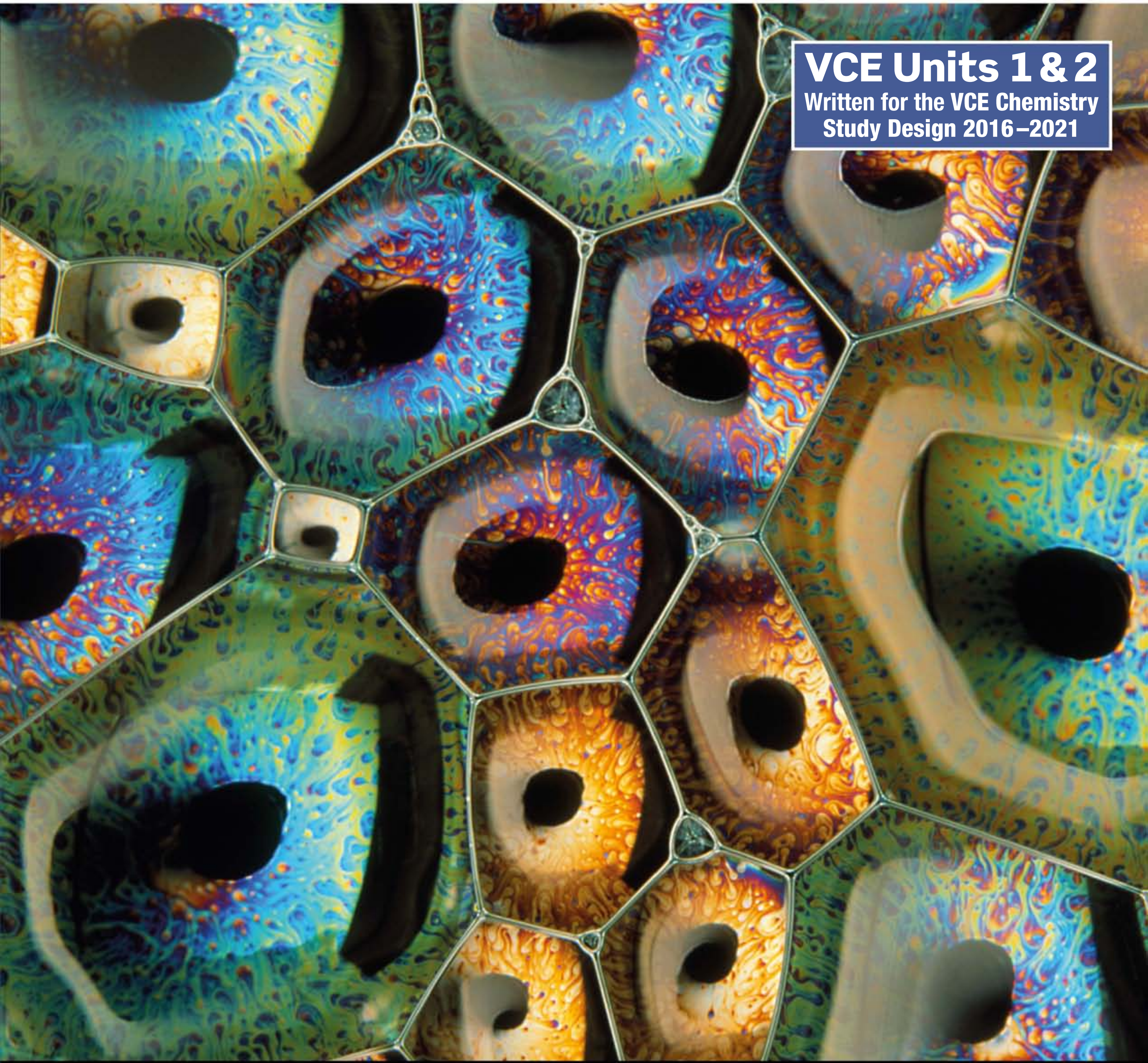
Heinemann

CHEMISTRY 1

5TH EDITION



VCE Units 1 & 2

Written for the VCE Chemistry Study Design 2016–2021

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The Chemistry Education Association was formed in 1977 by a group of chemistry teachers from secondary and tertiary institutions. It aims to promote the teaching of chemistry, particularly in secondary schools. The CEA has established a tradition of providing up-to-date text and electronic material and support resources for both students and teachers and professional development opportunities for teachers.

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

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Research investigation

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How do substances interact with water?

AREA OF STUDY 2

How are substances in water measured and analysed?

AREA OF STUDY 3

Practical investigation

How to use this book

Heinemann Chemistry 1 5th edition

Heinemann Chemistry 1 5th Edition has been written to the new VCE Chemistry Study Design 2016–2021. The book covers Units 1 and 2 in an easy-to-use resource. Explore how to use this book below.

Extension

Extension material goes beyond the core content of the Study Design. It is intended for students who wish to expand their depth of understanding.

Highlight

Focus on important information such as key definitions, formulas and summary points.

CHAPTER 04 Ionic bonding

Rocks, plates, molten lava and electrical insulators belong to a group of substances called ionic compounds. At the end of this chapter, you will be able to explain the structure and properties of these compounds.

Ionic compounds are made by the chemical combination of metallic and non-metallic elements. You will see that the properties of ionic compounds are a direct result of the bonding between the particles within these compounds.

The writing of chemical formulas and naming ionic compounds are other important skills that you will learn in this chapter.

Key knowledge

- Common properties of ionic compounds (brittleness, hardness, high melting point, difference in electrical conductivity in solid and liquid states) with reference to their formation, nature of ionic bonding and crystal structure, including limitations of representations. Experimental determination of the factors affecting crystal formation of ionic compounds
- The uses of ionic compounds

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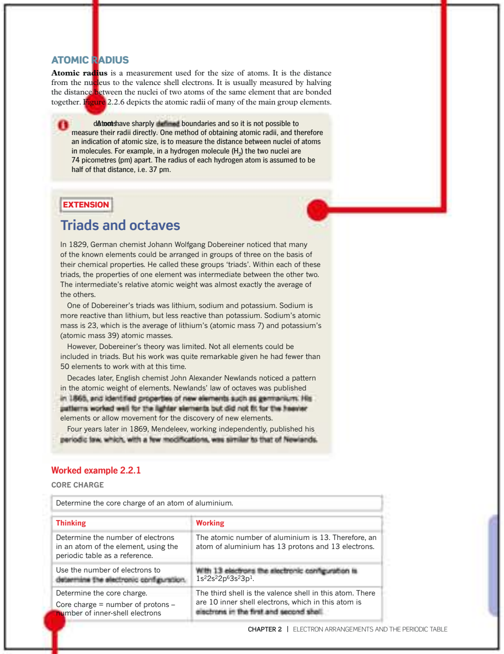
Chapter opener

Chapter opening pages link the Study Design to the chapter content. Key knowledge addressed in the chapter is clearly listed.

Chemistry in Action

Chemistry in Action place chemistry in an applied situation or relevant context. These refer to the nature and practice of chemistry, applications of chemistry and the associated issues and the historical development of concepts and ideas.



ATOMIC RADIUS

Atomic radius is a measurement used for the size of atoms. It is the distance from the nucleus to the valence shell electrons. It is usually measured by halving the distance between the nuclei of two atoms of the same element that are bonded together. Figure 2.2.6 depicts the atomic radii of many of the main group elements.

Atoms do not have sharply defined boundaries and so it is not possible to measure their radii directly. One method of obtaining atomic radii, and therefore an indication of atomic size, is to measure the distance between nuclei of atoms in molecules. For example, in a hydrogen molecule (H_2) the two nuclei are 74 picometres (pm) apart. The radius of each hydrogen atom is assumed to be half of that distance, i.e. 37 pm.

EXTENSION

Triads and octaves

In 1829, German chemist Johann Wolfgang Dobereiner noticed that many of the known elements could be arranged in groups of three on the basis of their chemical properties. He called these groups 'triads'. Within each of these triads, the properties of one element was intermediate between the other two. The intermediate's relative atomic weight was almost exactly the average of the others.

One of Dobereiner's triads was lithium, sodium and potassium. Sodium is more reactive than lithium, but less reactive than potassium. Sodium's atomic mass is 23, which is the average of lithium's (atomic mass 7) and potassium's (atomic mass 39) atomic masses.

However, Dobereiner's theory was limited. Not all elements could be included in triads. But his work was quite remarkable given he had fewer than 50 elements to work with at this time.

Decades later, English chemist John Alexander Newlands noticed a pattern in the atomic weight of elements. Newlands' law of octaves was published in 1865, and identified properties of new elements such as germanium. His patterns worked well for the lighter elements but did not fit for the heavier elements or allow movement for the discovery of new elements.

Four years later in 1869, Mendeleev, working independently, published his periodic law, which, with a few modifications, was similar to that of Newlands.

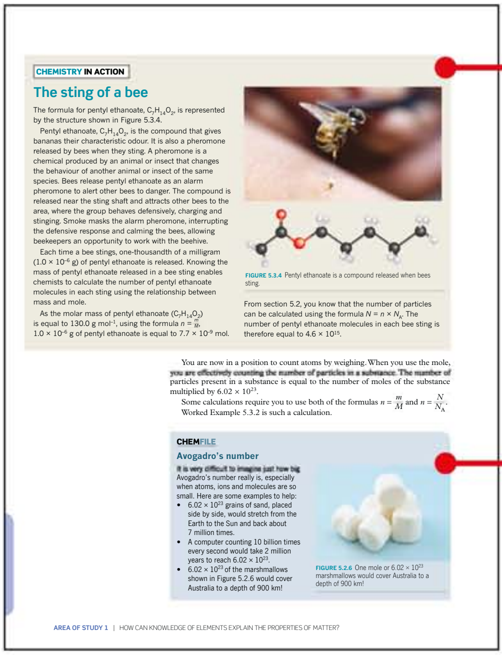
Worked example 2.2.1

CORE CHARGE

Determine the core charge of an atom of aluminium.

Thinking	Working
Determine the number of electrons in an atom of the element, using the periodic table as a reference.	The atomic number of aluminium is 13. Therefore, an atom of aluminium has 13 protons and 13 electrons.
Use the number of electrons to determine the electronic configuration.	With 13 electrons the electronic configuration is $1s^22s^22p^63s^23p^1$.
Determine the core charge. Core charge = number of protons – number of inner-shell electrons	The third shell is the valence shell in this atom. There are 10 inner shell electrons, which in this atom is electrons in the first and second shell.

CHAPTER 2 | ELECTRON ARRANGEMENTS AND THE PERIODIC TABLE



CHEMISTRY IN ACTION

The sting of a bee

The formula for pentyl ethanoate, $C_7H_{14}O_2$, is represented by the structure shown in Figure 5.3.4.

Pentyl ethanoate, $C_7H_{14}O_2$, is the compound that gives bananas their characteristic odour. It is also a pheromone released by bees when they sting. A pheromone is a chemical produced by an animal or insect that changes the behaviour of another animal or insect of the same species. Bees release pentyl ethanoate as an alarm pheromone to alert other bees to danger. The compound is released near the sting shaft and attracts other bees to the area, where the group behaves defensively, charging and stinging. Smoke masks the alarm pheromone, interrupting the defensive response and calming the bees, allowing beekeepers an opportunity to work with the beehive.

Each time a bee stings, one-thousandth of a milligram (1.0×10^{-6} g) of pentyl ethanoate is released. Knowing the mass of pentyl ethanoate released in a bee sting enables chemists to calculate the number of pentyl ethanoate molecules in each sting using the relationship between mass and mole.

As the molar mass of pentyl ethanoate ($C_7H_{14}O_2$) is equal to 130.0 g mol^{-1}, using the formula $n = \frac{m}{M}$, 1.0×10^{-6} g of pentyl ethanoate is equal to 7.7×10^{-9} mol.

FIGURE 5.3.4 Pentyl ethanoate is a compound released when bees sting.

From section 5.2, you know that the number of particles can be calculated using the formula $N = n \times N_A$. The number of pentyl ethanoate molecules in each bee sting is therefore equal to 4.6×10^{15}.

You are now in a position to count atoms by weighing. When you use the mole, you are effectively counting the number of particles in a substance. The number of particles present in a substance is equal to the number of moles of the substance multiplied by 6.02×10^{23}.

Some calculations require you to use both of the formulas $n = \frac{m}{M}$ and $n = \frac{N}{N_A}$. Worked Example 5.3.2 is such a calculation.

CHEMFILE

Avogadro's number

It is very difficult to imagine just how big Avogadro's number really is, especially when atoms, ions and molecules are so small. Here are some examples to help:

- 6.02×10^{23} grains of sand, placed side by side, would stretch from the Earth to the Sun and back about 7 million times.
- A computer counting 10 billion times every second would take 2 million years to reach 6.02×10^{23}.
- 6.02×10^{23} of the marshmallows shown in Figure 5.2.6 would cover Australia to a depth of 900 km!

FIGURE 5.2.6 One mole or 6.02×10^{23} marshmallows would cover Australia to a depth of 900 km!

AREA OF STUDY 1 | HOW CAN KNOWLEDGE OF ELEMENTS EXPLAIN THE PROPERTIES OF MATTER?

ChemFile

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

Worked examples

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

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

Fully worked solutions to all Try Yourself: Worked examples are available on *Heinemann Chemistry 5th Edition ProductLink*.

Chapter review

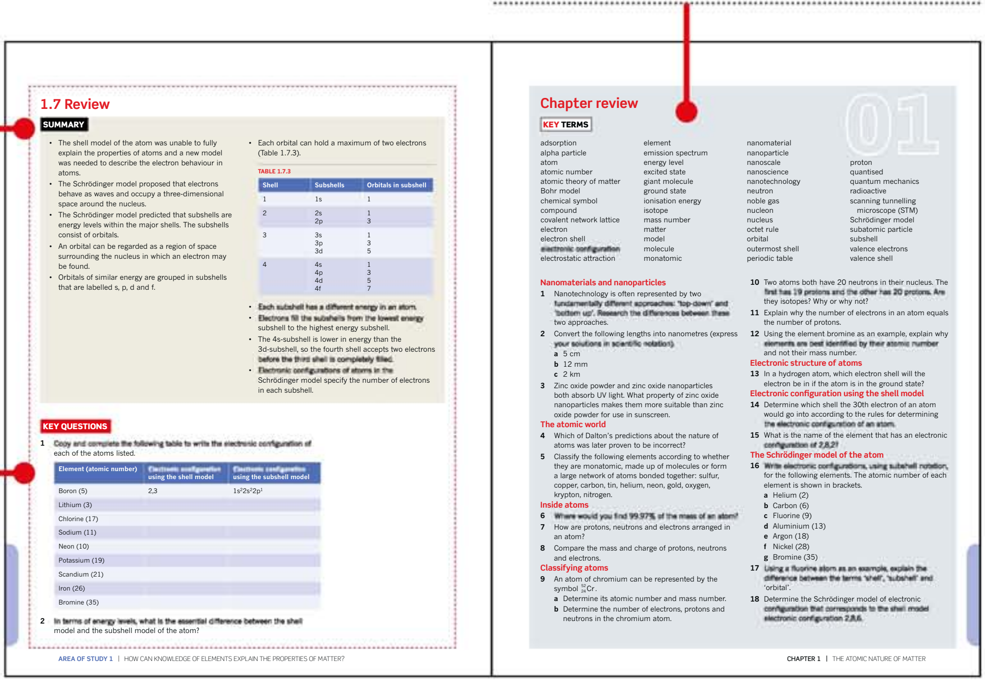
Each chapter finishes with a set of higher order questions to test students' ability to apply the knowledge gained from the chapter.

Section summary

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

Section review

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



1.7 Review

SUMMARY

- The shell model of the atom was unable to fully explain the properties of atoms and a new model was needed to describe the electron behaviour in atoms.
- The Schrödinger model proposed that electrons behave as waves and occupy a three-dimensional space around the nucleus.
- The Schrödinger model predicted that subshells are energy levels within the major shells. The subshells consist of orbitals.
- An orbital can be regarded as a region of space surrounding the nucleus in which an electron may be found.
- Orbitals of similar energy are grouped in subshells that are labelled s, p, d and f.
- Each orbital can hold a maximum of two electrons (Table 1.7.3).

TABLE 1.7.3

Shell	Subshells	Orbitals in subshell
1	1s	1
2	2s 2p	1 3
3	3s 3p 3d	1 3 5
4	4s 4p 4d 4f	1 3 5 7

- Each subshell has a different energy in an atom.
- Electrons fill the subshells from the lowest energy subshell to the highest energy subshell.
- The 4s-subshell is lower in energy than the 3d-subshell, so the fourth shell accepts two electrons before the third shell is completely filled.
- Electronic configurations of atoms in the Schrödinger model specify the number of electrons in each subshell.

KEY QUESTIONS

1 Copy and complete the following table to write the electronic configuration of each of the atoms listed.

Element (atomic number)	Electronic configuration using the shell model	Electronic configuration using the subshell model
Boron (5)	2,3	$1s^2 2s^2 2p^1$
Lithium (3)		
Chlorine (17)		
Sodium (11)		
Neon (10)		
Potassium (19)		
Scandium (21)		
Iron (26)		
Bromine (35)		

2 In terms of energy levels, what is the essential difference between the shell model and the subshell model of the atom?

AREA OF STUDY 1 | HOW CAN KNOWLEDGE OF ELEMENTS EXPLAIN THE PROPERTIES OF MATTER?

Chapter review

KEY TERMS

adsorption
alpha particle
atom
atomic number
atomic theory of matter
Bohr model
chemical symbol
compound
covalent network lattice
electron
electron shell
electronic configuration
electrostatic attraction
element
emission spectrum
energy level
excited state
giant molecule
ground state
ionisation energy
isotope
mass number
matter
model
molecule
monatomic
nanomaterial
nanoparticle
nanoscale
nanoscience
nanotechnology
neutron
noble gas
nucleon
nucleus
octet rule
orbital
outermost shell
periodic table
proton
quantised
quantum mechanics
radioactive
scanning tunnelling microscope (STM)
Schrödinger model
subatomic particle
subshell
valence electrons
valence shell

Nanomaterials and nanoparticles

1 Nanotechnology is often represented by two fundamentally different approaches: 'top-down' and 'bottom up'. Research the differences between these two approaches.

2 Convert the following lengths into nanometres (express your solutions in scientific notation).
  a 5 cm
  b 12 mm
  c 2 km

3 Zinc oxide powder and zinc oxide nanoparticles both absorb UV light. What property of zinc oxide nanoparticles makes them more suitable than zinc oxide powder for use in sunscreen.

The atomic world

4 Which of Dalton's predictions about the nature of atoms was later proven to be incorrect?

5 Classify the following elements according to whether they are monatomic, made up of molecules or form a large network of atoms bonded together: sulfur, copper, carbon, tin, helium, neon, gold, oxygen, krypton, nitrogen.

Inside atoms

6 Where would you find 99.97% of the mass of an atom?

7 How are protons, neutrons and electrons arranged in an atom?

8 Compare the mass and charge of protons, neutrons and electrons.

Classifying atoms

9 An atom of chromium can be represented by the symbol ${}^{52}_{24}\mathrm{Cr}$.
  a Determine its atomic number and mass number.
  b Determine the number of electrons, protons and neutrons in the chromium atom.

10 Two atoms both have 20 neutrons in their nucleus. The first has 19 protons and the other has 20 protons. Are they isotopes? Why or why not?

11 Explain why the number of electrons in an atom equals the number of protons.

12 Using the element bromine as an example, explain why elements are best identified by their atomic number and not their mass number.

Electronic structure of atoms

13 In a hydrogen atom, which electron shell will the electron be in if the atom is in the ground state?

Electronic configuration using the shell model

14 Determine which shell the 30th electron of an atom would go into according to the rules for determining the electronic configuration of an atom.

15 What is the name of the element that has an electronic configuration of 2,8,2?

The Schrödinger model of the atom

16 Write electronic configurations, using subshell notation, for the following elements. The atomic number of each element is shown in brackets.
  a Helium (2)
  b Carbon (6)
  c Fluorine (9)
  d Aluminium (13)
  e Argon (18)
  f Nickel (28)
  g Bromine (35)

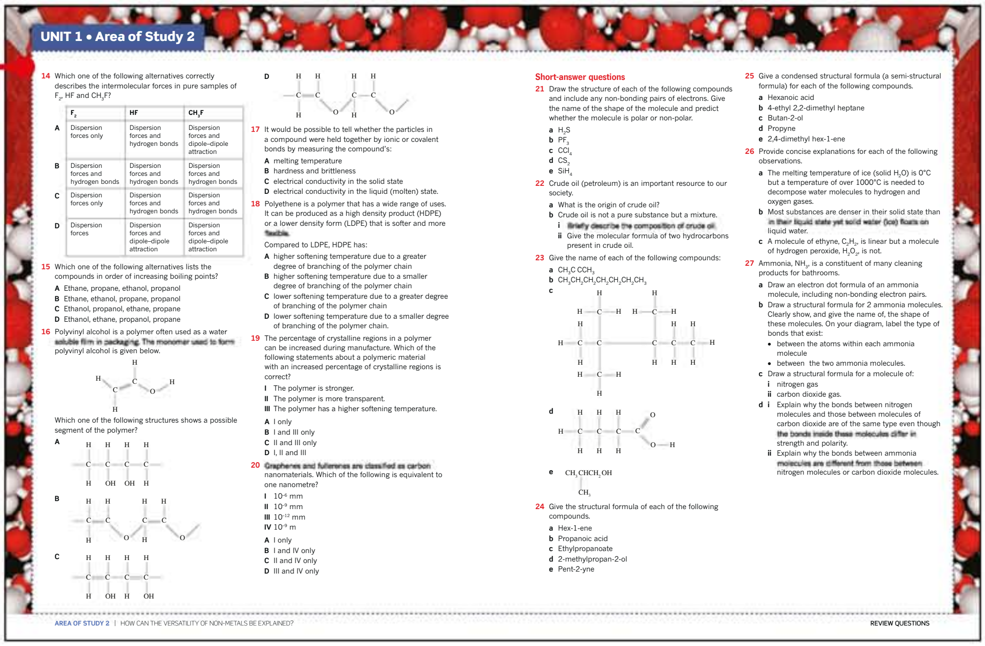
17 Using a fluorine atom as an example, explain the difference between the terms 'shell', 'subshell' and 'orbital'.

18 Determine the Schrödinger model of electronic configuration that corresponds to the shell model electronic configuration 2,8,6.

CHAPTER 1 | THE ATOMIC NATURE OF MATTER

Area of Study review

Each Area of Study finishes with a comprehensive set of exam-style questions, including multiple choice and extended response, that assist students to draw together their knowledge and understanding and apply it to this style of questions.



UNIT 1 • Area of Study 2

14 Which one of the following alternatives correctly describes the intermolecular forces in pure samples of F_2, HF and CH_3F?

	F_2	HF	CH_3F
A	Dispersion forces only	Dispersion forces and hydrogen bonds	Dispersion forces and dipole–dipole attraction
B	Dispersion forces and hydrogen bonds	Dispersion forces and hydrogen bonds	Dispersion forces and hydrogen bonds
C	Dispersion forces only	Dispersion forces and hydrogen bonds	Dispersion forces and hydrogen bonds
D	Dispersion forces	Dispersion forces and dipole–dipole attraction	Dispersion forces and dipole–dipole attraction

15 Which one of the following alternatives lists the compounds in order of increasing boiling points?
  A Ethane, propane, ethanol, propanol
  B Ethane, ethanol, propane, propanol
  C Ethanol, propanol, ethane, propane
  D Ethanol, ethane, propanol, propane

16 Polyvinyl alcohol is a polymer often used as a water soluble film in packaging. The monomer used to form polyvinyl alcohol is given below.

Which one of the following structures shows a possible segment of the polymer?
  A
  B
  C
  D

17 It would be possible to tell whether the particles in a compound were held together by ionic or covalent bonds by measuring the compound's:
  A melting temperature
  B hardness and brittleness
  C electrical conductivity in the solid state
  D electrical conductivity in the liquid (molten) state.

18 Polyethene is a polymer that has a wide range of uses. It can be produced as a high density product (HDPE) or a lower density form (LDPE) that is softer and more flexible.

Compared to LDPE, HDPE has:
  A higher softening temperature due to a greater degree of branching of the polymer chain
  B higher softening temperature due to a smaller degree of branching of the polymer chain
  C lower softening temperature due to a greater degree of branching of the polymer chain
  D lower softening temperature due to a smaller degree of branching of the polymer chain.

19 The percentage of crystalline regions in a polymer can be increased during manufacture. Which of the following statements about a polymeric material with an increased percentage of crystalline regions is correct?
  I The polymer is stronger.
  II The polymer is more transparent.
  III The polymer has a higher softening temperature.
  A I only
  B I and III only
  C II and III only
  D I, II and III

20 Graphenes and fullerenes are classified as carbon nanomaterials. Which of the following is equivalent to one nanometre?
  I 10^{-6} mm
  II 10^{-9} mm
  III 10^{-12} mm
  IV 10^{-9} m
  A I only
  B I and IV only
  C II and IV only
  D III and IV only

Short-answer questions

21 Draw the structure of each of the following compounds and include any non-bonding pairs of electrons. Give the name of the shape of the molecule and predict whether the molecule is polar or non-polar.
  a H_2S
  b PF_3
  c CCl_4
  d CS_2
  e SiH_4

22 Crude oil (petroleum) is an important resource to our society.
  a What is the origin of crude oil?
  b Crude oil is not a pure substance but a mixture.
    i Briefly describe the composition of crude oil.
    ii Give the molecular formula of two hydrocarbons present in crude oil.

23 Give the name of each of the following compounds:
  a $CH_3C\,CCH_3$
  b $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
  c
  d
  e

24 Give the structural formula of each of the following compounds.
  a Hex-1-ene
  b Propanoic acid
  c Ethylpropanoate
  d 2-methylpropan-2-ol
  e Pent-2-yne

25 Give a condensed structural formula (a semi-structural formula) for each of the following compounds.
  a Hexanoic acid
  b 4-ethyl 2,2-dimethyl heptane
  c Butan-2-ol
  d Propyne
  e 2,4-dimethyl hex-1-ene

26 Provide concise explanations for each of the following observations.
  a The melting temperature of ice (solid H_2O) is 0°C but a temperature of over 1000°C is needed to decompose water molecules to hydrogen and oxygen gases.
  b Most substances are denser in their solid state than in their liquid state yet solid water (ice) floats on liquid water.
  c A molecule of ethyne, C_2H_2, is linear but a molecule of hydrogen peroxide, H_2O_2, is not.

27 Ammonia, NH_3, is a constituent of many cleaning products for bathrooms.
  a Draw an electron dot formula of an ammonia molecule, including non-bonding electron pairs.
  b Draw a structural formula for 2 ammonia molecules. Clearly show, and give the name of, the shape of these molecules. On your diagram, label the type of bonds that exist:
    - between the atoms within each ammonia molecule
    - between the two ammonia molecules.
  c Draw a structural formula for a molecule of:
    i nitrogen gas
    ii carbon dioxide gas.
  d i Explain why the bonds between nitrogen molecules and those between molecules of carbon dioxide are of the same type even though the bonds inside these molecules differ in strength and polarity.
    ii Explain why the bonds between ammonia molecules are different from those between nitrogen molecules or carbon dioxide molecules.

AREA OF STUDY 2 | HOW CAN THE VERSATILITY OF NON-METALS BE EXPLAINED?

REVIEW QUESTIONS

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, Try Yourself: Worked examples, chapter review questions and Area of Study review questions are provided via *Heinemann Chemistry 5th Edition ProductLink.*

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 key terms.

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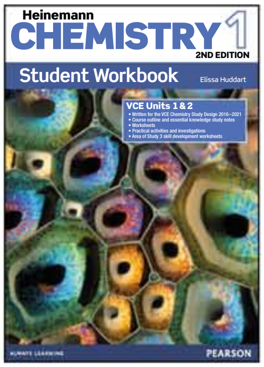
Student Book

Heinemann Chemistry 1 5th Edition has been written to fully align with the VCE Chemistry Study Design 2016–2021. The series includes the very latest developments and applications of Chemistry and incorporates best practice literacy and instructional design to ensure the content and concepts are fully accessible to all students.

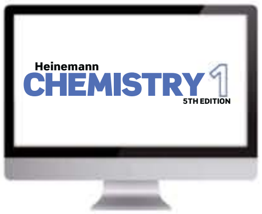
Pearson eBook 3.0

Pearson eBook 3.0 is the digital version of the student book. It retains the integrity of the printed page and is available online or offline on any device—PC/Mac, Android tablet, iPad.



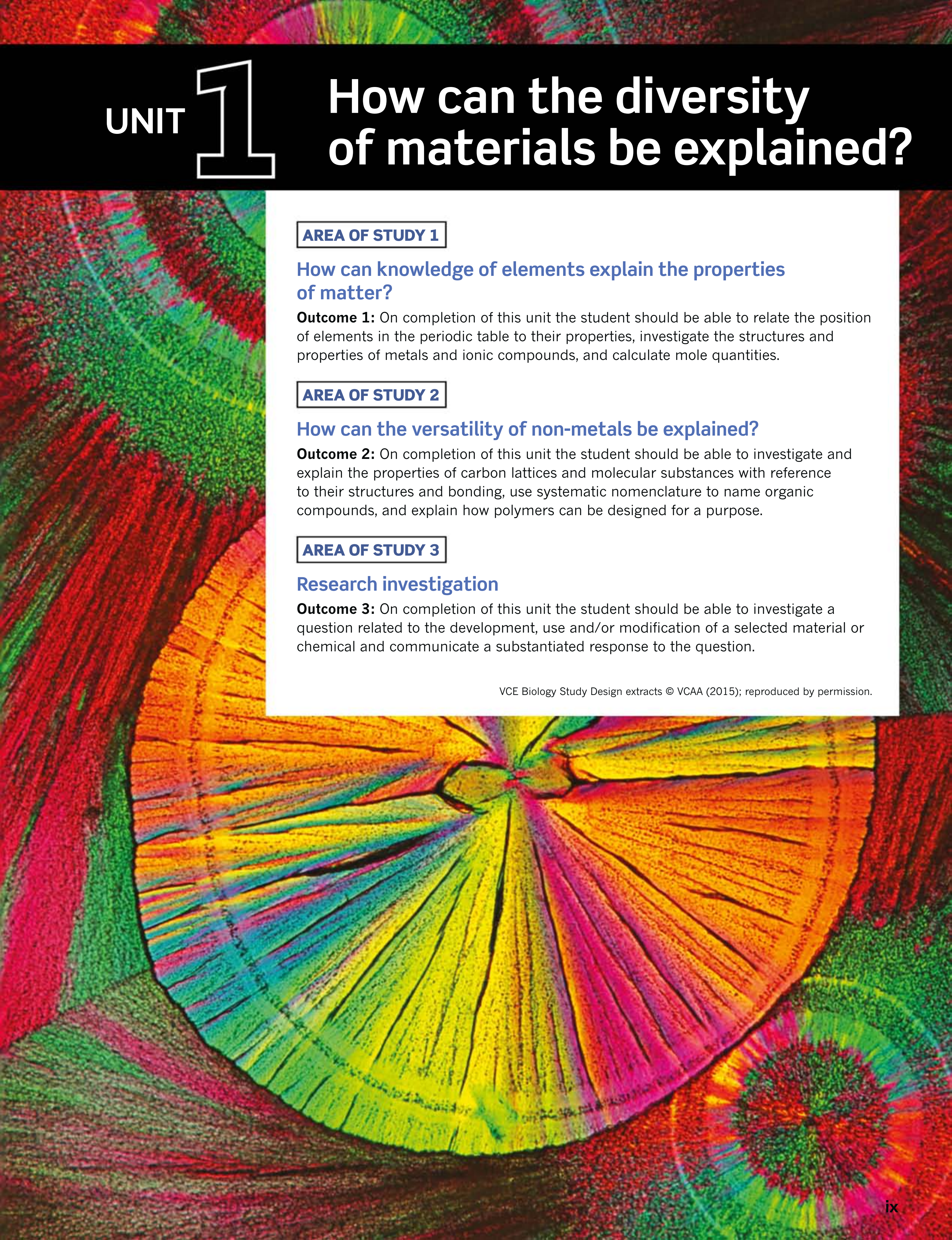
Student Workbook

Heinemann Chemistry 1 Student Workbook 2nd edition will give students the edge in preparing for all forms of assessment. New content has been written to ensure the workbook is fully aligned to the 2016–2021 Chemistry Study Design. Key features include study notes, worksheets, practical activities and guidance, and assessment practice and opportunities.



ProductLink

Heinemann Chemistry 5th Edition ProductLink provides comprehensive support for teachers and students completely free of charge. ProductLink includes comprehensive answers and worked solutions to all student book questions, tests, quizzes and practice exams, teaching programs, risk assessments and more.



UNIT 1

How can the diversity of materials be explained?

AREA OF STUDY 1

How can knowledge of elements explain the properties of matter?

Outcome 1: On completion of this unit the student should be able to relate the position of elements in the periodic table to their properties, investigate the structures and properties of metals and ionic compounds, and calculate mole quantities.

AREA OF STUDY 2

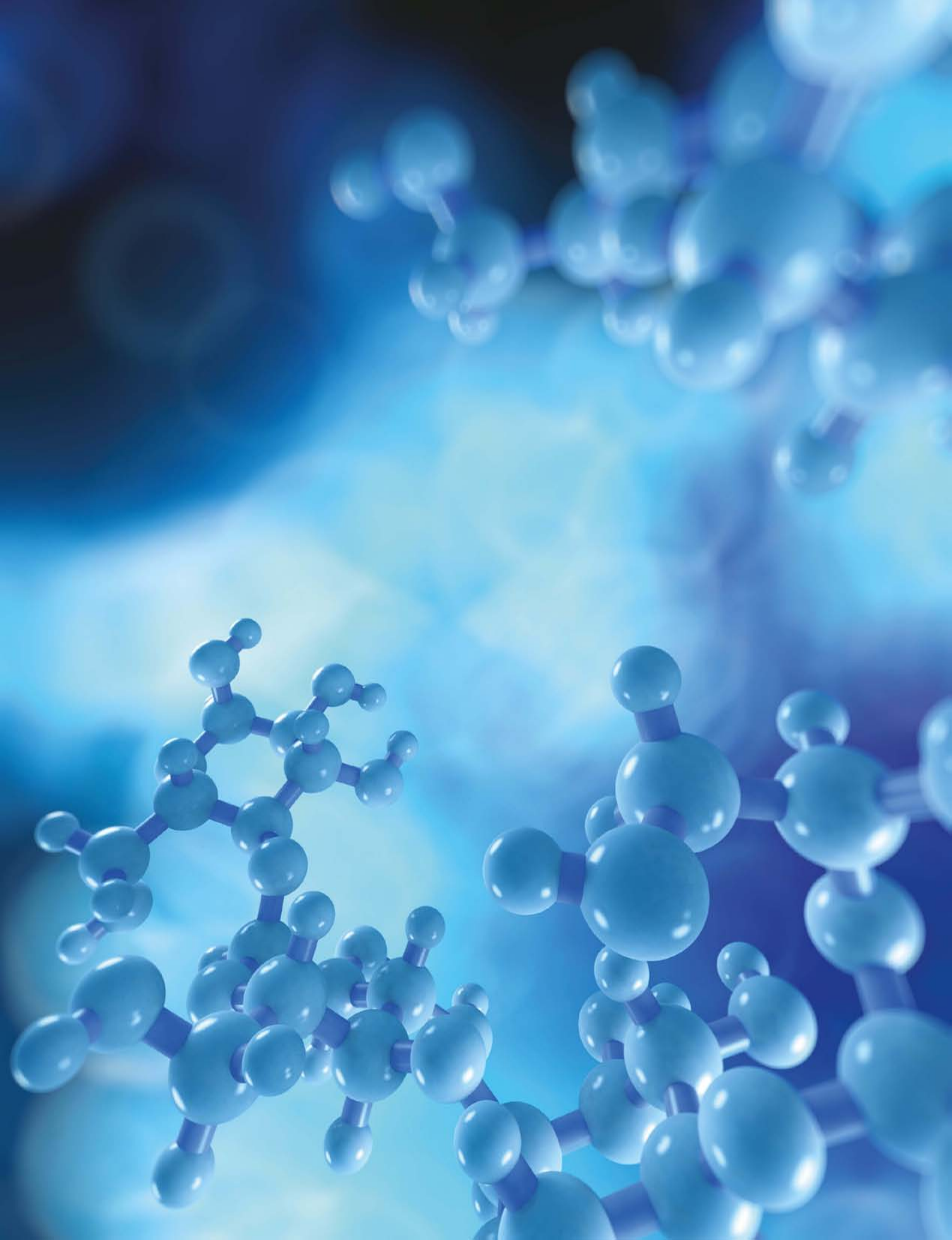
How can the versatility of non-metals be explained?

Outcome 2: On completion of this unit the student should be able to investigate and explain the properties of carbon lattices and molecular substances with reference to their structures and bonding, use systematic nomenclature to name organic compounds, and explain how polymers can be designed for a purpose.

AREA OF STUDY 3

Research investigation

Outcome 3: On completion of this unit the student should be able to investigate a question related to the development, use and/or modification of a selected material or chemical and communicate a substantiated response to the question.



CHAPTER

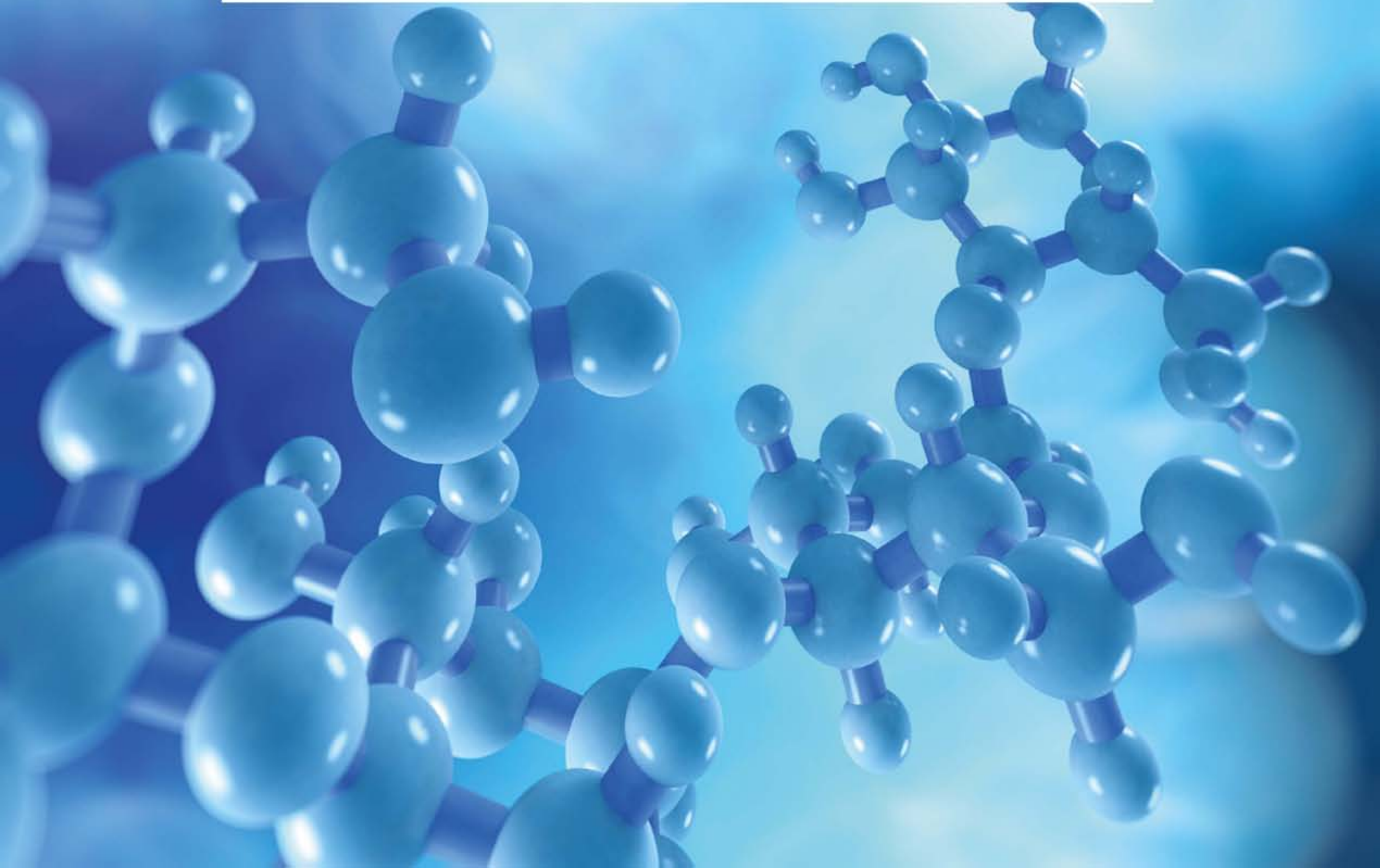
01

The atomic nature of matter

In this chapter, you will begin by examining how material science can create advanced materials by controlling matter on the atomic scale. Nanoparticles contain just a few hundred or thousands of atoms. You will then develop a detailed picture of the structure of atoms, which is the foundation for all chemistry.

Key knowledge

- Relative and absolute sizes of particles that are visible and invisible to the unaided eye: small and giant molecules and lattices; atoms and subatomic particles; nanoparticles and nanostructures
- The definition of an element with reference to atomic number and mass number
- Isotopic forms of an element using appropriate notation
- Spectral evidence for the Bohr model and for its refinement as the Schrödinger model
- Electronic configurations of elements 1 to 36 using the Schrödinger model of the atom, including s, p, d and f notations (with copper and chromium exceptions)



1.1 Nanomaterials and nanoparticles

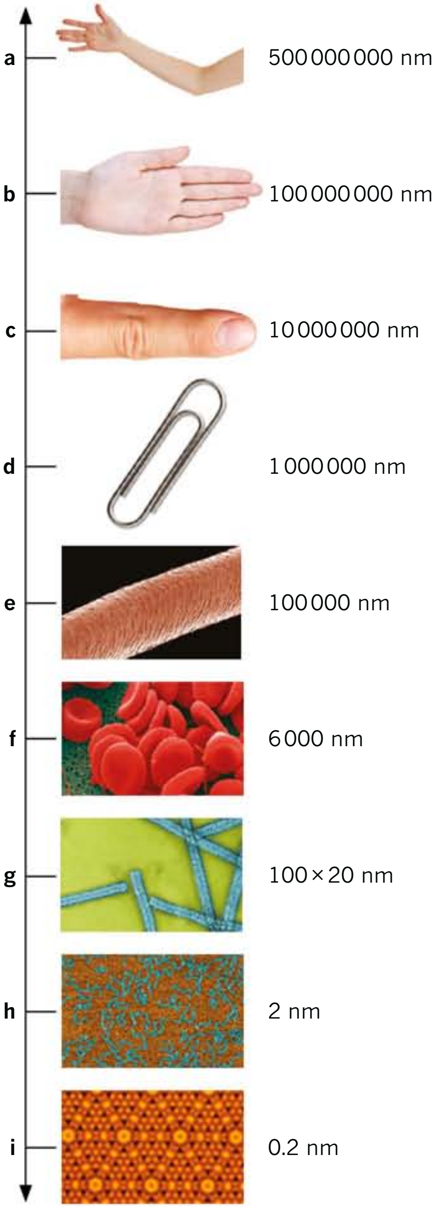


FIGURE 1.1.1 This scale compares the sizes of objects down to the nanometre size.
(a) The length of the average human arm is 0.5 m (500 000 000 nm).
(b) The width of the average hand is 10 cm (100 000 000 nm).
(c) The width of a finger is about 1 cm (10 000 000 nm).
(d) The width of a paperclip wire is approximately 1 mm (1 000 000 nm).
(e) The width of a human hair is approximately 100 000 nm.
(f) The diameter of red blood cells is 6000 nm.
(g) Tobacco mosaic virus is 100 nm long and 20 nm wide.
(h) DNA strands are about 2 nm wide.
(i) Silicon atoms are 0.2 nm across.

One of the most significant advances in materials science this century has been in the area of nanoscience. Nanoscience looks at materials at a very small scale—the nanoscale. The nanoscale is larger than the atomic scale, but is still far too small to be seen with the naked eye. By modifying and engineering materials at the nanoscale, scientists can fundamentally change the properties of the materials and therefore create new technologies.

Nanoscience is the study of nanoparticles and nanotechnology. **Nanotechnology** is the use of technologies that manipulate and investigate the properties of materials on the nanoscale.

Materials engineered on the nanoscale are already an important part of your everyday life. For example, microchips in computers and phones are made up of nanoscale transistors that process information at billions of bits per second. Lasers and light-emitting diodes (LEDs) also use materials engineered on the nanoscale. Even some sunscreens are made of nanoparticles designed specifically to absorb ultraviolet radiation.

'Nanotechnology' is no longer just a term used in science fiction. It is here today, and it has fundamentally changed the world you live in.

THE NANOSCALE

The prefix nano- refers to one-billionth or 10^{-9} in scientific notation. For example, a nanometre (nm) is one-billionth of a metre or 10^{-9} m. This is much smaller than anything you can see with the naked eye. Table 1.1.1 compares the nanometre to other metric units for length.

TABLE 1.1.1 Some metric units for length

Unit	Symbol	Relative to standard unit of length (m)
picometre	pm	10^{-12}
nanometre	nm	10^{-9}
micrometre	μm	10^{-6}
millimetre	mm	10^{-3}
metre	m	1
kilometre	km	10^{3}

For example, the width of a human hair or a pore on your skin is still thousands of times larger than the nanoscale features in nanomaterials. The **nanoscale** is used to describe objects that are about 1–100 nm wide. Figure 1.1.1 shows the sizes of different objects. You can see that tobacco mosaic virus and DNA belong to the nanoscale.

Worked example 1.1.1

CONVERTING MILLIMETRES TO NANOMETRES

Convert 15 mm into nanometres.

Thinking	Working
Write the length in metres.	15 mm = 0.015 m
Write the length in scientific notation.	0.015 m = 1.5×10^{-2} m
Multiply by 10^9 to convert to nanometres. (Hint: To do this, you just need to add 9 to the index on the number 10.)	$(1.5 \times 10^{-2}) \times 10^9 = 1.5 \times 10^{(-2+9)}$ nm $= 1.5 \times 10^7$ nm

Worked example: Try yourself 1.1.1

CONVERTING KILOMETRES TO NANOMETRES

Convert 2.43 km into nanometres.

NANOMATERIALS

Nanomaterials can have very different properties from those of the same material in bulk form. For example, carbon readily forms nanomaterials such as the carbon nanotubes shown in Figure 1.1.2. These nanostructures are nothing like soft, powdery charcoal, which we normally associate with carbon. Carbon nanotubes are extremely strong like diamond and conduct electricity like graphite. But unlike diamond and graphite, they are flexible and have a high tensile strength (resistance to stretching) and their conductivity can be engineered to make them insulating, conducting or semiconducting. You will look more closely at carbon nanomaterials in Chapter 8.

The term 'nanomaterial' is usually associated with modern, high-tech materials. However, nanomaterials have always been present in nature. For example, milk contains **nanoparticles** of proteins and fats. These particles scatter light and make milk appear white.

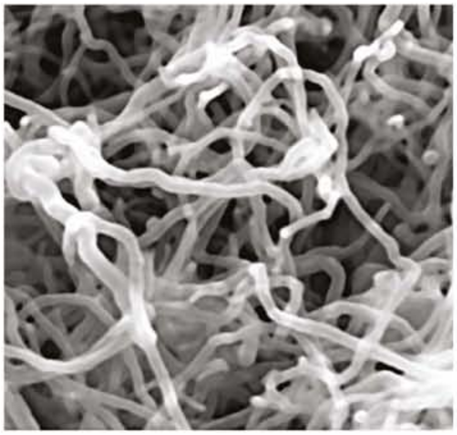


FIGURE 1.1.2 These carbon nanotubes have different properties from other materials made from carbon such as charcoal, graphite and diamond.

CHEMFILE

What do opals and butterflies have in common?

Opal is a nanomaterial made of tiny spheres of silica (Figure 1.1.3, top). These spheres diffract light to produce spectacular flashes of red, green and blue. Butterflies also get their coloured patterns from nanostructures on the surfaces of their wings.

FIGURE 1.1.3 (Top) An opal is made of tiny spherical nanoparticles of silica. (Bottom) The colour of a butterfly's wing is due to nanostructures in the wing.

Forming nanomaterials

Two processes are used to manufacture nanomaterials: the bottom-up method and the top-down method.

- The bottom-up method uses specially designed **molecules** or **atoms** in chemical reactions to gradually build up the new nanoparticle from the smaller atoms or molecular units.
- The top-down method uses the larger bulk material as the starting material. The bulk material is broken down into nanoparticles by mechanical or chemical means.

Even though the two methods start at opposite ends of the scale, the bottom-up and top-down approaches both produce materials that exist on the nanoscale and rely on physical and chemical processes to achieve these nanomaterials.

Manufactured nanomaterials

FIGURE 1.1.4 Silica gel sachets like this one are often placed with tablets and capsules to keep them dry. The silica gel works by adsorbing water from the atmosphere so the humidity does not affect the tablets and capsules. The silica gel is able to adsorb large amounts of water because of its nanostructure, shown in the inset. The nanostructure gives the gel an enormous surface area compared to its volume.

Scientists are learning more about how the structure of nanomaterials influences the properties of materials. This has allowed scientists to create new technologies based on nanomaterials. For example, materials such as silica gel (Figure 1.1.4) and activated charcoal can adsorb large amounts of liquids and gases. The term **adsorption** is used when a molecule attaches to a surface of a solid or liquid. This is different from absorption, where molecules are incorporated into the substance, as shown in Figure 1.1.5.

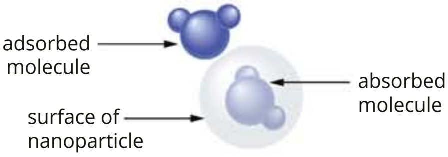


FIGURE 1.1.5 Molecules are adsorbed onto the surface of nanoparticles but are not usually absorbed by the particle. This diagram shows the difference between the two.

These products contain billions of nanoscale holes that trap unwanted molecules such as water and other gases. In activated charcoal, the holes are so tiny and so numerous that even a grain of the activated charcoal can have a surface area of several square metres. This means that only a small amount of activated charcoal is needed to adsorb a large number of gas molecules. For this reason, activated charcoal is used to store natural gas. Activated charcoal is also used in gas masks to adsorb dangerous gases from the atmosphere. Activated charcoal gas masks were invented in 1915 and were used in World War I to protect soldiers against poisonous gases.

Engineered nanomaterials

More recently, scientists have been able to engineer nanoscale features on the surfaces of materials to give the materials new and useful properties. A simple example is the patterning of the surface of a CD-ROM. Information is encoded on the surface of the CD-ROM as a series of nano-sized 'pits' or hollows, as shown in Figure 1.1.6. Improvements in the technology have meant that smaller pits can be made so that more information can be stored on a surface. This has led to the development of DVD and Blu-ray disks.

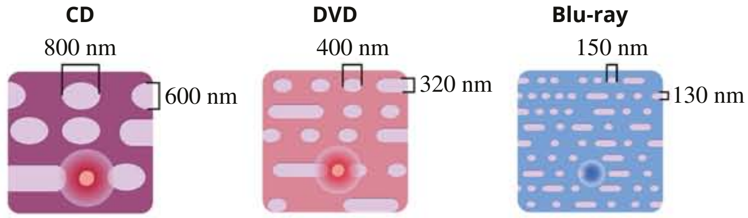


FIGURE 1.1.6 CD-ROMs store information as a series of nano-sized pits that are approximately 800 nm by 600 nm. DVDs are able to store more information because the pits are smaller: 400 nm by 320 nm. Blu-ray disks can store even more information because their pits are only 150 nm by 130 nm.

NANOPARTICLES

Nanoparticles are a specific type of nanomaterial with unique properties and a broad range of applications. Nanoparticles are usually spherical with diameters of 1–100 nm. They are used in chemotherapy and sunscreens and as industrial catalysts.

ℹ Nanoparticles range in diameter from 1 to 100 nm.

The importance of surface area

One of the most important properties of nanoparticles is their large surface area compared to their volume. In chemistry, surfaces are extremely important since surfaces are often where chemical reactions take place. Substances made of nanoparticles have very large surface areas because they are so small.

For example, consider a 1 m^3 cube. It has six sides, each exactly 1 m in length, and so has a total surface area of 6 m^2 and a volume of 1 m^3. If the cube is cut into eight 0.5 m cubes, the total volume of all the cubes stays the same (1 m^3), as shown in Figure 1.1.7. However, the surface area has doubled. This is because parts of the cube that were originally on the inside of the cube have now become part of the surface. The same block divided into 100 nm cubes has a surface area of 60 000 000 m^2 but the volume is still 1 m^3.

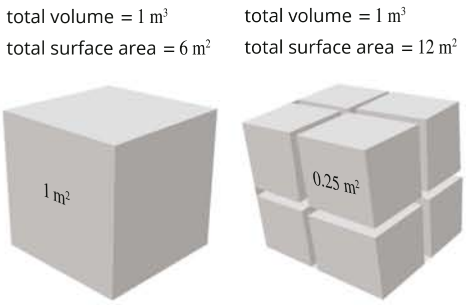


FIGURE 1.1.7 When a 1 m cube is divided into eight equal cubes, the volume stays the same but the surface area doubles.

A large surface area to volume ratio is one of the most important features of nanoparticles.

The large surface area of nanoparticles is important in three ways.

1. Adsorption of molecules: The large surface area of nanoparticles means that even a small volume of nanoparticles can adsorb a large number of molecules. Therefore, nanoparticles can be used to remove unwanted chemicals and gases in the same way that silica gel and activated charcoal are used.
2. Transportation of molecules: Nanoparticles can be used to transport the molecules that are adsorbed onto the nanoparticle. The nanoparticles' small size and large surface area mean that they can transport chemicals through air, skin and even cells. This feature of nanoparticles has a variety of applications in medicine for transporting drugs into the body and is already being used in some chemotherapy treatments for cancer.
3. Catalysts: The surfaces of some nanoparticles can be used to increase the rate of particular chemical reactions. The nanoparticles are acting as catalysts because they speed up the reaction but are not consumed (used up) by the reaction. The reactant molecules adsorb onto the surface of the nanoparticles, which allows reactant molecules to combine to form the product. The large surface area of nanoparticles means that many of these reactions can take place at the same time, which increases the rate of the reaction significantly.

CHEMISTRY IN ACTION

Professor Chengzhong Yu (from the Australian Institute for Biotechnology and Nanotechnology at the University of Queensland) was awarded the 2015 Le Févre Memorial Prize by the Australian Academy of Science. Professor Chengzhong Yu and a team of scientists are investigating using nanoparticles to improve the delivery of oral medications. Oral medications are subjected to changes in pH (high acid levels in the gut) and enzymatic breakdown in the mouth and stomach. This acid and enzyme attack means that many protein-based medications break down before they have a chance to act on the specific target tissue.

Professor Yu and his team are developing new, cost-effective nanomaterials that will improve delivery of vaccines, genes and drugs for human and animal health care.

Applications of nanotechnology in medicine are far-reaching. Figure 1.1.8 shows the targeted destruction of a tumour by nanoparticles. In medicine, nanotechnology could improve the analysis and treatment of cancers, genetic disorders and viral infections once thought untreatable.

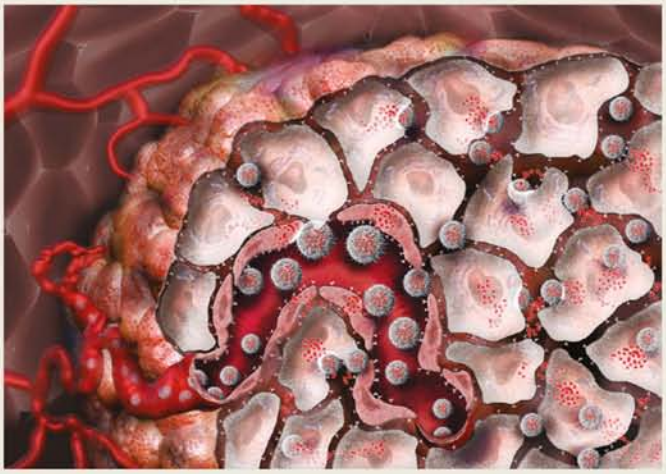


FIGURE 1.1.8 This computer illustration shows nanoparticles (spheres) containing cytotoxic drugs. The nanoparticles target tumour cells, leading to their destruction.

Other properties and applications

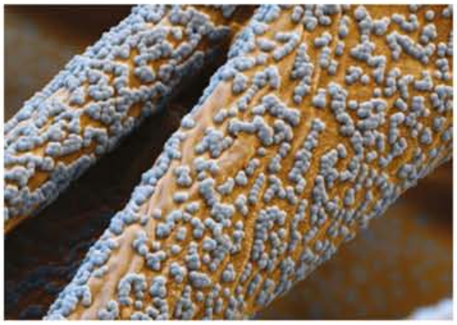


FIGURE 1.1.9 Water-repellent nanoparticles can be incorporated into cotton fibres to create a composite nanomaterial that is a water-resistant fabric.

FIGURE 1.1.10 These vials contain gold particles of various sizes. The different-sized particles are different colours because they interact with light differently.

Nanoparticles have many other useful properties. Their small size and unique structural properties mean they can be used for developing composite (made up of several parts) nanomaterials. Composite nanomaterials incorporate nanoparticles into other materials.

The stain-resistant cotton shown in Figure 1.1.9 is a composite nanomaterial. In this case, the cotton fibres are covered with water-resistant nanoparticles so that liquids cannot penetrate the material. This makes the fabric water-repellent and stain-resistant.

When a substance is processed into nanoparticles, its physical, chemical and optical properties can change. For example, when gold is in the form of nanoparticles, it loses its metallic lustre. Instead, it can take on a variety of colours depending on the size of the gold particles. For this reason, gold nanoparticles are often used to colour glass. Figure 1.1.10 shows samples containing gold nanoparticles of different sizes. All of the particles absorb white light, but they reflect different-coloured light, depending on the particle size.

The fact that nanoparticles interact differently with light makes them useful in sunscreens. Zinc oxide (ZnO) nanoparticles are commonly used in sunscreens. Zinc oxide absorbs a broad range of the UV spectrum and so provides excellent protection from the sun. Normally, sunscreens that contain metal oxides are milky white when applied to the skin. However, sunscreen that contains zinc oxide nanoparticles is clear, and therefore is preferred by beach-goers.

CHEMFILE

Nanoparticles: risks to health and the environment

Nanoparticles have opened up a range of technological possibilities. However, some people are concerned about the possible dangers to humans and the environment. Other useful materials such as asbestos have been found to have devastating side-effects. Scientists at Australia's CSIRO (Commonwealth Scientific and Industrial Research Organisation) and around the world are studying the potential dangers associated with nanoparticles and their applications.

THE PROBLEM WITH NANOPARTICLES

Nanoparticles are so small that they can travel through the air, through skin and into your bloodstream and even into cells. Inside the body, the particles may interact with biomolecules to cause unwanted chemical reactions. This makes nanoparticles potentially dangerous if breathed in or in contact with the skin (for example, in sunscreen, fabrics or cosmetics).

NANOPARTICLES IN SUNSCREENS

Scientists at CSIRO are looking at the zinc oxide nanoparticles used in sunscreens to determine whether they are safe. This research focuses on whether the nanoparticles can penetrate skin, their long-term health effects and how they might impact on the environment.

Initial studies suggest that small amounts of zinc oxide from sunscreens are absorbed into the body and can be detected in the blood and urine. It is still not clear whether the absorbed zinc oxide has any negative effects on the human body. The most recent research indicates that the cells of the immune system can break down the nanoparticles.

1.1 Review

SUMMARY

- Nanomaterials are materials with nanoscale features that determine important properties of the materials.
- Nanoparticles have diameters of 1–100 nm.
- Nanoparticles can have very different physical, chemical and optical properties from the bulk material.
- Nanoparticles can be made in two ways: the bottom-up and top-down methods.
- Nanoparticles have a large surface area compared to their volume.
- The surfaces of nanoparticles can be used to adsorb molecules, transport molecules and act as catalysts for chemical reactions.
- Nanoparticles can transport particles through the air and into the human body. This has raised concern about their safety for human health and the environment.
- Regulations are being developed to address the potential risks of nanomaterials.

KEY QUESTIONS

1 Convert 8.35 cm into nanometres.

2 Convert the following lengths into nanometres. Use scientific notation in your answers.

a 1.35 cm

b 4.2 mm

3 A human hair is about 0.050 mm wide, whereas a tobacco mosaic virus is 20 nm wide. How many times larger is the width of a human hair than the width of a tobacco mosaic virus?

4 **a** For the shapes in the following table, calculate the surface area, volume and then surface area to volume ratio.

Shape	Surface area	Volume	$\frac{\text{Surface area}}{\text{Volume}}$
Cube 2 cm × 2 cm × 2 cm			
Sphere of radius 1.38 cm			
Tube (cylinder) Radius of 1 cm Height of 2.82 cm			

Hint: The following formulas may be useful:

- Surface area of a sphere = $4\pi r^2$
- Surface area of a cylinder = $2\pi rh + 2\pi r^2$
- Volume of a sphere = $\frac{4}{3}\pi r^3$
- Volume of a cylinder = $\pi r^2 h$

b Which shape has the greatest surface area to volume ratio?

c Which shape would be the most useful to hold the greatest volume?

d Suggest an application where a big surface area to volume ratio is important and another application where small surface area to volume ratio is important.

5 Explain why the size of nanoparticles makes them useful for transporting medicines into the body.

1.2 The atomic world

The development of advanced materials such as nanoparticles is the result of centuries of scientific discovery. Over time, scientists have gained a deep understanding of the structure of atoms, which are the basic building blocks of **matter**. As scientists' understanding has increased, their ability to control matter on the atomic scale has also improved. However, atoms are too small to be seen with even the most powerful optical microscope. The average human can only see objects that are 0.04 mm wide. Therefore, much of what scientists know about atoms has come from theoretical models and indirect observations.

A scientific **model** is a description that scientists use to represent the important features of what they are trying to describe. They are able to test the consistency of their observations against various predictions of the model.

ATOMIC THEORY

FIGURE 1.2.1 John Dalton (1766–1844) proposed that matter was composed of atoms.

In 1802, an English scientist called John Dalton (Figure 1.2.1) presented the first **atomic theory of matter**. Dalton proposed that all matter is made up of tiny spherical particles, which are indivisible and indestructible.

Dalton also accurately described **elements** as materials containing just one type of atom and **compounds** as materials containing different types of atoms in fixed ratios. Elements cannot be broken down into simpler substances.

Subsequent experiments showed that Dalton's atomic theory of matter was mostly correct. However, scientists now know that atoms are not indivisible or indestructible. Atoms are made up of even smaller **subatomic particles**.

CHEMFILE

Viewing atoms

Dalton's atomic theory of matter assumed that atoms are spherical. However, atoms cannot be seen with conventional microscopes. Therefore, there was no way to confirm the shape of atoms. It wasn't until 1981 that a microscope capable of viewing atoms was developed by IBM researchers Gerd Binnig and Heinrich Rohrer. This type of microscope is known as a **scanning tunnelling microscope (STM)**. Using STMs, scientists confirmed that atoms are indeed spherical.

STMs use an extremely sharp metal tip to detect atoms. The tip is scanned, line-by-line, across the surface of a crystal. As the tip moves, the tip measures minute height differences in the crystal's surface due to the individual atoms. This is similar to the way sight-impaired people use their finger to sense braille on a page. The data from the tip is then sent to a computer that constructs an image of the atoms. An STM image of silicon atoms on the surface of a silicon wafer is shown in Figure 1.2.2.

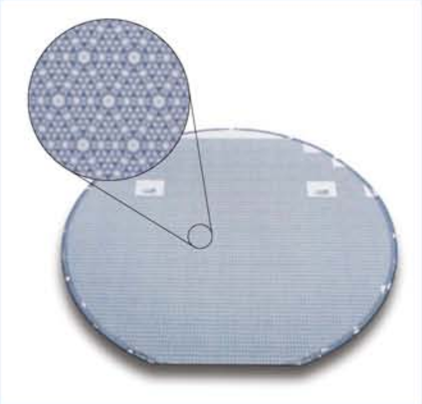
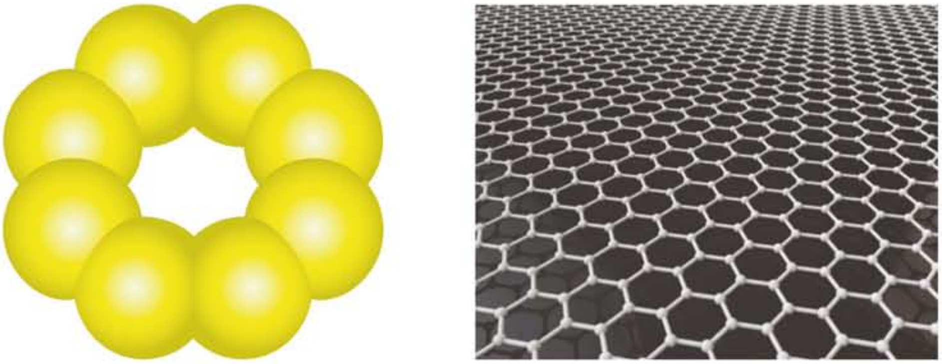


FIGURE 1.2.2 This image of the silicon atoms in a silicon wafer was taken by a scanning tunnelling microscope (STM).

Elements

As Dalton predicted, elements are made of just one type of atom and these atoms are identical. Most non-metallic elements, such as sulfur, form molecules with a definite number of sulfur atoms (8). However, some non-metals form **covalent network lattices** or **giant molecules**. Carbon is an example of such a non-metallic element. Diamond and graphite are both examples of covalent network lattices formed by carbon. Graphene is a giant molecule formed by carbon. (You will learn more about covalent network lattices formed from carbon in Chapter 8.) A comparison of the sizes of two different molecules is shown in Figure 1.2.3.



sulfur molecule

carbon giant molecule

FIGURE 1.2.3 Most non-metal elements, such as sulfur, form molecules. Other elements, such as carbon, form covalent network lattices or giant molecules given by the example here of graphene.

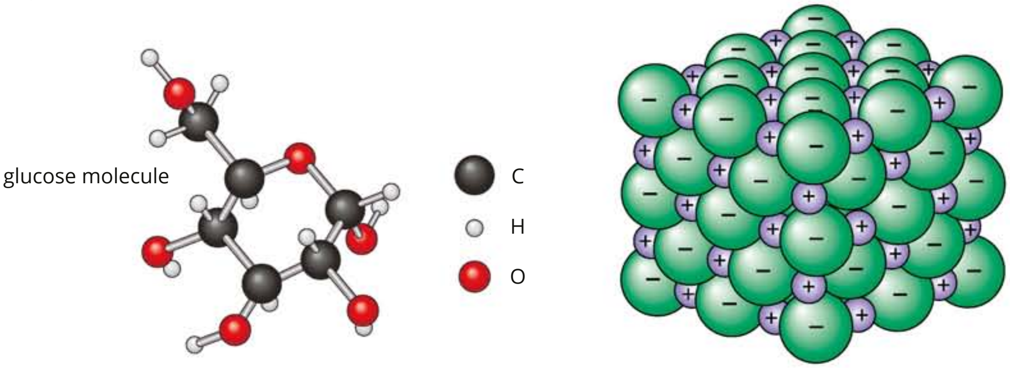
The metallic elements form a different type of network lattice structure, which you will look at in detail in Chapter 3.

Several non-metallic elements are **monatomic**, which means they exist as individual atoms. Monatomic elements are known as the **noble gases** because they are chemically inert (unreactive). The noble gases include helium, neon, argon, krypton, xenon and radon.

ⓘ Monatomic elements are those made up of only one atom. The prefix mon- (or mono-) is frequently used in science. It means only one, or single.

Compounds

Dalton also predicted correctly that different types of atoms could combine to form new substances. These substances are known as compounds. The atoms in compounds can also form molecules or large networks of atoms as shown in Figure 1.2.4.



glucose molecule

sodium chloride lattice

FIGURE 1.2.4 Compounds can be made up of molecules, like glucose, which contains carbon, oxygen and hydrogen atoms, or lattices like sodium chloride (table salt).

FIGURE 1.2.5 The red powder in this test-tube is mercury(II) oxide (HgO). If you look closely at the test-tube, you will see beads of liquid mercury forming from the decomposition of the compound.

To determine whether a pure substance is an element or a compound, you must determine if the substance can be broken down into simpler substances. For example, when heated, mercury(II) oxide (HgO) decomposes to liquid mercury (Hg) and oxygen gas (O_2). If it was not a compound, the mercury(II) oxide would not break down. The appearances of the compound mercury(II) oxide and the resulting mercury element can be seen in Figure 1.2.5. As oxygen is a colourless gas, you cannot see it. Oxygen is detected by placing a lit splint at the top of the test-tube. When oxygen is present, the splint ignites with a large flame.

Molecules are formed when two or more atoms join together chemically. Compounds contain different types of atoms in definite proportions.

ELEMENT SYMBOLS

Scientists have discovered 118 different elements. Only about 98 of these occur in nature (the exact number is debatable). The other elements have only been observed in the laboratory.

Each element has a unique name and **chemical symbol**. Table 1.2.1 lists the chemical symbols of some of the most common elements.

TABLE 1.2.1 Chemical symbols and names of some of the most common elements

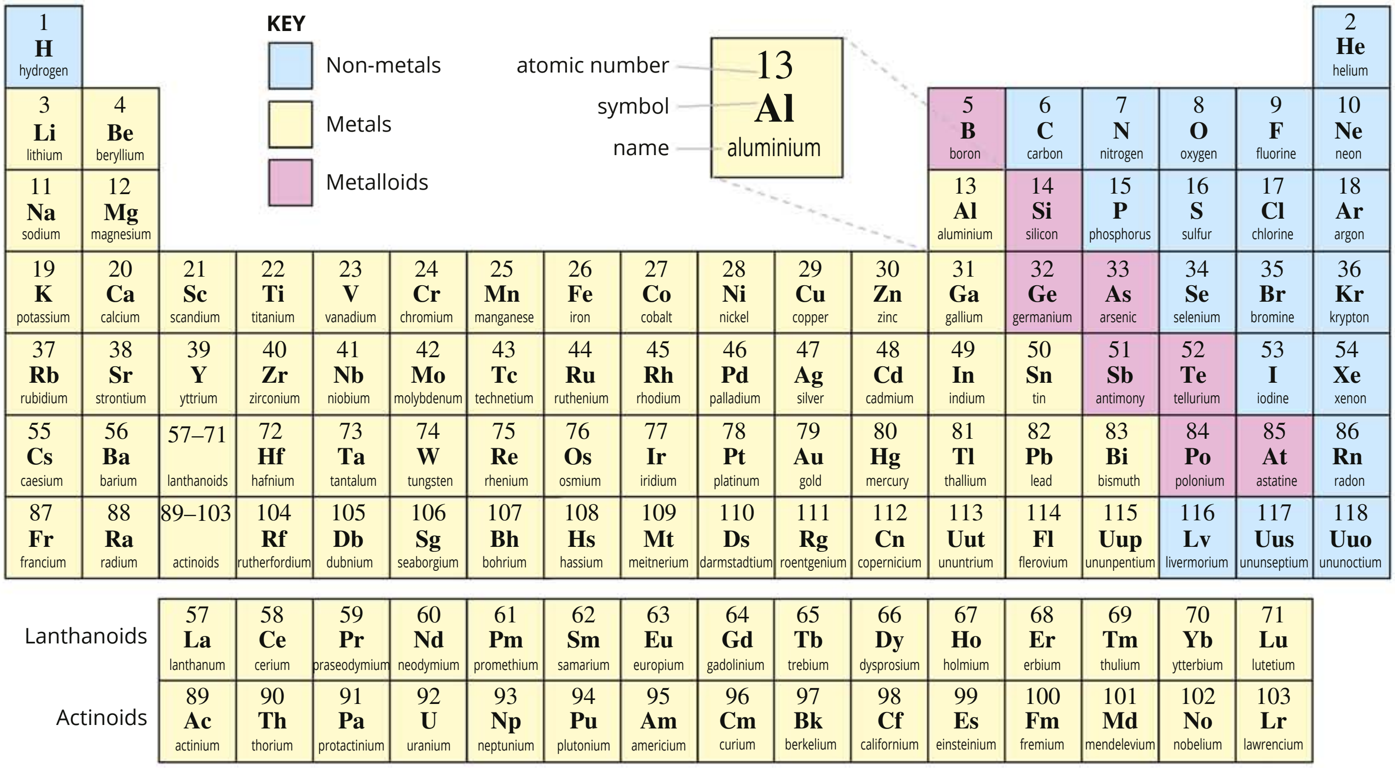
Element	Symbol	Element	Symbol
Aluminium	Al	Mercury	Hg
Argon	Ar	Nitrogen	N
Carbon	C	Oxygen	O
Chlorine	Cl	Potassium	K
Copper	Cu	Silver	Ag
Hydrogen	H	Sodium	Na
Iron	Fe	Uranium	U

The chemical symbol is usually made up of one or two letters. The first letter is always capitalised and subsequent letters are always lower case.

In many cases, the chemical symbol corresponds to the name of the element. For example, nitrogen has the chemical symbol N, chlorine has the chemical symbol Cl and uranium has the chemical symbol U.

However, some chemical symbols do not correspond to the name of the element. For example, sodium has the chemical symbol Na, potassium has the chemical symbol K and iron has the chemical symbol Fe. This is because the chemical symbols have been derived from the Latin or Greek names of the elements. In Latin, sodium is known as *natrium*, potassium is known as *kalium* and iron is known as *ferrum*.

The atomic symbols are usually displayed in a **periodic table** as shown in Figure 1.2.6. The periodic table helps to group elements that have similar chemical properties. You will learn more about the periodic table in Chapter 2.



KEY

🟦 Non-metals

🟨 Metals

🟪 Metalloids

atomic number — 13

symbol — Al

name — aluminium

1 H hydrogen																	2 He helium
3 Li lithium	4 Be beryllium											5 B boron	6 C carbon	7 N nitrogen	8 O oxygen	9 F fluorine	10 Ne neon
11 Na sodium	12 Mg magnesium											13 Al aluminium	14 Si silicon	15 P phosphorus	16 S sulfur	17 Cl chlorine	18 Ar argon
19 K potassium	20 Ca calcium	21 Sc scandium	22 Ti titanium	23 V vanadium	24 Cr chromium	25 Mn manganese	26 Fe iron	27 Co cobalt	28 Ni nickel	29 Cu copper	30 Zn zinc	31 Ga gallium	32 Ge germanium	33 As arsenic	34 Se selenium	35 Br bromine	36 Kr krypton
37 Rb rubidium	38 Sr strontium	39 Y yttrium	40 Zr zirconium	41 Nb niobium	42 Mo molybdenum	43 Tc technetium	44 Ru ruthenium	45 Rh rhodium	46 Pd palladium	47 Ag silver	48 Cd cadmium	49 In indium	50 Sn tin	51 Sb antimony	52 Te tellurium	53 I iodine	54 Xe xenon
55 Cs caesium	56 Ba barium	57–71 lanthanoids	72 Hf hafnium	73 Ta tantalum	74 W tungsten	75 Re rhenium	76 Os osmium	77 Ir iridium	78 Pt platinum	79 Au gold	80 Hg mercury	81 Tl thallium	82 Pb lead	83 Bi bismuth	84 Po polonium	85 At astatine	86 Rn radon
87 Fr francium	88 Ra radium	89–103 actinoids	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

Lanthanoids	57 La lanthanum	58 Ce cerium	59 Pr praseodymium	60 Nd neodymium	61 Pm promethium	62 Sm samarium	63 Eu europium	64 Gd gadolinium	65 Tb trebium	66 Dy dysprosium	67 Ho holmium	68 Er erbium	69 Tm thulium	70 Yb ytterbium	71 Lu lutetium
Actinoids	89 Ac actinium	90 Th thorium	91 Pa protactinium	92 U uranium	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fremium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium

FIGURE 1.2.6 The periodic table groups the chemical elements according to their chemical properties.

1.2 Review

SUMMARY

- All substances are made up of atoms.
- The atoms in elements can exist as individual atoms (monatomic), molecules, giant molecules or lattices.
- The atoms in compounds can exist as molecules or large networks of atoms.
- Every element has a chemical symbol that is usually made up of one or two letters. The first letter is capitalised and the second letter is lower case.
- Elements are organised into the periodic table.

KEY QUESTIONS

1 What special name is given to the group of elements that are monatomic at room temperature?

2 Classify each of the following as elements or compounds.

- **a** Copper
- **b** Sulfur
- **c** Water
- **d** Carbon dioxide
- **e** Diamond
- **f** Sodium chloride
- **g** Gold
- **h** Silicon carbide

3 Explain the difference between an element and a compound.

4 Identify the common name of each of the following elements from its non-English name.

- **a** Ferrum
- **b** Kalium
- **c** Wolfram
- **d** Plumbum

1.3 Inside atoms

FIGURE 1.3.1 A simplified model of the atom. The central glow represents the nucleus where the protons and neutrons are housed. The nucleus is surrounded by a cloud of electrons that orbit the nucleus.

Until the mid-1800s, scientists believed that atoms were hard spheres that couldn't be broken down into smaller parts. By the end of the 1800s, there was increasing evidence to suggest that atoms are made up of smaller particles. This led to a series of atomic models that attempted to explain the structure of atoms.

STRUCTURE OF ATOMS

The current model of the atom is based on the work of many scientists. All atoms are made up of a small, positively charged **nucleus** surrounded by a much larger cloud of negatively charged **electrons** as shown in Figure 1.3.1. The nucleus is in turn made up of two subatomic particles—**protons** and **neutrons**. The protons are positively charged and the neutrons have no charge.

Electrons

Electrons are negatively charged particles. You can imagine them forming a cloud of negative charge around the nucleus. This cloud gives the atom its size and volume.

An electron is approximately 1800 times smaller than a proton or neutron. Therefore, electrons contribute very little to the total mass of an atom. However, the space occupied by the cloud of electrons is 10 000–100 000 times larger than the nucleus.

Negative particles attract positive particles. This is called **electrostatic attraction**. Electrons are bound to the nucleus by the electrostatic attraction to the protons within the nucleus. The charge on an electron is equal but opposite to the charge on a proton. Electrons are said to have a charge of –1 whereas protons have a charge of +1.

In some circumstances, electrons can be easily removed from an atom. For example, when you rub a rubber balloon on a woollen jumper or dry hair, electrons are transferred to the balloon and the balloon develops a negative charge. The negative charge is observed as an electrostatic force that can stick the balloon to a wall or even move an aluminium can. You will look more closely at the removal of electrons from atoms when looking at ionic compounds in Chapter 4.

The electricity that powers lights and appliances is the result of electrons moving in a current through wires. Sparks and lightning are also caused by electrons moving through air.

CHEMFILE

Discovering the electron

In the 1850s, a series of experiments was carried out in which an electric current was passed through different gases in sealed tubes at very low pressures. The tubes were called cathode ray tubes.

When a high voltage was applied, the cathode ray tubes glowed with a coloured light and the glass on the wall opposite the negative electrode became fluorescent. This is shown in Figure 1.3.2.

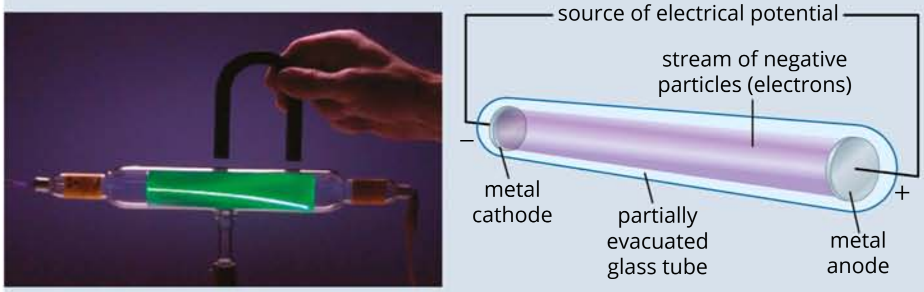


FIGURE 1.3.2 This glass tube contains a gas at low pressure. When an electric potential is applied, a green glow is observed on a phosphorescent screen.

In 1858, German physicist Julius Plucker conducted these experiments and suggested that the fluorescence was caused by invisible rays coming from the negative cathode. He called these cathode rays.

When an electric field was applied at right angles near the cathode, the position of the fluorescence moved away from the negative pole of the electric field. This can be seen in Figure 1.3.3.

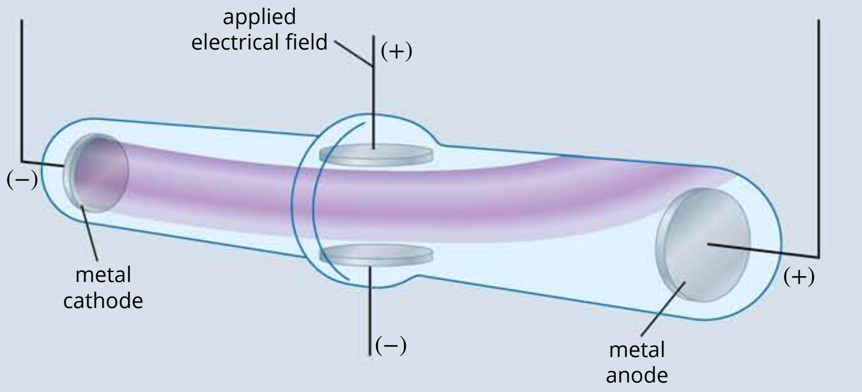


FIGURE 1.3.3 Cathode rays are deflected by an applied electric field.

In the late 1890s, English physicist Joseph John Thomson repeated these experiments, using different metals as electrodes and different gases in the tubes. In every case, the results were the same. The properties of the cathode rays were independent of both the gas and the metal. From his experiments, Thomson deduced that:

- the rays were a stream of particles
- the particles came from the negative electrode (cathode) and were negatively charged
- the particles must be found in all matter and therefore were subatomic particles
- atoms must also contain positive subatomic particles since atoms have no overall charge.

Thomson's research laid the foundation for other scientists to build the modern model of the atom. For his discovery of the electron, Thomson was awarded the 1906 Nobel Prize in Physics.

The nucleus

The nucleus of an atom is approximately 10 000–100 000 times smaller than the size of the atom. To put this in perspective, if an atom were the size of the Melbourne Cricket Ground (Figure 1.3.4), then the nucleus would be about the size of a pea. Nonetheless, the nucleus contributes around 99.97% of the atom's mass. This means that atomic nuclei are extremely dense.

The subatomic particles in the nucleus, the protons and neutrons, are referred to collectively as **nucleons**. Protons are positively charged particles with a mass of approximately 1.673×10^{-27} kg. Neutrons are almost identical in mass.

Table 1.3.1 summaries the properties of protons, neutrons and electrons.

TABLE 1.3.1 Properties of the subatomic particles

Particle	Symbol	Charge	Size relative to a proton	Mass (kg)
Proton	p	+1	1	1.673×10^{-27}
Neutron	n	0	1	1.675×10^{-27}
Electron	e	–1	$\frac{1}{1800}$	9.109×10^{-31}

FIGURE 1.3.4 If an atom were the size of the Melbourne Cricket Ground, then the nucleus would be the size of a pea.

CHEMFILE

Discovering the nucleus

The secrets of the nucleus were unlocked by New Zealand physicist Ernest Rutherford. Between 1899 and 1911, Rutherford conducted experiments in which he fired a beam of **alpha particles** (positively charged particles) at a piece of extremely thin gold foil. The vast majority of the alpha particles passed straight through the gold foil. From this observation, Rutherford deduced that the gold atoms were made up almost entirely of empty space. Figure 1.3.5 shows the apparatus and observations of Rutherford's experiments.

However, Rutherford was surprised to discover that occasionally, an alpha particle would bounce straight back. He stated: 'It was about as incredible as if you had fired a 16-inch shell at a piece of tissue paper and it came back and hit you!'

This remarkable observation suggested that the centre of the atom is very small, positive and extremely dense. This central region was later named the nucleus.

Rutherford proposed that the nucleus contained positive particles (because the positive alpha particles were deflected or rebounded), which he termed 'protons'. James Chadwick confirmed the existence of neutrons in 1932.

Rutherford's model (1911) proposed the following.

- Most of the mass of an atom, and all of the positive charge must be located in a tiny central region called the nucleus.
- Most of the volume of an atom is empty space, occupied only by electrons.
- The electrons move in circular orbits around the nucleus.
- The force of the attraction between the positive nucleus and the negative electrons is electrostatic.

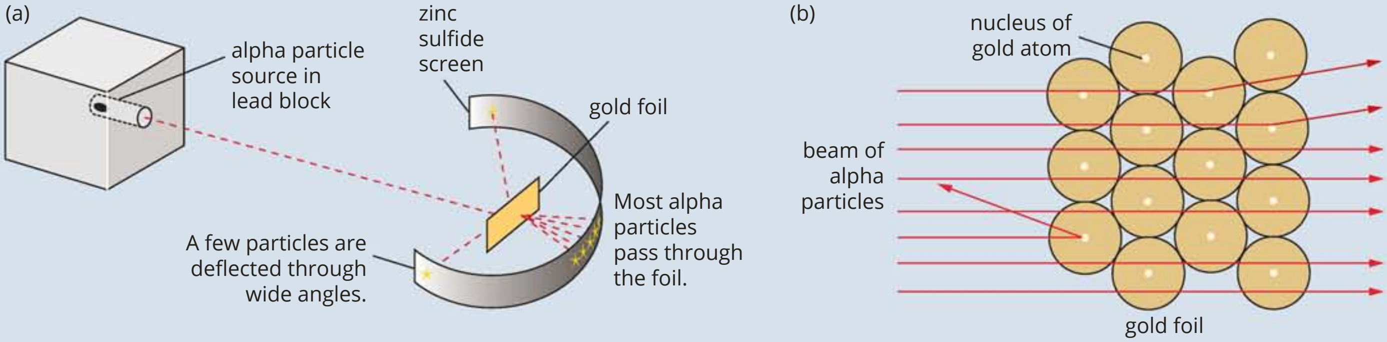


FIGURE 1.3.5 (a) Ernest Rutherford's apparatus that provided evidence for the discovery of nuclei in atoms. (b) Only those alpha particles that closely approach the nuclei in the gold foil are deflected significantly. Most particles pass almost directly through the foil.

1.3 Review

SUMMARY

- All atoms are composed of a small, positively charged nucleus surrounded by a negatively charged cloud of electrons.
- The mass of an atom is mostly determined by the mass of the nucleus, while the size of an atom is determined by the cloud of electrons.
- The nucleus is made up of two subatomic particles—protons and neutrons. These particles are referred to as nucleons.
- Protons have a positive charge, electrons have a negative charge and neutrons have no charge.
- Protons and neutrons are similar in size and mass while electrons are approximately 1800 times smaller.
- The charges on protons and electrons are equal but opposite.

KEY QUESTIONS

1 How many times larger is the atom compared to its nucleus?

2 What subatomic particles make up the most mass of an atom and where are they found?

3 How are electrons held within the cloud surrounding the nucleus?

1.4 Classifying atoms

DIFFERENT TYPES OF ATOMS

Each element is made up of one type of atom. The type of atom that makes up each element is determined by the number of protons in the nucleus.

The number of protons in an atom's nucleus is known as the **atomic number** and is represented by the symbol Z.

All atoms that belong to the same element must have the same number of protons and therefore have the same atomic number, Z. For example, all hydrogen atoms have $Z = 1$, all carbon atoms have $Z = 6$ and all gold atoms have $Z = 79$.

The number of protons and neutrons in the nucleus is known as the **mass number** and is represented by the symbol A. The mass number represents the total mass of the nucleus.

As all atoms are electrically neutral, the number of protons in an atom is equal to the number of electrons in an atom. The atomic number therefore tells you both the number of protons and the number of electrons. For example, carbon atoms, with $Z = 6$, have six protons and six electrons.

STRUCTURE OF ATOMS

The number of protons, neutrons and electrons defines the basic structure of an atom. The standard way of representing an atom is to show its atomic and mass numbers as shown in Figure 1.4.1.

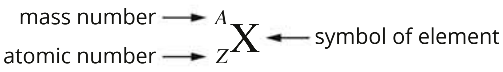


FIGURE 1.4.1 The standard way of representing an atom to show its atomic number and mass number.

For an aluminium atom, this would be written as shown in Figure 1.4.2.

$$^{27}_{13}\text{Al}$$

FIGURE 1.4.2 This representation of an aluminium atom indicates the number of protons, neutrons and electrons in the atom.

From this representation, you can determine that the:

- number of protons is 13 because the number of protons is equal to the atomic number (Z)
- number of neutrons is 14 because the number of neutrons plus the number of protons is equal to the mass number. Therefore you can subtract the atomic number from the mass number to determine the number of neutrons ($A - Z$)
- number of electrons is 13 because atoms have no overall charge. Therefore the number of electrons must equal the number of protons.

Worked example 1.4.1

CALCULATING THE NUMBER OF SUBATOMIC PARTICLES

Calculate the number of protons, neutrons and electrons for the atom with this atomic symbol:

$${}^{40}_{18}\text{Ar}$$

Thinking	Working
The atomic number is equal to the number of protons.	The number of protons = Z = 18
Find the number of neutrons. Number of neutrons = mass number – atomic number	The number of neutrons = $A - Z$ = 40 – 18 = 22
Find the number of electrons. The number of electrons is equal to the atomic number because the total negative charge is equal to the total positive charge.	Number of electrons = Z = 18

Worked example: Try yourself 1.4.1

CALCULATING THE NUMBER OF SUBATOMIC PARTICLES

Calculate the number of protons, neutrons and electrons for the atom with this atomic symbol:

$${}^{235}_{92}\text{U}$$

ISOTOPES

All atoms that belong to the same element have the same number of protons in the nucleus and therefore the same atomic number, Z. However, not all atoms that belong to the same element have the same mass number, A. For example, hydrogen atoms can have mass numbers of 1, 2 or 3. In other words, hydrogen atoms may contain just a single proton, a proton and a neutron, or a proton and two neutrons as shown in Figure 1.4.3. Atoms that have the same number of protons (atomic number) but different numbers of neutrons (and therefore different mass numbers) are known as **isotopes**.

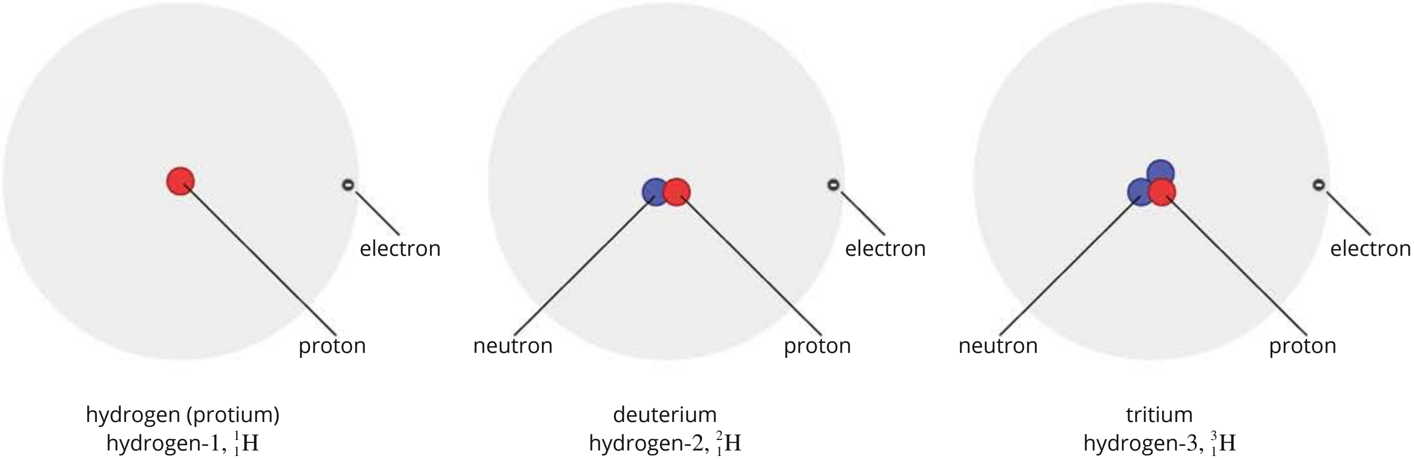


FIGURE 1.4.3 The three isotopes of hydrogen are given special names. A hydrogen atom with just one proton in its nucleus is known as hydrogen or protium. A hydrogen atom with one proton and one neutron is known as deuterium. A hydrogen atom with one proton and two neutrons is known as tritium.

Carbon also has three naturally occurring isotopes. These three isotopes are known as carbon-12, carbon-13 and carbon-14. Carbon-12 atoms have a mass number of 12, carbon-13 atoms have a mass number of 13 and carbon-14 atoms have a mass number of 14. In the 1950s and 1960s, nuclear weapons testing caused a spike in carbon-14 in the atmosphere. This has been declining in the last 50 years. These three carbon isotopes can be represented as:

$^{12}_{6}\mathrm{C}$	$^{13}_{6}\mathrm{C}$	$^{14}_{6}\mathrm{C}$
carbon–12	carbon–13	carbon–14

Isotopes have identical chemical properties but different physical properties such as mass and density. In particular, some isotopes are **radioactive**.

CHEMFILE

Isotopes

In nature, different elements have different numbers of isotopes. Gold has only one isotope, whereas lead has four and mercury seven isotopes.

CHEMISTRY IN ACTION

Carbon-14 and the war against poachers

Isotopes are important in the war against ivory poaching in Africa. Living organisms take up carbon-14 from the environment. Over time, the amount of carbon-14 in tissues of plants and animals decreases as the isotope radioactively decays. By looking at the levels of the carbon-14 isotope in elephant tusks and ivory (Figure 1.4.4), scientists can determine how old they are.

If the authorities know the age of the ivory, then legal action can be taken against the poachers and sellers of the product. Ivory products prior to 1989 are allowed to be traded. Since 1989, the trade on ivory has been made illegal world-wide.

FIGURE 1.4.4 These tusks are from African elephants killed for their ivory.

1.4 Review

SUMMARY

- You can determine the number of subatomic particles in an atom from an element's atomic number and mass number.
- The atomic number indicates how many protons or electrons an atom has.
- The mass number tells you how many protons and neutrons are in the nucleus of the atom.
- Isotopes are atoms with the same atomic number but different mass numbers, i.e. they have the same number of protons but different numbers of neutrons.
- Isotopes have the same chemical properties but different physical properties such as mass, density and radioactivity.

KEY QUESTIONS

1. What term is given to the number of protons and neutrons in the nucleus of an atom?
2. Calculate the numbers of protons, neutrons and electrons in the atom $^{31}_{15}\mathrm{P}$.
3. What is the correct name of the element that has an atom with seven protons and eight neutrons?
4. Explain the similarities and differences between isotopes of the same element.
5. How many more neutrons does an atom of carbon-14 have than an atom of the carbon-12 isotope?

1.5 Electronic structure of atoms

When fireworks explode, they create a spectacular show of coloured lights (Figure 1.5.1). The light is produced by metal atoms that have been heated by the explosion. These coloured lights posed a significant problem for early scientists. The models the scientists were using could not explain the source of the light. However, the light was a clue that ultimately led to a better understanding of the arrangement of electrons in atoms.

FIGURE 1.5.1 The spectacular colours in this New Year's Eve fireworks display are emitted by metal atoms that have been heated to very high temperatures.

EMISSION SPECTRA

When atoms are heated, they give off electromagnetic radiation or light. If the light passes through a prism, it produces a spectrum with a black background and a number of coloured lines. Figure 1.5.2 shows the apparatus used to produce these spectra.

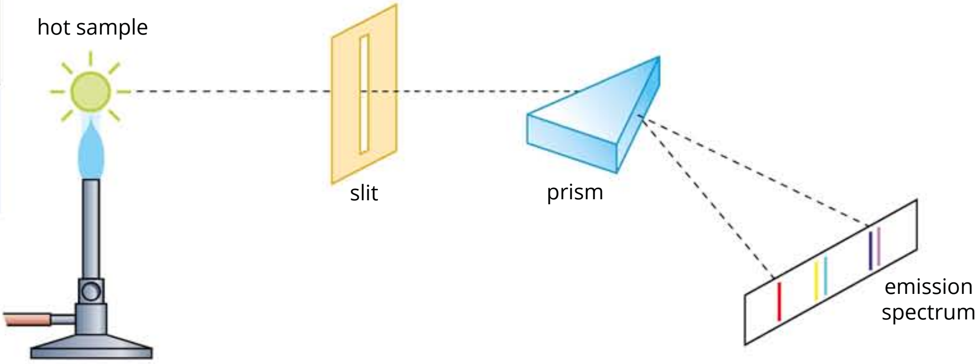


FIGURE 1.5.2 The apparatus used to analyse the light given out when an element is heated. The coloured lines are called an emission spectrum.

These spectra are known as line spectra or **emission spectra** and are related to the electronic structure within the atoms. Each emission spectrum is unique for a particular element and can be used to identify different elements.

The line spectrum produced by helium is shown in Figure 1.5.3.

FIGURE 1.5.3 The emission spectrum of helium is made up of lines ranging from violet to red in colour.

CHEMFILE

How helium got its name

Helium was discovered on the Sun before being discovered on Earth. The French astronomer Jules Janssen discovered helium in 1868 while studying the light from a solar eclipse in India similar to the solar eclipse shown in Figure 1.5.4. Although the spectrum showed the full range of colours, the bright yellow line in the helium spectrum stood out. The line could not be matched to the line spectra of any of the known elements. It was concluded that the line belonged to an unknown element. This element was named helium after the Greek Sun god, Helios.

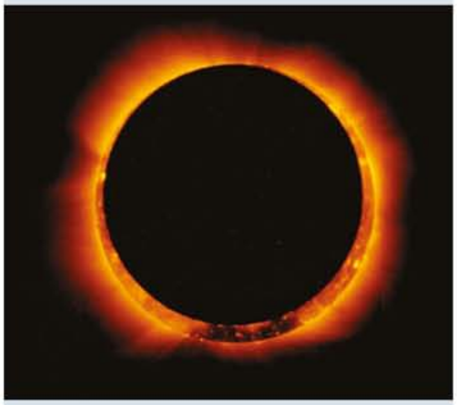


FIGURE 1.5.4 The emission spectrum of helium was first detected in sunlight of a solar eclipse like the one shown here.

Each line in the spectrum corresponds to light of a different energy. Violet lines correspond to light with high energies. As the colour of the light changes to blue, green, yellow and orange, the energy of the light decreases. Red light is the lowest energy light visible to the human eye.

Information from emission spectra

Emission spectra give clues about the electronic structure of atoms. Two important clues are:

1. atoms of the same element produce identical line spectra
2. each element has a unique line spectrum and therefore a unique electronic structure.

THE BOHR MODEL

In 1913, Niels Bohr developed a new model of the hydrogen atom that explained emission spectra. The **Bohr model** proposed the following.

- Electrons revolve around the nucleus in fixed, circular orbits.
- The electrons' orbits correspond to specific **energy levels** in the atom.
- Electrons can only occupy fixed energy levels and cannot exist between two energy levels.
- Orbits of larger radii correspond to energy levels of higher energy.

In the Bohr model, it is possible for electrons to move between the energy levels by absorbing or emitting energy in the form of light. Bohr's model (Figure 1.5.5) gave close agreement between the calculated energies for lines in the hydrogen spectrum and the observed values in the spectrum.

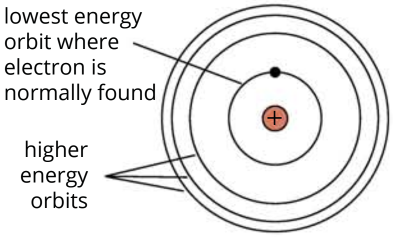


FIGURE 1.5.5 The Bohr model of a hydrogen atom. Bohr suggested that electrons moved in orbits of particular energies.

Electron shells

Scientists quickly extended Bohr's model of the hydrogen atom to other atoms. Scientists proposed that electrons were grouped in different energy levels, called **electron shells.** The electron shells are labelled with the number $n = 1, 2, 3 \ldots$, as shown in Figure 1.5.6.

The orbit in which an electron moved depended on the energy of the electron; electrons with low energy are in orbits close to the nucleus while high-energy electrons are in outer orbits.

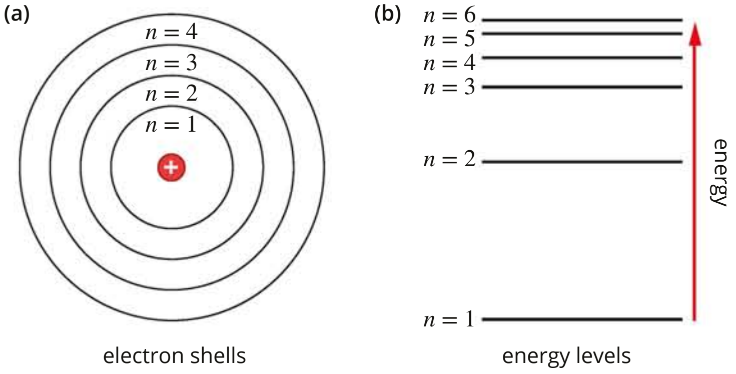


FIGURE 1.5.6 (a) The electron shells of an atom (*n*) are labelled using integers. The first shell is the shell closest to the nucleus and the radii of the shells increase as the shell number increases. (b) Each shell corresponds to an energy level that electrons can occupy. The first shell has the lowest energy and the energy increases as the shell number increases.

The lowest energy shell is the shell closest to the nucleus and is labelled $n = 1$. Shells with higher values of n correspond to higher energy levels. As the values of n increase, the energy levels get closer together.

Emission spectra and the shell model

Heating an element can cause an electron to absorb energy and jump to a higher energy state. Shortly afterwards, the electron returns to the lower energy state, releasing a fixed amount of energy as light. The electron can return in a number of different ways, some of which are shown in Figure 1.5.7 as coloured arrows. Each one of the particular pathways produces light of a particular colour in the emission spectrum.

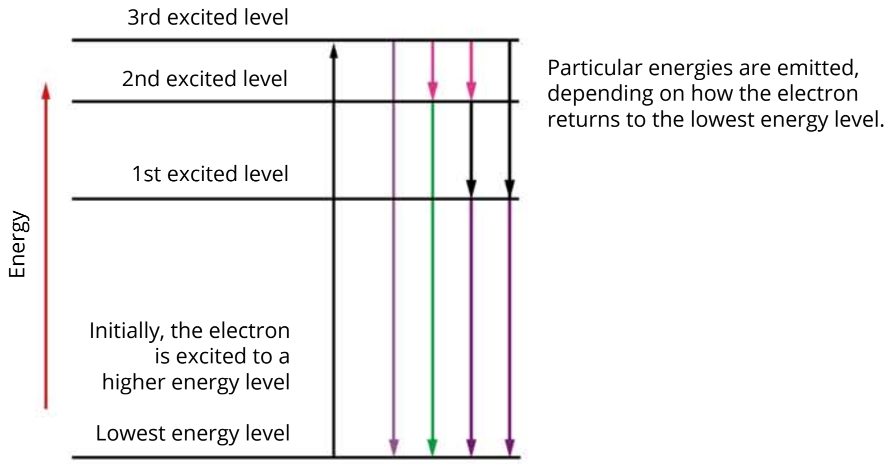


FIGURE 1.5.7 Emission of energy as electrons move from a higher to a lower energy state.

Consider a hydrogen atom with one proton and one electron. Usually, the electron exists in the $n = 1$ shell. This is the lowest energy state of the atom and is called the **ground state**.

When the hydrogen atom is heated, the electron absorbs energy and jumps to a higher energy level. This is known as an **excited state**.

Shortly afterwards, the electron returns to the ground state. The electron may return directly to the ground state or may move to other energy levels before returning to the ground state. For example, an electron in the $n = 4$ shell may move to the $n = 2$ shell before returning to the $n = 1$ ground state.

As the electron falls to a lower energy shell, it emits energy in the form of light. This energy is exactly equal to the energy difference between the two energy levels. Each transition corresponds to a specific energy of light and therefore one line in the line spectrum of hydrogen shown in Figure 1.5.8.

FIGURE 1.5.8 The emission spectrum of the hydrogen atom has four lines in the visible range—violet, blue, green and red.

1.5 Review

SUMMARY

- When atoms are heated, they emit electromagnetic radiation or light.
- When the light is passed through a prism, it produces a spectrum made up of lines of different colours. These spectra are known as emission or line spectra.
- The emission spectra produced by atoms of the same element are identical.
- Each element has a unique emission spectrum.
- The Bohr model of the atom was the first atomic model to explain the origin of emission spectra.
- The Bohr model assumes that electrons can only exist in fixed, circular orbits of specific energies. These orbits later came to be known as energy levels or shells.
- When an electron absorbs energy (e.g. heat or light), the electron can jump from one shell to a higher energy shell.
- When an electron falls from a higher energy shell to a lower energy shell, it emits energy in the form of light.
- Each line in the emission spectrum corresponds to a specific electron transition between two shells.

KEY QUESTIONS

1. Explain how emission spectra are evidence for electron shells in the Bohr model.
2. What four assumptions did Bohr make about the electronic structure of the atom?
3. What form of energy is emitted when an electron moves from a higher energy shell to a lower energy shell?

1.6 Electronic configuration and the shell model

Bohr's model of the hydrogen atom gave close agreement between his calculated energies for lines in hydrogen's emission spectra and the observed values. In Bohr's model, electrons are confined to specific energy levels or shells. In this section, you will look at how scientists were able to determine the electronic arrangement in other atoms.

IONISATION ENERGY

Evidence for the existence of energy levels in atoms was obtained from studies of successive **ionisation energies** in atoms of different elements. The ionisation energy is the energy needed to remove an electron from an atom. For example, a sodium atom contains 11 electrons. As each successive electron is removed, these ionisation energies can be measured. Figure 1.6.1 shows that the first electron to be removed has the lowest ionisation energy and is therefore the easiest to remove. The following eight electrons are slightly more difficult, and finally, the last two require substantially more energy to remove.

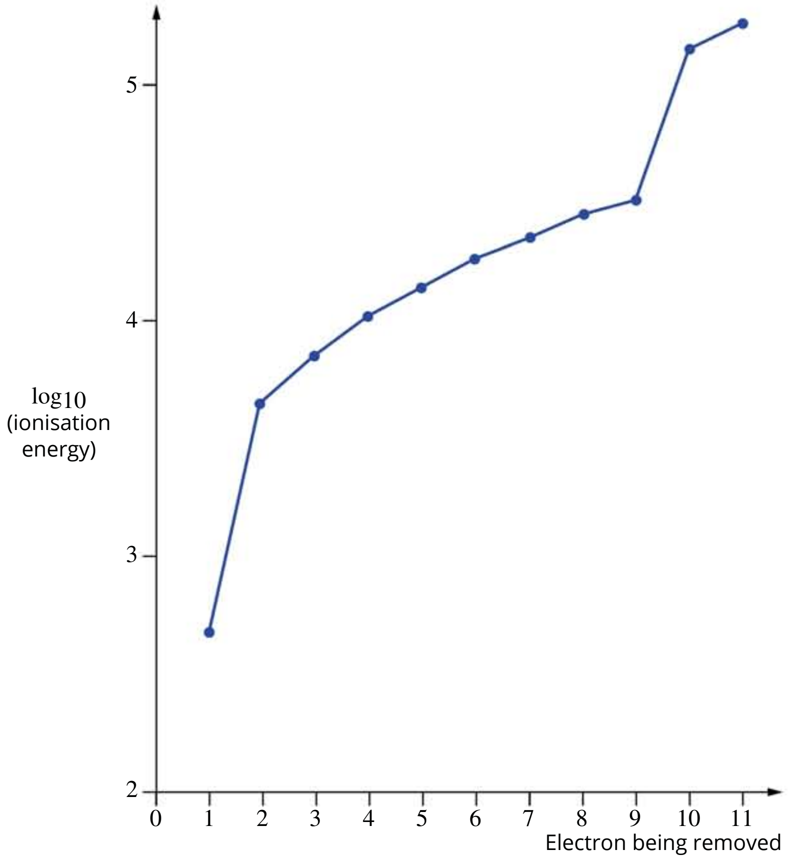


FIGURE 1.6.1 Graph of the ionisation energies of a sodium atom. (The logarithm of ionisation energy is used to provide a more convenient vertical scale.)

Once scientists had determined the successive ionisation energies for a large number of elements, they concluded that electrons were grouped in different energy levels, which they called electron shells. Electrons in the same shell:

- are about the same distance from the nucleus
- have about the same energy.

If an atom has six electrons, then each can be removed in turn. The electron that is least strongly attracted to the nucleus will be removed most easily. The amount of energy this requires is known as the first ionisation energy. Each one of the remaining five electrons will have a specific ionisation energy. The second ionisation energy will be greater than the first. The third will be greater than the second and so on.

The different energy levels or shells can hold different numbers of electrons. The arrangement of these electrons around the nucleus is called the **electronic configuration**.

ELECTRONIC CONFIGURATION IN SHELLS

In all atoms, the electrons are as close to the nucleus as possible. This means that electrons will generally occupy inner shells before outer shells. For example, an atom of lithium has three electrons. Two electrons will occupy the first shell as that is all it can hold. The third electron is in the second shell.

A Bohr diagram is a simple diagram that shows the arrangement of electrons around the nucleus. In such diagrams, only the shells that are occupied are drawn. The Bohr diagram for lithium is shown in Figure 1.6.2.

It is possible to determine the basic electronic configuration of any atom by applying the following rules.

- Rule 1. Each shell can only contain a maximum number of electrons. Table 1.6.1 shows how many electrons can occupy the first four shells.

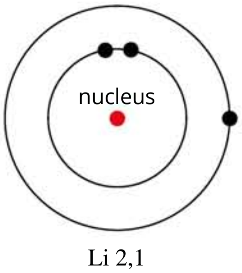


FIGURE 1.6.2 The Bohr diagram for the lithium atom with three electrons.

TABLE 1.6.1 The number of electrons held by each shell of an atom. Shell 1 is the shell closest to the nucleus.

Electron shell (*n*)	Maximum number of electrons
1	2
2	8
3	18
4	32
n	$2n^2$

- Rule 2. Lower energy shells fill before higher energy shells.

Using these rules, it is possible to accurately predict the electronic configuration of the first 18 elements.

Oxygen has eight electrons, so the first shell will hold two electrons and the second shell will hold six electrons. Its electronic configuration is therefore 2,6.

Figure 1.6.3 shows the electronic configuration of a sodium atom, which has 11 electrons. The first two electrons fill the first shell. Then the next eight electrons fill the second shell. The remaining electron occupies the third shell. The electronic configuration for this atom is written as 2,8,1 to indicate the arrangement of electrons in each shell.

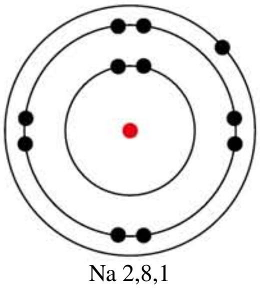


FIGURE 1.6.3 The electronic configuration of a sodium atom.

- Rule 3. Electron shells fill in a particular order. The first two electrons go into the first shell. The next eight electrons go into the second shell. The third shell can hold 18 electrons but once it contains eight electrons, the next two electrons go into the fourth shell. Only then does the third shell fill up.

A potassium atom contains 19 electrons. The first shell holds two electrons. The second shell holds eight and the third shell holds eight. The fourth shell will hold one electron. This arrangement can be seen in Figure 1.6.4.

This pattern of shell filling continues until the third shell contains the maximum number of electrons it can hold (18). Therefore, an atom with 30 electrons has electronic configuration of 2,8,18,2.

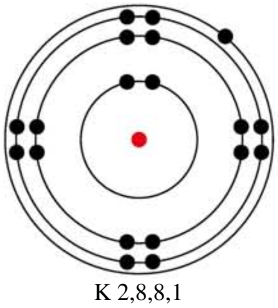


FIGURE 1.6.4 The electronic configuration of potassium.

Worked example 1.6.1

ELECTRONIC CONFIGURATION FOR UP TO 36 ELECTRONS

Apply the rules of the shell model to determine the electronic configuration of an atom with 28 electrons.

Thinking	**Working**
Recall the maximum number of electrons that each shell can hold.	Shell (*n*) Maximum number of electrons 1 2 2 8 3 18 4 32
Place the first 18 electrons in the shells from the lowest energy to the highest energy. Do not exceed the maximum number of electrons allowed.	Shell (*n*) Electrons in atom 1 2 2 8 3 8 4
Place the next two electrons in the fourth shell.	Shell (*n*) Electrons in atom 1 2 2 8 3 8 4 2
Continue filling the third shell until it holds up to 18 electrons. Put any remaining electrons in the fourth shell.	Shell (*n*) Electrons in atom 1 2 2 8 3 16 4 2 The 8 remaining electrons from the previous step have gone into the third shell.
Write the electronic configuration by listing the number of electrons in each shell separated by commas.	The electronic configuration is: 2,8,16,2

Worked example: Try yourself 1.6.1

ELECTRONIC CONFIGURATIONS FOR UP TO 36 ELECTRONS

Apply the rules of the shell model to determine the electronic configuration of an atom with 34 electrons.

VALENCE ELECTRONS

The **outermost shell** of an atom is known as the atom's **valence shell**. The electrons in the outer shell are called **valence electrons**. These electrons require the least amount of energy to be removed. The valence electrons are involved in chemical reactions. Consequently, if you know the number of valence electrons in the atoms of an element, then you can predict the chemical properties of the element.

In Chapters 3, 4 and 6, you will learn about how atoms tend to lose, gain or share valence electrons in order to achieve eight electrons in their outer shell when they are involved in chemical reactions. This is known as the **octet rule**.

Worked example 1.6.2

CALCULATING THE NUMBER OF VALENCE ELECTRONS IN AN ATOM

How many valence electrons are present in an atom of magnesium, which has an atomic number of 12?

Thinking	**Working**
Recall the maximum number of electrons that each shell can hold.	Shell (*n*) Maximum number of electrons 1 2 2 8 3 18 4 32
Place 12 electrons in the shells from the lowest energy to the highest energy. Do not exceed the maximum number of electrons allowed.	Shell (*n*) Electrons in atom 1 2 2 8 3 2 4
Write the electronic configuration by listing the number of electrons in each shell separated by commas.	The electronic configuration is: 2,8,2
Determine the number of electrons in the outer shell or valence shell.	The number of electrons in the valence shell is 2.

Worked example: Try yourself 1.6.2

CALCULATING THE NUMBER OF VALENCE ELECTRONS IN AN ATOM

How many valence electrons are present in an atom of sulfur, which has an atomic number of 16?

1.6 Review

SUMMARY

- The electronic configuration of an atom indicates the arrangement of electrons in each shell.
- Bohr diagrams can be used to show the electronic configurations of atoms.
- Each shell can have a maximum number of electrons. This is summarised in Table 1.6.2.

TABLE 1.6.2 Number of electrons in each electron shell

Electron shell (*n*)	Maximum number of electrons
1	2
2	8
3	18
4	32
n	$2n^2$

- The lowest energy shells fill first until they are full or have eight electrons. At that point, the next energy shell accepts two electrons before the unfilled shell with eight electrons continues filling.
- The outer shell cannot contain more than eight electrons.
- The outer shell is called the valence shell.
- Electrons in the outer shell are called valence electrons.

KEY QUESTIONS

1 Construct the electronic configurations for atoms with:
  - **a** 5 electrons
  - **b** 12 electrons
  - **c** 20 electrons
  - **d** 35 electrons.

2 Write the electronic configuration of:
  - **a** Be
  - **b** S
  - **c** Ar
  - **d** Mg
  - **e** Ne

3 Draw the Bohr diagram for one atom of scandium.

4 Write the name and symbol of the element with the electronic configuration:
  - **a** 2
  - **b** 2,7
  - **c** 2,8,3
  - **d** 2,5
  - **e** 2,8,7

5 What is the number of valence electrons for an atom with 35 electrons?

1.7 The Schrödinger model of the atom

The shell model of the atom that developed from the work of Niels Bohr mathematically explained the lines in the emission spectrum of hydrogen atoms. However, there were some things that the model could not explain. The shell model:

1. cannot accurately predict the emission spectra of atoms with more than one electron
2. is unable to explain why electron shells can only hold $2n^2$ electrons
3. does not explain why the fourth shell accepts two electrons before the third shell is completely filled.

These failings of the shell model indicate that the model is incomplete. Obtaining a better model of the atom required scientists to think about electrons in an entirely different way.

A QUANTUM MECHANICAL VIEW OF ATOMS

The Bohr model of the atom was revolutionary when it was proposed. Before Bohr, Rutherford and other scientists believed that electrons could orbit the nucleus at any distance from the nucleus. This picture of the electrons was based on how scientists observed the world around them. For example, planets can revolve at any distance around the Sun. However, Bohr's theory stated that electrons only occupy specific, circular orbits. This was the first suggestion that the physics inside atoms might be very different from the physics we experience in our daily lives.

Quantum mechanics

The word 'quantum' means a specific amount. In the Bohr model, the electrons can only have specific amounts of energy depending on which shell they are in. The energy of the electrons is said to be **quantised**.

In 1926, the German scientist Erwin Schrödinger proposed that electrons behaved as waves around the nucleus. Using a mathematical approach and this wave theory, Schrödinger developed a model of the atom called **quantum mechanics**. This is the model of the atom that scientists use today.

Quantum mechanics describes the behaviour of extremely small particles like electrons. You rarely experience quantum mechanics in your everyday life. As a result, the predictions of quantum mechanics are often difficult to imagine. Nonetheless, quantum mechanics accurately predicts the behaviour of electrons in atoms.

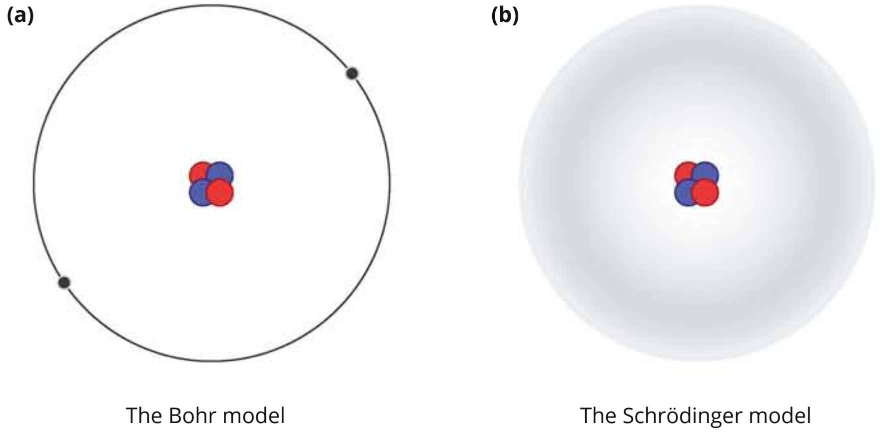
CHEMFILE

Quantum mechanics and large objects

Quantum mechanics even accounts for the motion of larger objects such as footballs, people and stars. When the laws of quantum mechanics are applied to the study of these larger objects, they give results that are virtually identical to those obtained using the laws of classical physics.

The Schrödinger model

The fundamental difference between the Bohr model and the **Schrödinger model** of the atom is the way they view the electrons. Bohr viewed electrons as tiny, hard particles that revolve around the nucleus in circular orbits. Schrödinger viewed electrons as having wave-like properties. In this model, the electrons occupy a three-dimensional space around the nucleus known as an **orbital**. Figure 1.7.1 compares the Bohr model and the Schrödinger model.



The Bohr model

The Schrödinger model

FIGURE 1.7.1 (a) Bohr regarded electrons as particles that travel along a defined path in circular orbits. (b) In Schrödinger's quantum mechanical approach, the electrons behave as waves and occupy a three-dimensional space around the nucleus. The region occupied by the electrons is known as an orbital.

By assuming that electrons have wave-like properties, Schrödinger found the following.

- There are major energy levels in an atom that, for historical reasons, were called shells.
- These shells contain separate energy levels of similar energy, called **subshells**, which he labelled s, p, d and f. Each subshell can only hold a certain number of electrons.
- The first shell ($n = 1$) contains only an s-subshell. The second shell contains s- and p-subshells. The third shell contains s-, p- and d-subshells and so on. The subshells for the first four shells are summarised in Table 1.7.1.

TABLE 1.7.1 Energy levels within an atom

Shell number (n)	Subshells	Number of orbitals in subshell	Maximum number of electrons per subshell	Maximum number of electrons per shell
1	1s	1	2	2
2	2s 2p	1 3	2 6	8
3	3s 3p 3d	1 3 5	2 6 10	18
4	4s 4p 4d 4f	1 3 5 7	2 6 10 14	32

- Each subshell is made up of smaller components known as orbitals. Orbitals can be described as regions of space surrounding the nucleus of an atom in which electrons may be found. An s-subshell has just one orbital. A p-subshell has three orbitals. A d-subshell has five orbitals and an f-subshell has seven. The number of orbitals in each subshell for the first four shells is summarised in Table 1.7.1.
- The total number of orbitals in a shell is given by n^2. Each orbital can contain a maximum of two electrons. Therefore, the total number of electrons per shell is given by $2n^2$. For example, the second shell contains s- and p-subshells and so contains a total of $1 + 3 = 4$ orbitals. Each orbital contains two electrons so the second shell contains $2 \times 4 = 8$ electrons. The number of electrons in each subshell and shell for the first four shells is summarised in Table 1.7.1.

Note that the Schrödinger model accurately predicts the maximum number of electrons that each shell can hold. This is something that the Bohr model could not explain.

ELECTRONIC CONFIGURATIONS AND THE SCHRÖDINGER MODEL

The electronic configurations for the Schrödinger model are more complicated than the electronic configurations of the shell model. This is because the Schrödinger model specifies subshells that electrons occupy. The electronic configuration of a sodium atom is shown in Figure 1.7.2.

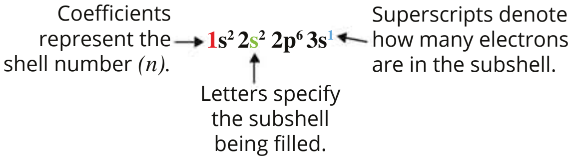


FIGURE 1.7.2 The electronic configuration of a sodium atom. It shows that there are 2 electrons in the 1s-subshell, 2 electrons in the 2s-subshell, 6 electrons in the 2p-subshell and 1 electron in the 3s-subshell.

Sodium has 11 electrons. The electronic configuration in Figure 1.7.2 indicates that for sodium, there:

- are two electrons in the s-subshell in the first shell
- are two electrons in the s-subshell of the second shell
- are six electrons in the p-subshell of the second shell
- is one electron in the s-subshell of the third shell.

Although the electronic configurations may look complicated, the rules for constructing them are simple.

- The lowest energy orbitals are always filled first.
- Each orbital contains a maximum of two electrons.

The order of energy levels of the subshells are:

$1s < 2s < 2p < 3s < 3p < 4s < 3d \ldots.$

This is shown in Figure 1.7.3. In this diagram, each dashed line represents an orbital that can hold two electrons.

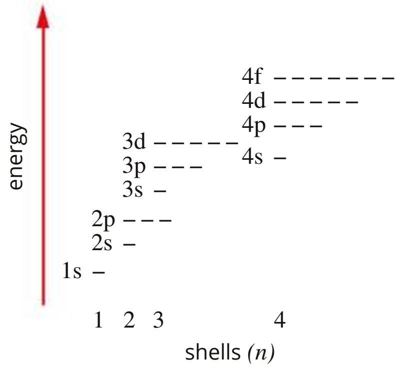


FIGURE 1.7.3 The relative energies of subshells. Each dashed line represents an orbital in a subshell. Each orbital can contain two electrons.

The geometric pattern shown in Figure 1.7.4 is a commonly used and convenient way of remembering the order in which the subshells are filled.

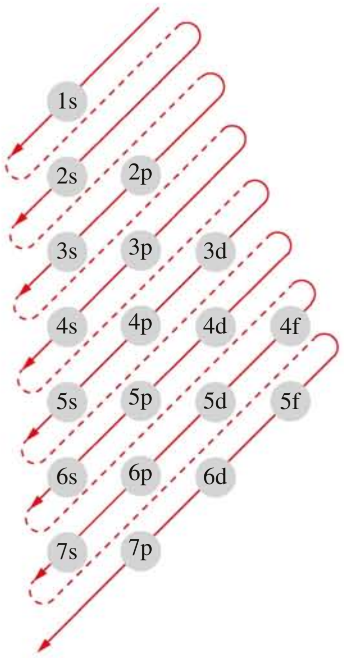


FIGURE 1.7.4 This geometric pattern shows the order in which the subshells are filled. Note that in this diagram the fourth shell starts filling before the third shell is completely filled. This is because the 4s-orbital is lower in energy than the 3d-orbitals. As a result, the 4s-orbital accepts two electrons after the 3s- and 3p-orbitals are filled but before the 3d-orbital begins filling.

Figure 1.7.5 shows how the energy levels are filled in a neon atom, which has 10 electrons. The first two electrons fill the 1s-subshell, the second two electrons go into the next highest energy level, the 2s-subshell. The last six electrons then fill the next highest energy level, the 2p-subshell. The electronic configuration is written as $1s^2 2s^2 2p^6$.

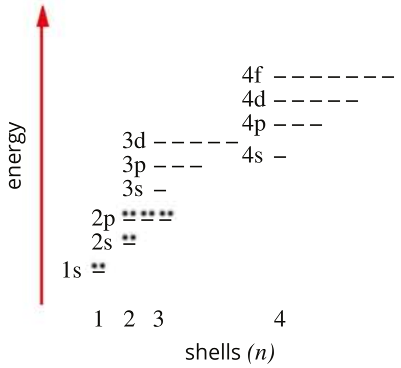
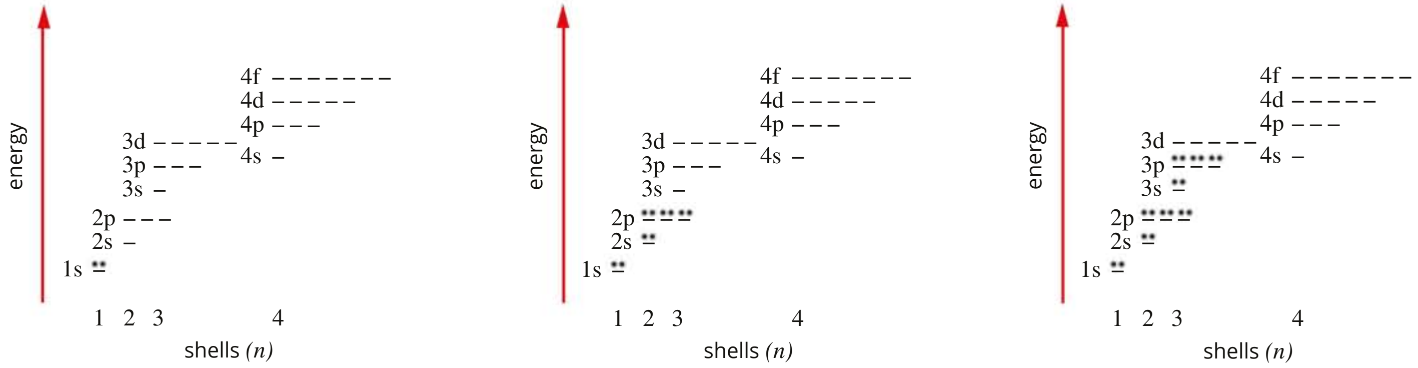


FIGURE 1.7.5 This electron shell diagram shows how the orbitals in a neon atom are filled to give an electronic configuration.

Figure 1.7.6 on page 30 shows how to add electrons to atoms with more than 20 electrons. The first two electrons fill the 1s-orbital in the first shell. The next eight electrons fill the s- and p-orbitals in the second shell. The next eight electrons fill the s- and p-orbitals in the third shell. The 4s-orbital is then filled with two electrons because this orbital is lower in energy than the 3d-orbitals. Once the 4s-orbital is filled, the next 10 electrons are placed in the 3d-orbitals.

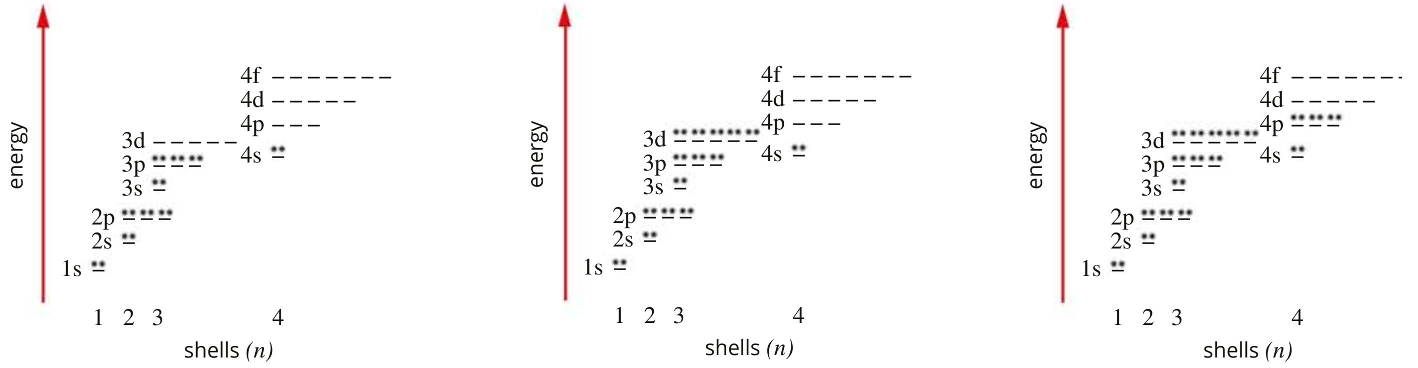
Finally, the remaining six electrons fill the 4p-orbitals.



He $1s^2$

Ne $1s^2 2s^2 2p^6$

Ar $1s^2 2s^2 2p^6 3s^2 3p^6$



Ca $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Zn $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

Kr $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

FIGURE 1.7.6 Adding electrons to atoms with more than 20 electrons

Krypton has 36 electrons. According to the order of subshell filling, its electronic configuration is:

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$

Although the 4s-subshell is filled before the 3d-subshell, the subshells of the third shell are usually grouped together. Therefore, the electronic configuration for a krypton atom is written as:

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

Chromium and copper – exceptions

The electronic configurations for most elements follow the rules described above. There are two notable exceptions: element 24, chromium, and element 29, copper. Table 1.7.2 shows these exceptions.

TABLE 1.7.2 The electronic configurations for chromium and copper

Element	Electronic configuration predicted according to the rules above	Actual electronic configuration
Chromium, Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
Copper, Cu	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

Each orbital can hold two electrons. In the d-subshell there are five orbitals and therefore 10 electrons that can be held within them. Scientists have determined that as a subshell fills, a single electron is placed in each orbital first. Then a second electron is entered into the orbitals until the filling process is complete.

Chemists calculate that there is very little difference in energy between 3d- and 4s-orbitals, and the $3d^5 4s^1$ configuration for chromium is slightly more stable than the $3d^4 4s^2$ configuration. This is because each of the five d-orbitals is exactly half filled with one d-orbital empty.

Similarly for copper, the $3d^{10} 4s^1$ arrangement with five completely filled d-orbitals is more stable than the $3d^9 4s^2$ configuration with partially filled d-orbitals.

Worked example 1.7.1

WRITING ELECTRONIC CONFIGURATIONS USING THE SCHRÖDINGER MODEL

Write the Schrödinger model of electronic configuration for a manganese atom with 25 electrons.

<table>
<tr><th>Thinking</th><th>Working</th></tr>
<tr><td>Recall the order in which the subshells fill by listing them from lowest energy to highest energy and the number of orbitals in each.</td><td>1s, 1 orbital
2s, 1 orbital
2p, 3 orbitals
3s, 1 orbital
3p, 3 orbitals
4s, 1 orbital
3d, 5 orbitals
4p, 3 orbitals</td></tr>
<tr><td>Fill the subshells by assigning two electrons per orbital, starting from the lowest energy subshells until you have reached the total number of electrons in your atom.</td><td><table>
<tr><th>Subshell</th><th>Electrons in subshell</th><th>Progressive total of electrons</th></tr>
<tr><td>1s</td><td>2</td><td>2</td></tr>
<tr><td>2s</td><td>2</td><td>4</td></tr>
<tr><td>2p</td><td>6</td><td>10</td></tr>
<tr><td>3s</td><td>2</td><td>12</td></tr>
<tr><td>3p</td><td>6</td><td>18</td></tr>
<tr><td>4s</td><td>2</td><td>20</td></tr>
<tr><td>3d</td><td>5</td><td>25</td></tr>
<tr><td>4p</td><td></td><td></td></tr>
</table></td></tr>
<tr><td>Write the electronic configuration by writing each subshell with the number of electrons as a superscript. Remember to group subshells from the same shell.</td><td>$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$</td></tr>
</table>

Worked example: Try yourself 1.7.1

WRITING ELECTRONIC CONFIGURATIONS USING THE SCHRÖDINGER MODEL

Write the Schrödinger model of electronic configuration for a vanadium atom with 23 electrons.

1.7 Review

SUMMARY

- The shell model of the atom was unable to fully explain the properties of atoms and a new model was needed to describe the electron behaviour in atoms.
- The Schrödinger model proposed that electrons behave as waves and occupy a three-dimensional space around the nucleus.
- The Schrödinger model predicted that subshells are energy levels within the major shells. The subshells consist of orbitals.
- An orbital can be regarded as a region of space surrounding the nucleus in which an electron may be found.
- Orbitals of similar energy are grouped in subshells that are labelled s, p, d and f.
- Each orbital can hold a maximum of two electrons (Table 1.7.3).

TABLE 1.7.3

Shell	Subshells	Orbitals in subshell
1	1s	1
2	2s 2p	1 3
3	3s 3p 3d	1 3 5
4	4s 4p 4d 4f	1 3 5 7

- Each subshell has a different energy in an atom.
- Electrons fill the subshells from the lowest energy subshell to the highest energy subshell.
- The 4s-subshell is lower in energy than the 3d-subshell, so the fourth shell accepts two electrons before the third shell is completely filled.
- Electronic configurations of atoms in the Schrödinger model specify the number of electrons in each subshell.

KEY QUESTIONS

1 Copy and complete the following table to write the electronic configuration of each of the atoms listed.

Element (atomic number)	Electronic configuration using the shell model	Electronic configuration using the subshell model
Boron (5)	2,3	$1s^2 2s^2 2p^1$
Lithium (3)		
Chlorine (17)		
Sodium (11)		
Neon (10)		
Potassium (19)		
Scandium (21)		
Iron (26)		
Bromine (35)		

2 In terms of energy levels, what is the essential difference between the shell model and the subshell model of the atom?

Chapter review

KEY TERMS

adsorption
alpha particle
atom
atomic number
atomic theory of matter
Bohr model
chemical symbol
compound
covalent network lattice
electron
electron shell
electronic configuration
electrostatic attraction
element
emission spectrum
energy level
excited state
giant molecule
ground state
ionisation energy
isotope
mass number
matter
model
molecule
monatomic
nanomaterial
nanoparticle
nanoscale
nanoscience
nanotechnology
neutron
noble gas
nucleon
nucleus
octet rule
orbital
outermost shell
periodic table
proton
quantised
quantum mechanics
radioactive
scanning tunnelling microscope (STM)
Schrödinger model
subatomic particle
subshell
valence electrons
valence shell

Nanomaterials and nanoparticles

1 Nanotechnology is often represented by two fundamentally different approaches: 'top-down' and 'bottom up'. Research the differences between these two approaches.

2 Convert the following lengths into nanometres (express your solutions in scientific notation).

- **a** 5 cm
- **b** 12 mm
- **c** 2 km

3 Zinc oxide powder and zinc oxide nanoparticles both absorb UV light. What property of zinc oxide nanoparticles makes them more suitable than zinc oxide powder for use in sunscreen.

The atomic world

4 Which of Dalton's predictions about the nature of atoms was later proven to be incorrect?

5 Classify the following elements according to whether they are monatomic, made up of molecules or form a large network of atoms bonded together: sulfur, copper, carbon, tin, helium, neon, gold, oxygen, krypton, nitrogen.

Inside atoms

6 Where would you find 99.97% of the mass of an atom?

7 How are protons, neutrons and electrons arranged in an atom?

8 Compare the mass and charge of protons, neutrons and electrons.

Classifying atoms

9 An atom of chromium can be represented by the symbol $^{52}_{24}\text{Cr}$.

- **a** Determine its atomic number and mass number.
- **b** Determine the number of electrons, protons and neutrons in the chromium atom.

10 Two atoms both have 20 neutrons in their nucleus. The first has 19 protons and the other has 20 protons. Are they isotopes? Why or why not?

11 Explain why the number of electrons in an atom equals the number of protons.

12 Using the element bromine as an example, explain why elements are best identified by their atomic number and not their mass number.

Electronic structure of atoms

13 In a hydrogen atom, which electron shell will the electron be in if the atom is in the ground state?

Electronic configuration using the shell model

14 Determine which shell the 30th electron of an atom would go into according to the rules for determining the electronic configuration of an atom.

15 What is the name of the element that has an electronic configuration of 2,8,2?

The Schrödinger model of the atom

16 Write electronic configurations, using subshell notation, for the following elements. The atomic number of each element is shown in brackets.

- **a** Helium (2)
- **b** Carbon (6)
- **c** Fluorine (9)
- **d** Aluminium (13)
- **e** Argon (18)
- **f** Nickel (28)
- **g** Bromine (35)

17 Using a fluorine atom as an example, explain the difference between the terms 'shell', 'subshell' and 'orbital'.

18 Determine the Schrödinger model of electronic configuration that corresponds to the shell model electronic configuration 2,8,6.

19 Explain how the Schrödinger model of the atom explains why the fourth electron shell begins filling before the third shell is completely filled.

20 Explain why the 4s-subshell in chromium and copper is only half-filled compared to almost all other elements.

Connecting the main ideas

21 Our model describes an atom as consisting of rapidly moving electrons at a relatively large distance from a very small central nucleus. What is there *between* those electrons and the nucleus?

22 New models for the atom evolve as scientists become aware of inconsistencies between current models and experimental data. Outline the problems with the existing model of the atom that led to the modifications suggested by the following scientists.

- **a** Rutherford
- **b** Bohr
- **c** Schrödinger

CHAPTER

02

Electron arrangements and the periodic table

At the end of this chapter, you will be able to explain how the periodic table was developed. You will be able to use the periodic table to explain trends that are observed in the structures and properties of the elements within the groups and periods of the table. In particular, you will look at the trends in characteristics and properties of the elements such as their electronic configuration, atomic size, behaviour as metals or non-metals, and reactivity.

Key knowledge

- The periodic table as an organisational tool to identify patterns and trends in, and relationships between, the structures (including electronic configurations and atomic radii) and properties (including electronegativity, first ionisation energy, metallic or non-metallic character and reactivity) of elements

2.1 The periodic table

Chapter 1 looked at research into elements and the nature of atoms, the existence of subatomic particles, their charge and mass, the way these particles are arranged in an atom and the way they behave. As scientists' understanding of the atom improved, and more elements were discovered, a way of organising this knowledge was needed.

The **periodic table** (Figure 2.1.1) is one of the most useful reference tools available to chemists. It minimises the need to memorise isolated facts about different elements, and provides a framework on which to organise our understanding. By knowing the properties of particular elements and trends within the table, chemists are able to organise what would otherwise be an overwhelming collection of disorganised information.

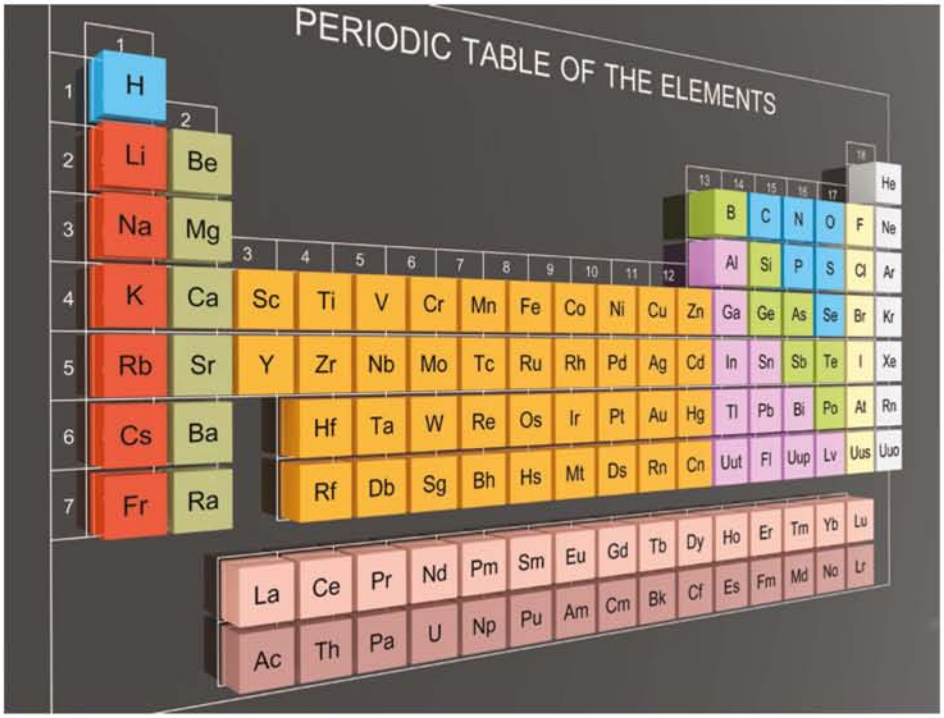


FIGURE 2.1.1 There are many versions of the modern periodic table of the elements. This is one of them.

EARLY FORMS OF THE PERIODIC TABLE

In the 19th century, chemists wanted to use information they had gathered about the elements to organise the elements into a useful and practical format. The work of these scientists led to what we now know as the periodic table. The early forms of the periodic table were very different from the one we use today; many elements had not been discovered and scientists only had limited information about some other elements. An early form of the periodic table created by a Russian chemist, Dimitri Mendeleev, is shown in Figure 2.1.2 on page 37.

At the time the early periodic table was being constructed, the existence of subatomic particles was unknown, and so the elements were placed in order of the increasing mass of the atoms. Mendeleev recognised that the chemical properties of the elements varied periodically with increasing atomic mass. He arranged elements with similar properties in vertical columns. Mendeleev proposed his **periodic law**: The properties of elements vary periodically with their atomic weights.

CHEMFILE

Atomic mass

The property of an element that Mendeleev called atomic weight is now called atomic mass. Atomic mass should not be confused with the mass number. Scientists at the time of Mendeleev did not know about subatomic particles. They only knew the relative masses of atoms of each element.

Group Period	I	II	III	IV	V	VI	VII	VIII
1	H = 1							
2	Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5	
4	K = 39	Ca = 40	? = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56 Co = 59 Ni = 59
5	Cu = 63	Zn = 65	? = 68	? = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	? = 100	Ru = 104 Rh = 104 Pd = 106
7	Ag = 108	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	J = 127	
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140				
9								
10			?Er = 178	?La = 180	Ta = 182	W = 184		Os = 195 Ir = 197 Pt = 198
11	Au = 199	Hg = 200	Tl = 204	Pb = 207	Bi = 208			
12				Th = 231		U = 240		

FIGURE 2.1.2 A representation of Mendeleev's periodic table. Notice the spaces left for undiscovered elements.

EXTENSION

Triads and octaves

In 1829, German chemist Johann Wolfgang Dobereiner noticed that many of the known elements could be arranged in groups of three on the basis of their chemical properties. He called these groups 'triads'. Within each of these triads, the properties of one element was intermediate between the other two. The intermediate's relative atomic weight was almost exactly the average of the others.

One of Dobereiner's triads was lithium, sodium and potassium. Sodium is more reactive than lithium, but less reactive than potassium. Sodium's atomic mass is 23, which is the average of lithium's (atomic mass 7) and potassium's (atomic mass 39) atomic masses.

However, Dobereiner's theory was limited. Not all elements could be included in triads. But his work was quite remarkable given he had fewer than 50 elements to work with at this time.

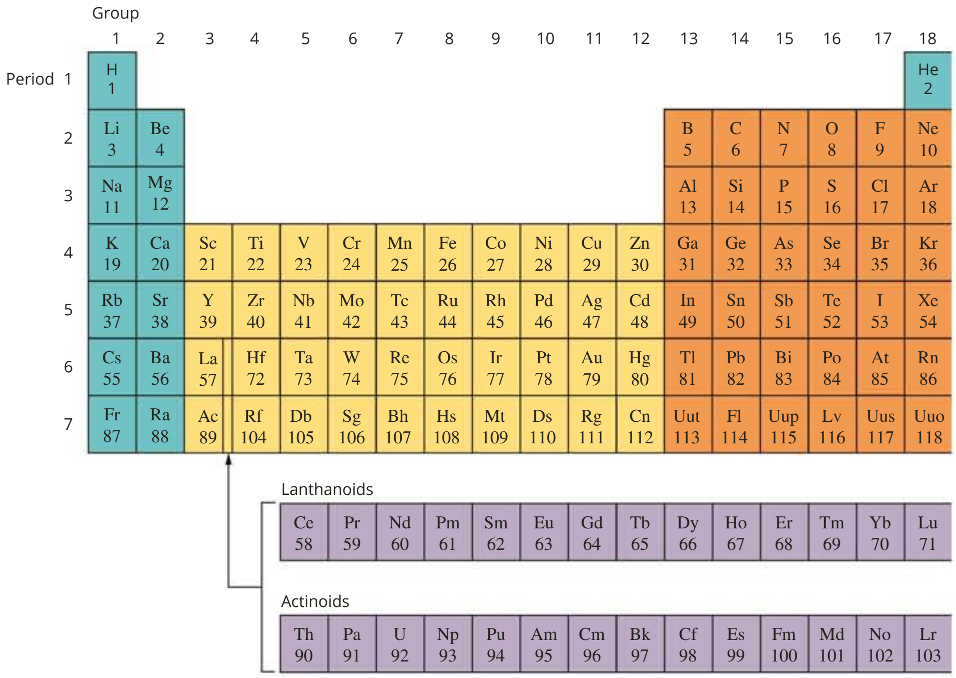
Decades later, English chemist John Alexander Newlands noticed a pattern in the atomic weight of elements. Newlands' law of octaves was published in 1865, and identified properties of new elements such as germanium. His patterns worked well for the lighter elements but did not fit for the heavier elements or allow for the discovery of new elements.

Four years later in 1869, Mendeleev, working independently, published his periodic law, which, with a few modifications, was similar to that of Newlands.

THE MODERN PERIODIC TABLE

We now know that the number of protons (the **atomic number**) is what makes one element fundamentally different from another element. The elements in the modern periodic table are therefore arranged in rows in order of increasing atomic number.

Chemists use the number of electrons in the outer shell, called the valence electrons (see Chapter 1), to organise the elements into columns. The form of the periodic table in common use is shown in Figure 2.1.3.



Group

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period 1	H 1																	He 2
2	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
3	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6	Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
7	Fr 87	Ra 88	Ac 89	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	Uut 113	Fl 114	Uup 115	Lv 116	Uus 117	Uuo 118

Lanthanoids

Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71

Actinoids

Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

FIGURE 2.1.3 This is the most common form of the periodic table in use.

The modern periodic table has several key features.

- The periodic table is arranged in order of increasing atomic number.
- The horizontal rows are known as **periods** and are labelled 1–7.
- The vertical columns are known as **groups** and are labelled 1–18.
- **Main group elements** are elements in groups 1, 2 and 13–18.
- The elements in groups 3–12 are known as **transition metals**.

Some periodic tables you will see also indicate other properties of the elements such as boiling point or whether the element is a solid, liquid or gas at room temperature.

CHEMFILE

Element 117 and the Canberra scientists

Four atoms of a super heavy element known as number 117 have been created in a German laboratory as part of a collaboration with Professor David Hinde (Figure 2.1.4), director of the heavy ion accelerator facility at the Department of Nuclear Physics at the Australian National University.

Because the element is radioactive, the atoms disappeared within one-tenth of a second, but the scientists were able to confirm the element's first observation in 2010. This new element has been given the temporary name of ununseptium ('one-one-seven' in Latin), but will soon be given a name by the International Union of Pure and Applied Chemistry (IUPAC) that will possibly reflect the Russian scientists who produced the first atom in 2010. The atoms of element 117 equal the heaviest atoms ever observed, being 40% heavier than an atom of lead.

Professor Hinde said that because such an extremely small amount of the element was synthesised, it will not be practical to use it. But the Australian researchers will continue to concentrate on the quantum science behind the element's synthesis and attempt to produce the next super-heavy element.

FIGURE 2.1.4 Professor David Hinde is director of the heavy ion accelerator facility at the Department of Nuclear Physics at the Australian National University in Canberra.

GROUPS

Elements in the periodic table are arranged into vertical columns called groups. For main group elements, the group number can be used to determine the number of valence electrons (outer-shell electrons) in an atom of the element.

In groups 1 and 2, the number of valence electrons is equal to the group number. For example, magnesium is in group 2 and therefore has two valence electrons.

In groups 13–18, the number of valence electrons is equal to the group number minus 10. For example, oxygen is in group 16 so oxygen has six outer-shell electrons. Similarly, neon is in group 18 so neon has eight valence electrons. Helium is an important exception. It is located in group 18 but only has two valence electrons. Helium is placed in group 18 because it is unreactive, like other group 18 elements. This information is summarised in Table 2.1.1.

TABLE 2.1.1 The number of valence electrons in elements belonging to each group

Group	Number of valence electrons
1	1
2	2
13	3
14	4
15	5
16	6
17	7
18	8*

*Helium has two valence electrons.

GROUPS OF ELEMENTS

The electrons in the outer shell of an atom (the valence electrons) are the electrons that are involved in chemical reactions. As a consequence, the number of valence electrons determines many of the chemical properties that an element exhibits.

Table 2.1.2 shows the names of some groups in the periodic table.

TABLE 2.1.2 Names of different groups in the periodic table

Group	Name
1	Alkali metals
2	Alkaline earth metals
17	Halogens
18	Noble gases

Because elements in the same group have the same number of valence electrons, elements in the same group have similar properties. For example, the alkali metals are elements in group 1 (with the exception of hydrogen). They are all relatively soft metals and are highly reactive with water and oxygen. Consider the electronic configurations of the atoms of the first three metals of this group:

Li $1s^2 2s^1$
Na $1s^2 2s^2 2p^6 3s^1$
K $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

The valence shell of each atom of each element in group 1 contains one electron in an s-subshell. This similarity in the valence shell structure gives these elements similar chemical properties.

Fluorine, chlorine, bromine and iodine are halogens (group 17). They are all coloured and highly reactive. Their electronic configurations are:

F $1s^2 2s^2 2p^5$
Cl $1s^2 2s^2 2p^6 3s^2 3p^5$
Br $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$
I $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5 4d^{10} 5s^2 5p^5$

Notice how all these elements have a highest-energy subshell electronic configuration of s^2p^5.

The noble gases (group 18) are a particularly interesting group. The noble gases have a very stable electron arrangement: helium has a full outer shell and the other members of this group have a stable octet of valence electrons (eight electrons). Chemical reactions involve the rearrangement of valence electrons to achieve a stable outer shell. Noble gases have a stable electronic configuration, so they do not tend to lose or gain electrons. This means that the noble gases have low reactivity.

The arrangement of electrons in atoms is responsible for the **periodicity** (periodic pattern) of element properties.

PERIODS

The horizontal rows in the periodic table are called periods. Periods are numbered 1–7. The number of a period gives information about the electronic configuration of an element. The period an element is located within is equal to the number of occupied electron shells in the element's atoms. For example, the outer shell of magnesium and chlorine is the third shell and both of these elements are in period 3:

Mg $1s^2 2s^2 2p^6 3s^2$
Cl $1s^2 2s^2 2p^6 3s^2 3p^5$

Similarly, the elements in period 5 all have outer shell electrons in the fifth shell.

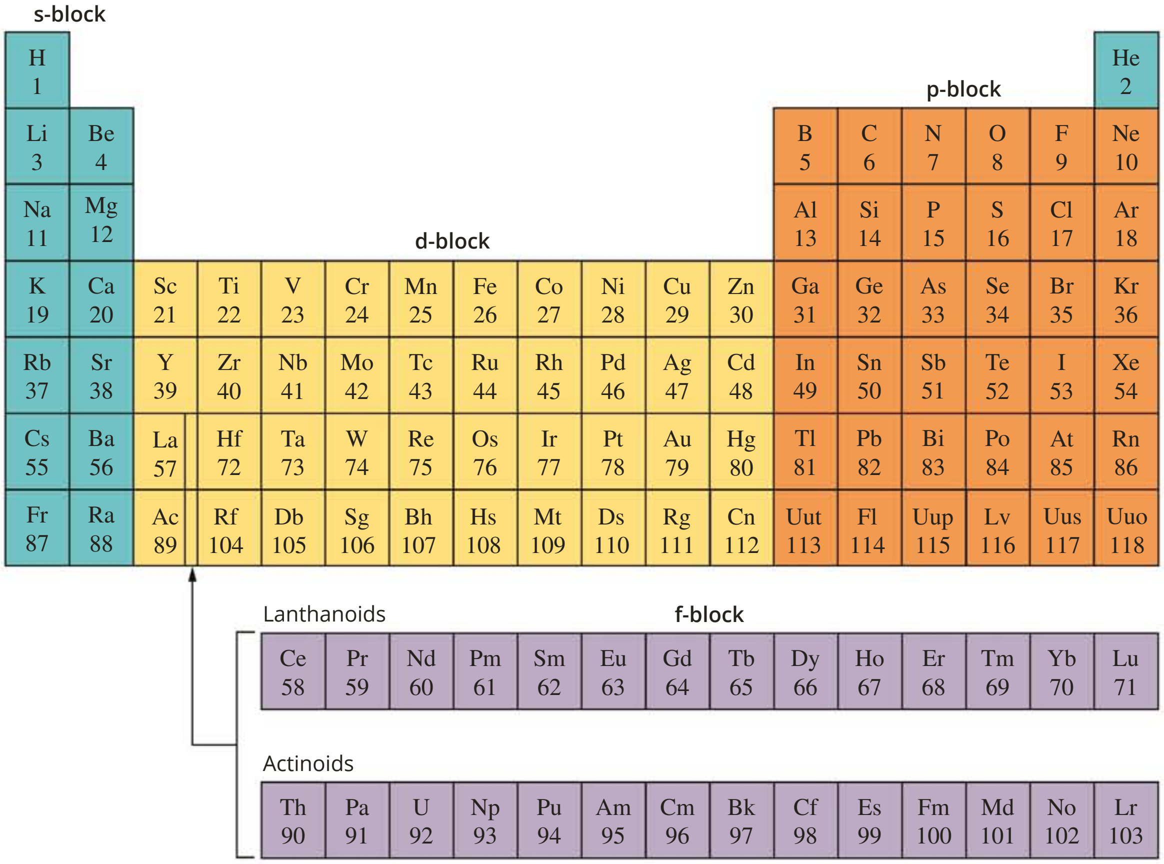
BLOCKS

The periodic table has four main **blocks**. The elements in each block have the same type of subshell (s, p, d or f) as their highest energy subshell. For example, the highest energy subshell of an element in the s-block is the s-subshell.

The s-block contains the elements in group 1 (alkali metals), group 2 (alkaline earth metals), hydrogen and helium. These elements have a half-filled or fully filled s-subshell, that is, s^1 or s^2, as the highest energy subshell configuration. Table 2.1.3 and Figure 2.1.5 show which groups of elements fall into the four different blocks.

TABLE 2.1.3 Elements in the different blocks of the periodic table

Block	Elements	Highest energy subshell configurations
s-block	Groups 1 and 2 and helium	s^1 or s^2
p-block	Groups 13–18 (except helium)	s^2p^1 to s^2p^6
d-block	Groups 3–12	d^1s^2 to $d^{10}s^2$
f-block	Lanthanoids and actinoids	4f-subshell progressively being filled in the lanthanoids 5f-subshell progressively being filled in the actinoids



H 1																	He 2
Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Ac 89	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	Uut 113	Fl 114	Uup 115	Lv 116	Uus 117	Uuo 118

Lanthanoids

Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71

Actinoids

Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

FIGURE 2.1.5 Colour is used to distinguish between the s, p, d and f-blocks of elements.

2.1 Review

SUMMARY

- The periodic table is a tool for organising elements according to their chemical and physical properties.
- The elements of the periodic table are arranged in order of increasing atomic number.
- Columns in the periodic table are known as groups and are numbered 1–18.
- The number of valence electrons in an atom of an element can be determined by the group in which it is located (Table 2.1.1).
- The main group elements are in groups 1, 2 and 13–18 in the periodic table.
- Elements in between the main group elements (groups 3–12) are known as transition metals.
- Rows in the periodic table are known as periods and are numbered 1–7.
- The number of occupied electron shells of an atom of an element is equal to the number of the element's period.
- The periodic table has four main blocks of elements; the elements in each block have the same type of subshell (s, p, d or f) as their highest energy subshell (Table 2.1.3).

KEY QUESTIONS

1 Main group elements are elements that belong to specific groups in the periodic table. Which groups are these?

2 How many valence electrons are in atoms of elements found in:

- **a** group 1?
- **b** group 15?
- **c** group 17?
- **d** group 2?

3 What is the electronic configuration of an atom of an element in period 3 and group 2?

4 Use the periodic table in Figure 2.1.3 on page 38 to answer these questions.

- **a** In which group of the periodic table will you find the following?
  - **i** B
  - **ii** Cl
  - **iii** Na
  - **iv** Ar
  - **v** Si
  - **vi** Pb
- **b** In which period of the periodic table will you find the following?
  - **i** K
  - **ii** F
  - **iii** He
  - **iv** H
  - **v** U
  - **vi** P
- **c** What is the name, symbol and electronic configuration of the:
  - **i** second element in group 14?
  - **ii** second element in period 2?
  - **iii** element that is in group 18 and period 3?

5 Why are elements in the periodic table arranged in order of atomic number rather than relative atomic mass?

2.2 Trends in the periodic table—Part 1

The periodic table does not just provide information about an element's electronic configuration. It can also be used as a tool for summarising the relative properties of elements and explaining the trends observed in those properties.

You have already seen how the group number of an element determines how many valence electrons an atom of that element has. The period indicates how many electron shells are occupied in an atom of an element. Properties such as atomic radii, electronegativity and ionisation energy show common trends in the periodic table.

Periodic trends were observed by Dimitri Mendeleev and formed the basis of the table of the elements that he first published in 1869. Mendeleev described the way the properties of the elements vary as the periodic law.

ELECTRONIC CONFIGURATION

To understand the reason for the periodicity of element properties, look at two groups of elements that Mendeleev recognised as being similar. The first group is the alkali metals (group 1). The elements in this group (lithium, sodium, potassium, rubidium and caesium) are all relatively soft metals and are highly reactive with water and oxygen.

Consider their electronic configurations:

Li $1s^22s^1$
Na $1s^22s^22p^63s^1$
K $1s^22s^22p^63s^23p^64s^1$
Rb $1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^1$
Cs $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^66s^1$

These elements have similar valence shell electronic configurations – all have one electron in an s-subshell. This similarity in a group's arrangement of electrons gives elements similar properties and is responsible for the periodicity of element properties.

You can also see that the number of electron shells increases moving down the group. The increase in electron shells means that the valence electrons are in higher energy subshells and have a weaker attraction to the nucleus. The decrease in the attractive force between the valence electrons and the nucleus as you move down a group causes trends in properties to be observed within a group.

CORE CHARGE

The **core charge** of an atom is a measure of the attractive force felt by the valence shell electrons towards the nucleus. Core charge can be used to predict the properties of elements and explain trends observed in the periodic table.

Consider an atom of lithium, which has an atomic number of three. It has three protons in its nucleus, two electrons in the first shell and one electron in the second shell (Figure 2.2.1).

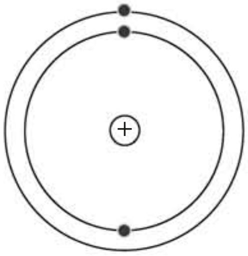


FIGURE 2.2.1 A lithium atom with one valence electron and two electrons in the inner shell. The atom has a core charge of +1.

The valence shell electron is attracted to the three positive charges in the nucleus. This electron is also repelled by the two electrons in the inner shell. The electrons in the inner shell shield the valence shell electron from the attraction of the nucleus. The valence shell electron is effectively attracted to the nucleus as if there were a +1 nuclear charge. This atom is therefore said to have a core charge of +1.

In atoms with two or more shells filled with electrons, the attraction between the nucleus and valence shell electrons is reduced by repulsion between the inner shell electrons and the valence shell electrons.

In general:

Core charge = number of protons in the nucleus – number of total inner-shell electrons

For example, an atom of chlorine (Figure 2.2.2) has 17 protons and seven valence shell electrons; the number of electrons in the inner shells is 10. The core charge of a chlorine atom is 17 – 10 = +7.

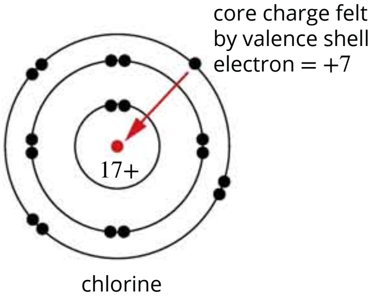


FIGURE 2.2.2 A Bohr diagram for the chlorine atom showing the valence shell electron shielded by 10 electrons in shells $n = 1$ and $n = 2$.

Worked example 2.2.1

CORE CHARGE

Determine the core charge of an atom of aluminium.

Thinking	Working
Determine the number of electrons in an atom of the element, using the periodic table as a reference.	The atomic number of aluminium is 13. Therefore, an atom of aluminium has 13 protons and 13 electrons.
Use the number of electrons to determine the electronic configuration.	With 13 electrons the electronic configuration is $1s^22s^22p^63s^23p^1$.
Determine the core charge. Core charge = number of protons – number of inner-shell electrons	The third shell is the valence shell in this atom. There are 10 inner-shell electrons, which in this atom are electrons in the first and second shell. Core charge = 13 – 10 = +3

Worked example: Try yourself 2.2.1

CORE CHARGE

Determine the core charge of an atom of fluorine.

Consider the atoms of two different elements in group 1, lithium and sodium shown in Figure 2.2.3.

As for all group 1 elements, the valence electron of a lithium atom and a sodium atom experience a core charge of +1.

Moving down a group you can see that the:

- core charge remains constant but the number of electron shells increases
- valence electrons are further from the nucleus. Consequently, they will be pulled less strongly towards the nucleus.

Now consider sodium and chlorine. They are both in period 3 in the periodic table (Figure 2.2.4).

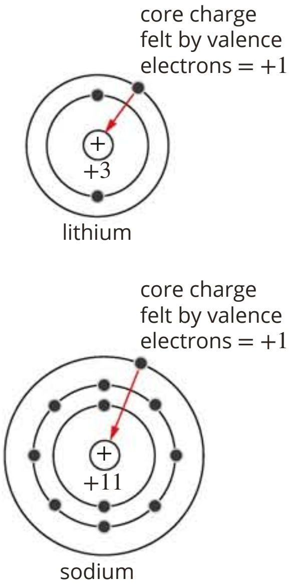


FIGURE 2.2.3 Lithium and sodium atoms both have a core charge of +1.

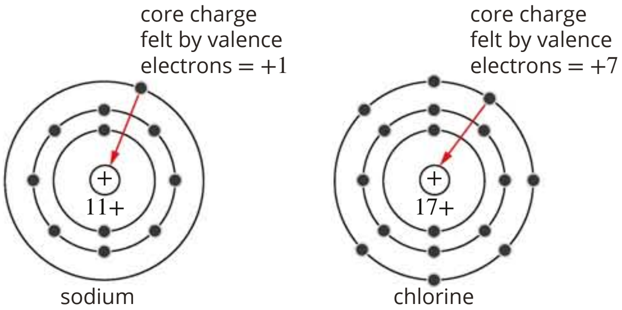


FIGURE 2.2.4 The core charges of two period 3 elements, sodium and chlorine, are +1 and +7 respectively.

TABLE 2.2.1 Core charges of main group elements

Group	Core charge
1	+1
2	+2
13	+3
14	+4
15	+5
16	+6
17	+7
18*	+8

*Helium has a core charge of +2.

The core charge experienced by the valence shell electrons in atoms of elements increases from left to right across a period, as you have seen for sodium and chlorine. The core charge of an atom of a main group element is equal to the number of valence electrons in the atom, as summarised in the Table 2.2.1.

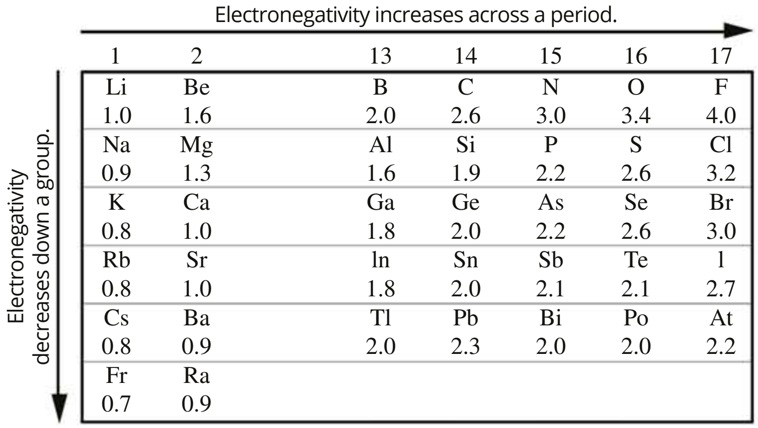
Table 2.2.2 summarises how the attraction between the nucleus and valence electrons changes in the periodic table.

TABLE 2.2.2 The changes in attraction between the nucleus and valence electrons within groups and periods of the periodic table

	Trend in core charge	Trend in attraction between the nucleus and valence electrons
Down a group	Remains constant	Core charge stays constant down a group, but the valence electrons are held less strongly as they are further from the nucleus (there are more shells in the atom).
Left to right across a period	Increases	The valence electrons are more attracted to the nucleus as the core charge increases.

ELECTRONEGATIVITY

Electronegativity is the ability of an atom to attract electrons towards itself. The more strongly the valence electrons of an atom are attracted to the nucleus of the atom, the greater the electronegativity. Therefore, the greater the core charge of an atom, the greater the electronegativity. Figure 2.2.5 shows the electronegativity of many of the main group elements.



1	2	13	14	15	16	17
Li 1.0	Be 1.6	B 2.0	C 2.6	N 3.0	O 3.4	F 4.0
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2
K 0.8	Ca 1.0	Ga 1.8	Ge 2.0	As 2.2	Se 2.6	Br 3.0
Rb 0.8	Sr 1.0	In 1.8	Sn 2.0	Sb 2.1	Te 2.1	I 2.7
Cs 0.8	Ba 0.9	Tl 2.0	Pb 2.3	Bi 2.0	Po 2.0	At 2.2
Fr 0.7	Ra 0.9					

FIGURE 2.2.5 The electronegativity of elements generally decreases down a group and increases across a period, from left to right.

The trends observed in the electronegativity of the elements are summarised in Table 2.2.3.

TABLE 2.2.3 Trends in electronegativity in groups and periods of the periodic table

	Trend in electronegativity	Explanation
Down a group	Decreases	The core charge stays constant and the number of shells increases down a group. Therefore, valence electrons are less strongly attracted to the nucleus as they are further from the nucleus. As a result, electronegativity decreases.
Left to right across a period	Increases	The number of occupied shells in the atoms remains constant but the core charge increases across a period. Therefore, the valence electrons become more strongly attracted to the nucleus. As a result, electronegativity increases.

ATOMIC RADIUS

Atomic radius is a measurement used for the size of atoms. It can be regarded as the distance from the nucleus to the valence shell electrons. It is usually measured by halving the distance between the nuclei of two atoms of the same element that are bonded together. Figure 2.2.6 depicts the atomic radii of many of the main group elements.

Atoms do not have sharply defined boundaries and so it is not possible to measure their radii directly. One method of obtaining atomic radii, and therefore an indication of atomic size, is to measure the distance between nuclei of atoms in molecules. For example, in a hydrogen molecule (H_2) the two nuclei are 74 picometres (pm) apart. The radius of each hydrogen atom is assumed to be half of that distance, i.e. 37 pm.

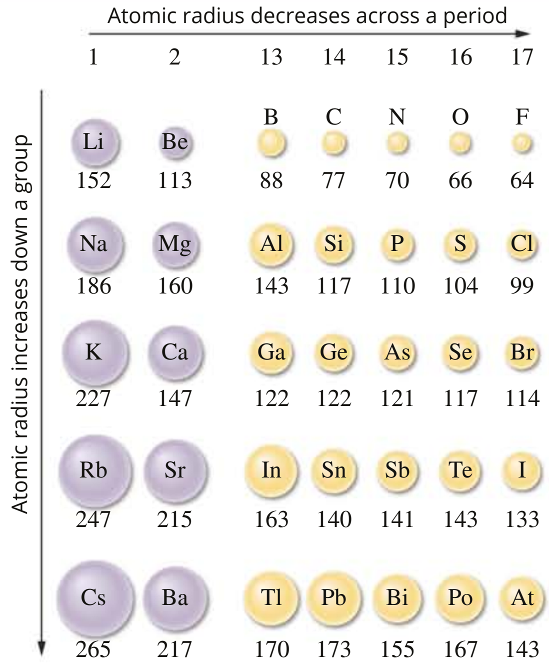


FIGURE 2.2.6 The relative sizes of atoms of selected main group elements. The atomic radii are given in picometres (pm). A picometre is 10^{-12} m.

Table 2.2.4 explains the trends in atomic radii in the periodic table.

TABLE 2.2.4 Trends in atomic radii in the periodic table

	Trend in atomic radii	Explanation
Down a group	Increases	Core charge stays constant and the number of shells increases as you move down a group. As a result, atomic radii increases.
Left to right across a period	Decreases	As you move across a period, the number of occupied shells in the atoms remains constant but the core charge increases. The valence electrons become more strongly attracted to the nucleus, so atomic radii decreases across a period.

2.2 Review

SUMMARY

- The core charge of an atom is a measure of the attractive force felt by the valence electrons towards the nucleus.
- The core charge is calculated by subtracting the total number of inner-shell electrons from the number of protons in the nucleus.
- Electronegativity is the ability of an element to attract electrons towards itself.
- Atomic radius is a measurement used for the size of atoms. It can be regarded as the distance from the nucleus to the outermost electrons.
- Table 2.2.5 summarises how these properties have specific trends within the groups and periods of the periodic table.

TABLE 2.2.5 Trends in properties that occur across a period and down a group

Property	Down a group	Across a period (left to right)
Core charge	No change	Increases
Electronegativity	Decreases	Increases
Atomic radius	Increases	Decreases

KEY QUESTIONS

1 What is the core charge of an atom of carbon?

2 Explain the relationship between electronegativity and core charge.

3 Figure 2.2.5 gives electronegativity values for the elements in groups 1, 2 and 13–17 of the periodic table.

- **a** Give the name and symbol of the element that has the:
  - **i** highest electronegativity
  - **ii** lowest electronegativity.
- **b** In which group do you see the:
  - **i** greatest change in electronegativity as you go down the group?
  - **ii** smallest change in electronegativity as you go down the group?
- **c** Why are the elements of group 18 usually omitted from tables that give electronegativity values?

2.3 Trends in the periodic table—Part 2

You have learnt that the core charge and the number of electron shells in an atom of an element can be used to predict some properties of elements. You will remember that the core charge of an atom is the attractive force felt by the valence electrons towards the nucleus. Core charge increases as you move across a period. As you move down a group, the core charge stays constant but atomic radius increases due to the additional electron shell in each period. The changes in core charge and atomic radii account for periodic trends in ionisation energy, reactivity and metallic character.

FIRST IONISATION ENERGY

When an element is heated, its electrons can move to higher energy shells. If an atom is given sufficient energy, an electron can be completely removed from the atom. If this occurs, the atom will now have one less electron than the number of protons in the nucleus, and becomes a positively charged **ion**. A positively charged ion is called a **cation**. You will learn more about ions in Chapter 4.

The process of removing an electron from an atom and forming an ion is called **ionisation**. The valence electrons are removed first because they are the furthest electrons from the nucleus and the least strongly held.

An ion is any atom of an element with more or fewer electrons than protons. If an atom loses electrons, it becomes positively charged as there are now more protons than electrons. A positively charged ion is called a cation. If an atom gains electrons, it becomes negatively charged and is called an **anion**.

The energy required to remove one electron from an atom of an element in the gas phase is called the **first ionisation energy**. For example, the ionisation energy of sodium is 494 kJ per mole of sodium atoms.

Figure 2.3.1 shows the first ionisation energies of most main group elements.

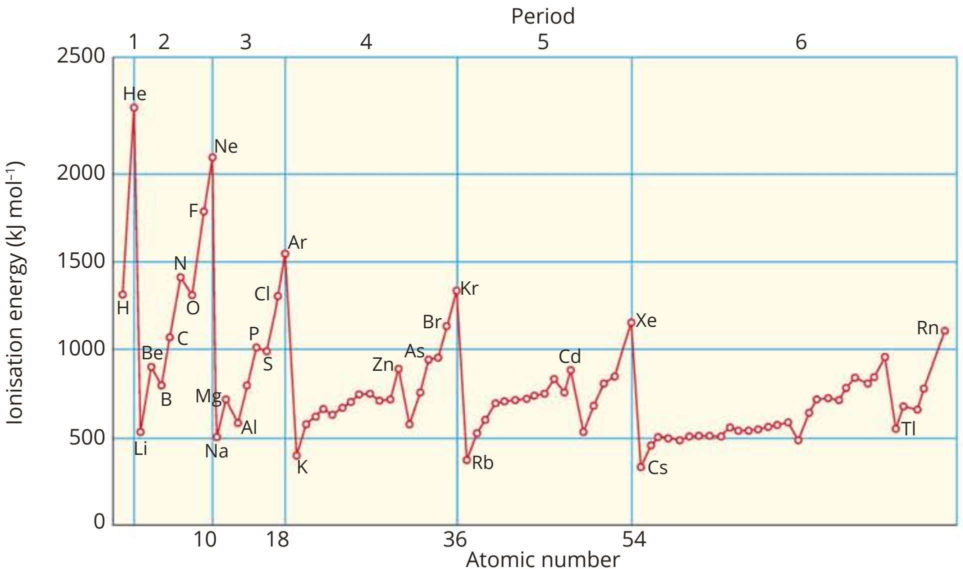


FIGURE 2.3.1 The first ionisation energy generally increases from left to right across a period.

The magnitude of the first ionisation energy reflects how strongly the valence electrons are attracted to the nucleus of the atoms. The more strongly the valence electrons are attracted to the nucleus, the more energy is required to remove them from the atom and the higher the first ionisation energy.

TABLE 2.3.1 The trend in ionisation properties in groups and periods of the periodic table

	Trend in ionisation energy	Explanation
Down a group	Decreases	Core charge stays constant and the number of shells increases down a group. Therefore, the valence electrons are less attracted to the nucleus as they are further from the nucleus. As a result, the energy required to overcome the attraction between the nucleus and the valence electron is less, and the first ionisation energy decreases down a group.
Left to right across a period	Increases	Core charge increases and the number of occupied shells remains constant across a period. As a result, the valence electrons become more strongly attracted to the nucleus, and more energy is required to remove an electron. Therefore, first ionisation energy increases across a period.

The s- and p-block elements of the periodic table follow these patterns. As the core charge increases across a period, so too does the ionisation energy. As atomic radius increases down a group (due to the additional electron shell), the electrons are further from the nucleus. Therefore, the valence electrons in elements lower in a group can be removed more easily, meaning the ionisation energy decreases.

EXTENSION

Trends in d- and f-block elements

The d-block elements are the transition metals. The f-block elements are the lanthanoids and actinoids (also called the lanthanides and actinides). The trends in the d-block and in f-block are more complex than those in the first three periods. Between elements within the same group in periods 4, 5 and 6 a new pattern emerges.

Between periods 4 and 5 for d-block elements, the atomic radius increases. When the 4f-subshell starts filling in period 6, the core charge increases. With this increase in core charge, the valence electrons are more closely attracted to the nucleus, and the atoms become denser with smaller atomic radii.

The pattern is true for the transition metals in the sixth period. For example, in group 6, chromium (period 4) has an atomic radius of 125 pm. Molybdenum (period 5) has a higher atomic radius at 137 pm because of the additional electron shell. Tungsten (period 6) also has an atomic radii of 137 pm even with an additional electron shell filled. This is because, as the electrons fill the 4f-subshell, the core charge increases.

This change in density and atomic radius also affects other properties of the transition metals. With increasing density, melting point also increases. Tungsten has the highest melting temperature of any metal at 3410°C.

METALLIC CHARACTER

Metals conduct electricity and are usually solids at room temperature. Conversely, non-metallic elements usually do not conduct electricity and many are gases at room temperature.

The differences between the properties of metals and non-metals are related to the number of electrons in the outer shell of their atoms. In general, elements with atoms containing one, two or three valence electrons tend to behave as metals, whereas those with four or more valence electrons behave as non-metals. You will study this in more detail in Chapter 3.

Metals are located on the left side of the periodic table and non-metals are on the right. Elements known as the **metalloids** are located between the metals and non-metals. The metalloids exhibit both metallic and non-metallic properties. Silicon is one of the most abundant metalloids. It is a brittle solid, which is a common property of non-metals. However, it is also a semiconductor, meaning it exhibits electrical conductivity, making it useful in many electronic devices such as computers and calculators.

REACTIVITY

The **reactivity** of an element is an indication of how easily an atom of that element loses or gains electrons.

Reactivity of metals

When metals react, they lose electrons. Therefore, the reactivity of metals is a measure of how easily an atom of a metallic element can lose electrons. The weaker the attraction of the valence electrons to the nucleus, the more easily the electrons can be lost.

Moving down a group, there is an increasing number of electron shells in the atoms and therefore a weaker attractive force between the nucleus and valence electrons. This means that reactivity of metals increases down a group. The rate at which metals react with water indicates their relative reactivity.

Table 2.3.2 describes the reaction of some of the group 1 and 2 metals with water.

TABLE 2.3.2 Reaction of some group 1 and 2 metals with water. In each case, a reaction results in the formation of hydrogen gas

Period	Group	Element	Reaction with water
3	1	Sodium	Vigorous, producing enough energy to melt the sodium, which fizzes and skates on the water surface
4	1	Potassium	Violent, making crackling sounds as the heat evolved ignites the hydrogen produced by the reaction
5	1	Rubidium	Violent explosion
3	2	Magnesium	No reaction at room temperature but will react with steam
4	2	Calcium	Slow reaction at room temperature

For the five metals in Table 2.3.2:

- those in group 1 are more reactive in water than those in group 2
- down a group, the reactivity of the metal in water increases.

These generalisations agree with the results of experiments with other metals.

From left to right across the periodic table, the core charge of the atoms increases and it becomes more difficult for the element to lose electrons. Within the metals, this means there is a decrease in reactivity.

In summary, the reactivity of metals:

- increases down a group as it is easier for a metal with a greater number of shells to lose electrons
- decreases across the period as the increasing core charge makes it more difficult for a metal to lose electrons.

Reactivity of non-metals

Atoms of non-metallic elements undergo chemical reactions to gain electrons and form a stable octet arrangement. The more easily a non-metal can attract or share electrons, the more reactive that non-metal is. Elements that have fewer electron shells and higher core charges will have a greater attractive force between the nucleus and valence electrons and thus be more reactive.

Therefore, the reactivity of non-metals:

- decreases down a group as it is harder for a non-metal atom to attract electrons into its valence shell with a greater number of shells
- increases across the period as the increasing core charge makes it easier for a non-metallic atom to attract electrons.

2.3 Review

SUMMARY

- The first ionisation energy is the energy required to remove one electron from an atom of an element in the gas phase.
- First ionisation energy decreases down a group but increases across a period.
- Chemical reactivity is the ease with which an element undergoes a reaction. Metals tend to lose electrons, and non-metals tend to gain electrons. From left to right across a period in the periodic table, the elements change from metals to metalloids to non-metals.
- Chemical reactivity for metals increases down a group but decreases across a period.
- Chemical reactivity of non-metals decreases down a group but increases across a period.
- Many trends in the physical properties of elements in the periodic table can be explained using two key ideas.
  - From left to right across a period, the core charge of atoms increases, so the attractive force felt between the valence electrons and the nucleus increases.
  - Down a group, the number of shells in an atom increases so that the valence electrons are further from the nucleus and are held less strongly.

KEY QUESTIONS

1 **a** Explain the meaning of ionisation energy.
  b What factors need to be considered when predicting the trend in ionisation energies across a period?

2 What is a metalloid?

3 Explain why ionisation energy increases from left to right across a period.

Chapter review

02

KEY TERMS

anion
atomic number
atomic radius
block (periodic table)
cation
core charge
electronegativity
first ionisation energy
group (periodic table)
ion
ionisation
main group element
metalloid
periodic law
periodic table
period
periodicity
reactivity
transition metal

The periodic table

1 Use the periodic table to determine the period and block of the following elements.

- **a** Hydrogen
- **b** Carbon
- **c** Phosphorus
- **d** Copper
- **e** Uranium

2 Determine the period and group of the elements with the following electronic configurations.

- **a** $1s^2 2s^2$
- **b** $1s^2 2s^2 2p^6 3s^2 3p^2$
- **c** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$
- **d** $1s^2$

3 In the periodic table, explain why there are:

- **a** two groups of elements in the s-block
- **b** six groups of elements in the p-block
- **c** 10 elements in each transition series
- **d** 14 elements in the actinoids and lanthanoids.

4 Name an element with properties similar to those of:

- **a** carbon
- **b** rubidium
- **c** iodine
- **d** phosphorus.

Trends in the periodic table—Part 1

5 Across a period, the number of subatomic particles in an atom increases but the size of an atom decreases. Why?

6 Account for the fact that it takes more energy to remove an electron from the outer shell of atoms of:

- **a** phosphorus than magnesium
- **b** fluorine than iodine.

7 **a** Give the electronic configuration of nitrogen.

- **b** What period and group does nitrogen belong to in the periodic table?
- **c** How many valence electrons does nitrogen have?
- **d** What is nitrogen's core charge?

Trends in the periodic table—Part 2

8 Consider the elements in period 2 of the periodic table: lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine. Describe the changes that occur across the period. Consider:

- **a** the sizes of atoms
- **b** metallic character
- **c** electronegativity.

9 **a** Order the following elements from least reactive to most reactive: rubidium, sodium, lithium, potassium.

- **b** Explain your reasoning.

10 **a** Select the most reactive non-metal from the following list: magnesium, sulfur, chlorine, fluorine, aluminium, oxygen.

- **b** Explain your reasoning.

11 From each set of elements, select the element that has the largest first ionisation energy.

- **a** Phosphorus, arsenic, nitrogen
- **b** Silicon, chlorine, sulfur
- **c** Bromine, chlorine, sulfur

12 How does the reactivity of elements change from left to right across period 3 in the periodic table?

Connecting the main ideas

13 What concepts or ideas are the two versions of the periodic table in Figure 2.4.1 trying to convey? Search the internet for other versions of the periodic table.

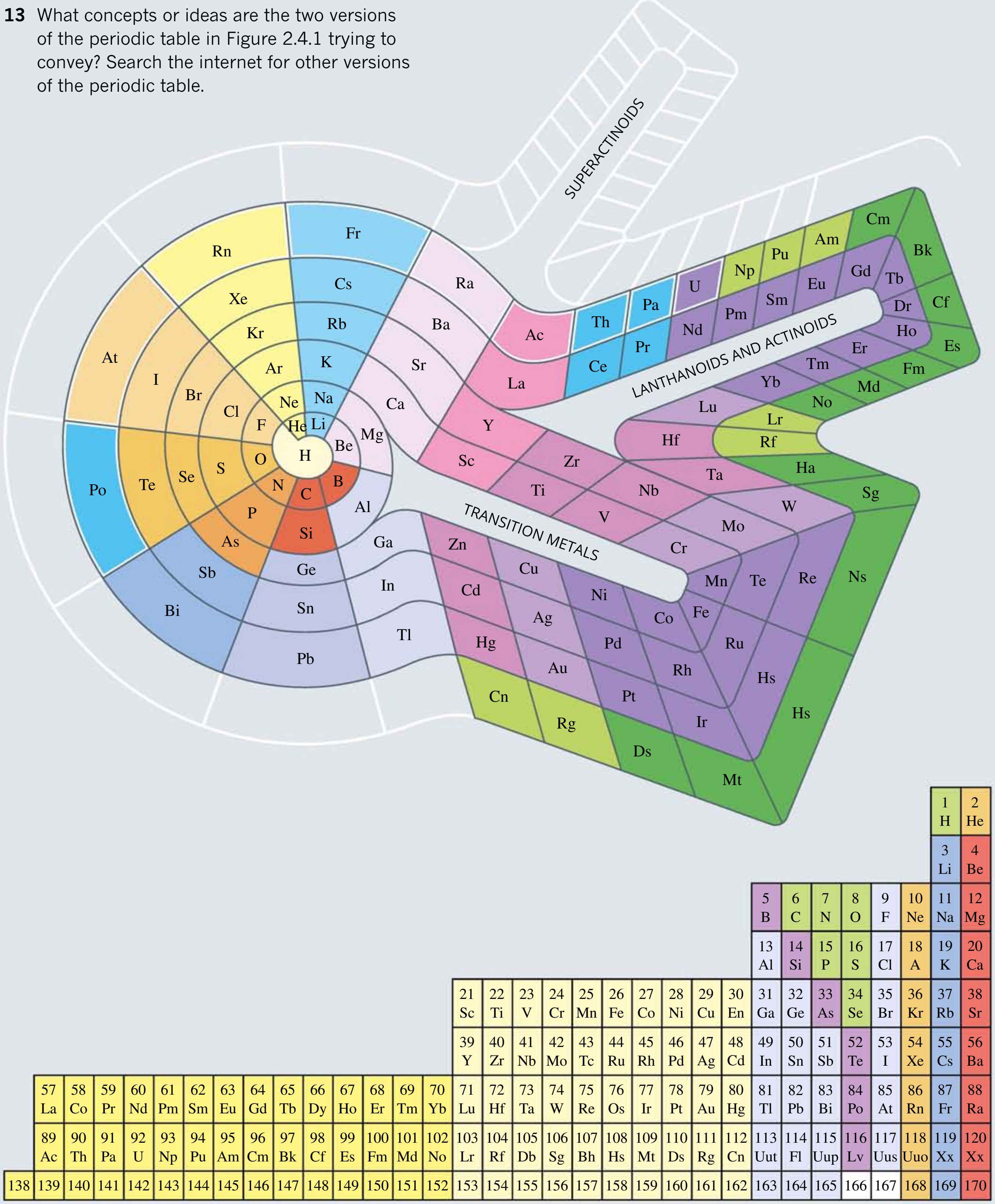
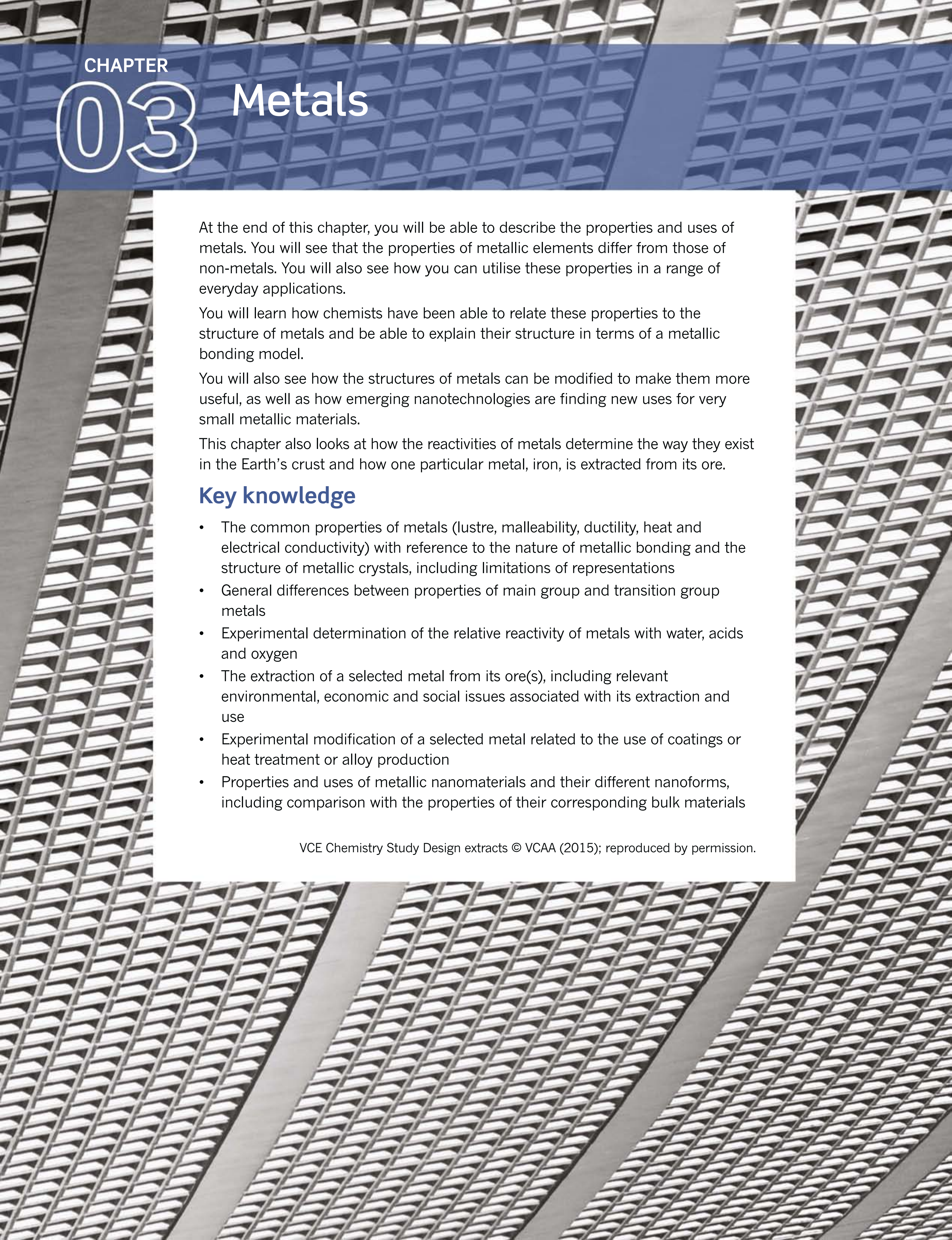


FIGURE 2.4.1



CHAPTER

03

Metals

At the end of this chapter, you will be able to describe the properties and uses of metals. You will see that the properties of metallic elements differ from those of non-metals. You will also see how you can utilise these properties in a range of everyday applications.

You will learn how chemists have been able to relate these properties to the structure of metals and be able to explain their structure in terms of a metallic bonding model.

You will also see how the structures of metals can be modified to make them more useful, as well as how emerging nanotechnologies are finding new uses for very small metallic materials.

This chapter also looks at how the reactivities of metals determine the way they exist in the Earth's crust and how one particular metal, iron, is extracted from its ore.

Key knowledge

- The common properties of metals (lustre, malleability, ductility, heat and electrical conductivity) with reference to the nature of metallic bonding and the structure of metallic crystals, including limitations of representations
- General differences between properties of main group and transition group metals
- Experimental determination of the relative reactivity of metals with water, acids and oxygen
- The extraction of a selected metal from its ore(s), including relevant environmental, economic and social issues associated with its extraction and use
- Experimental modification of a selected metal related to the use of coatings or heat treatment or alloy production
- Properties and uses of metallic nanomaterials and their different nanoforms, including comparison with the properties of their corresponding bulk materials

3.1 Properties of metals

More than 80% of the elements in the periodic table are metals.

Metals have been important to human beings since early times. The development of civilisation can be measured by the way we have used metals. The Copper Age (5000–3000 BCE) was followed by the Bronze Age (3000–1000 BCE) and the Iron Age (from 1000 BCE).

Gold, silver and copper can be found on Earth in an almost pure form. These metals were employed by prehistoric humans to make ornaments, tools and weapons. As humans' knowledge of metallurgy (the science of modifying metals) developed, metals have played a central role in fields as diverse as construction, agriculture, art, medicine and transport.

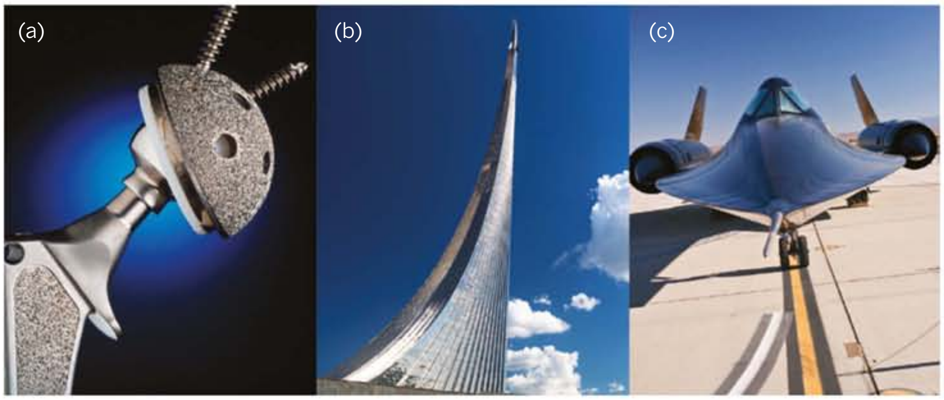


FIGURE 3.1.1 Titanium has many uses: (a) a replacement hip socket, (b) the spectacular curved space museum building in Moscow and (c) the SR-71 Blackbird reconnaissance aircraft. The SR-71 aircraft is the fastest manned aircraft that uses oxygen directly from the atmosphere.

The diverse properties of different metals make them suitable for many purposes. Table 3.1.1 shows the uses of some metals. For example, titanium (Figure 3.1.1) is a very strong, relatively unreactive metal with a low density that is close to that of bone. Consequently, it is used in surgical implants that can last up to 20 years with little effect on the body. Titanium is also used in the aerospace industry, in art and architecture, and in sporting products such as golf clubs.

TABLE 3.1.1 Properties and uses of some metals

Metal	Properties	Uses
Iron	Soft, malleable, magnetic, good thermal and electrical conductor, fairly reactive, readily forms alloys	Can corrode and is usually converted to more stable steel, which is used in buildings and bridges, automobiles, machinery and appliances
Aluminium	Low density, relatively soft when pure, excellent thermal and electrical conductor, malleable and ductile, good reflector of heat and light, readily forms alloys	Saucepans, frying pans, drink cans, cooking foil, food packaging, roofing, window frames, appliance trim, decorative furniture, electrical cables, aircraft and boat construction
Titanium	Very strong, high melting point, low density, low reactivity, readily forms alloys	Medical devices within the body, wheelchairs, computer cases; lightweight alloys are used in high-temperature environments such as spacecraft and aircraft
Gold	Shiny gold appearance, excellent thermal and electrical conductor, unreactive, readily forms alloys	Electrical connections, jewellery, monetary standard, dentistry

In this section, you will examine the properties of metals. Then, in the next section, you will learn about the bonding model that chemists have developed to explain these properties. This model has helped chemists and materials engineers to understand why metals behave the way they do and how metals can be modified to create useful new materials.

PROPERTIES OF METALS

Table 3.1.2 gives the properties of some metals and non-metals. Despite the different properties of metals, most metals:

- exhibit a range of melting points and relatively high boiling points
- are good **conductors** of electricity
- are good conductors of heat
- generally have high **densities**.

TABLE 3.1.2 Properties of some metallic and non-metallic elements

Element	Melting point (°C)	Boiling point (°C)	Electrical conductivity (MS m^{-1})*	Thermal conductivity (J s^{-1} m^{-1} K^{-1})†	Density (g mL^{-1})
Metals					
Gold	1063	2970	45	310	19.3
Iron	1540	3000	9.6	78	7.86
Mercury	–39	357	1	8.4	13.5
Potassium	64	760	14	100	0.86
Silver	961	2210	60	418	10.5
Sodium	98	892	21	135	0.97
Non-metals					
Carbon (diamond)	3550	‡	10^{-17}	—	3.51
Oxygen	–219	183	—	0.026	1.15 (liquid)

*MS m^{-1} = megasiemens per metre.
†Thermal conductivity measures the conductance of heat.
‡Diamond sublimes (changes straight from a solid to a gas) when heated.

Not all metals have all of these properties. Mercury is a liquid at room temperature—it has an unusually low melting point. The group 1 elements (the **alkali metals**) have some properties that make them different from most other metals. They are all soft enough to be cut with a knife and they react vigorously with water to produce hydrogen gas. Both mercury and the group 1 elements exhibit most of the other properties listed above and are classified as metals.

Metals also generally have the following characteristics in common. They:

- are **malleable**—they can be shaped by beating or rolling
- are **ductile**—they can be drawn into a wire
- are lustrous or reflective when freshly cut or polished
- are often hard, with high **tensile strength**
- have low **ionisation energies** and electronegativities.

These properties can allow different metals to be used together in order to solve many engineering problems. The power transmission tower in Figure 3.1.2 is made of a few metals to take advantage of their different properties.

FIGURE 3.1.2 This power transmission tower relies on the strength of iron in steel for its structural integrity. The electricity cables are made from aluminium, utilising its ductility and electrical conductivity.

Generally, metals are shaped for use in different applications by hammering, exploiting their malleability. Some metals, such as gold, copper and aluminium, are very malleable at room temperature. Other metals, such as iron, must be heated before they can be shaped.

Generally, metals are good conductors of electricity and heat. They are malleable, ductile, and have high tensile strength and low ionisation energies.

Most metals are similar in appearance, being lustrous (reflective) and silvery-grey. Gold and copper are notable exceptions. Gold is a yellow coloured metal; copper is reddish.

FORMING METAL IONS

In Chapter 1, you saw that there is a general tendency for atoms to combine so that they have eight electrons in the outer shell (the **octet rule**).

Metallic elements are found on the left-hand side of the periodic table. The atoms of metals are generally larger than the atoms of non-metallic elements within a period and the **core charge** of their atoms is lower. It takes less energy to remove electrons from an outer shell when an atom is large, so the ionisation energy of metals is usually lower than for non-metals in the same period. As a consequence, metal atoms tend to lose their outer-shell electrons to form positive ions, called **cations**.

Atoms of simple metals have one, two or three electrons in their outer shell. The cations that are formed when these metal atoms lose these valence electrons have a stable noble gas electronic configuration, with eight electrons in their outer shell.

CHEMFILE

Beryllium

Beryllium is the fourth element in the periodic table. It is one of the lightest metals, its density being two-thirds the density of aluminium. Beryllium is non-magnetic and has six times the stiffness of steel. The Space Shuttle and the Spitzer Space Telescope both use beryllium due to its strength and light weight. NASA's next-generation James Webb Space Telescope shown in Figure 3.1.3, scheduled for launch in 2018, will depend on a 6.5-metre mirror constructed using beryllium to see objects 200 times fainter than those previously visible.

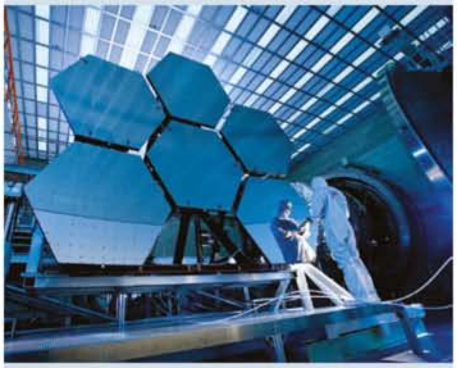


FIGURE 3.1.3 Some of the 18 mirror segments of the James Webb Space Telescope. The mirrors are supported by beryllium ribs that maintain the mirror's shape under extreme conditions.

Worked example 3.1.1

DETERMINING CHARGES

Determine the charge of a calcium cation.

Thinking	Working
Unreacted calcium atoms have the same number of protons and electrons.	Atomic number (*Z*) of calcium is 20: number of protons is 20, number of electrons is 20
The electrons in an atom are in shells.	Shell configuration of calcium: 2,8,8,2
Only the outer-shell electrons will be lost.	Outer shell contains two electrons, 20 – 2 = 18 electrons remaining
Cation charge = number of protons – number of electrons	Cation charge = 20 – 18 = +2

Worked example: Try yourself 3.1.1

DETERMINING CHARGES

Determine the charge of an aluminium cation.

TRANSITION METALS

Between group 2 and group 13 in the periodic table is a block of elements known as the **transition metals**. These elements generally have unfilled d-subshells and are often referred to as the d-block. (See the periodic table at the end of the book.) They include metals such as iron and nickel that are used to build cities, bridges, cars and railway lines, and precious metals such as silver and gold that have ornamental and economic uses. Most transition metals are silver-coloured and are similar in appearance, as can be seen in Figure 3.1.4.

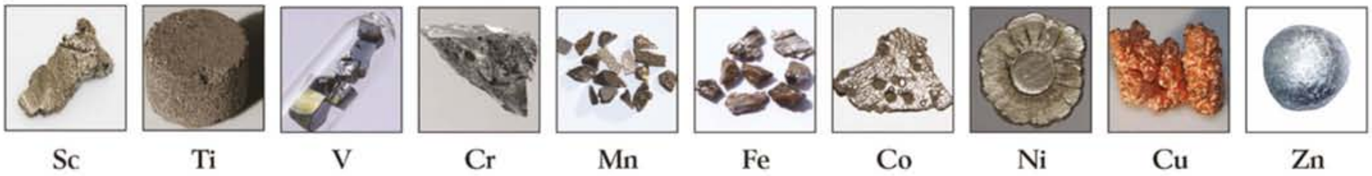


FIGURE 3.1.4 The first row of transition metals.

The transition metals are very important to Australian industry. All of the metals in the first row are found in Australia and many are being mined today.

Iron is by far the most important metal to us. Nearly ten times more iron is mined than all other metals combined. Iron obtained directly from a blast furnace is relatively **brittle** and corrodes easily. Carbon and other transition metals are combined with iron to produce mixtures or **alloys**, called **steel**. Steel has more desirable characteristics than pure iron. (Alloys are covered in more detail in section 3.5.)

Copper is one of the few transition metals that is mainly used in its pure form. It is highly electrical conductive and so it is used for most of the millions of kilometres of electrical wires that enable the transmission of electric energy for heating, lighting, telephones, radio and television.

Transition metals are not only important for industry, they are also important for life. All the transition metals in the first row, except scandium and titanium, are essential for animal life. Your body relies on the presence of trace elements to carry out certain biochemical reactions. For example, chromium, which you get from meat and bread, assists in the production of energy from glucose.

Properties of transition metals

Compared to the main group metals, transition metals have the following properties.

- They tend to be harder.
- They have higher densities.
- They have higher melting points.
- Some of them have strong magnetic properties.

The hardness, higher densities and higher melting points are due to the atoms of transition metals generally being a smaller size due to their greater core charge. This allows them to pack together more tightly with stronger bonds.

The high tensile strength of transition metals makes them suitable for use in the construction of buildings, cars, bridges and numerous other objects.

Transition metal compounds

Transition metal compounds display a wide range of different colours. They are extensively used as pigments in paints, and to colour glass, ceramics and enamel. In Figure 3.1.5 on page 58, the colours used by the artists are caused by the different transition metals present and the colours are still as vivid today as when they were painted.

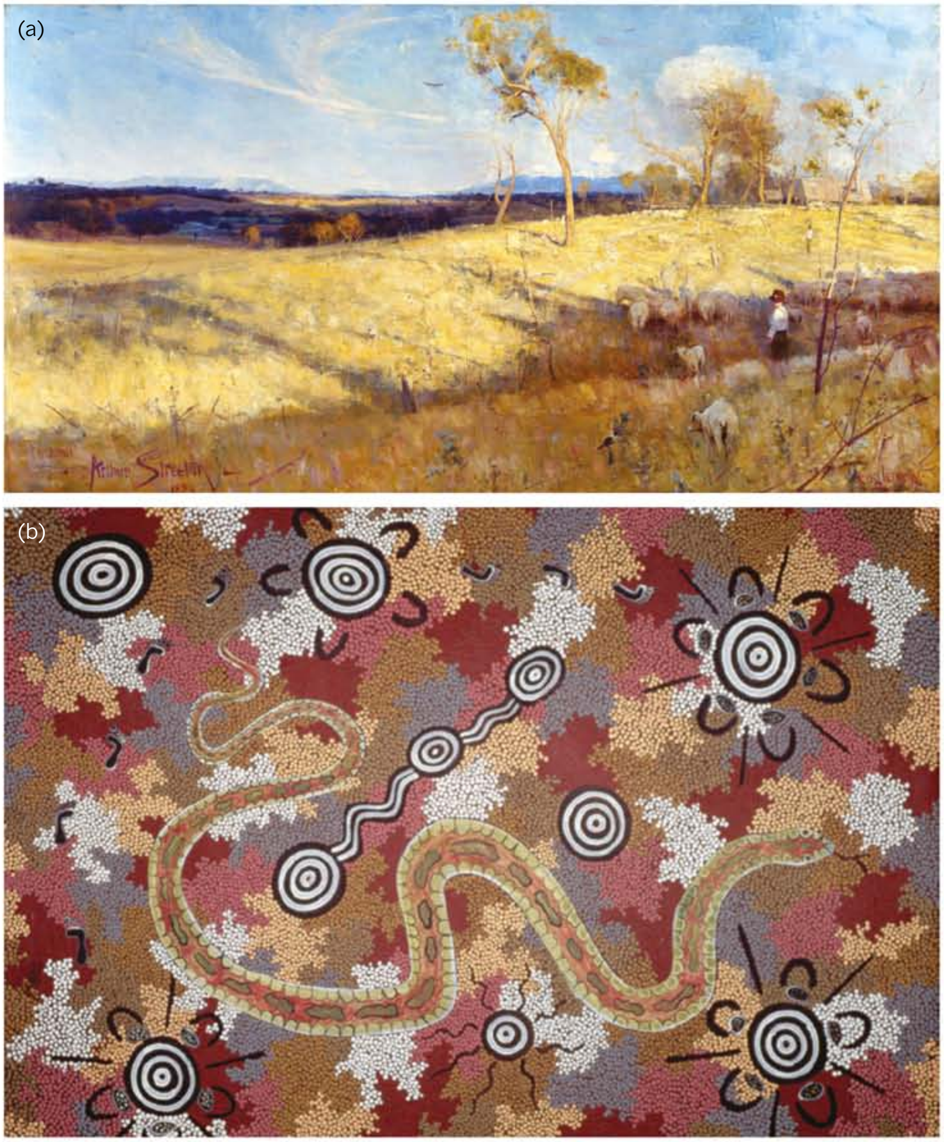


FIGURE 3.1.5 (a) Arthur Streeton's 'Golden summer, Eaglemont', 1889. (b) An Australian Aboriginal abstract painting.

FIGURE 3.1.6 Blue sapphires get their colour from impurities of titanium and iron.

Ochre is a type of hard clay that contains iron oxides and hydroxides, which can be found naturally in many colours, including red, pink, white and yellow. Ground into a powder and mixed with liquids, ochre forms a paste that has been used for millennia by Aboriginal and Torres Strait Islander people in Australia for body decoration, cave painting, bark painting and other artwork.

The colours of many gemstones are also due to the presence of transition metals. For example, sapphires (Figure 3.1.6) contain traces of titanium and iron in a crystal **lattice** of aluminium oxide.

The colours arise when electrons within the metal ions in the compounds absorb light of particular wavelengths and move to higher energy levels. Absorbance of light with some wavelengths and transmission of light with other wavelengths results in the compounds appearing coloured. By contrast, compounds of group 1 and group 2 metals are usually colourless.

3.1 Review

SUMMARY

- Metals have the following characteristic properties:
  - high boiling points
  - good conductors of electricity in solid and liquid states
  - malleable and ductile
  - high densities
  - good conductors of heat
  - lustrous
  - low electronegativities
  - low ionisation energies
  - react by losing electrons.
- The main differences between the properties of main group and transition metals are:
  - transition metals are harder
  - transition metals are more dense
  - transition metals have higher melting points
  - some transition metals have strong magnetic properties
  - transition metal compounds tend to be brightly coloured.

KEY QUESTIONS

1. Determine the charge of the cations formed from the following metals if they lost all of their outer-shell electrons.
   a Li
   b Mg
   c Ga
   d Ba
2. **a** Potassium is classed as a metal. Which of its properties are similar to those of the metal gold? In what ways is it different?
   b Identify another element in Table 3.1.2 on page 55 that has similar properties to potassium.
   c Identify another metal in Table 3.1.2 on page 55 that has similar properties to gold.
   d Where are these four metals in the periodic table?
3. **a** Which metals would you select if you wanted a good electrical conductor?
   b What other factors might influence your choice?
4. Sodium and iron have very different physical properties. Explain why this is so based on where these metals are found in the periodic table.
5. Suggest some properties not included in Table 3.1.2 on page 55 that you would need to consider before choosing between aluminium and iron for building a bridge.

3.2 Metallic bonding

In this section, you will learn how the properties of metals can be explained in terms of the structure of the particles in metals. You will also learn about the bonding model that chemists have developed to explain these properties. The metallic bonding model has helped chemists and materials engineers to understand why metals behave as they do and how metals can be modified to create useful new materials.

CONNECTING PROPERTIES AND STRUCTURE

The properties of metals are listed in Table 3.2.1. Each of these properties gives some information about the structure and bonding of particles in metals.

TABLE 3.2.1 The physical properties of metals and resulting conclusions about metal structure and bonding

Property	What this tells us about structure
Metals are usually hard and tend to have high boiling points.	The forces between the particles must be strong.
Metals conduct electricity in the solid state and in the molten liquid state.	Metals have charged particles that are free to move.
Metals are malleable and ductile.	The attractive forces between the particles must be stronger than the repulsive forces between the particles when the layers of particles are moved.
Metals generally have high densities.	The particles are closely packed in a metal.
Metals are good conductors of heat.	There must be a way of quickly transferring energy throughout a metal object.
Metals are lustrous or reflective.	Free electrons are present, so metals can reflect light and appear shiny.
Metals tend to react by losing electrons.	Electrons must be relatively easily removed from metal atoms.

Chemists have developed a model for the structure of metals to explain all the properties that have been mentioned so far. You can deduce from the information in Table 3.2.1 that the metallic bonding model must include:

- charged particles that are free to move and conduct electricity
- strong forces of attraction between atoms throughout the metal structure
- some electrons that are relatively easily removed.

METALLIC BONDING MODEL

Electrons are the particles that enable metals to conduct electricity. They are able to move between the lattice (tightly packed arrangement) of metal atoms. Negatively charged electrons can be lost from the outer shell of metal atoms, forming positive ions (cations). As shown in Figure 3.2.1, the freed electrons **delocalise** (spread through a large area) to form a 'sea' of electrons throughout the entire metal structure due to the strong attraction to the metal cations.

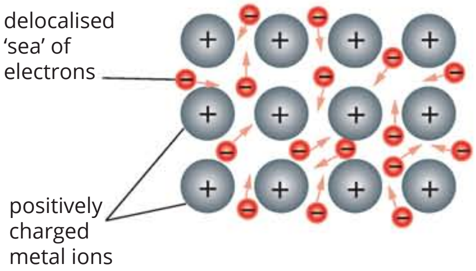


FIGURE 3.2.1 The metallic bonding model. Positive metal cations are surrounded by a mobile sea of delocalised electrons. This diagram shows just one layer of metal ions.

Chemists believe that, in a solid sample of a metal:

- positive ions are arranged in a closely packed structure. This structure is described as a regular, three-dimensional network of positive ions. The cations occupy fixed positions in the lattice
- negatively charged electrons move freely throughout the lattice. These electrons are called **delocalised electrons** because they belong to the lattice as a whole, rather than staying in the shell of a particular atom
- the delocalised electrons come from the outer shells of the atoms. Inner-shell electrons are not free to move throughout the lattice and remain firmly bonded to individual cations

- the positive cations are held in the lattice by the electrostatic force of attraction between these cations and the delocalised electrons. This attraction extends throughout the lattice and is called **metallic bonding**.

Together, these ideas make up the metallic bonding model. An example of how a metal, such as sodium, could be represented using this model is shown in Figure 3.2.2.

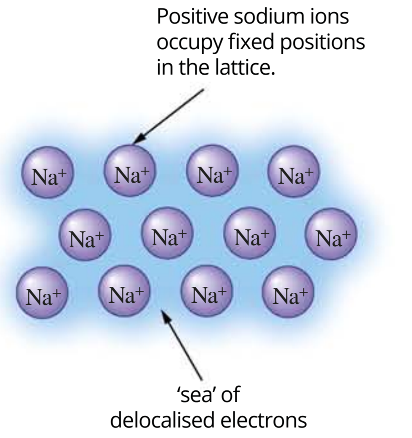


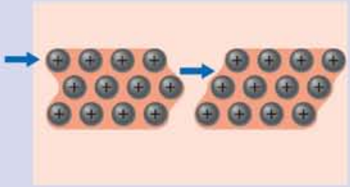
FIGURE 3.2.2 A representation of a sodium metal lattice. Each sodium atom loses its one valence electron. This electron is shared with all atoms in the lattice to form a sea of delocalised electrons.

In the metallic bonding model, positive metal cations are surrounded by a sea of delocalised electrons.

EXPLAINING THE PROPERTIES OF METALS

Table 3.2.2 shows how the metallic bonding model is consistent with the relatively high boiling point, electrical conductivity, malleability and ductility of metals.

TABLE 3.2.2 Physical properties of metals and explanations from metallic bonding model

Property	Explanation	
Metals are hard and have relatively high boiling points.	Strong electrostatic forces of attraction between positive metal ions and the sea of delocalised electrons holds the metallic lattice together.	
Metals are good conductors of electricity.	Free-moving delocalised electrons will move towards a positive electrode and away from a negative electrode in an electric circuit.	
Metals are malleable and ductile.	When a force causes metal ions to move past each other, layers of ions are still held together by the delocalised electrons between them.	

Other properties of metals

Metals generally have a high density. The cations in a metal lattice are closely packed. The density of a metal depends on the mass of the metal ions, their radius and the way in which they are packed in the lattice.

Metals are good conductors of heat. When the delocalised electrons bump into each other and into the metal ions, they transfer energy to their neighbour. Heating a metal gives the ions and electrons more energy and they vibrate more rapidly. The electrons, being free to move, transmit this energy rapidly throughout the lattice.

Metals are lustrous. Because of the presence of free electrons in the lattice, metals reflect light of all wavelengths and appear shiny.

Metals tend to react by losing electrons. The delocalised electrons in metals may participate in reactions anywhere on the metal's surface. The reactivity of a metal depends on how easily electrons can be removed from its atoms. This is covered in more detail in section 3.3.

Limitations of the metallic bonding model

Although this model of metallic bonding explains many properties of metals, some cannot be explained so simply. These include the:

- range of melting points, hardness and densities of different metals

- differences in electrical conductivities of metals
- magnetic nature of metals such as cobalt, iron and nickel.

In order to deal with such questions, you would need a more complex model of metallic bonding, which is beyond the scope of this book.

Worked example 3.2.1

ELECTRONIC CONFIGURATION OF ALUMINIUM

With reference to the electronic configuration of aluminium, explain why solid aluminium can conduct electricity.

Thinking	Working
Using the atomic number of the element, determine the electronic configuration of its atoms. (You may need to refer to a periodic table.)	Al has an atomic number of 13. This means a neutral atom of aluminium has 13 electrons. The electronic configuration is $1s^22s^22p^63s^23p^1$.
From the electronic configuration, find how many outer-shell electrons are lost to form cations that have a stable, noble gas electronic configuration. These electrons become delocalised.	Al has 3 electrons in its outer shell (the $3s^23p^1$ electrons). Al atoms will tend to lose these 3 valence electrons to form a cation with a charge of 3+. The outer-shell electrons become delocalised and form the sea of delocalised electrons within the metal lattice.
An electric current occurs when there are free-moving charged particles.	If the Al is part of an electric circuit, the delocalised electrons are able to move through the lattice towards a positively charged electrode.

Worked example: Try yourself 3.2.1

ELECTRONIC CONFIGURATION OF MAGNESIUM

With reference to the electronic configuration of magnesium, explain why solid magnesium can conduct electricity.

3.2 Review

SUMMARY

- Metallic bonding is the electrostatic force of attraction between a lattice of positive ions and delocalised valence electrons. The lattice of cations is surrounded by a sea of delocalised electrons.
- The metallic bonding model can be used to explain the properties of metals, including their malleability, thermal conductivity, generally high melting point and electrical conductivity.

KEY QUESTIONS

1 The properties of calcium mean that it is classed as a metal.

- **a** Draw a diagram to represent a calcium metal lattice.
- **b** Describe the forces that hold this lattice together.

2 Barium is an element in group 2 of the periodic table. It has a melting point of 850°C and conducts electricity in the solid state. Describe how the properties of barium can be explained in terms of its bonding and structure.

3 Graphite is a non-metallic substance that can be lustrous and conducts electricity and heat. It is not malleable, but breaks if a force is applied.

- **a** What properties does graphite share with metals?
- **b** What inferences can you make about the structure of graphite given it shares these properties with metals?

3.3 Reactivity of metals

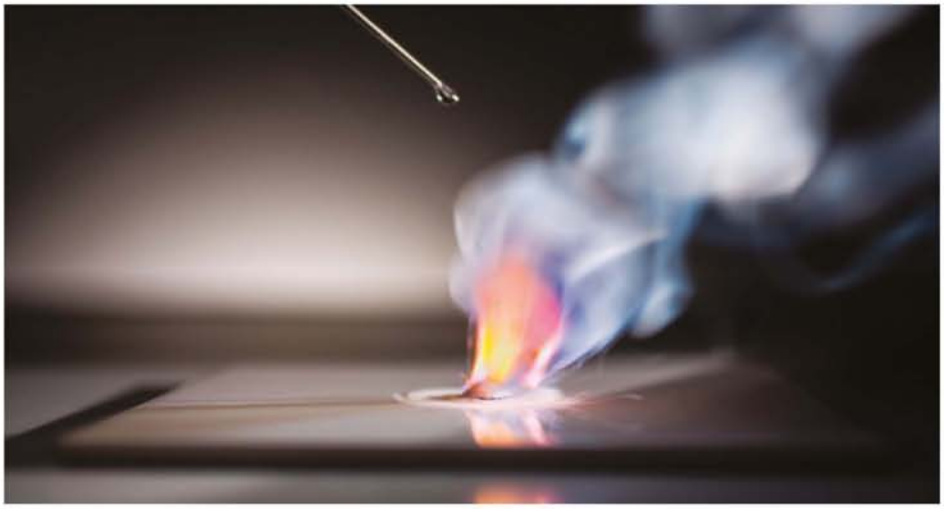
In the previous section, you learned that metals have many common properties. Metallic elements can also have very different properties. These include their **reactivity** with water, acids and oxygen. Some metals are extremely reactive and others are much less so.

This section will look at how the reactivity of different metals can be determined experimentally and what are some of the periodic patterns that exist.

DETERMINING THE REACTIVITY OF METALS

Reactivity with water

The way metals react with water can indicate their relative reactivity.



potassium + water → potassium hydroxide + hydrogen gas

FIGURE 3.3.1 When water is dropped onto metallic potassium, hydrogen gas is produced.

Figure 3.3.1 shows the reaction of potassium, a group 1 metal, with water. Enough heat is generated to instantly melt the potassium and ignite the hydrogen. The vigour of the reaction is an indication of the reactivity of the metal. Potassium has high reactivity with water, which is characteristic of the group 1 metals.

Table 3.3.1 describes the reaction of some group 1 and group 2 metals with water. In each case, a reaction results in the formation of hydrogen gas.

TABLE 3.3.1 Reaction of selected group 1 and 2 metals with water

Period	Group	Element	Reaction with water
3	1	Sodium	Reacts vigorously, producing enough energy to melt the sodium, which fizzes and skates on the water surface
4	1	Potassium	Reacts violently, making crackling sounds as the heat evolved ignites the hydrogen produced by the reaction
5	1	Rubidium	Explodes violently on contact with water
3	2	Magnesium	Will not react with water at room temperature but will react with steam
4	2	Calcium	Reacts slowly with water at room temperature

From these and other experimental observations we can say that, in general:

- metals in group 1 of the periodic table (i.e. Na, K and Rb) are more reactive in water than those in group 2 (i.e. Mg and Ca)
- going down a group, the reactivity of the metal in water increases.

CHEMFILE

Reactivity of group 1 metals

Group 1 metals are so reactive that they must be handled with great care. They need to be stored under oil to prevent the metal coming into contact with moisture in the atmosphere.

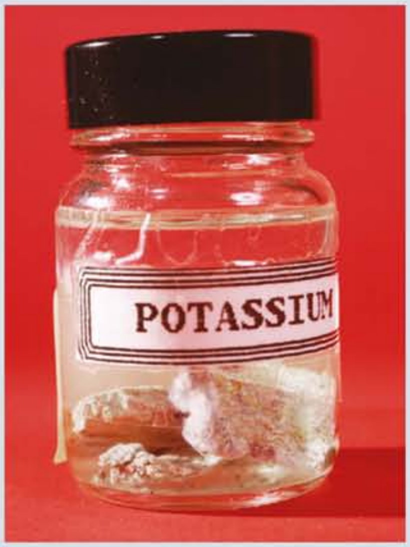


FIGURE 3.3.2 Potassium metal is stored under oil to prevent contact with moisture.

Transition metals

Transition metals are generally less reactive with water than group 1 and 2 metals are. For example, iron reacts fairly slowly with water. Gold and platinum are essentially unreactive.

Reactivity with acids

The reactivity of different metals with acids follows the same general patterns as the reactivity of metals with water. Metals are normally more reactive with acids than with water. More metals react with acids and the reactions tend to be more energetic.

Metals can be placed in an order of their relative reactivity. In Figure 3.3.3, the reactions of magnesium, iron and copper with an acid are shown. The large amount of bubbling and the mist produced show that magnesium is the most reactive metal of the three, whereas copper is the least.

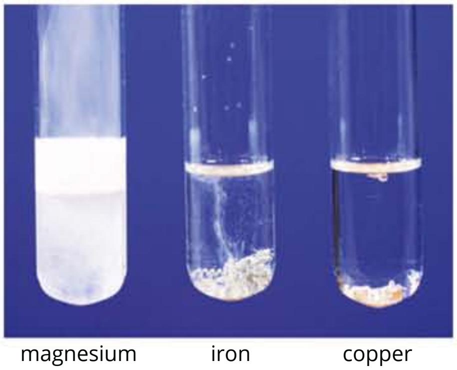


FIGURE 3.3.3 Metals reacting with an equal amount of dilute acid. From left to right: magnesium ribbon, iron filings and copper turnings.

Reactivity with oxygen

Many metals also react with oxygen. The group 1 metals all react rapidly with oxygen. Figure 3.3.4 shows sodium metal burning in a container of pure oxygen. The metal atoms and oxygen molecules rearrange to form a new compound, sodium oxide. The word equation for this reaction is:

sodium + oxygen → sodium oxide

The group 2 metals also react with oxygen to form oxides (compounds containing the O^{2-} **anion**), although not as rapidly as group 1 metals. Heat is usually required to start the reaction.

While the transition metals are less reactive with oxygen than the metals in groups 1 and 2, their reactions are also important. Iron forms rust (iron oxide) when exposed to oxygen and water over a period of time. Many transition metals needed by society cannot be found in nature as a pure element but often exist as oxides.

Iron, copper, titanium and aluminium are all mined as the oxides and must be processed to obtain the finished metal. Figure 3.3.5 shows a cluster of crystals of rutile, the oxide from which titanium is extracted. The production of iron from iron oxide is covered in detail in section 3.4.

Gold and platinum, which are much less reactive than most other metals, are found in the Earth's crust in their pure form. Gold is often found in rock formations called seams alongside quartz, as shown in Figure 3.3.6.

FIGURE 3.3.4 Sodium burning in pure oxygen.

FIGURE 3.3.5 Rutile is a mineral that contains titanium dioxide.

FIGURE 3.3.6 Gold, an unreactive metal, exists in the Earth's crust in its metallic elemental form.

REACTIVITY SERIES OF METALS

Chemists have used experimental data from the reactions of metals to produce a **reactivity series of metals**, as shown in Figure 3.3.7. Group 1 metals are at the top of the series, while transition metals appear at the bottom.

Reasons for different reactivities of metals

In general, the reactivity of main group metals increases going down a group in the periodic table and decreases across a period. This trend in reactivity can be explained in terms of the relative attractions of valence electrons to the nucleus of atoms.

When metals react, their atoms tend to form positive ions by donating one or more of their valence electrons to other atoms. The metal atoms that require less energy to remove electrons tend to be most reactive. The most reactive metals tend to be those with the lowest ionisation energies, which are found in the bottom left-hand corner of the periodic table.

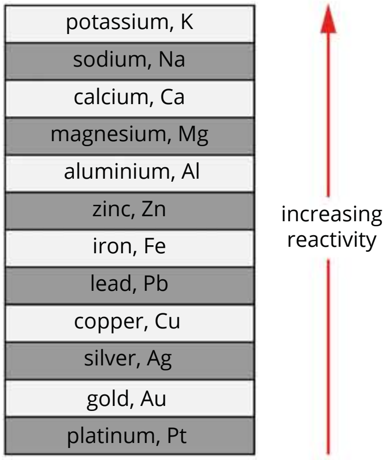


FIGURE 3.3.7 The reactivity series of some common metals.

3.3 Review

SUMMARY

- The reactivity of different metals with water, acid and oxygen can be determined experimentally.
- Group 1 metals are very reactive with water.
- Metals tend to be more reactive with acids than with water.
- The experimental results of metals reacting with acids are used to place metals in an order of reactivity called the reactivity series.
- The most reactive metals are found at the bottom left-hand side of the periodic table.
- Although the reactivities of transition metals vary, they are usually less reactive than the main group metals.

KEY QUESTIONS

1 Predict the products of the reaction between potassium and water and write a word equation for this reaction.

2 **a** Describe the trend in reactivity with water down the group 1 metals.

b What atomic property accounts for this trend in reactivity?

3 Pieces of iron, zinc and gold metal were each placed into test-tubes containing hydrochloric acid. Table 3.3.2 summarises the observations from each test. On the basis of the reactions, list the metals in order of reactivity.

TABLE 3.3.2 Summary of observations from tests in which iron, zinc and gold were added to hydrochloric acid

Metal	Evidence of reaction
Iron	Bubbles of gas are slowly produced. Iron metal disappears after a very long time.
Zinc	Bubbles of gas are rapidly produced. Zinc metal disappears.
Gold	No signs of a chemical reaction. Gold does not change appearance.

4 Using the reactivity series of some common metals (Figure 3.3.7), determine whether calcium, platinum or aluminium would react most vigorously with oxygen in the air.

3.4 Extraction of iron from its ore

Australia is the world's largest exporter of iron **ore** (a natural compound containing a metal). Australia exported a record 747 million tonnes of iron ore in 2014–15, which was worth around $57 billion.

Modern society is very dependent on iron. About 98% of world iron production is used to make steel, which you will learn more about in section 3.5. The steel in turn is used in bridges, buildings and all forms of transport. It also has many other uses (Figure 3.4.1).

FIGURE 3.4.1 Steel is used in (a) the Sydney Harbour Bridge, (b) building frames in construction, (c) train tracks and (d) surgical instruments.

Deposits of iron ore occur in all Australian states and territories. Most of the identified deposits—almost 93% (totalling 64 billion tonnes)—are found in Western Australia. Massive deposits of iron ore in the Pilbara region of Western Australia are mined by open-cut methods.

Iron ore is composed mainly of **iron oxide** combined with rocky material. The iron must be extracted from the ore before it can be used to make steel.

There are various ways of extracting a metal from its ore. This section will examine, as a case study, the main method used to extract iron from its ore. It will also examine the environmental, economic and social issues associated with this method of extraction.

IRON ORE

Iron ore is a **mineral** that occurs in the Earth's crust. Minerals are naturally occurring solid substances with a definite chemical composition, structure and properties.

Most metals in the Earth's crust are in the form of mineral compounds such as oxides, sulfides or silicates. The only metals in the Earth's crust that are found entirely in their elemental state are platinum and gold. Gold and platinum are so unreactive as to be considered chemically **inert**. They do not generally react with water, acids or oxygen.

Most deposits of iron ore occur in sedimentary rocks, which are more than 600 million years old. They formed from chemical reactions that combined iron and oxygen in marine and fresh waters.

In Australia, the iron oxides in iron ore are usually in the form of **haematite** (Fe_2O_3) (Figure 3.4.2). This mineral is dark and reflective when polished, but a red layer forms on its surface after exposure to oxygen. Many of Australia's deserts have red sands due to the presence of this red oxide.

Other common iron minerals are magnetite (Fe_3O_4) and pyrite (FeS_2). Magnetite is a black mineral that has been known since ancient times as lodestone. It is magnetic and was used to make early compasses. Pyrite is a shiny, yellow coloured mineral that is often referred to as 'fool's gold' due to its striking resemblance to gold (Figure 3.4.3). Pyrite is used extensively as a source of sulfur by the chemical industry.

FIGURE 3.4.2 The mineral haematite (Fe_2O_3) is mined as the main source of iron. This sample has been partially polished, removing most of the red oxide coating that forms upon exposure to air.

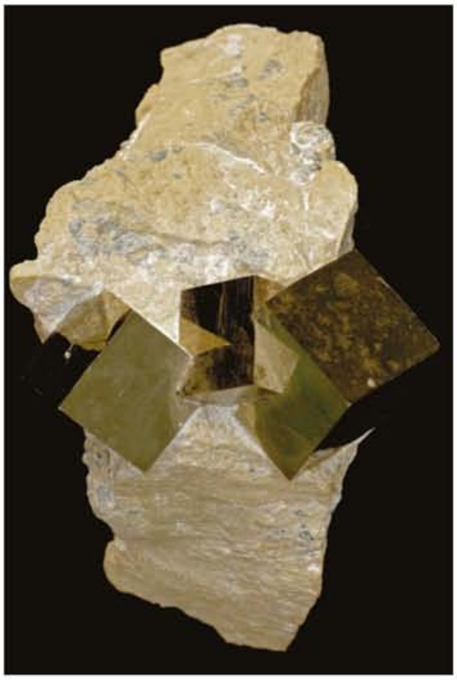


FIGURE 3.4.3 Cubic crystals of pyrite.

EXTRACTING IRON FROM ITS ORE

Raw materials

The raw materials used in the extraction of iron are:

- iron ore
- **coke**
- **limestone**
- air.

Iron ore

Iron ore is mined from the ground and taken in trucks for processing. In Australia, this is done by open-cut mining methods. A haul truck (large dump truck) capable of carrying up to 400 tonnes is shown moving iron ore within a mine in Figure 3.4.4.

FIGURE 3.4.4 Iron ore is sourced from open-cut mines in Australia.

Coke

Coke is a solid that contains 80–90% carbon. The coke used for iron production is made by strongly heating coal in air-tight ovens for about 15 hours. This is performed on the same site where iron is extracted from the ore. A number of useful by-products are obtained from this process, including:

- fuel gas, which is burnt to provide heat in various furnaces on the site
- tar, benzene, toluene and ammonium sulfate, which are used as the raw materials for other chemical industries.

Limestone

Limestone is a sedimentary rock that is mainly composed of calcium carbonate. Limestone is obtained by mining or quarrying and is crushed before use.

FIGURE 3.4.5 A blast furnace used to extract iron from iron ore. Iron ore is added continuously to the top of the furnace by the conveyor belts on the left-hand side.

The blast furnace

Extraction of iron from ore and the removal of unwanted materials is carried out in a tall, bottle-shaped tower called a **blast furnace**. A building containing a modern blast furnace and external conveyer belts is shown in Figure 3.4.5. These furnaces are heated to very high temperatures and are operated continuously for many years.

Figure 3.4.6 shows a diagram of the inside of a blast furnace. Pre-heated air is blasted into the bottom part of the furnace, while solid 'charges' (scoops) of iron ore, coke and limestone are continuously added to the top. The construction of the furnace causes different temperature zones where different reactions can take place.

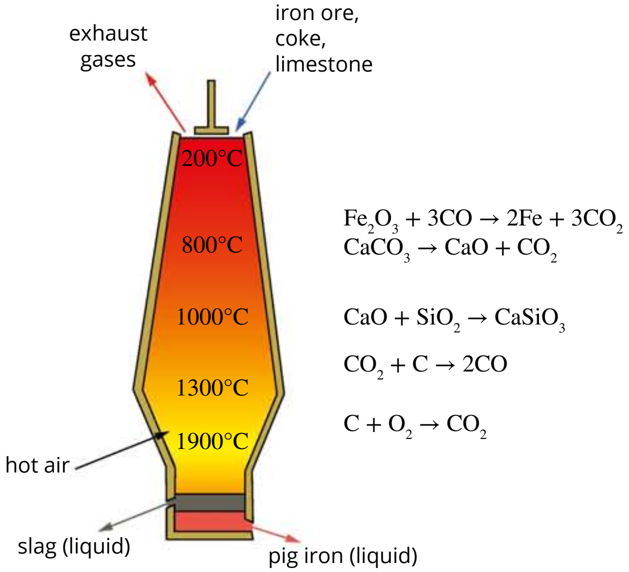


FIGURE 3.4.6 A diagram of a blast furnace. Hot air jets blast air in at the bottom. Iron ore, coke and limestone are added at the top.

Part 1: Coke reacts with oxygen

As the air rises through the furnace and meets the descending charge, oxygen reacts with coke to produce carbon dioxide, which then reacts further with the coke to produce carbon monoxide. These reactions are represented by the following equations:

$$\text{carbon} + \text{oxygen} \rightarrow \text{carbon dioxide}$$
$$C + O_2 \rightarrow CO_2$$
$$\text{carbon dioxide} + \text{carbon} \rightarrow \text{carbon monoxide}$$
$$CO_2 + C \rightarrow 2CO$$

The first reaction releases considerable heat energy and helps to maintain the high temperature that provides the fast rate of reaction required for metal production in the furnace. No external source of heat is needed to achieve temperatures up to 1800°C within the furnace.

Part 2: Carbon monoxide reacts with iron ore

Extraction of iron from iron oxide occurs in a series of steps in which carbon monoxide is the main reactant. The steps occur in different temperature zones within the blast furnace. Iron ore (Fe_2O_3) is first converted to another iron oxide (Fe_3O_4), then another (FeO) and finally to the metal (Fe). The process is summarised by the single chemical equation:

$$\text{carbon monoxide} + \text{iron oxide} \rightarrow \text{iron} + \text{carbon dioxide}$$
$$3CO + Fe_2O_3 \rightarrow 2Fe + 3CO_2$$

Function of limestone in the blast furnace

Iron ore is not pure iron oxide. It also contains rocky material such as silica (silicon dioxide), alumina and manganese oxides. These would not melt in the heat of the furnace and would eventually clog it up.

The limestone ($CaCO_3$) added to the top of the furnace breaks down in the furnace to form calcium oxide (CaO) and carbon dioxide. Calcium oxide can react with the unwanted materials to form a new compound called **slag**. Most of the slag is calcium silicate ($CaSiO_3$) due to the high amount of silica in iron ore.

Both the iron and slag are **molten** (melted) and sink to the bottom of the furnace. The slag is less dense and floats on top of the molten iron. This provides a cover that prevents the iron from reacting with the incoming air and re-forming iron oxide.

Collection of the iron

Holes at the base of the furnace are opened and the molten iron and slag are drained out and separated. In a steel works, the iron is usually transferred, while still molten, directly to a steel-making furnace. The slag may be used as a road-surfacing material or to manufacture cement.

ENVIRONMENTAL, ECONOMIC AND SOCIAL ISSUES

Modern society is literally built on and driven by iron and steel. Since the early 1960s, iron ore mining and export has shaped many aspects of life in Australia.

Mining and metal extraction processes raise environmental, economic and social issues. Some of issues involved with the mining of iron ore and the production of iron are listed in Table 3.4.1.

TABLE 3.4.1 Some of the environmental, economic and social issues associated with the extraction of iron from iron ore

Environmental issues	Economic issues	Social issues
• Loss of landscape due to mining, processing and transporting iron ore, coke and limestone • Air pollution from extraction process • Disposal of slag • Noise pollution	• Significant financial benefit for Australia • Significant gaps can occur in wages paid to mining staff and those who work locally in service industries	• Negotiations with indigenous groups to ensure fair access to iron-rich land • Land use conflicts between mining, agriculture and tourism • Iron ore mines are located in remote locations. Workers usually fly to mines to work for a number of days before flying home, which has an impact on family life

3.4 Review

SUMMARY

- The raw materials used in the extraction of iron are iron ore, coke, limestone and air.
- Iron ore is a mixture of iron oxides and other rocky material.
- Extraction of iron from iron ore occurs in a blast furnace. A series of reactions occur involving the iron ore, air and coke:
  carbon + oxygen → carbon dioxide
  $C + O_2 \rightarrow CO_2$
  carbon dioxide + carbon → carbon monoxide
  $CO_2 + C \rightarrow 2CO$
  carbon monoxide + iron oxide → iron + carbon dioxide
  $3CO + Fe_2O_3 \rightarrow 2Fe + 3CO_2$
- Limestone ($CaCO_3$) reacts with unwanted substances in the iron ore to produce slag, which is removed.
- Molten iron is collected from the bottom of the blast furnace.
- There are many environmental, economic and social issues associated with the mining and extraction of iron from ore.

KEY QUESTIONS

1 Classify each of the following statements about iron extraction in a blast furnace as true or false.
   a Slag is denser than iron.
   b Iron ore is a rock that contains purely iron oxide.
   c Limestone is a source of calcium carbonate.
   d Air is pre-heated before being added through the bottom of the furnace.
   e The furnace must be continually heated by external sources to achieve the temperatures required to extract iron.

2 Write the word equation for the production of iron from the reaction of carbon monoxide and the ore magnetite.

3 One of the very important issues with the production of iron in a blast furnace is environmental pollution. Name one source of gas pollution and write a word equation in which it is produced.

4 When choosing a suitable location for the production of iron, miners consider other factors as well as the availability of iron ore. What other factors might affect the selection of a suitable site?

3.5 Modifying metals

The way in which a metal can be used is determined by the metal's physical and chemical properties. Although some metals are valuable in their pure state, most metals need to be modified to make them more useful.

Modified metals have a wide range of applications. In Figure 3.5.1, you can see a number of uses of modified metals. In each case, a metal with desirable properties has been chosen and improved by the processes covered in this section.

FIGURE 3.5.1 (a) Modified metals are used in aeroplanes, which need to be made from materials that are strong, durable and light. (b) The Oscar statuettes are made of britannium (a mixture of tin, copper and antimony) and then coated successively in layers of copper, nickel, silver and gold. (c) Blacksmiths use heat and hammering tools to modify the properties of the metal used for horseshoes.

A metal can be modified in one of three main ways:

- through alloy production
- by heat treatment
- with a coating.

Section 3.4 described the extraction of iron from its ores. In this section, iron will again be used as a case study so you can look at the different ways metals are modified and the effect of these modifications on the metal's properties and uses.

MAKING ALLOYS

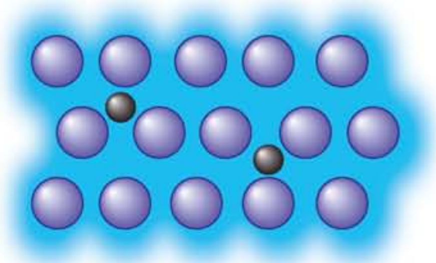
Often, metals are mixed with small amounts of another substance, usually a metal or carbon. The substances are melted together, mixed and then allowed to cool. The resultant solid is an alloy.

By varying the composition of alloys, you can obtain materials with specific properties. Generally, an alloy is harder and melts at a lower temperature than the pure metal. This is because atoms of different sizes are now included in the metal lattice. As these atoms do not pack in the same way as the main metal, they will not allow the lattice to shift and bend in the same way. This disruption of the regular metallic lattice also accounts for the lowered melting point.

Steel: alloys of iron

Currently, almost all of the iron mined around the world is used to make the alloy steel. The simplest steel is made by adding a small amount of carbon to iron to make carbon steel.

Carbon steel is a type of **interstitial alloy**. In interstitial alloys, a small proportion of an element with significantly smaller atoms is added to a metal. The added atoms sit in interstices (very small spaces) between metal cations in the metallic lattice, as shown in Figure 3.5.2.



The smaller carbon atoms occupy some of the spaces between the iron atoms.

FIGURE 3.5.2 Steel is an interstitial alloy of iron and carbon. Note the relative sizes and position of the atoms in an interstitial alloy.

CHEMFILE

Gold

Pure gold is 24-carat gold. It is so soft that it can be moulded by hand. Gold in jewellery is a substitutional alloy. Nine-carat gold is 9/24 gold, which is 37.5% gold and 62.5% other metals. White gold is an alloy of gold and a metal such as nickel, manganese or palladium. The purity of white gold is also expressed in carats.

FIGURE 3.5.4 Gold jewellery is typically made from alloys. Pure gold (24-carat purity) is not often used for jewellery because it is too soft.

Carbon steel is generally harder and less malleable than pure iron. Varying the amount of carbon in the mixture produces steels with different properties, as shown in Table 3.5.1. This allows the steel with the best properties to be used in specific applications.

TABLE 3.5.1 A summary of the properties and uses of some different carbon steels

Type of carbon steel	Percentage of carbon	Properties	Typical use
Low carbon steel	Less than 0.3%	Strong, easily shaped	Bridges, buildings, ships and vehicles
Medium carbon steel	0.3–0.45%	Increased hardness and tensile strength, decreased ductility	Large machinery parts
High carbon steel	0.45–0.75%	Very strong, more brittle	Springs and high-strength wires
Very high carbon steel	Up to 2.5%	Hard, more brittle	Cutting tools

Other elements can also be added in addition to carbon to make steels with improvements to different properties. Examples of some of these are listed in Table 3.5.2.

TABLE 3.5.2 Some elements that are alloyed with iron to make steels

Alloying element	General effects on properties	Example
Manganese	Increases strength and toughness	Bicycle frames
Chromium	Increases hardness and tensile strength Resists corrosion	Stainless steel for cutlery, kitchen sinks
Nickel	Increases toughness, tensile strength and hardness Resists corrosion	Stainless steel
Cobalt	Improves magnetic properties Resists high temperatures	Alnico magnets, jet propulsion engines

The steels in Table 3.5.2 are not considered to be interstitial alloys, as the added atoms are too big to fit into the spaces in the metallic lattice. The atoms of the elements added replace some of the iron cations and the mixture is called a **substitutional alloy**. In general, the metallic elements added to make substitutional alloys have fairly similar chemical properties and form cations of a similar size to the main metal.

Stainless steel is a substitutional alloy of nickel and chromium. The nickel and chromium atoms take the place of some of the iron atoms in the lattice (Figure 3.5.3). All the metal cations are attracted to the sea of electrons, so the lattice is still strongly bonded. However, because the different kinds of atoms are slightly different in size, the layers within the lattice cannot move as easily past each other. This makes the alloy harder and less malleable than pure iron.

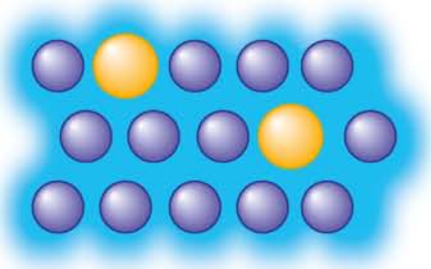


FIGURE 3.5.3 The iron, nickel and chromium atoms in stainless steel are relatively similar in size. The alloy is harder than any of these metals alone.

When other metals or carbon are added to melted metals, the substance that is produced is called an alloy. Alloys tend to have improved properties compared to the original metal, making them more useful in society.

Common alloys

Many common materials are made of alloys in order to make the metal more suited to a particular purpose. Metals are blended together to combine properties, such as strength, colour, reflectivity and chemical stability. The resulting alloy will have different properties from the individual elements. A number of examples of substitutional alloys are shown in Table 3.5.3.

TABLE 3.5.3 Substitutional alloys found in everyday objects

Alloy	Metals used	
Australian 20-cent coin	Copper (75%) and nickel (25%)	
Australian $2 coin	Copper (92%), aluminium (6%) and nickel (2%)	
Dental mercury amalgam	Mercury and zinc	
Brass	Copper (65%) and zinc (35%)	
Bronze	Copper (90%) and tin (10%)	

WORK HARDENING AND HEAT TREATMENT

The way a metal object is prepared also affects how it behaves. Many metals are prepared in the liquid state and then cooled. The rate at which a metal is cooled affects the properties of the solid.

The model that you have been developing for the structure of metals describes the arrangement of particles within a single metal **crystal**. A crystal is a region in a solid where the particles are arranged in a regular way. A sample of solid metal consists of many small crystals. Each crystal is a continuous regular arrangement of cations surrounded by a sea of delocalised electrons, but the arrangement of individual crystals with respect to one another is random like those shown in Figure 3.5.5. As you can see in Figure 3.5.5, the regular lattice is disrupted at the point where one crystal meets another.

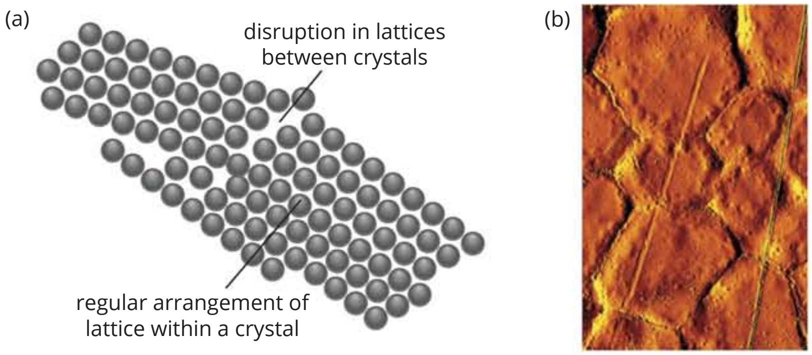


FIGURE 3.5.5 (a) Metals are made of a number of crystals, which have boundaries between them. (b) An electron micrograph shows the individual crystals that formed as the molten metal mixture cooled down and solidified.

The way a metal behaves—its malleability and brittleness—will depend on the size and arrangement of the crystals. Generally, smaller crystals result in harder metals as there is less free movement of layers of cations over each other. Smaller crystals also have more areas of disruption between them, and this usually means that these metals will be more brittle.

The crystal structure of metals can be altered in a number of ways. Two of these ways are **work hardening** and **heat treatment**.

Work hardening

Hammering or working cold metals causes the crystals to rearrange as they are pushed and deformed. This can result in the hardening of the metal as the crystals are flattened out and pushed closer together. Figure 3.5.6 shows a gold ring being hammered on a round tool, called a triblet, to harden and strengthen it.

FIGURE 3.5.6 The crystal structure of metals like this gold ring can be altered by work hardening. Care is needed as the gold becomes more brittle through this process.

CHEMFILE

Work hardening with paperclips

You can see work hardening by bending a paperclip. If you bend it once, it remains fairly pliable, but if you bend it backwards and forwards several times, it snaps. Bending rearranges the crystal grains, making the metal harder but more brittle.

Heat treatment

The physical properties of a metal can be altered by controlled heating and cooling. The three main methods of heat treatment (**annealing**, **quenching** and **tempering**) of metals and the effects on the metal's properties and structure are summarised in Table 3.5.4.

TABLE 3.5.4 Summary of the heat treatment methods and the effect on metal properties

Treatment	Process	Effect on metal structure	Effect on metal properties
Annealing	A metal is heated to a moderate temperature and allowed to cool slowly.	Larger metal crystals form.	The metal is softer with improved ductility.
Quenching	A metal is heated to a moderate temperature and cooled quickly (sometimes by plunging into water).	Tiny metal crystals form.	The metal is harder and brittle.
Tempering	A quenched metal is heated (to a lower temperature than is used for quenching) and allowed to cool.	Crystals of intermediate size form.	The metal is hard but less brittle.

When metals are heated above a critical temperature, the individual crystals merge. When the metal is allowed to cool, the crystals re-form. The rate of cooling determines how large the new crystals will be. Faster cooling leads to smaller crystals; slower cooling allows more time for crystals to grow larger.

Steels respond well to heat treatment. Annealing steels reduces their strength or hardness, increases uniformity of crystals and so reduces stresses and restores ductility. Hardening of steels by quenching and tempering increases the strength and wear properties (Figure 3.5.7).

CHEMFILE

Swords

The art of producing a superior sword blade was a highly valued skill in ancient Japan. It required knowledge of the properties of alloys and the effects of heat-treating and work hardening. The blade was heated and plunged into cold water to harden the edge. To avoid the blade becoming too brittle, the sword was then tempered. The wavy line along the blade shows the interface between hard and flexible regions within the metal.

FIGURE 3.5.7 Japanese swordsmiths had to understand the properties of alloys and the effects of heat-treating and work hardening.

COATINGS

Metals can be given a coating in order to make them even more suitable for their intended application. The coating can be decorative, functional or both. For example, stainless steel frying pans (Figure 3.5.8) are strong, hard and durable, have a high melting point and conduct heat very well. Coating the frying pan with the polymer Teflon makes the frying pan non-stick and more resistant to rust.

Iron and the other elements that make up steel alloys react with air and other substances, which can damage the steel object. Surface coatings, such as tin (Figure 3.5.9), paint and powder coating, protect the steel by forming a physical barrier on the surface to prevent exposure to damaging chemicals.

FIGURE 3.5.8 A stainless steel frying pan with a non-stick Teflon coating.

FIGURE 3.5.9 'Tin' cans constructed from steel with a thin coating of tin make the can resistant to rusting.

FIGURE 3.5.10 Powder coating uses fine particles of pigment and resin to protect the metal underneath.

Powder coating is a method of applying a decorative and protective finish. The powder is a mixture of finely ground particles of pigment and resin, which is sprayed onto a surface electrostatically (Figure 3.5.10). The charged powder particles adhere to the surface. When heated, the particles fuse to form a smooth surface that is resistant to scratching and marking.

Another approach involves coating steel with metals that chemically protect the surface. A common example is galvanising (Figure 3.5.11), which will be described further in section 16.3. Galvanised steel has a protective coating of zinc, which prevents rusting. The zinc coating reacts with oxygen and carbon dioxide in the air to slow corrosion.

The surface coatings applied to a car body consists of many layers that offer both physical and chemical barriers to protect the steel from rusting (Figure 3.5.12).

FIGURE 3.5.11 These galvanised nails have been coated with a protective layer of zinc.

FIGURE 3.5.12 The special paint used on cars is a decorative and functional coating.

3.5 Review

SUMMARY

- Most metals can be modified to alter their properties and make them more useful.
- An alloy is a mixture of a metallic element with other elements.
- Alloys are often harder and melt at a lower temperature than pure metals.
- Heat treatment changes the size and arrangement of crystals in metals.
- Different coatings can be applied to metals to provide additional decorative and/or functional properties.

KEY QUESTIONS

1 Consider the alloys that make up a 20-cent coin and high-carbon steel.
  - **a** List the elements present.
  - **b** Draw a diagram to show how the atoms of these elements are arranged in the alloy.

2 Dentists fit partial dentures by means of small metal hooks. The hooks attach the denture to the remaining teeth. The hooks are easily bent at first to fit snugly in individual mouths. However, if the hooks are bent backwards and forwards too often, then they become brittle and snap. Explain why this happens.

3 Before shaping aluminium into objects by hammering, it is usually annealed to make it more malleable. The final product of this shaping process is then usually quenched to increase its strength. Use the metallic bonding model to explain why:
  - **a** annealing makes aluminium more malleable
  - **b** quenching can increase the strength of the final aluminium object.

4 During the manufacture of a metal object, many different modifications may be needed. Propose a series of modifications to produce a steel chisel that has a flexible and strong shaft with a hard blade.

3.6 Metallic nanomaterials

Metallic **nanomaterials** consist of metal atoms arranged to make nano-sized structures. Metallic nanomaterials have very different properties when compared to a bulk sample of the same type of metal. Scientists have long been fascinated by the effects of nanomaterials. For example, gold–silver alloyed nanoparticles change the colour of glass (Figure 3.6.1).

As you learned in section 1.1 on page 2, emerging technologies have allowed scientists to manipulate metals at the nanoscale. This section will introduce you to some of the different forms of metallic **nanoparticles**, as well as some examples of their current applications.

FIGURE 3.6.1 As light passes through this stained glass window containing gold–silver alloyed nanoparticles, it causes the glass to change colour.

FORMS OF METALLIC NANOMATERIALS

Materials exist in many different forms at the nanoscale level, just as they do on the macroscale level. These forms include:

- particles
- rods
- wires
- tubes.

Metallic nanoparticles

Nanoparticles range from about 0.1 to 100 nm in size (where $1\,\text{nm} = 10^{-9}\,\text{m}$). They have a very high surface area to volume ratio compared to the bulk material of similar volume.

The gold nugget shown in Figure 3.6.2 consists of many billions of cations and delocalised electrons. The properties of gold and other metals, such as electrical and thermal conductivity and metallic lustre, are explained in terms of the movement of delocalised electrons.

However, scientists have found that in a metal crystal with less than a certain number of atoms, the number of valence electrons released is too small to behave as a 'sea' of delocalised electrons. Metal nanoparticles that contain only 100 or so atoms have properties in-between those of metals and non-metals. In general, the nanoparticles have different optical properties and are more sensitive to heat.

For example, gold takes on a ruby colour when the gold particles are reduced to nano-size. You can see this in the stained glass window in Figure 3.6.3. The deep yellow colour is caused by silver nanoparticles.

FIGURE 3.6.2 Bulk gold has a characteristic colour and typical metallic properties.

FIGURE 3.6.3 The red colour in this stained glass window is caused by gold nanoparticles trapped in the glass. The deep yellow colour is caused by silver nanoparticles.

Metallic nanorods

Nanorods are nanoscale rods in which each dimension ranges from 1 to 100 nm. They have a length to width ratio of 3:1–5:1 (Figure 3.6.4). Nanorods of metals such as gold and silver have been synthesised in the laboratory. Their applications are diverse, including in display technologies and microelectronics, powering everything from solar cells to mobile phones.

FIGURE 3.6.4 A group of nanorods.

Metallic nanowires

A **nanowire** is a nano-sized wire. The diameter of a nanowire is measured on the nanoscale, but its length is unrestricted. Nanowires differ from nanorods because they are much longer, as shown in Figure 3.6.5. Platinum nanowires have promising applications as catalysts and in electronics.

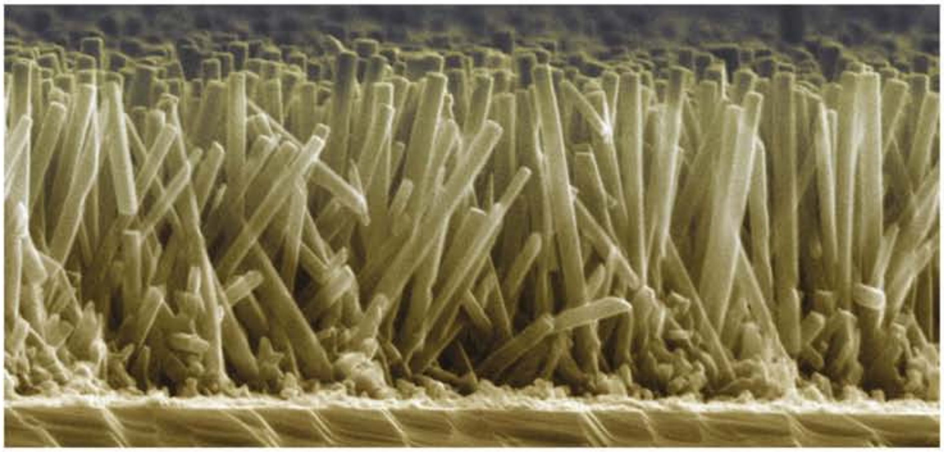


FIGURE 3.6.5 Zinc oxide nanowires.

USES OF METALLIC NANOMATERIALS

Nanomaterials have unique electrical, catalytic, magnetic, mechanical, thermal and imaging characteristics. This makes them attractive for use in medical, pharmaceutical, electronic and different engineering sectors.

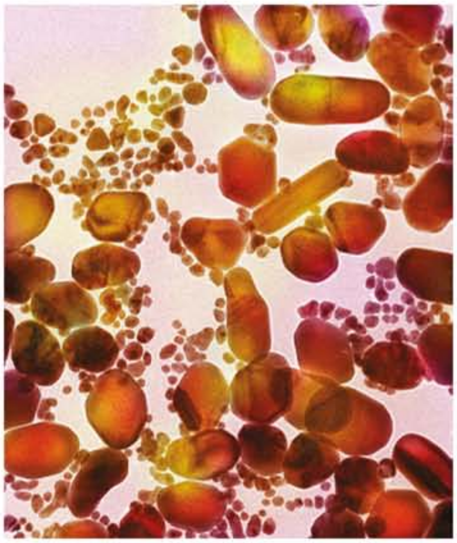


FIGURE 3.6.6 Applications of gold nanoparticles include cancer treatment research and detecting biological toxins.

Gold nanoparticles in cancer treatment

Gold nanoparticles are the subject of substantial research with a wide range of applications (Figure 3.6.6). One area of development is in using gold nanoparticles as a targeted chemotherapy treatment method.

Gold nanoparticles can be attached to molecules of a tumour-killing agent known as tumour necrosis factor (TNF). The nanoparticles hide the molecule from the body's immune system.

The nanoparticles carrying the TNF tend to accumulate in cancer tumours, allowing TNF to destroy tumours. The nanoparticles do not appear to accumulate in other regions of the body, which means healthy cells are not affected.

CHEMFILE

Gold nanorods target cancer cells

Scientists at Swinburne University of Technology in Victoria have shown that gold nanorods can inhibit cancer cell growth in cervical cancer.

Dr Chiara Paviolo used tiny gold nanorods to act as blocking agents to interfere with the activity of cell receptors and prevent growth factors from stimulating the growth of cancer cells. Growth factors are involved in 20% of cancers.

Silver nanoparticles kill bacteria

FIGURE 3.6.7 A wound dressing with silver nanoparticles to kill bacteria.

Silver ions have long been known to kill bacteria. The ions can rapidly penetrate bacterial membranes and interact with proteins in the bacteria, destroying the cell structure of the bacteria and preventing them from reproducing.

Technology has enabled silver nanoparticles to be included in many different types of wound dressings. When the dressing (Figure 3.6.7) comes into contact with moisture from the wound, silver nanoparticles are slowly but continuously released from the wound pad. They then enter the wound and kill bacteria.

In similar antibacterial applications, Samsung has created and marketed a material called Silver Nano, which adds silver nanoparticles to the surfaces of household appliances. Silver nanoparticles have been embedded in the surfaces of plastic storage bins, as well as in fabrics used by astronauts, babies and outdoor enthusiasts.

Copper nanoparticles go to space

Solder is a filler metal used to join two or more metals. Solders are essential to plumbing and metal constructions, including in satellites and spacecraft. For most of history, solders have contained a high amount of lead. Concerns about the toxicity of lead have driven the development of lead-free solder.

The complex electronics in satellites, such as the solar-powered satellite in Figure 3.6.8, must be reliable and efficient over a very long time. Space scientists have developed a nanotechnology copper-based solder that offers far superior performance over the materials currently in use. It is expected that the new solder material will produce joins with up to 10 times the electrical and thermal conductivity of current solders, with a wide range of space and defence applications.

FIGURE 3.6.8 A nanotechnology copper-based solder has advantages in situations where long life and reliability are critical.

Iron nanoparticles remove pollution in ground water

Iron nanoparticles are being used to clean up the pollutant carbon tetrachloride (CCl_4) from ground water (Figure 3.6.9). Carbon tetrachloride is a manufactured toxic chemical that has been shown to cause cancer in animals. Spills of carbon tetrachloride can spread through soil and create large areas of contamination.

Iron nanoparticles can quickly and effectively break down carbon tetrachloride to a mixture of relatively harmless products. It may be possible to inject the nano-sized iron deep into the ground where it can treat contaminated ground water.

FIGURE 3.6.9 Nanoparticles of iron are being investigated as a way of eliminating a range of environmental pollutants.

3.6 Review

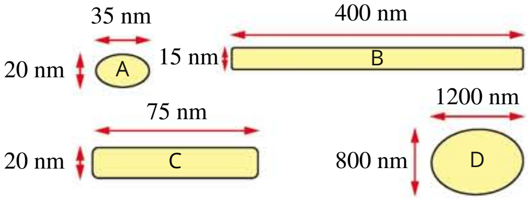
SUMMARY

- Nanomaterials range in size between 1 and 100 nm, where 1 nm = 10^{-9} m.
- Metallic nanomaterials are nano-sized particles of metals.
- Different forms of metallic nanomaterials include nanoparticles, nanorods and nanowires.
- Metallic nanomaterials have applications in medical, pharmaceutical, electronic, environmental and engineering sectors.

KEY QUESTIONS

1 Explain why you would not expect a sample of pure gold nanoparticles to reflect light.

2 Classify the metallic nanoparticles shown in the illustration.



3 Iron nanoparticles must be stored away from oxygen as they will react quickly to produce iron oxide. Write a word equation for the reaction of iron nanoparticles with oxygen.

Chapter review

03

KEY TERMS

alkali metal
alloy
anion
annealing
blast furnace
brittle
cations
coke
conductor
core charge
crystal
delocalise
delocalised electron
density
ductile
haematite
heat treatment
inert
interstitial alloy
ionisation energy
iron oxide
lattice
limestone
malleable
metallic bonding
metallic bonding model
mineral
molten
nanomaterials
nanoparticles
nanorods
nanowire
octet rule
ore
quenching
reactivity
reactivity series of metals
slag
steel
substitutional alloy
tempering
tensile strength
transition metals
work hardening

Properties of metals

1 Which of the following metals would have similar properties to beryllium?

Ca, Cs, Cu, Pb, Mg, Zn, Sr, K

2 Use the data in Table 3.1.2 on page 55 to answer the following questions.

- **a** Which metal is the best conductor of heat?
- **b** Why is this metal not used in saucepans?
- **c** What metals are used to make saucepans?

3 Which property most clearly distinguishes the metals from the non-metals listed in Table 3.1.2 on page 55?

4 What do you think is the most important property of each of the following metals that has led to its widespread use?

- **a** Aluminium
- **b** Copper
- **c** Iron

5 The atomic number of calcium is 20. How many electrons are in an atom of calcium and in a Ca^{2+} cation?

6 Determine the electronic configuration of an aluminium atom and the configuration of its most stable cation.

7 What is the meaning of the term 'ductile' when referring to metals?

Metallic bonding

8 Use the metallic bonding model to explain each of the following observations.

- **a** Copper wire conducts electricity.
- **b** A metal spoon used to stir a boiling mixture becomes too hot to hold.
- **c** Iron has a high melting point, 1540°C.
- **d** Lead has a density of 11.4 g mL^{-1}, which is much higher than for a non-metal such as sulfur.
- **e** Copper can be drawn out to form a wire.

9 Consider the metallic bonding model used to describe the structure and bonding of metals.

- **a** What is meant by the following terms?
  - **i** Delocalised electrons
  - **ii** A lattice of cations
  - **iii** Metallic bonding
- **b** Which electrons are delocalised in a metal?

10 Describe the arrangement of particles in a metal wire and how they allow the wire to conduct electricity.

11 Use a diagram to describe what is meant by the term 'metallic lattice'.

Reactivity of metals

12 Look at the periodic table at the end of the book.

- **a** Name a metal that would have similar properties to calcium.
- **b** In which part of the periodic table are magnetic metals found?

13 Which of the following metals would you expect to be the least reactive with water?

Aluminium, sodium, rubidium, indium

14 When a reactive metal is added to water, bubbles or fizzing can be observed. Explain the appearance of the bubbles.

15 The following image shows similar-sized pieces of iron and silver in test-tubes of sulfuric acid of the same concentration. Describe the reactivity of the two metals and identify which metal is on the left and which is on the right.

16 Observations of the reaction of metals A, B and C with dilute hydrochloric acid are summarised below. Identify which metal is aluminium, copper and sodium.

- Metal A does not react with dilute hydrochloric acid.
- Metal B is stored in oil because of its high reactivity, and it undergoes a violent reaction with dilute hydrochloric acid.
- Metal C reacts very slowly with dilute hydrochloric acid.

17 Identify the following statements about the reactivity of metals as true or false.

- **a** All metals react with acid to produce hydrogen gas.
- **b** Hydrogen is a flammable gas.
- **c** The most reactive metals are located at the top of a group in the periodic table.
- **d** A metal that is very reactive with water is likely to be less reactive with a solution of a dilute acid.
- **e** When metals react with oxygen in the air, they release energy.

18 Write the word equation for the reaction that occurs when magnesium is heated strongly in air.

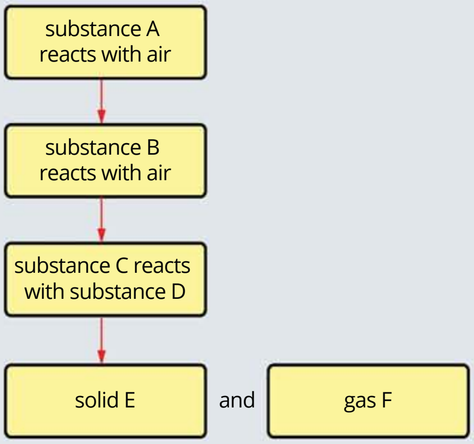
Extraction of iron from its ore

19 Explain why iron is not found in its pure form in nature.

20 Define:

- **a** iron ore
- **b** mineral
- **c** haematite
- **d** iron oxide.

21 Consider the following flow chart describing the extraction of iron from iron ore in a blast furnace.



- **a** Which two letters would represent carbon dioxide?
- **b** What is substance A likely to be?
- **c** Is solid D likely to be a mixture or an element?
- **d** What other substance is also added to the blast furnace for proper operation?

22 Identify the four raw materials used in the extraction of iron from its ore and explain the role of each.

23 Write a word equation to show the formation of slag (calcium silicate) from silica in a blast furnace.

Modifying metals

24 Alloys are modified metals. In each example, state the metals used and one property that is different from the original metals.

- **a** An Australian one dollar coin
- **b** Solder
- **c** 9-carat gold
- **d** Stainless steel
- **e** Dental mercury amalgam

25 A student wishes to make an iron needle more malleable. She heats three needles strongly in a Bunsen burner flame. She then treats each needle differently.

- Needle 1 is allowed to cool slowly on the bench.
- Needle 2 is cooled quickly by dropping it into a beaker of cold water.
- Needle 3 is cooled quickly in the beaker of water then reheated in the flame before being allowed to cool more slowly on the bench.

Place the resulting needles in order of least malleable to most malleable.

26 Horseshoes are often made from steel that is worked into shape by a process of heating and hammering the metal. Explain how this process results in a better horseshoe than one simply made of iron.

Metallic nanomaterials

27 A scientist synthesises a new material in the laboratory. It is a solid substance with a diameter of 15 nm and a length of 2300 nm. Which form of nanomaterial is this substance?

28 A scientist synthesised a tiny particle for use in solar cells, with a diameter of 8.34×10^{-7} m. Would this particle be classified as a nanomaterial?

29 Explain why a nanowire can be longer than 3000 nm but still be considered a metallic nanomaterial.

Connecting the main ideas

30 Metals have many uses in modern society.

- **a i** Name one metal that is used in large quantities in the building industry.
  - **ii** What properties make it suitable for this use?
  - **iii** What properties limit its use in buildings?
- **b i** Name one metal that is used in large quantities for making electrical wires.
  - **ii** What properties make it suitable for use in wires?
- **c i** Name two metals that are used in large quantities in the jewellery trade.
  - **ii** What properties make them suitable for this use?

31 Draw a concept map using the following terms: metal, cation, delocalised electron, lattice, electrostatic attraction.

32 Some metals are found as elements in nature; others are found as compounds, combined with other elements such as oxygen and sulfur in ores. Australia has natural reserves of many metals and ores, with mining producing large quantities of metals, including aluminium, copper, gold, iron and silver.

- **a** Give the chemical symbol for each of these metals.
- **b** In which group, period and block of the periodic table are each of these metals found?
- **c** Which of these metals are found in nature as elements rather than compounds?
- **d** Which of these metals are transition elements?
- **e** Which of these elements is the rarest?

33 It has been shown using X-rays that metals have a crystalline structure in the solid state.

- **a** Explain, using the metallic bonding model, why metals form crystals.
- **b** What problems can this crystalline structure of metals cause?

34 The boiling points of three metals—sodium, potassium and calcium—are given in Table 3.7.1.

TABLE 3.7.1 Boiling points of three metals

Metal	Boiling point (°C)
Na	892
K	760
Ca	1490

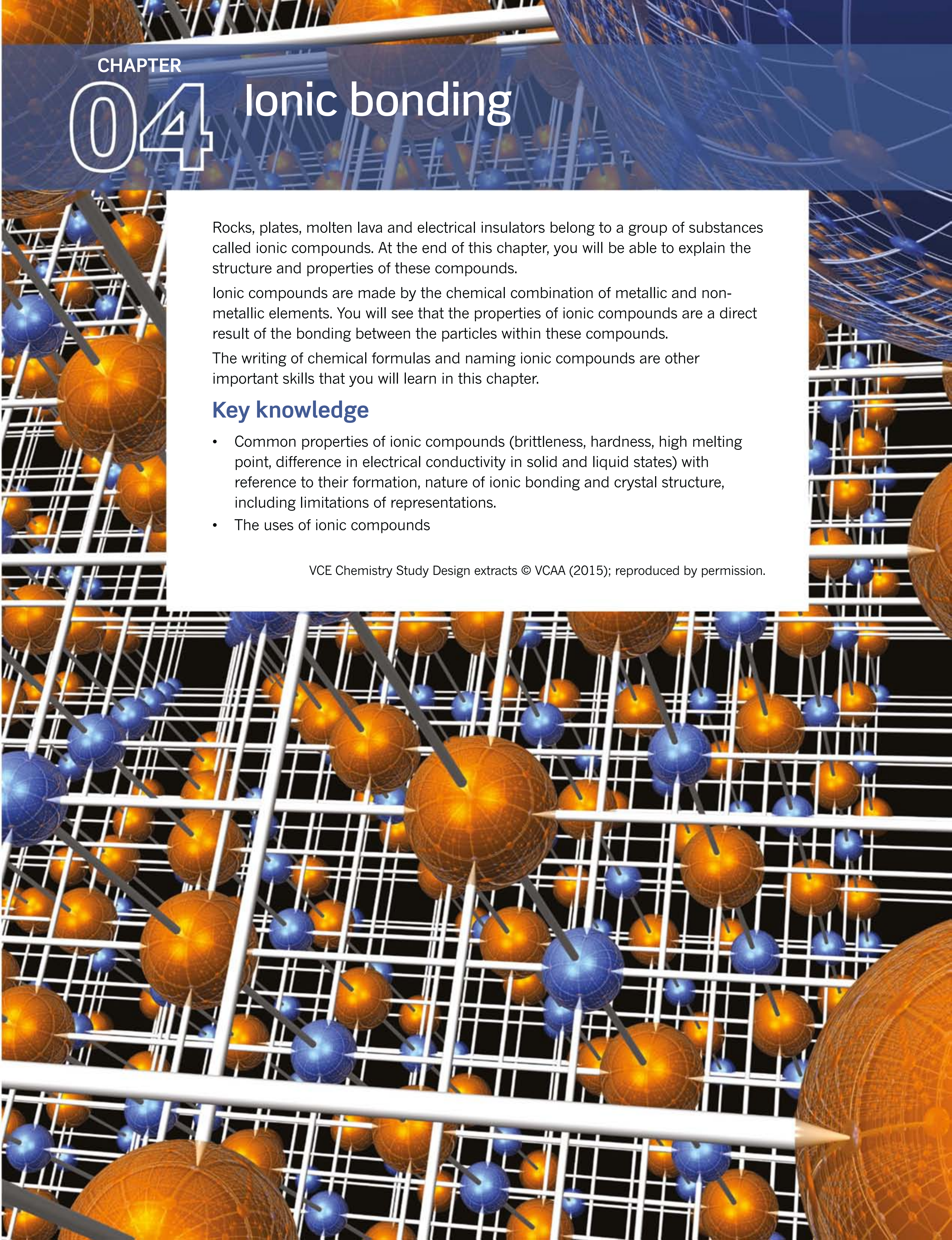
- **a** In which group and period of the periodic table are these metals found?
- **b** Write the electronic configuration for each of the three metals.
- **c** Use the metallic bonding model to suggest why:
  - **i** sodium has a higher boiling point than potassium
  - **ii** calcium has a much higher boiling point than potassium.

35 Aluminium is the most abundant metal in the Earth's crust. Why was aluminium not available before 1886?

CHAPTER

04

Ionic bonding



Rocks, plates, molten lava and electrical insulators belong to a group of substances called ionic compounds. At the end of this chapter, you will be able to explain the structure and properties of these compounds.

Ionic compounds are made by the chemical combination of metallic and non-metallic elements. You will see that the properties of ionic compounds are a direct result of the bonding between the particles within these compounds.

The writing of chemical formulas and naming ionic compounds are other important skills that you will learn in this chapter.

Key knowledge

- Common properties of ionic compounds (brittleness, hardness, high melting point, difference in electrical conductivity in solid and liquid states) with reference to their formation, nature of ionic bonding and crystal structure, including limitations of representations.
- The uses of ionic compounds

4.1 Properties and structures of ionic compounds

FIGURE 4.1.1 Many gemstones are made from ionic compounds.

In this chapter, you will study the structure and properties of a group of substances called **ionic compounds**. Ionic compounds are made by the chemical combination of metallic and non-metallic elements.

These materials are very common in the natural world because the Earth's crust is largely made up of complex ionic compounds. Most rocks, minerals and **gemstones** (Figure 4.1.1) are ionic compounds. Soil contains weathered rocks mixed with decomposed organic material, so soil contains large quantities of ionic compounds.

Ceramics, kitchen crockery and bricks are made from clays. Clays are formed by the weathering of rocks, so these materials also contain ionic compounds. Kitchen crockery and bricks contain mixtures of different ionic compounds. Table salt (sodium chloride) is a pure ionic compound.

PROPERTIES OF IONIC COMPOUNDS

If you think about the characteristics of rocks, kitchen crockery and table salt, you will recognise that these materials, and therefore ionic compounds, have some properties in common.

Table 4.1.1 lists some properties of typical ionic compounds. These compounds can be found in materials you might encounter in everyday life. Note that the compounds listed are simple ionic compounds, whereas rocks, ceramics and bricks contain more complex ionic compounds.

TABLE 4.1.1 Properties of typical ionic compounds

Ionic compound	Melting point (°C)	Conductive as solid	Conductive as liquid	Conductive in aqueous solution (0.1 mol L^{-1})	Solubility in water at 25°C (g/100 g water)	Example of commercially available product containing the compound
Copper(II) sulfate	Decomposes 110	No	Yes	Yes	22	Bluestone spray (used to kill pathogens on fruit)
Sodium chloride	801	No	Yes	Yes	36	Food salt
Calcium carbonate	1339*	No	Yes	–	0.0013	Main component in marble
Zinc oxide	1975	No	Yes	–	Insoluble	Zinc cream
Sodium hydroxide	318	No	Yes	Yes	114	Oven cleaner

*Melting point determined under pressure to prevent decomposition of compound.

Lists of data about ionic compounds such as those in the Table 4.1.1 have allowed chemists to summarise their properties. Generally, ionic compounds:

- have high melting and boiling points. They are all solids at room temperature
- are hard but **brittle**, unlike metals. Therefore, they are neither malleable nor ductile
- do not conduct electricity in the solid state
- are good conductors of electricity in the liquid state or when dissolved in water
- vary from very soluble to insoluble in water. They are not soluble in **non-polar solvents** such as oil.

DEDUCING THE STRUCTURE OF A COMPOUND FROM ITS PROPERTIES

You will remember from Chapter 3 that the properties of metals indicate something about the structure of metals; that is, how particles are arranged in a metallic lattice. The properties of ionic compounds also provide evidence for how the particles are arranged in ionic compounds.

From Table 4.1.1, you can see that some of the physical properties of ionic compounds are different from those of metals. Chemists have concluded that the particles in ionic compounds, and how they are arranged in the solid state, are different from those present in metals.

Table 4.1.2 lists the observed properties of one particular ionic compound, sodium chloride (table salt). Beside each property is a description of the nature of the particles and therefore the types of forces between the particles. These descriptions can be inferred from the different properties of sodium chloride.

TABLE 4.1.2 Properties of sodium chloride and the information this provides about its structure

Property	What this tells us about structure
High melting point	Forces between the particles are strong
Hard, brittle crystals	Forces between the particles are strong
Does not conduct electricity in the solid state	No free-moving charged particles are present in solid sodium chloride
Conducts electricity in the molten state	Free-moving charged particles are present in molten sodium chloride

In summary, for ionic compounds generally:

- the forces between the particles are strong
- there are no free-moving electrons present, as there are in metals
- there are charged particles present, but in the solid state they are not free to move
- when an ionic compound melts, the charged particles are free to move and then the compound will conduct electricity.

THE IONIC BONDING MODEL

Now that you understand some of the details of the structure of ionic compounds, the next step is to work out how the particles in these compounds are arranged in the solid state.

When metallic and non-metallic atoms react to form ionic compounds, the following steps occur.

- Metal atoms lose electrons to non-metallic atoms and so become positively charged metal ions (called **cations**).
- Non-metal atoms gain electrons from metal atoms and so become negatively charged non-metal ions (called **anions**).

(You will remember from Chapter 1, page 12, how electrons arrange themselves into shells around the nucleus. Atoms are at their most stable when there are eight electrons in the valence shell. Therefore, an atom's ability to form a cation or anion depends on how many electrons it needs to gain or lose to achieve this stable arrangement.)

Cations and anions then arrange themselves in the following way:

- Large numbers of cations and anions combine to form a three-dimensional lattice.
- The three-dimensional lattice is held together strongly by electrostatic forces of attraction between the oppositely charged ions. The electrostatic forces of attraction holding the ions together is called **ionic bonding**.

- In the case of sodium chloride, sodium (electronic configuration 2,8,1) loses one electron, so it has a stable eight electrons in the second electron shell (electronic configuration 2,8). Losing one electron makes it positively charged and it is given the symbol Na^+. A chlorine atom normally has the electronic configuration of 2,8,7. Therefore, it only needs to gain one electron to become an anion, Cl^-. Its electronic configuration in this arrangement becomes 2,8,8.
- In sodium chloride, in order to maximise the forces of attraction, each sodium ion is surrounded by six chloride ions and each chloride ion is surrounded by six sodium ions, as shown in Figure 4.1.2.
- Even though each chloride ion is close to another chloride ion (Figure 4.1.2), the attractive force they have towards the sodium ions outweighs the repulsive force from the chloride ions so the lattice is held together quite strongly.

Electrostatic forces of attraction result from the attraction between positive and negative charges.

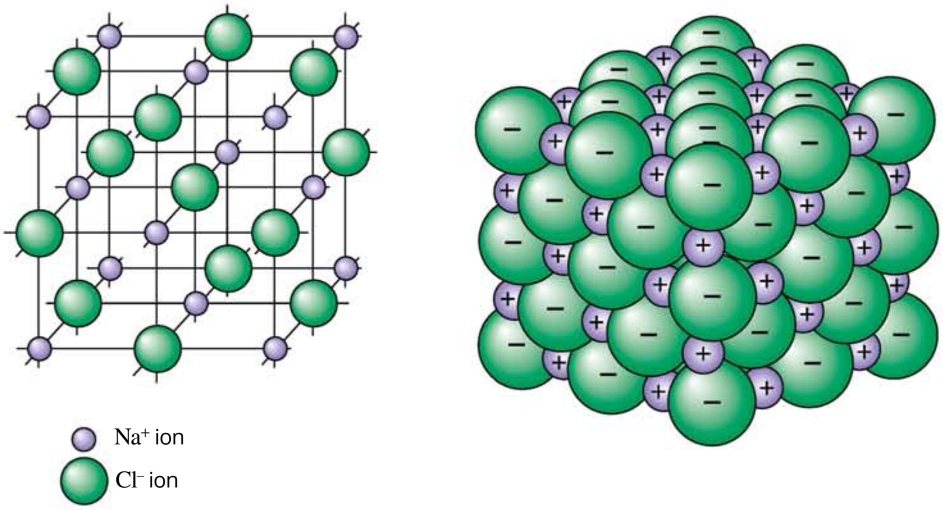


FIGURE 4.1.2 Two representations of part of the crystal lattice of the ionic compound sodium chloride. Forces of attraction between oppositely charged ions result in strong bonding.

The formula of sodium chloride

The **chemical formula** of sodium chloride is written as NaCl. However, it is important to note that in a solid sample of an ionic compound, such as sodium chloride, individual pairs of sodium and chloride ions do not exist. The solid is also not built up of discrete NaCl molecules.

Instead, the solid is made up of a continuous lattice of alternating Na^+ and Cl^- ions. All sodium ions are an equal distance from six chloride ions and all chloride ions are an equal distance from six sodium ions. The overall ratio of sodium ions to chloride ions in the lattice is 1:1, so that is why the formula is written as NaCl.

4.1 Review

SUMMARY

- Ionic compounds form a crystal lattice made up of metals and non-metals.
- The particles that make up the crystal lattice are cations and anions.
- Cations are positive ions and anions are negative ions.
- The three-dimensional lattice is held together strongly by electrostatic forces of attraction between the cations and anions. The electrostatic forces of attraction are called ionic bonding.
- In the case of sodium chloride, in order to maximise the forces of attraction, each sodium ion (Na^+) is surrounded by six chloride ions (Cl^-) and each chloride ion is surrounded by six sodium ions.
- Ionic compounds have high melting and boiling points. They are solids at room temperature.
- Ionic compounds are hard but brittle. Unlike metals, they are neither malleable nor ductile.
- Ionic compounds do not conduct electricity in the solid state.
- Ionic compounds are good conductors of electricity in the liquid state or when dissolved in water.
- In water, ionic compounds vary from very soluble to insoluble.

KEY QUESTIONS

1 Some properties of four different substances are described below. Which substance is most likely to be an ionic compound?

A Substance A has a melting point of 842°C and conducts electricity at 700°C.

B Substance B has a melting point of 308°C. It does not conduct electricity at 250°C but will conduct electricity at 350°C.

C Substance C has a melting point of 180°C and can be drawn into a wire.

D Substance D is a white solid that melts at 660°C and will not conduct electricity at 700°C.

2 Sodium chloride does not conduct electricity in the solid state but does conduct when molten (liquid).

a How could you use Figure 4.1.2 on page 86 to explain why solid sodium chloride does not conduct electricity?

b Explain why molten sodium chloride conducts electricity.

3 Explain why aluminium would be more likely to form a cation than an anion.

4 Explain why the crystal lattice is held together so strongly in sodium chloride, even though the number of cations is equal to the number of anions.

4.2 Using the ionic bonding model to explain properties

In Chapter 3, you saw that the metallic bonding model represents the structure of metals as a lattice of positively charged metal ions held together by delocalised electrons. This model explains many of the properties of metals, such as why metals generally have high melting points and conduct electricity in the solid state.

In this section, you will see how the ionic bonding model explains the properties of ionic compounds.

FIGURE 4.2.1 Bricks made from the ionic compound magnesium oxide are used to line furnaces and kilns.

FIGURE 4.2.2 Ceramic brake discs work more effectively than steel ones at high temperatures. A ceramic brake disc contains ionic compounds that have very high melting temperatures and withstand the heat produced by braking better than metals.

HIGH MELTING POINTS

To melt an ionic solid such as sodium chloride, you must provide energy to allow the ions to break free and move. Sodium chloride has a high melting point (801°C). This indicates that a large amount of energy is needed to overcome the electrostatic attraction between oppositely charged ions and allow them to move freely. Therefore, the ionic bonds between the positive sodium ions and negative chloride ions must be strong, which explains why a high temperature is required to melt solid sodium chloride.

The high melting point of ionic compounds is put to use in the bricks that line furnaces and kilns (Figure 4.2.1) and in the ceramic materials used to make brake discs for high-performance cars (Figure 4.2.2).

HARDNESS AND BRITTLENESS

There are strong electrostatic forces of attraction between ions in an ionic compound, so a strong force is needed to disrupt the **crystal lattice**. Therefore, one of the properties of ionic compounds is that they are hard. This means that a sodium chloride crystal cannot be scratched easily.

The strength of house bricks, concrete bridges and cobbled streets can be attributed to the ionic bonding within their structures.

CHEMFILE

Early tools

Some of the earliest tools used by humans were axes, spearheads and coarse needles used for weaving. Each application required a material that was hard and could be shaped. Certain types of rocks that are composed of ionic compounds served this purpose well.

Figure 4.2.3 shows a primitive axe used during the Stone Age. The Stone Age ended at different times in different parts of the world, as humans learned to smelt (fuse or melt) metals such as copper from their ores to create more refined and lighter tools. Their metallic nature meant that they were not as hard as the original tools (made of rock composed of ionic compounds).

FIGURE 4.2.3 The hardness of ionic compounds is the reason why axes were once made from rocks.

Although a salt crystal is hard, a strong force such as a hammer blow will shatter the crystal. Therefore, it is said to be brittle. This is because the layers of ions will move relative to each other due to the force of the blow.

During this movement, ions of like charge are shifted so they are next to each other, as seen in Figure 4.2.4. The resulting repulsion between the similarly charged ions causes the crystal to shatter.

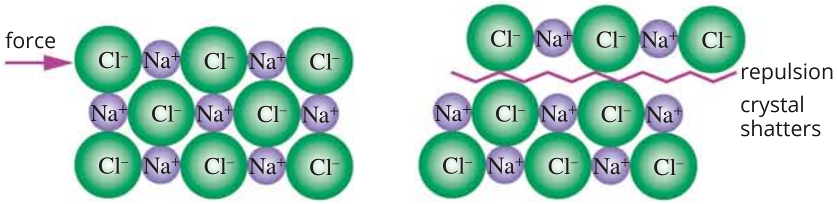


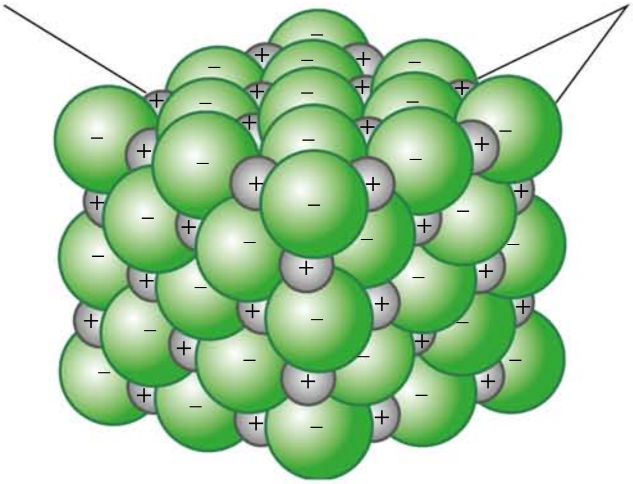
FIGURE 4.2.4 A lattice of an ionic compound shattering. Note that just before shattering, the Cl^- ions are adjacent to other Cl^- ions and the Na^+ ions are also next to each other.

Materials made from clay, such as kitchen crockery (Figure 4.2.5), ceramic tiles and bricks are hard, but they are also brittle.

FIGURE 4.2.5 A coffee cup being smashed.

ELECTRICAL CONDUCTIVITY

In the solid form, ions in sodium chloride are held in the crystal lattice and are not free to move, so solid sodium chloride does not conduct electricity. Remember that for a substance to conduct electricity, it must contain charged particles that are free to move. Figure 4.2.7 shows how the particles are arranged in an ionic compound in solid form.



The force of attraction between oppositely charged ions is strong, so ionic compounds are hard and have high melting points.

In the solid state oppositely charged ions are held strongly within the lattice and cannot move. Solid ionic compounds do not conduct electricity.

FIGURE 4.2.7 The arrangement of ions within a solid ionic compound form a crystal lattice.

The non-conducting property of ionic compounds is used in ceramic insulators, which are used to keep high-voltage power lines insulated from electricity poles and electric fence wires (Figure 4.2.8).

CHEMFILE

Porcelain

Porcelain is a type of chinaware made from a clay called kaolin. Figure 4.2.6 shows a dinner setting made from porcelain. Clay is weathered rock and consists of a mixture of complex ionic compounds. The chemical formula for kaolin is $Al_2Si_2O_5(OH)_4$. The ions in kaolin are aluminium (Al^{3+}), silicate ($(Si_2O_5)^{2-}$) and hydroxide (OH^-).

FIGURE 4.2.6 Porcelain cups and plates are made from clay, which contains ionic compounds. Therefore, porcelain is hard and brittle.

Porcelain is made by moulding the object from kaolin and then heating it to about 1300°C in a kiln. Because it is made from ionic compounds, the resulting porcelain is hard but brittle. Be careful not to drop the family heirloom chinaware as it will most likely shatter!

FIGURE 4.2.8 A ceramic insulator on the post of an electric fence.

When solid ionic compounds melt, the ions become free to move, enabling the cations and anions in the molten compound to conduct electricity.

Similarly, when ionic compounds **dissolve** in water, ionic bonds in the lattice are broken and the ions are separated and move freely in solution.

When an electric current is applied to either a molten ionic compound or a solution of the compound in water, positive ions move towards the negatively charged electrode and negative ions move towards the positively charged electrode, resulting in an electric current as shown in Figure 4.2.9.

For an object to conduct electricity, it must contain charged particles that are free to move. Solid ionic compounds are made up of a crystal lattice, so the particles are not free to move and they cannot conduct electricity. When molten (melted) or mixed with water, the charged particles are free to move and conduct.

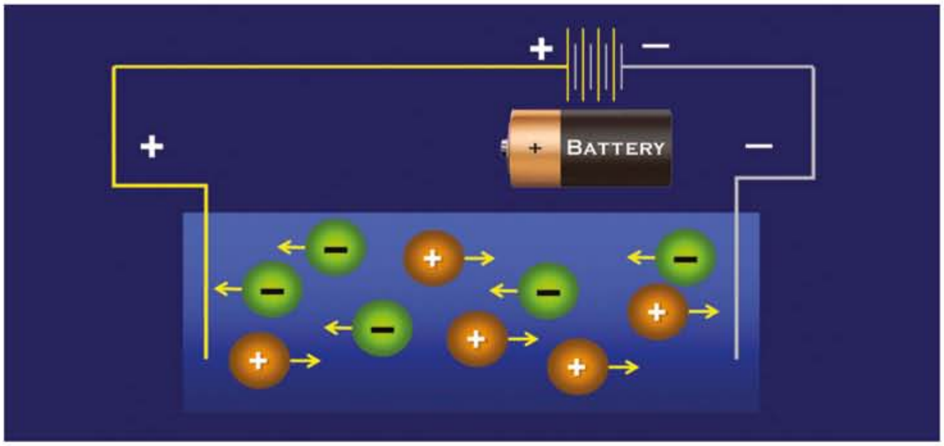


FIGURE 4.2.9 A molten ionic compound will conduct an electric current.

A solution or molten substance that conducts electricity by means of the movement of ions is called an **electrolyte**.

EXTENSION

Electrolysis

When an electric current passes through a molten ionic compound, or a solution of the compound, chemical reactions occur at the positive and negative electrodes. This process is known as **electrolysis** and is used to make a variety of chemicals. Chemicals formed by electrolysis are often difficult to obtain by other means.

For example, the final stage in the industrial production of aluminium involves passing an electric current through a molten liquid containing aluminium oxide (alumina). Aluminium metal is deposited at the negatively charged electrode.

Sodium metal is a starting material for the manufacture of a range of organic chemicals, including dyes. It is also produced on a large scale by electrolysis. In this case, electricity is passed through molten sodium chloride to make sodium. During this process, sodium ions move towards the negative electrode where they become sodium metal, and chloride ions move to the positive electrode and are converted into chlorine gas (Figure 4.2.10).

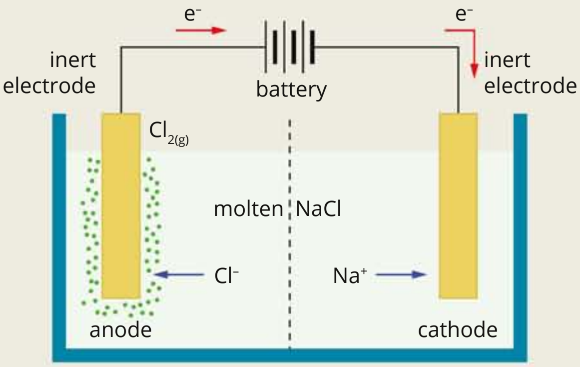


FIGURE 4.2.10 The production of sodium and chlorine by the electrolysis of molten sodium chloride.

SOLUBILITY

Some ionic compounds are very soluble in water, whereas others are very insoluble. When a soluble ionic compound is added to water, the ions break away from the ionic lattice and mix with the water molecules. If an insoluble compound is added to water, the ions remain bonded together in the ionic lattice and do not form a solution.

Whether an ionic compound is soluble or insoluble depends on the relative strength of the forces of attraction between the:

- positive and negative ions in the lattice
- water molecules and the ions.

You will look at the solubility of ionic compounds in water in more detail in Chapter 12.

USES OF IONIC COMPOUNDS

Ionic compounds have a wide variety of uses. Some of these uses are related directly to the physical properties of the compounds, such as hardness, high melting points and their ability to conduct electricity in solution. A number of ionic compounds and their uses in relation to their characteristic properties are described below.

Hardness

- Calcium phosphate is a constituent of bone tissue that gives it strength.
- Calcium sulfate in the form of gypsum is used to make plasterboard for lining the walls and ceilings of houses.
- Granite, limestone and sandstone are used as building stone.
- Bricks, tiles and crockery are made from clay, a material that contains particles held together by strong ionic bonding.

High melting point

- Magnesium oxide and other ionic compounds are used to line furnaces.
- Ceramics are materials that contain a mixture of strong ionic and covalent bonds. They are used in some engine parts.

Electrical conductivity

- Ammonium chloride is used as an electrolyte in dry cell batteries. Electrolytes contain ions in solution and this allows a current to flow in the battery.
- Potassium hydroxide is used as an electrolyte in the 'button' cells used in small electronic devices such as watches and calculators.

Other uses of ionic compounds

- Sodium hydrogen carbonate (bicarbonate of soda or baking soda) is used in baking to cause cakes to rise when placed in a hot oven. This occurs because the compound decomposes when heated to produce carbon dioxide gas.
- Sodium chloride has many uses, including as a flavouring agent and preservative in food.
- Sodium hypochlorite is used as a bleach and in swimming pools to kill microorganisms.

CHEMISTRY IN ACTION

Salt of the Earth

Salt is added to many foods as a preservative or to 'improve' the flavour. It is rarely essential to add salt—a diet that has meat and milk provides enough sodium for our needs (Tables 4.2.1 and 4.2.2). It is the sodium part of sodium chloride that we should limit in our diets.

TABLE 4.2.1 The sodium content of some natural foods

Food	Sodium content (g Na/100 g food)
Beef	0.06
Chicken	0.1
Fish	0.1
Crab meat	0.35
Rice	–
Cow's milk	0.06
Celery	0.15
Silverbeet	0.7
Fresh fruit	–
Most vegetables	0.1

TABLE 4.2.2 The sodium content of some processed foods

Food	Sodium content (g Na/100 g food)
Sausage	1.2
Ham	1.1
Cheddar cheese	0.7
Meat pie	0.5
Tomato sauce	1.2
Soy sauce	7.0
Bread	0.5
Potato chips	1.0
Olives	2.3
Salted nuts	4.0
Doughnuts	0.5
Ice-cream	0.08

A healthy adult requires about 2 grams of sodium a day to replace the sodium they excrete in urine and lose when they perspire (sweat). Salt plays a role in the passage of nerve impulses and helps control the movement of water in and out of cells. A salt deficiency can lead to muscular cramps, loss of appetite and reduced brain function.

Doctors are increasingly critical of the amount of salt in our diets because of the connection between dietary salt and hypertension, or high blood pressure. The average Australian consumes 11 grams of salt daily. When you consider that a take-away meal can contain about 3.5 grams of salt, it is easy to see how you could reach this level. Food manufacturers have responded to public demand by decreasing the salt content in processed foods.

The body attempts to maintain the salt concentration within narrow limits. After a salty meal, you feel thirsty—your body's response to the increased salt concentration in the blood. You drink water to dilute the salt. This excess fluid remains in your body until the kidneys have removed the excess salt.

Ancient civilisations recognised that we need salt in our diets. Settlements were based in regions where salt occurred naturally or on salt trade routes. Wars were even fought over salt, with Roman soldiers being paid a salt allowance (the word 'salary' comes from the Latin word for salt). Salt is harvested from salt lakes, salt mines or the sea (Figure 4.2.11). Solar energy is commonly used to extract salt from seawater.

FIGURE 4.2.11 Harvesting salt from evaporation lakes.

Salinity

Salinity is the presence of salt in groundwater and soil. Plants, like animals, can only tolerate a limited range of salt concentrations. Some plants growing on sand dunes tolerate higher amounts of salt than others. However, if the salt concentration in the soil is too high, even those plants die.

Salinity is caused by increasing amounts of groundwater (water found under the surface of the Earth). As groundwater increases, the water table (water level) rises, bringing dissolved salts, in this case sodium chloride, closer to the surface. The increased salinity of water near the soil surface leads to poor plant growth and reduces the productivity of agricultural land that is used for grazing animals and growing crops.

The rise in the water table has been caused by excess water from irrigation flowing down through the soil, and the clearing of trees, which would otherwise have absorbed this water through their roots.

Reducing salinity

A number of organisations are working to reduce soil and water salinity. Strategies include:

- using irrigation water more efficiently
- improving drainage on the surface of the land
- improving drainage under the surface
- growing trees to soak up excess water
- sealing irrigation channels to prevent leakage.

These are long-term projects, although reduced salinity is apparent in some areas already.

One property of salt that has the potential to cause environmental damage is its ability to dissolve in water (Figure 4.2.12).

FIGURE 4.2.12 Land that is affected by salinity.

4.2 Review

SUMMARY

- Ionic compounds are hard and have high melting and boiling points. This is because of the strong forces of attraction between the positively and negatively charged ions in the ionic lattice.
- When an ionic compound is hit, the ions move within the lattice so that like-charged ions line up opposite each other and then repel, causing the lattice to be disrupted. This makes ionic compounds brittle.
- Ionic compounds do not conduct electricity in the solid state. Although the solid ionic lattice contains charged particles, the particles are not free to move.
- When ionic compounds are added to water or are in molten form, the charged particles are free to move, which means they can conduct electricity.
- In water, ionic compounds vary from very soluble to insoluble. The solubility depends on whether the forces between the water molecules and the ions in the lattice are strong enough to pull the ions out of the lattice.
- Ionic compounds are useful because of their physical properties such as hardness and high melting points.

KEY QUESTIONS

1 Why do ionic compounds have such high melting and boiling points?

2 **a** Explain why the lattice breaks apart in an ionic compound when hit with a heavy blow.

b How does this give ionic compounds their brittle property?

3 Use the ionic bonding model to explain why ionic compounds that have been heated above their melting point conduct electricity but will not when in solid form.

4 Sodium chloride or common salt is an essential part of our diet. Throughout history, it has also been used to preserve food in the absence of refrigeration. So important was sodium chloride to daily life that many words or expressions in the English language have been derived from the word salt. ‘Salary’ and ‘salinity’ are two of them. Can you think of any others?

4.3 Formation of ionic compounds

Some of the reactions that occur between metals and non-metals to form ionic compounds are very vigorous. The reaction between sodium and chlorine to form sodium chloride produces a lot of heat. You will remember from Chapter 3 that sodium is very reactive. At high temperatures, the production of sodium chloride from sodium metal and chlorine gas is very explosive, producing a flame and large amounts of energy.

In the previous sections, you saw that the positive and negative ions that are formed in this reaction are arranged to form a three-dimensional lattice. In this section, you will learn how these positive and negative ions are formed from the atoms. You will also learn how the ratio of each type of atom in the compound is determined.

FORMING IONS

When metal atoms react with non-metal atoms to form an ionic compound, two things occur.

- Metal atoms lose electrons to form positively charged ions (cations).
- Non-metal atoms gain electrons to form negatively charged ions (anions).

From Chapter 3, you will remember that most metals have low ionisation energies and low electronegativities. This means that non-metal atoms are usually more electronegative than metal atoms. In other words, non-metals have a stronger attraction for electrons than metals. In reactions that form ionic compounds, non-metal atoms take one or more electrons from the outermost shell of metal atoms.

Most importantly, the ions that are formed usually have eight electrons in their outer shell—a stable electronic configuration. The tendency for elements to react in such a way that their atoms have eight electrons in their outer shell (valence shell) is known as the **octet rule**.

Noble gases (group 18) are elements that already have the most stable valence shell configuration. Therefore, another way of thinking about the octet rule is that atoms tend to gain or lose electrons to gain a stable electronic configuration identical to that of the noble gas nearest to them on the periodic table. The formation of stable ions is a powerful driving force in reactions between metals and non-metals when they produce ionic compounds.

For example, when sodium reacts with chlorine, each sodium atom loses one electron and each chlorine atom gains one electron.

After the reaction, the:

- sodium ion has the stable electron shell configuration of 2,8 (the same as a neon atom)
- chloride ion has the stable electron shell configuration of 2,8,8 (the same as an argon atom).

Note that, for simplicity, you will look at the arrangement of electrons just in shells of atoms (rather than in subshells).

Figure 4.3.1 illustrates how, when sodium reacts with chlorine, an electron is lost by a sodium atom and gained by a chlorine atom. A diagram of this type is called an **electron transfer diagram**.

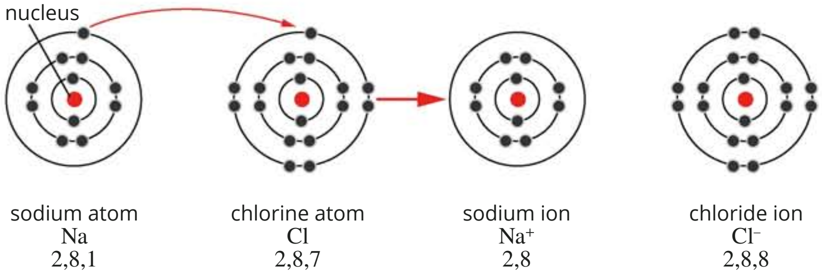


FIGURE 4.3.1 Electron transfer diagram showing the formation of sodium and chloride ions.

The reaction between lithium and oxygen atoms is illustrated in Figure 4.3.2. In this reaction, an oxygen atom needs to gain two electrons to have eight electrons in its outer shell and form a stable ion. To allow this to happen, one oxygen atom will react with two lithium atoms, taking one electron from each atom.

After the reaction, there are just two electrons in what is now the outer shell of the Li^+ ion, which is the same as the electronic configuration of a helium atom.

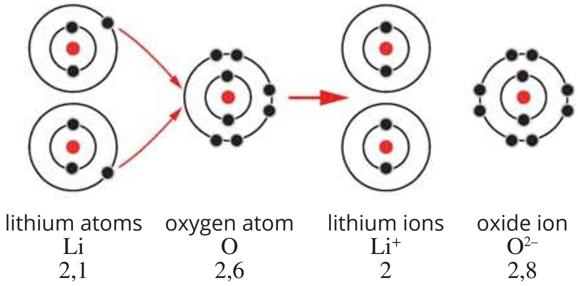


FIGURE 4.3.2 An electron transfer diagram showing the formation of lithium and oxide ions.

In Chapter 2, you learned that atoms of elements in group 1 of the periodic table have electronic configurations with one electron in the valence shell. Therefore, elements in this group often form cations with a charge of +1 as they readily lose this one outer-shell electron. For example, potassium has an electronic configuration of 2,8,8,1. It will readily lose the one electron in the valence shell to have an electronic configuration similar to that of argon (the nearest noble gas). The potassium ion now has an electronic configuration of 2,8,8.

Metals in group 2 of the periodic table have electronic configurations with two electrons in their valence shells. Therefore, they readily form ions with a charge of +2 as they lose these electrons. Magnesium is a metal in group 2 of the periodic table. An electron transfer diagram for magnesium is shown in Figure 4.3.3.

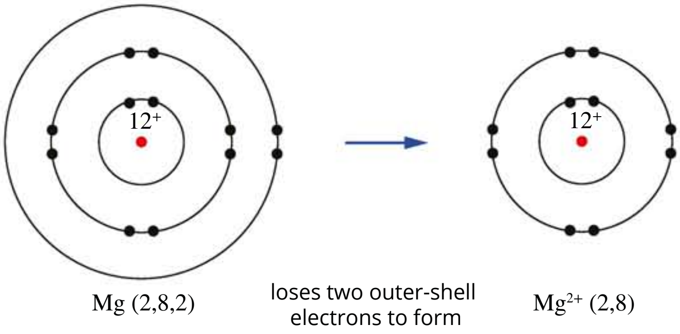


FIGURE 4.3.3 The electron transfer diagram for magnesium, showing the new electronic configuration when the ion Mg^{2+} is formed.

EXTENSION

Beryllium is an exception in group 2

Beryllium is found in group 2 of the periodic table. However, beryllium behaves very differently from the other alkaline earth metals in this group.

Beryllium has an electronic configuration of 2,2. It could lose two electrons to form an ion similar to lithium with just one remaining valence shell (that is, full with two electrons). However, it does not do this because beryllium has a very high electronegativity compared with the rest of the group 2 metals. It tends to hold on to these two electrons. Beryllium mostly forms covalent compounds (which you will learn about in Chapter 6). For example, beryllium covalently bonds with two chlorine atoms to form beryllium chloride ($BeCl_2$). Beryllium chloride is used in the production of beryllium by electrolysis.

Non-metals in group 16 have six electrons in their valence shells. Therefore, they electrons to form anions with a charge of –2.

Group 17 non-metals have seven electrons in their valence shell. They readily gain one electron to fill the valence shell according to the octet rule. This means they form anions with a charge of –1.

Atoms are at their most stable when they have a valence shell containing eight electrons. An exception to this is lithium. As lithium has only one electron in the second shell, it loses this and the first shell becomes the valence shell. The first shell can only hold two electrons so a lithium ion is stable with an electronic configuration of 2. This configuration is the same as that of the noble gas closest to it, helium.

ELECTRON TRANSFER DIAGRAMS

Electron transfer diagrams can be used to show how electrons are transferred from metallic atoms to non-metallic atoms to form an ionic compound. Figure 4.3.4 shows such a diagram for the reaction of magnesium with oxygen.

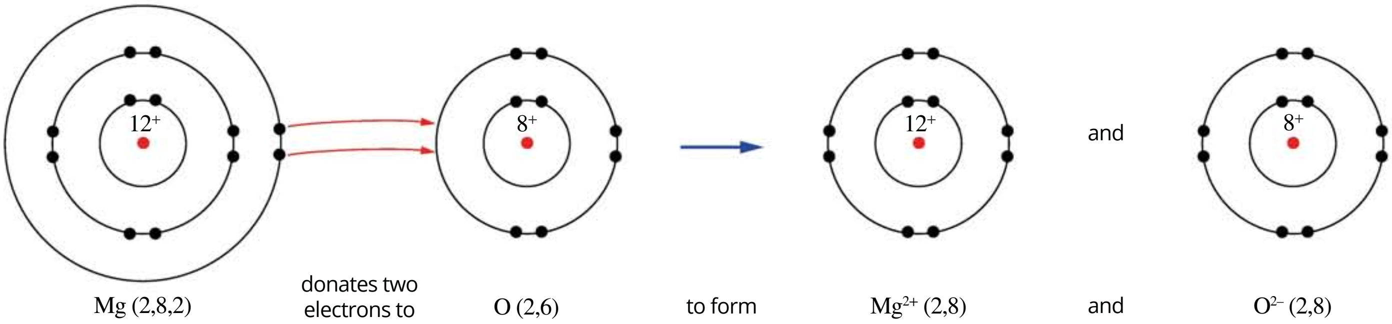


FIGURE 4.3.4 An electron transfer diagram showing the transfer of electrons when magnesium atoms react with oxygen atoms.

Figure 4.3.5 shows the diagram for the reaction of magnesium with chlorine. A magnesium atom has an electronic configuration of 2,8,2 so it will readily lose its two outer-shell electrons. A magnesium ion (Mg^{2+}) is formed so that it now has the electronic configuration of the nearest noble gas, neon (2,8). Each chlorine atom has an electronic configuration of 2,8,7, so each will gain one outer-shell electron. A chloride ion (Cl^-) has the electronic configuration of the noble gas argon (2,8,8). Because magnesium readily donates two electrons, it is found with two chlorine atoms, each chlorine atom taking one electron each from magnesium.

When an atom loses electrons, it becomes more positively charged as the number of protons no longer equals the number of electrons. The ion formed is written with a superscript + sign indicating the charge. If there are two additional electrons, it is written as 2+. When an atom gains electrons, in the case of anions, they become negatively charged. This is written with a superscript –. If three electrons are gained, the charge is written as 3– in superscript.

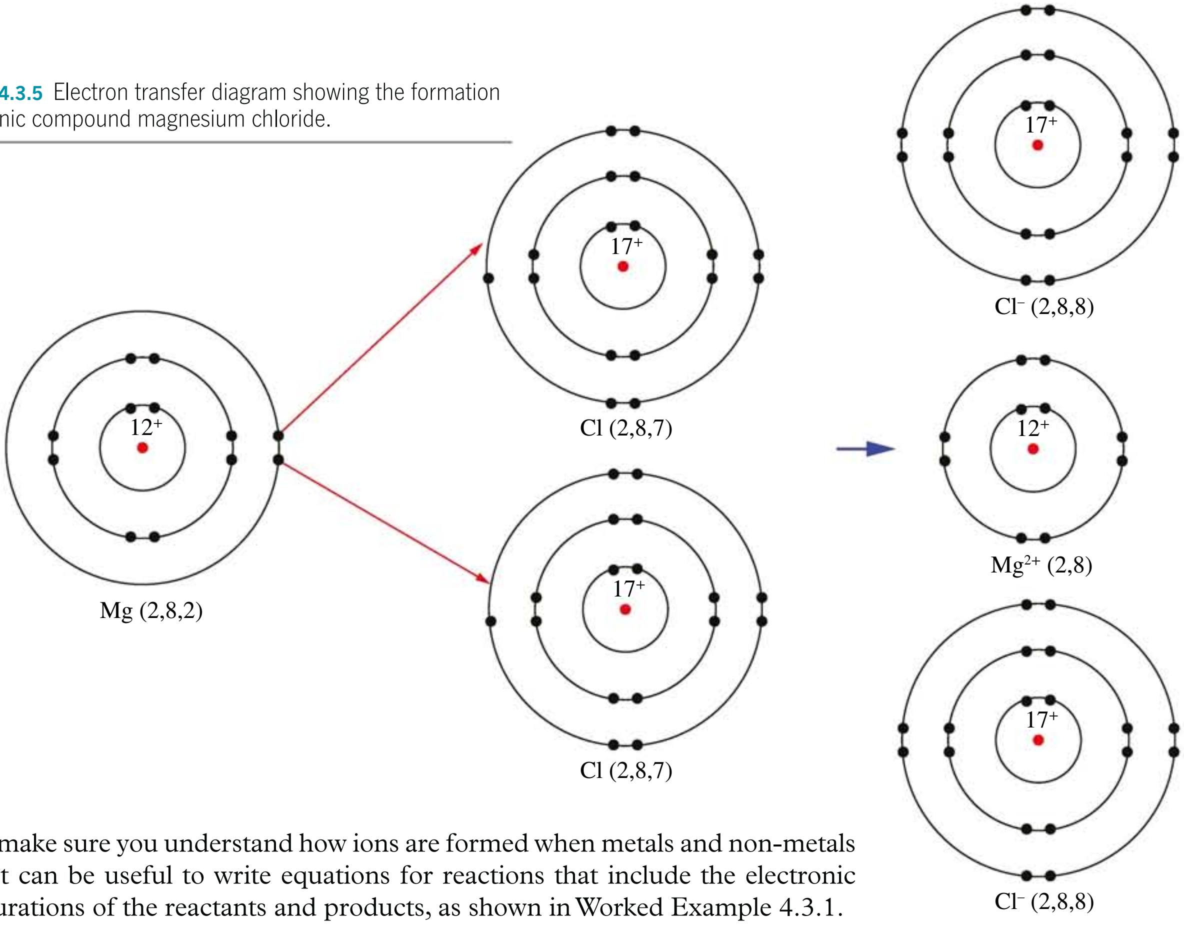


FIGURE 4.3.5 Electron transfer diagram showing the formation of the ionic compound magnesium chloride.

To make sure you understand how ions are formed when metals and non-metals react, it can be useful to write equations for reactions that include the electronic configurations of the reactants and products, as shown in Worked Example 4.3.1.

Worked example 4.3.1

WRITING EQUATIONS FOR REACTIONS BETWEEN METALS AND NON-METALS ATOMS

Write an equation for the reaction between lithium and nitrogen atoms. Show the electronic configurations for each element before and after the reaction.

Thinking	Working
Write the symbol and electronic configuration for the metal atom.	Li (2,1)
How many electrons will the metal atom lose from its outer shell when it reacts?	1
Write the symbol and electronic configuration of the metal ion that will be formed.	Li^+ (2)
Write the symbol and electronic configuration for the non-metal atom.	N (2,5)
How many electrons will the non-metal atom gain in its outer shell when it reacts?	3
Write the symbol and electronic configuration of the non-metal ion that will be formed.	N^{3-} (2,8)
The total number of electrons lost by metal atoms must equal the total number of electrons gained by non-metal atoms. What is the lowest number ratio of metal atoms to non-metal atoms that will allow this to happen?	metal atom : non-metal atom = 3:1
Using the ratio of metal ion : non-metal ion calculated above, write a balanced equation for the reaction. Show the electronic configurations for both the reactant atoms and the product ions.	$3Li\ (2,1) + N\ (2,5) \rightarrow 3Li^+\ (2) + N^{3-}\ (2,8)$

Worked example: Try yourself 4.3.1

WRITING EQUATIONS FOR REACTIONS BETWEEN METALS AND NON-METALS ATOMS

Write an equation for the reaction between calcium and phosphorus atoms. Show the electronic configurations for each element before and after the reaction.

4.3 Review

SUMMARY

- During the formation of ionic compounds, metal atoms lose electrons to form positively charged ions (cations).
- During the formation of ionic compounds, non-metal atoms gain electrons to form negatively charged ions (anions).
- The ions present in an ionic compound have a stable electronic configuration identical to that of the noble gas nearest to them on the periodic table.
- Electron transfer diagrams can be used to represent the formation of an ionic compound from its elements.
- When an ionic compound is formed from positively charged metal ions and negatively charged non-metal ions, the ions combine in proportions that produce an ionic compound with an overall zero charge.

KEY QUESTIONS

1 Indicate whether the following atoms will form cations or anions and explain why.
  - **a** Calcium
  - **b** Nitrogen
  - **c** Fluorine
  - **d** Aluminium
  - **e** Phosphorus

2 Use diagrams similar to Figure 4.3.1 on page 94 to show the formation of ions in the reactions between:
  - **a** potassium and fluorine
  - **b** magnesium and sulfur
  - **c** aluminium and fluorine
  - **d** sodium and oxygen
  - **e** aluminium and oxygen.

3 Why are group 2 metals of the periodic table likely to form cations with a charge of +2?

4 Explain why potassium chloride has the formula KCl, whereas the formula of calcium chloride is $CaCl_2$.

5 Using the technique demonstrated in Worked Example 4.3.1, write an equation for the reaction between the following metal and non-metal atoms. Show the electronic configurations for each element before and after the reaction.
  - **a** Sodium and chlorine atoms
  - **b** Magnesium and oxygen atoms
  - **c** Aluminium and sulfur atoms

4.4 Chemical formulas of simple ionic compounds

You have seen that ionic compounds contain oppositely charged ions that are arranged in three-dimensional lattices. The ions can have different charges. For example, aluminium forms ions with a +3 charge, whereas oxygen forms an ion with a –2 charge.

In this section, you will learn how to use your knowledge of the charges on ions to write an overall formula for an ionic compound.

WRITING THE FORMULA OF AN IONIC COMPOUND

Because ionic compounds are electrically neutral, the total number of positive charges on the metal ions must equal the total number of negative charges on the non-metal ions. This is the most important guiding principle when you are trying to work out the formula of an ionic compound.

This can be seen with the formula of the ionic compound sodium chloride.

- A sodium ion (Na^+) has a +1 charge.
- A chloride ion (Cl^-) has a –1 charge.
- Therefore, in a crystal of sodium chloride, the ratio of sodium ions to chloride ions is 1:1 and the formula of sodium chloride is NaCl.

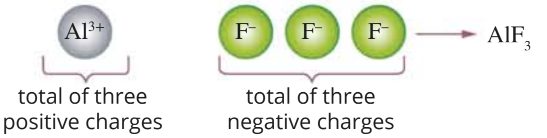
Using the same steps, you can work out the formula of magnesium chloride.

- A magnesium ion (Mg^{2+}) has a +2 charge.
- A chloride ion (Cl^-) has a –1 charge.
- Therefore, in a crystal of magnesium chloride, two chloride ions are needed to provide two negative charges so that they balance the +2 charge on every magnesium ion. Therefore, the ratio of magnesium ions to chloride ions in the crystal is 1:2 and the formula of magnesium chloride is $MgCl_2$.

Figure 4.4.1 illustrates how formulas for some other ionic compounds can be determined.

Tables 4.4.1 and 4.4.2 list some of the more common positively and negatively charged ions. You may use these when you are writing formulas for ionic compounds.

(a) Aluminium fluoride, AlF_3



(b) Copper(II) nitride, Cu_3N_2

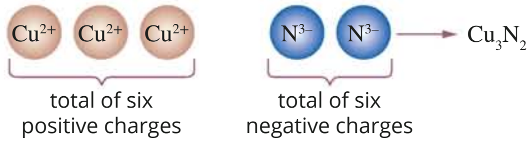


FIGURE 4.4.1 How to deduce chemical formulas from the charges on ions.

TABLE 4.4.1 Names and formulas of some common cations

Charge			
+1	+2	+3	+4
Caesium, Cs^+	Barium, Ba^{2+}	Aluminium, Al^{3+}	Lead(IV), Pb^{4+}
Copper(I), Cu^+	Cadmium(II), Cd^{2+}	Chromium(III), Cr^{3+}	Tin(IV), Sn^{4+}
Gold(I), Au^+	Calcium, Ca^{2+}	Gold(III), Au^{3+}	
Hydrogen, H^+	Cobalt(II), Co^{2+}	Iron(III), Fe^{3+}	
Lithium, Li^+	Copper(II), Cu^{2+}		
Potassium, K^+	Iron(II), Fe^{2+}		
Rubidium, Rb^+	Lead(II), Pb^{2+}		
Silver, Ag^+	Magnesium, Mg^{2+}		
Sodium, Na^+	Manganese(II), Mn^{2+}		
	Mercury(II), Hg^{2+}		
	Nickel, Ni^{2+}		
	Strontium, Sr^{2+}		
	Tin(II), Sn^{2+}		
	Zinc, Zn^{2+}		

TABLE 4.4.2 Names and formulas of some common anions

Charge		
–1	–2	–3
Bromide, Br^-	Oxide, O^{2-}	Nitride, N^{3-}
Chloride, Cl^-	Sulfide, S^{2-}	
Fluoride, F^-		
Iodide, I^-		

Rules for writing chemical formulas

Here are some simple rules to follow when you are writing chemical formulas.

- Write the symbol for the positively charged ion first.
- Use subscripts to indicate the number of each ion in the formula. Write the subscripts after the ion they refer to.
- If there is just one ion present in the formula, omit the subscript '1'.
- Do not include the charges on the ions in the balanced formula.

These rules are illustrated in Figure 4.4.2.

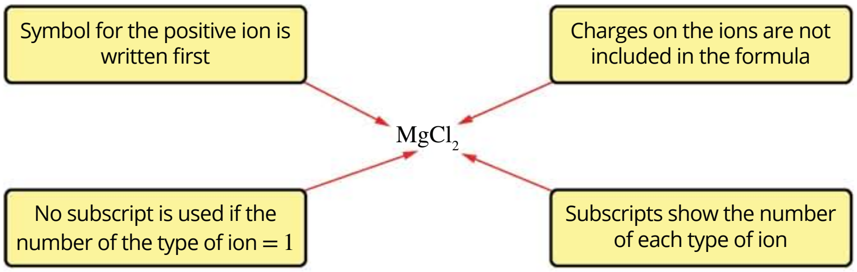


FIGURE 4.4.2 This diagram summarises the information provided by a chemical formula.

Worked example 4.4.1

STEPS IN WRITING A CHEMICAL FORMULA

Determine the chemical formula of the ionic compound formed between zinc and nitride ions. You may need to refer to Tables 4.4.1 and 4.4.2 on page 99.

Thinking	Working
Write the symbol and charge of the two ions forming the ionic compound.	Zn^{2+} and N^{3-}
Calculate the lowest common multiple of the two numbers in the charges of the ions.	$2 \times 3 = 6$
Calculate how many positive ions are needed to equal the lowest common multiple.	Three Zn^{2+} ions
Calculate how many negative ions are needed to equal the lowest common multiple.	Two N^{3-} ions
Use the answers from the previous two steps to write the formula for the ionic compound. Write the symbol of the positive ion first. (Note that 1 is not written as a subscript.)	Zn_3N_2

Worked example: Try yourself 4.4.1

STEPS IN WRITING A CHEMICAL FORMULA

Determine the chemical formula of the ionic compound formed between barium and fluoride ions. You may need to refer to Tables 4.4.1 and 4.4.2 on page 99.

4.4 Review

SUMMARY

- When considering the formula of an ionic compound, the total number of positive charges on the metal ions must equal the total number of negative charges on the non-metal ions.
- When writing formulas of ionic compounds:
  - the symbol for the positively charged ion is written first
  - subscripts are used to indicate the number of each ion in the formula
  - the charges on the ions are not included in the balanced formula.

KEY QUESTIONS

1 A_2B is an ionic compound. Both of the ions in A_2B have the same electronic configuration as an argon atom. What is the identity of A_2B?

A Calcium chloride
B Potassium sulfide
C Calcium sulfide
D Sodium oxide

2 Listed below are pairs of metal and non-metal ions. When the ions in each pair combine to form ionic compounds, what will be the ratio of metal ion to non-metal ion?

a K^+ and S^{2-}
b Al^{3+} and F^-
c Ca^{2+} and N^{3-}
d Al^{3+} and P^{3-}
e Mg^{2+} and Cl^-

3 Use the information in Tables 4.4.1 and 4.4.2 on page 99 to write formulas for the following ionic compounds.

a Sodium chloride
b Potassium bromide
c Zinc chloride
d Potassium oxide
e Barium bromide
f Aluminium iodide
g Silver bromide
h Zinc oxide
i Barium oxide
j Aluminium sulfide

4 Use the information in Tables 4.4.1 and 4.4.2 on page 99 to name the ionic compounds with the following formulas.

a KCl
b CaO
c MgS
d K_2O
e NaF

4.5 Writing formulas of more complex ionic compounds

The chemical formulas you have written for ionic compounds so far contain simple ions—ions that contain only one atom of an element. In this section, you will look at the formulas of some compounds containing more complex ions. You will also learn rules to help you name ionic compounds.

FORMULAS CONTAINING POLYATOMIC IONS

Simple ions contain only one atom, as you have seen in section 4.4. However, other ions contain two or more atoms, which may be of different elements. These ions are called **polyatomic ions**.

In polyatomic ions:

- if different elements are present, then they are combined in a fixed ratio
- the group of atoms behaves as a single unit with a specific charge
- subscripts are used to indicate the number of each kind of atom in the ion.

For example, a carbonate ion (CO_3^{2-}) contains one carbon atom and three oxygen atoms combined together to form an ion. The carbonate ion has a charge of –2. Other polyatomic ions are nitrate (NO_3^-), hydroxide (OH^-) and phosphate (PO_4^{3-}). The formulas of a number of polyatomic ions can be seen in Table 4.5.1.

TABLE 4.5.1 Common polyatomic cations and anions

Charge			
+1	–1	–2	–3
Ammonium, NH_4^+	Cyanide, CN^- Dihydrogen phosphate, $H_2PO_4^-$ Ethanoate, CH_3COO^- Hydrogen carbonate, HCO_3^- Hydrogen sulfide, HS^- Hydrogen sulfite, HSO_3^- Hydrogen sulfate, HSO_4^- Hydroxide, OH^- Nitrite, NO_2^- Nitrate, NO_3^- Permanganate, MnO_4^-	Carbonate, CO_3^{2-} Chromate, CrO_4^{2-} Dichromate, $Cr_2O_7^{2-}$ Hydrogen phosphate, HPO_4^{2-} Oxalate, $C_2O_4^{2-}$ Sulfite, SO_3^{2-} Sulfate, SO_4^{2-}	Phosphate, PO_4^{3-}

The alternative, common name for the ethanoate ion is acetate. The alternative name for the hydrogen carbonate ion is bicarbonate.

Polyatomic ions are ions that are made up of two or more different atoms that have an overall charge. They need to be written within brackets if there is more than one present in an ionic compound. Subscripts are used to indicate the ratio of ions in the crystal lattice.

If more than one polyatomic ion is required in a formula to balance the charge, then it is placed in brackets with the required number written as a subscript after the brackets. Some examples are:

- magnesium nitrate, $Mg(NO_3)_2$
- aluminium hydroxide, $Al(OH)_3$
- ammonium sulfate, $(NH_4)_2SO_4$.

Note that brackets are not required for the formula of sodium nitrate ($NaNO_3$), where there is only one NO_3^- ion present for each sodium ion.

A formula that is expressed in terms of the simplest whole-number ratio of particles (in this case the particles are ions) is called an **empirical formula**. You will learn more about empirical formulas in Chapter 5.

The formulas of several other ionic compounds containing polyatomic ions are shown in Figure 4.5.1.

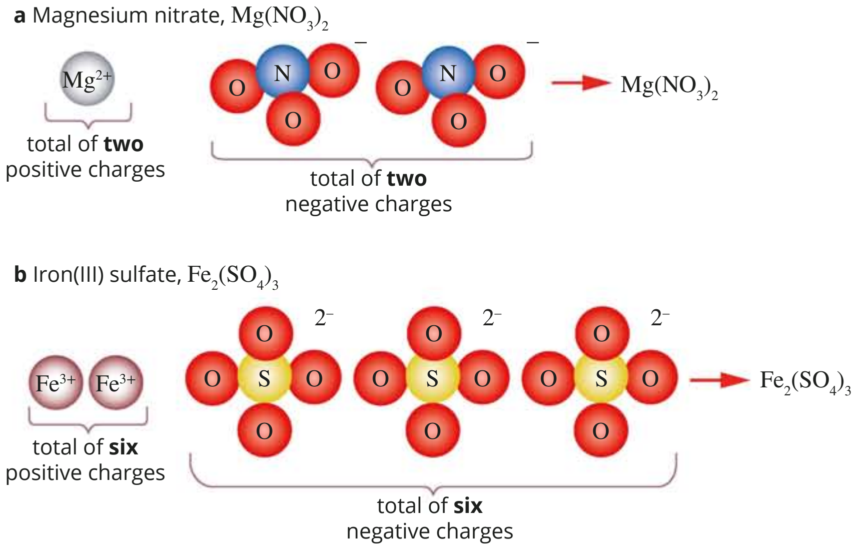


FIGURE 4.5.1 The chemical formulas of ionic compounds containing polyatomic ions.

Formulas involving elements with multiple electrovalencies

The **electrovalency** of an ion is the charge on the ion. Some transition metals can form ions with several electrovalencies. For example, copper can form Cu^+ ions with a charge of +1 and Cu^{2+} ions with a charge of +2.

Some other metals with ions of variable electrovalency are:

- lead (Pb^{2+} and Pb^{4+})
- iron (Fe^{2+} and Fe^{3+})
- tin (Sn^{2+} and Sn^{4+}).

For compounds of these metals, you need to specify the charge on the ion when naming the compound. This is done by placing a Roman numeral immediately after the metal in the name of the compound. For example:

- iron(II) chloride contains the Fe^{2+} ion and so the formula is $FeCl_2$
- iron(III) chloride contains the Fe^{3+} ion and so the formula is $FeCl_3$
- copper(I) sulfide contains the Cu^+ ion and so the formula is Cu_2S.

Some transition metals can form ions with variable charges. To indicate the charge on the metal, write a Roman numeral in brackets immediately after the metal in the name of the compound.

NAMING IONIC COMPOUNDS

There are some basic conventions that are followed when naming ionic compounds:

- The name of a positively charged metal ion (cation) is the same as the name of the metal. For example, the cation of a sodium atom is called a sodium ion; the cation of an aluminium atom is an aluminium ion.
- For simple non-metal ions (anions), the name of the ion is similar to that of the atom, but ends in '-ide'. For example, the anion of the chlorine atom is chloride; the anion of the oxygen atom is oxide.
- For polyatomic anions containing oxygen, the name of the ion will usually end in '-ite' or '-ate'. For example, the NO_2^- ion is called a nitrite ion; the NO_3^- ion is called a nitrate ion. (For two different ions of the same element with oxygen, the name of the ion with the smaller number of oxygen atoms usually ends in '-ite' and the one with the larger number of oxygen atoms ends in '-ate'.)

4.5 Review

SUMMARY

- When writing formulas for ionic compounds, these rules apply.
  - Ions that contain two or more atoms of different elements are called polyatomic ions.
  - If a chemical formula contains more than one polyatomic ion, the formula of the ion is placed in brackets with the number of ions written as a subscript after the brackets.
  - For metals that form ions with different charges, the charge on the ion is shown by placing a Roman numeral after the name of the metal.
- When naming ionic compounds, the following rules apply.
  - The name of the metal ion is the same as the name of the metal.
  - Simple non-metal ions take the name of the atom, but end in '-ide'.
  - Polyatomic anions containing oxygen usually end in '-ite' or '-ate'.
- The charge of an ion is called its electrovalency.

KEY QUESTIONS

1 Use the information in Tables 4.4.1 and 4.4.2 on page 99 and Table 4.5.1 on page 102 to write formulas for the following ionic compounds.

a Sodium carbonate
b Barium nitrate
c Aluminium nitrate
d Calcium hydroxide
e Zinc sulfate
f Potassium hydroxide
g Potassium nitrate
h Zinc carbonate
i Potassium sulfate
j Barium hydroxide

2 Use the information in Tables 4.4.1 and 4.4.2 on page 99 and Table 4.5.1 on page 102 to write formulas for the following ionic compounds.

a Copper(I) chloride
b Iron(III) oxide
c Copper(II) oxide
d Chromium(III) sulfate
e Iron(II) oxide
f Lead(II) nitrate
g Lead(IV) oxide
h Tin(II) nitrate

3 Use the information in Tables 4.4.1 and 4.4.2 on page 99 and Table 4.5.1 on page 102 to name the following ionic compounds.

a $Mg(OH)_2$
b Na_2CO_3
c $FeSO_4$
d $CuSO_4$
e $Ba(NO_3)_2$
f Cu_2SO_4
g $Fe_2(SO_4)_3$
h NH_4NO_3
i Na_2HPO_4

Chapter review

04

KEY TERMS

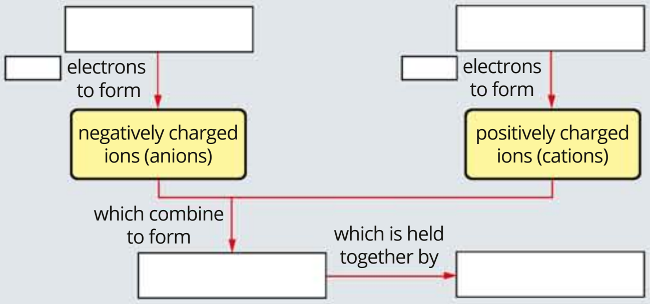
anion
brittle
cation
ceramic
chemical formula
crystal lattice
dissolve
electrolysis
electrolyte
electron transfer diagram
electrovalency
empirical formula
gemstone
ionic bonding
ionic compound
non-polar solvent
octet rule
polyatomic ion
salinity

Properties and structures of ionic compounds

1 Describe an experiment you could carry out to demonstrate each of the following properties of the compounds given. In each case:
   - **i** sketch the equipment you would use
   - **ii** describe what you would expect to observe.
   - **a** Solid magnesium chloride does not conduct electricity.
   - **b** Molten sodium chloride does conduct electricity.
   - **c** Solid sodium chloride is hard and brittle.

2 State whether the following properties relate to metallic lattices only, ionic lattices only or both metallic and ionic lattices.
   - **a** They contain both positively and negatively charged particles.
   - **b** The lattice is held together by forces of attraction between positively and negatively charged particles.
   - **c** They are hard.
   - **d** They are brittle.
   - **e** They conduct electricity in the molten state.

3 Copy and complete the following diagram to show what happens when ionic compounds are formed from metallic and non-metallic elements.



Using the ionic bonding model to explain properties

4 Use the ionic bonding model to explain the following properties of ionic compounds.
   - **a** They generally have high melting points.
   - **b** They are hard and brittle.
   - **c** They do not conduct electricity in the solid state but will conduct when molten or dissolved in water.

5 The melting point of sodium chloride is 801°C, whereas that of magnesium oxide is 2800°C.
   - **a** What particles are present in the two solids?
   - **b** Which solid has the stronger forces between its particles?
   - **c** Give some possible differences in the structure and bonding of the two solids that would explain the large difference in melting point.

6 Describe what happens to the forces between particles as sodium chloride is heated and melts.

7 The following is a list of some of the uses of ionic compounds. For each use, explain what property of ionic compounds enables them to be used in this way.
   - **a** Insulators on electrified fences
   - **b** Bricks for building the wall of a house
   - **c** One of the chemicals in a battery

Formation of ionic compounds

8 Use diagrams to show the electron transfer that occurs when:
   - **a** lithium reacts with chlorine
   - **b** magnesium reacts with fluorine
   - **c** potassium reacts with sulfur
   - **d** magnesium reacts with nitrogen.

9 Give the electronic configurations of the following ions.
   - **a** Na^+
   - **b** O^{2-}
   - **c** Mg^{2+}
   - **d** N^{3-}

10 The electronic configurations of some metallic and non-metallic elements are given. (The symbols shown for the elements are not their real ones.) Write formulas for the compounds they are most likely to form if they react together. The first example has been done for you.

a	A: 2,1	B: 2,6	A_2B
b	C: 2,8,3	D: 2,7	
c	E: 2,8,8,2	F: 2,8,6	
d	G: 2,8,8,1	H: 2,5	
e	K: 2,8,2	L: 2,6	

11 Refer to the periodic table at the end of the book and, for each general formula given, identify two elements that will react to form an ionic compound with that formula. (Remember the metal ion, as represented by X, is written first in each formula.)

a XY_2
b XY
c X_2Y
d X_3Y
e XY_3
f X_3Y_2

12 Explain why elements in group 17 of the periodic table are likely to forms ions with a –1 charge.

13 Write an equation for the reaction between the following metal and non-metal atoms. Show the electronic configurations for each element before and after the reaction.

a Magnesium and chlorine atoms
b Aluminium and oxygen atoms

Chemical formulas of simple ionic compounds

14 Write the empirical formula for the ionic compound formed in the reaction between:

a potassium and bromine
b magnesium and iodine
c calcium and oxygen
d aluminium and fluorine
e calcium and nitrogen.

15 Write the empirical formula for each of the following ionic compounds.

a Copper(I) chloride
b Silver oxide
c Lithium nitride
d Potassium iodide

16 What do subscripts in the formula of an ionic compound tell you about the arrangement of the metal and non-metal ions?

Writing formulas of more complex ionic compounds

17 The elements X, Y and Z form ionic compounds when they react with other elements. The following compounds are formed: Ca_3X_2, Y_2CO_3 and Al_2Z_3.

a What is the electrovalency (charge) of the ion formed by:
  i element X?
  ii element Y?
  iii element Z?

b Use these charges on the ions to write correct chemical formulas for the:
  i sulfate salt of Y
  ii potassium salt of Z
  iii ionic compound formed between X and Y
  iv ionic compound formed between Y and Z.

18 Write the empirical formulas for the following ionic compounds.

a Copper(I) nitrate
b Chromium(II) fluoride
c Potassium carbonate
d Magnesium hydrogen carbonate
e Nickel(II) phosphate.

19 Name the ionic compounds with the following chemical formulas.

a $(NH_4)_2CO_3$
b $Cu(NO_3)_2$
c $CrBr_3$

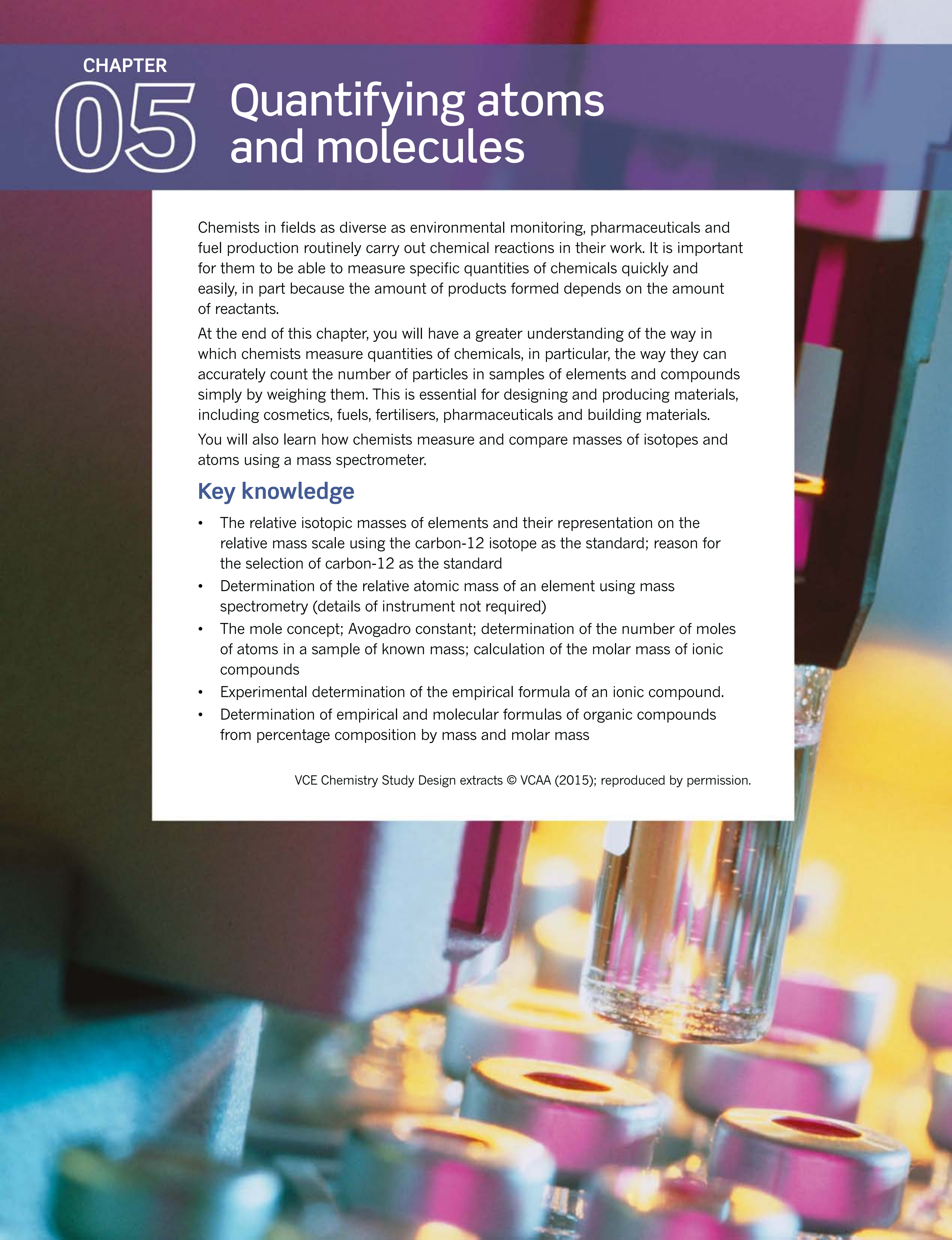
Connecting the main ideas

20 A student compares the structure and bonding in metals and ionic compounds and makes the following statements.

a Metals and ionic solids both contain positive ions in a regular arrangement.
b In metals and ionic solids, there is attraction between one particle and all the neighbouring particles of opposite charge.
c In metals and ionic solids, there will be forces of repulsion between particles with like charges.
d In metals and ionic solids that contain metal cations, energy has been used to remove valence electrons from metal atoms.
e A metal will conduct electricity, whereas an ionic solid will not because electrons are much smaller than negative ions.

Comment on each of these statements, explaining clearly why you either agree or disagree.

21 Construct a concept map to show the connection between the terms: metal, non-metal, atom, valence electron, anion, cation, electrostatic attraction, ionic bonding.



CHAPTER

05

Quantifying atoms and molecules

Chemists in fields as diverse as environmental monitoring, pharmaceuticals and fuel production routinely carry out chemical reactions in their work. It is important for them to be able to measure specific quantities of chemicals quickly and easily, in part because the amount of products formed depends on the amount of reactants.

At the end of this chapter, you will have a greater understanding of the way in which chemists measure quantities of chemicals, in particular, the way they can accurately count the number of particles in samples of elements and compounds simply by weighing them. This is essential for designing and producing materials, including cosmetics, fuels, fertilisers, pharmaceuticals and building materials.

You will also learn how chemists measure and compare masses of isotopes and atoms using a mass spectrometer.

Key knowledge

- The relative isotopic masses of elements and their representation on the relative mass scale using the carbon-12 isotope as the standard; reason for the selection of carbon-12 as the standard
- Determination of the relative atomic mass of an element using mass spectrometry (details of instrument not required)
- The mole concept; Avogadro constant; determination of the number of moles of atoms in a sample of known mass; calculation of the molar mass of ionic compounds
- Experimental determination of the empirical formula of an ionic compound.
- Determination of empirical and molecular formulas of organic compounds from percentage composition by mass and molar mass

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5.1 Masses of particles

Atoms are particles so small that they cannot be counted individually or even in groups of thousands or millions. The mass of one atom is incredibly small. For example, one atom of carbon has a mass of approximately 2×10^{-23} g.

Figure 5.1.1 shows a model of a glucose molecule. Glucose is a type of sugar used as an energy source by almost all living organisms on Earth. One glucose molecule contains 6 carbon atoms, 12 hydrogen atoms and 6 oxygen atoms bonded together. One glucose molecule has an actual mass of 3×10^{-22} g. This means that the teaspoon of glucose crystals shown in Figure 5.1.1 contains approximately 1.4×10^{22} glucose molecules.

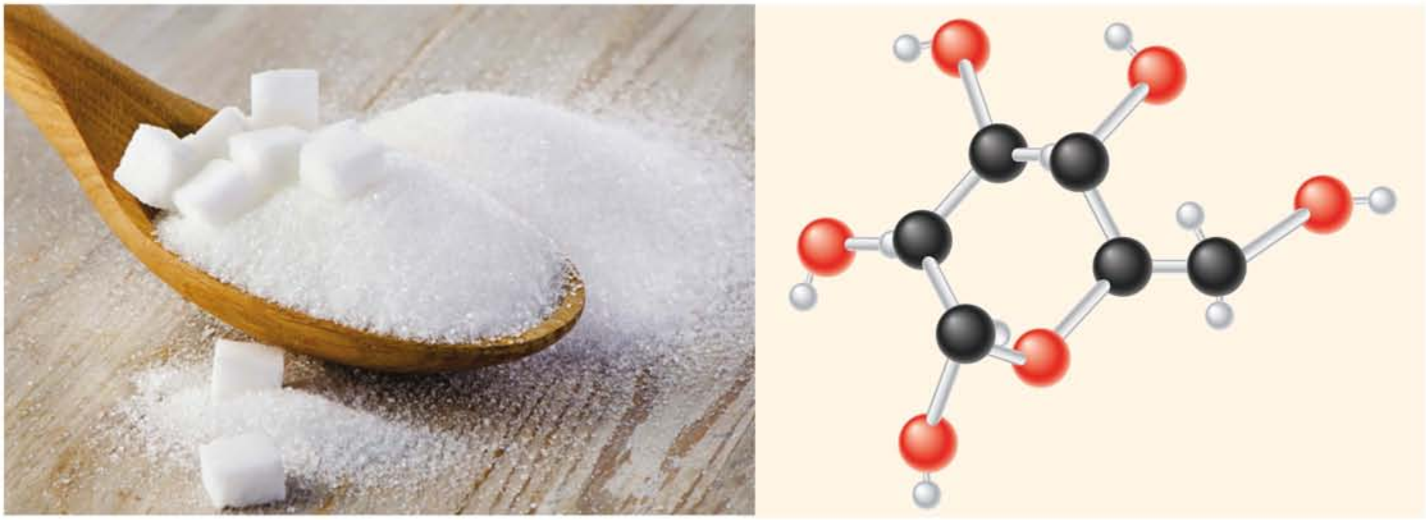


FIGURE 5.1.1 A teaspoon of glucose crystals contains an incredibly large number of extremely small glucose molecules. The single glucose molecule pictured contains 6 carbon atoms (black), 12 hydrogen atoms (white) and 6 oxygen atoms (red) bonded together.

Such small masses are not easily measured and can be inconvenient to use in calculations. This section will introduce you to the ways scientists determine and use the masses of different particles.

RELATIVE MASSES

From Chapter 1, you will remember that isotopes are atoms of the same element that have different numbers of neutrons in their nucleus. So isotopes have the same atomic number but different mass number.

The masses used most frequently in chemistry are relative masses, rather than actual masses. The standard to which all masses are compared is the mass of an atom of the common **isotope** of carbon, **carbon-12** or ^{12}C, which is given a mass of exactly 12. Carbon-12 was selected as the standard in 1961. Before then, oxygen was used as the standard.

Physicists and chemists could not agree on a way of assigning a standard mass to oxygen. Chemists assigned a mass of exactly 16 to the average mass of oxygen atoms. Physicists assigned a mass of exactly 16 to the oxygen-16 isotope. This resulted in two different tables of slightly different atomic masses.

Making carbon-12 the standard was a compromise. Assigning carbon-12 a mass of exactly 12 created a new scale, which was adopted universally.

RELATIVE ISOTOPIC MASSES

The individual isotopes of each element have a **relative isotopic mass**. Table 5.1.1 shows the approximate mass of various isotopes relative to the carbon-12 isotope taken as 12 units exactly.

TABLE 5.1.1 Approximate mass of various isotopes relative to the ^{12}C isotope, which is taken as exactly 12 units

Isotope	Diagram of nucleus	Number of protons in nucleus	Number of neutrons in nucleus	Total number of protons and neutrons	Approximate mass of atom relative to carbon-12 isotope
Hydrogen $^{1}_{1}H$		1	0	1	$\frac{1}{12}$ of 12 = 1
Helium $^{4}_{2}He$		2	2	4	$\frac{4}{12}$ of 12 = 4
Lithium $^{7}_{3}Li$		3	4	7	$\frac{7}{12}$ of 12 = 7
Carbon $^{12}_{6}C$		6	6	12	12

As shown in Figure 5.1.2, there are two different isotopes of the element chlorine:

- $^{35}_{17}Cl$, which contains 17 protons and 18 neutrons
- $^{37}_{17}Cl$, which contains 17 protons and 20 neutrons.

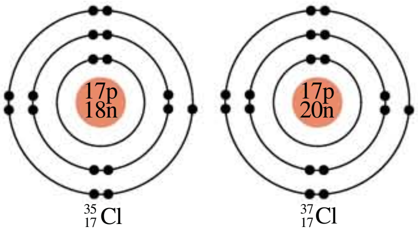


FIGURE 5.1.2 The two isotopes of the element chlorine. Different numbers of neutrons in the nuclei of these atoms give the atoms different masses.

The isotopes have different masses because of the different numbers of neutrons. Remember that the mass of an atom is mainly determined by the number of protons and neutrons in their nucleus, since the mass of the electrons is relatively small.

The relative isotopic masses of the two chlorine isotopes are experimentally determined to be 34.969 (^{35}Cl) and 36.966 (^{37}Cl). Since the masses of a proton and a neutron are similar and close to 1 on the $^{12}C = 12$ scale, the relative isotopic mass of an isotope is almost, but not exactly, equal to the number of protons plus neutrons in the nucleus.

The relative isotopic mass of an isotope is the mass of an atom of that isotope relative to the mass of an atom of carbon-12 (^{12}C) taken as 12 units exactly.

Relative isotopic abundance

Naturally occurring chlorine is made up of the two isotopes shown in Figure 5.1.2: 75.80% of the lighter isotope and 24.20% of the heavier isotope. This composition is virtually the same no matter the source of the chlorine. The percentage abundance of an isotope in the natural environment is called its **relative isotopic abundance**.

Most elements, like chlorine, are a mixture of two or more isotopes. Details of the isotopes of some common elements are shown in Table 5.1.2.

TABLE 5.1.2 Isotopic composition of some common elements

Element	Isotopes	Relative isotopic mass	Relative isotopic abundance (%)
Hydrogen	^{1}H	1.008	99.986
	^{2}H	2.014	0.014
	^{3}H	3.016	0.0001
Oxygen	^{16}O	15.995	99.76
	^{17}O	16.999	0.04
	^{18}O	17.999	0.20
Silver	^{107}Ag	106.9	51.8
	^{109}Ag	108.9	48.2

The mass spectrometer

Relative isotopic masses of elements and their isotopic abundances are determined by using an instrument called a **mass spectrometer**, which was invented by Francis Aston in 1919.

A mass spectrometer separates the individual isotopes in a sample of an element and determines the mass of each isotope, relative to the carbon-12 isotope, and the relative abundances of the isotopes.

CHEMFILE

Mass spectrometry reveals history

Scientists can use mass spectrometry to determine the relative abundance of one isotope to another in tissues taken from a dead animal. This can help scientists determine important features about that organism's life.

For example, archaeologists can analyse the fossil jawbone shown in Figure 5.1.3 to calculate how long ago the short-necked giraffe lived, to study its diet, or to determine the habitat where the animal lived. Isotope analysis of a number of related fossils can help track the evolution of this species.

FIGURE 5.1.3 Ancient fossil jawbone from an extinct short-necked giraffe. Isotopic analysis using a mass spectrometer provides archaeologists with information about the organism's life.

EXTENSION

Operation of a mass spectrometer

A mass spectrometer, like the one in Figure 5.1.4, is a laboratory instrument used to detect isotopes of an element and determine both the relative mass and abundance of each isotope.

The construction of a mass spectrometer is shown in Figure 5.1.5.

Several different stages are involved in the operation of a mass spectrometer:

- A sample of the element is vapourised and the gas is injected into the ionisation chamber.
- In the ionisation chamber, positive ions are formed when a beam of bombarding electrons dislodges electrons from the sample atoms.
- The positive ions enter an electric field, which accelerates them to high speeds.
- The fast-moving positive ions then enter a magnetic field perpendicular to their path. This causes the ions to be deflected, or move in a curved path with a radius that depends upon the mass-to-charge ratio (*m*/*z* or *m*/*e*) of the ions.
- Ions of a certain mass and charge reach a detector, which measures the current produced by a particular ion.
- The accelerating voltage and strength of the magnetic field are varied to allow different ions to reach the detector, which measures the mass of the ions and their relative abundance. This data is recorded as a mass spectrum.

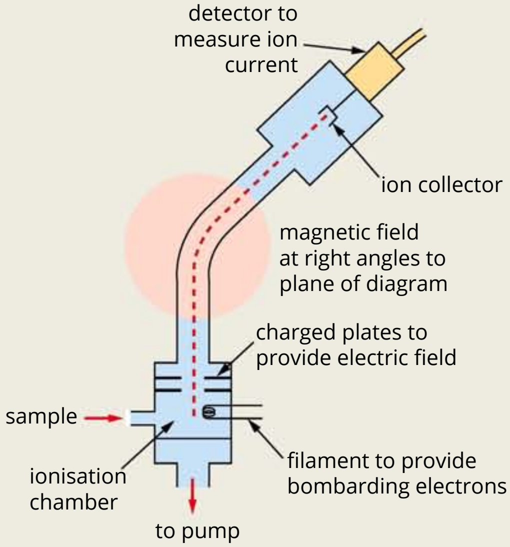


FIGURE 5.1.5 The construction of a mass spectrometer. The sample is **ionised** and the ions pass through an electric field and a magnetic field before reaching the detector.

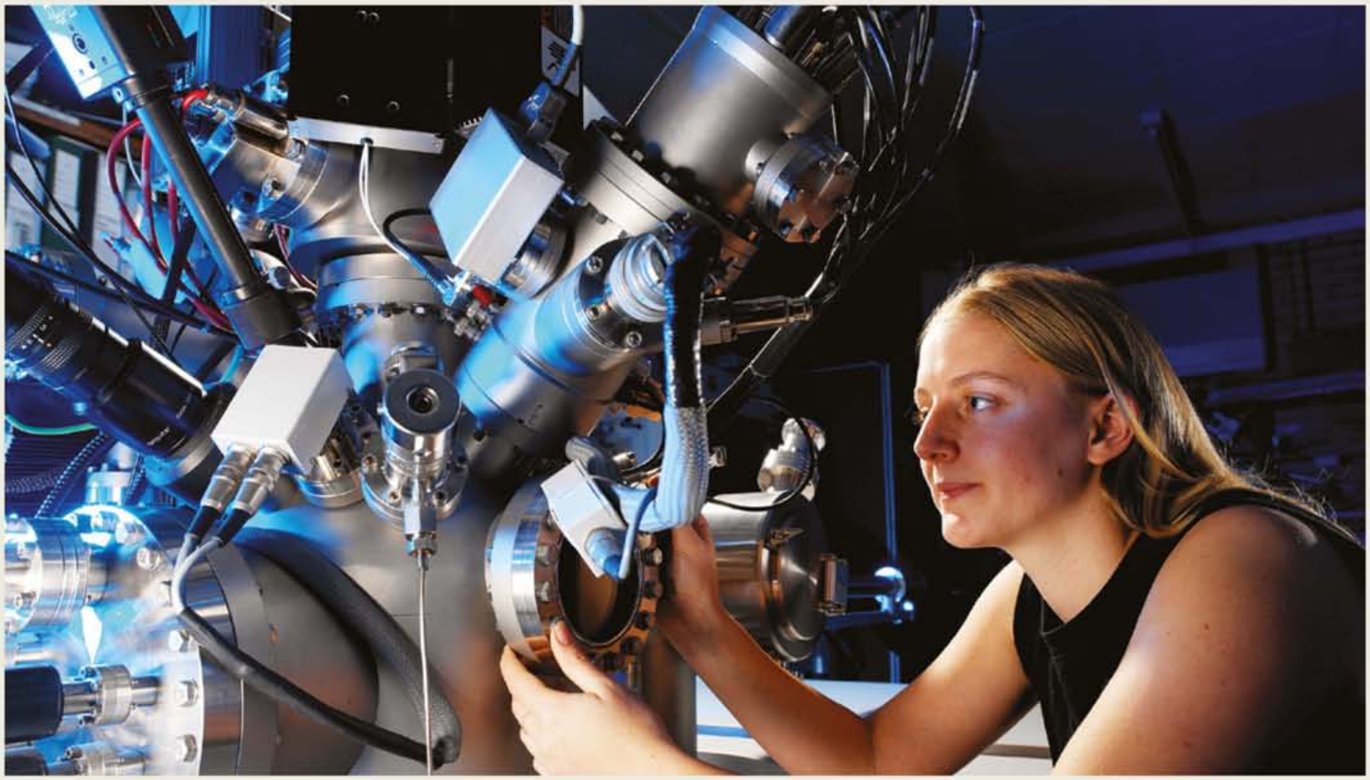


FIGURE 5.1.4 A mass spectrometer is used to determine the relative masses of different isotopes.

Mass spectra

The output obtained from a mass spectrometer is called a **mass spectrum**. Figure 5.1.6 shows the mass spectrum of chlorine. In this mass spectrum, the:

- number of peaks indicates the number of isotopes, in this case, two
- horizontal axis indicates the relative mass of each isotope present in an element according to the isotope's mass-to-charge ratio, which is given the symbol *m*/*z* or *m*/*e*. (The charge on most ions reaching the detector is +1, so the mass of an isotope can be read directly from the horizontal axis.) The two isotopes of chlorine have relative masses of 35 and 37
- vertical axis indicates the abundance of each isotope in the sample: 75% ^{35}Cl, and 25% ^{37}Cl.

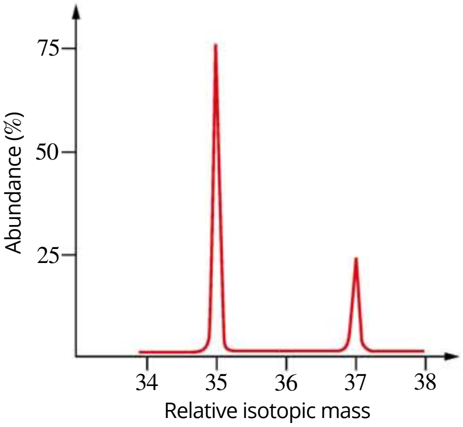


FIGURE 5.1.6 The mass spectrum of chlorine. The two peaks indicate there are two isotopes. The most abundant isotope has a relative isotopic mass of 35 and an abundance of 75%. The other isotope has a relative isotopic mass of approximately 37 and an abundance of approximately 25%.

In summary, in the mass spectrum of an element, the:

- number of peaks indicates the number of isotopes
- position of each peak on the horizontal axis indicates the relative isotopic mass
- relative heights of the peaks correspond to the relative abundance of the isotopes.

RELATIVE ATOMIC MASS

Most elements consist of a mixture of isotopes. For the purpose of the calculations you will be doing later in this chapter, it is convenient to know the average relative mass of an atom in this mixture. This average is called the **relative atomic mass** of an element, and given the symbol A_r.

The relative atomic mass of an element is the weighted average of the relative masses of the isotopes of the element on the ^{12}C scale.

In order to calculate the average of the relative masses of the isotopes that exist in a naturally occurring mixture of an element, you must consider the relative abundances of each isotope.

Data obtained from the mass spectrum of chlorine shown in Figure 5.1.6 is summarised in Table 5.1.3.

The data about the two isotopes is used to calculate the relative atomic mass of chlorine. A weighted average mass is calculated by using the relative isotopic masses and abundances to find the total mass of 100 atoms. This mass is then divided by 100 to find the average mass of one atom.

TABLE 5.1.3 The isotopic composition of chlorine

Isotope	Relative isotopic mass	Relative abundance (%)
^{35}Cl	34.969	75.80
^{37}Cl	36.966	24.20

The relative atomic mass (A_r) of an element with two isotopes can be calculated using the formula:

$$A_r = \frac{(\text{relative isotopic mass} \times \%\ \text{abundance}) + (\text{relative isotopic mass} \times \%\ \text{abundance})}{100}$$

The periodic table at the end of the book provides relative atomic masses, calculated by taking into account the relative abundances of all the natural isotopes of each element.

Worked example 5.1.1

CALCULATING RELATIVE ATOMIC MASS FROM ISOTOPIC MASSES AND PERCENTAGE ABUNDANCES

Determine the relative atomic mass of chlorine from the data obtained from its mass spectrum. (Refer to Figure 5.1.6 and Table 5.1.3.)

Thinking	**Working**
Determine the relative isotopic masses and abundances of each isotope.	Two peaks on the spectrum indicate two isotopes: First isotope: relative isotopic mass 34.969; abundance 75.80% Second isotope: relative isotopic mass 36.966; abundance 24.20%
Substitute the relative isotopic masses and abundances into the formula for calculating relative atomic mass: $A_r = \frac{(\text{relative isotopic mass} \times \%\ \text{abundance}) + (\text{relative isotopic mass} \times \%\ \text{abundance})}{100}$	$A_r = \frac{(34.969 \times 75.80) + (36.966 \times 24.20)}{100}$
Calculate the relative atomic mass.	$A_r = \frac{2650.65 + 894.58}{100}$ $= 35.452$
Express the answer to two decimal places.	$A_r(\text{Cl}) = 35.45$

Worked example: Try yourself 5.1.1

CALCULATING RELATIVE ATOMIC MASS FROM ISOTOPIC MASSES AND PERCENTAGE ABUNDANCES

Boron has two isotopes. Their relative isotopic masses and percentage abundances are provided. Calculate the relative atomic mass of boron.

Isotope	Relative isotopic mass	Relative abundance (%)
^{10}B	10.013	19.91
^{11}B	11.009	80.09

CHEMISTRY IN ACTION

Significant figures

In calculations in chemistry, the accuracy of an answer is limited by the accuracy of the information given. An answer has the same number of significant figures as there are in the least accurate piece of information. In Worked Example 5.1.1, relative isotopic masses have five significant figures, but the relative abundances have only four significant figures. Therefore, the answer to this question has four significant figures. (See the Appendix at the end of the book for a more detailed treatment of significant figures.)

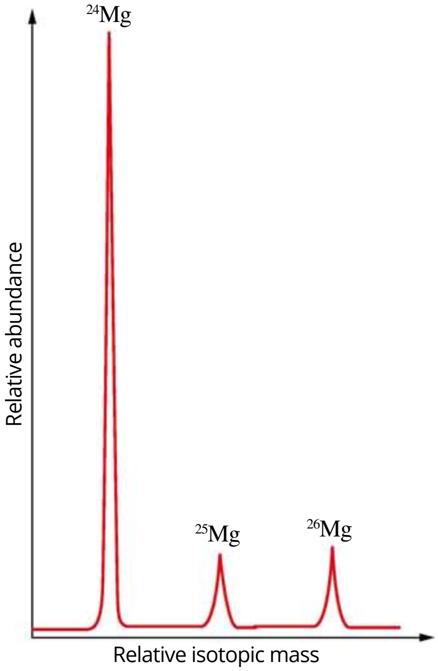


FIGURE 5.1.7 Mass spectrum of magnesium.

Worked example 5.1.2

CALCULATING PERCENTAGE ABUNDANCE OF EACH ISOTOPE FROM THE MASS SPECTRUM

Figure 5.1.7 shows a simplified mass spectrum of magnesium. From this mass spectrum, calculate the percentage abundance of each of its three isotopes.

Thinking	**Working**
Measure the peak height for each isotope using a ruler.	From the spectrum, the height of each peak is: ^{24}Mg = 7.9 cm ^{25}Mg = 1.0 cm ^{26}Mg = 1.1 cm
Calculate the total peak height for the three isotopes by adding the individual peak heights.	Total peak height = 7.9 + 1.0 + 1.1 = 10.0 cm
Substitute the peak height for each isotope into the formula: % abundance = $\frac{\text{peak height}}{\text{total peak height}} \times 100\ \%$	% abundance ^{24}Mg = $\frac{7.9}{10.0} \times 100 = 79\%$ % abundance ^{25}Mg = $\frac{1.0}{10.0} \times 100 = 10\%$ % abundance ^{26}Mg = $\frac{1.1}{10.0} \times 100 = 11\%$

Worked example: Try yourself 5.1.2

CALCULATING PERCENTAGE ABUNDANCE OF EACH ISOTOPE FROM THE MASS SPECTRUM

Figure 5.1.8 shows a simplified mass spectrum of lead. From this mass spectrum, calculate the percentage abundance of each of its three isotopes.

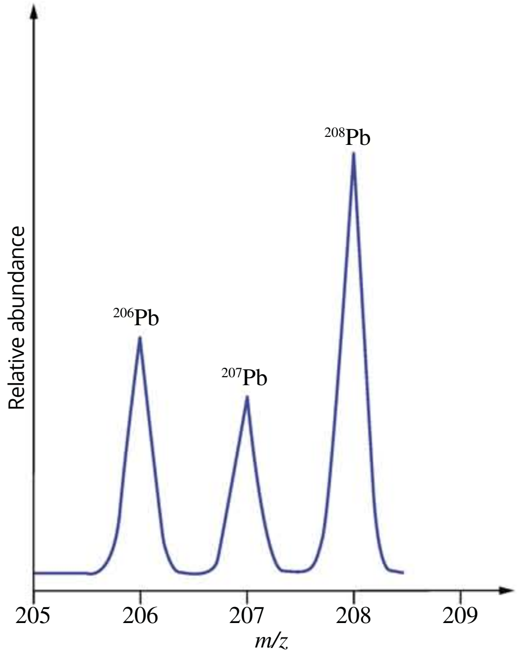


FIGURE 5.1.8 Mass spectrum of lead.

Worked example 5.1.3

CALCULATING PERCENTAGE ABUNDANCES FROM RELATIVE ATOMIC MASS AND THE RELATIVE ISOTOPIC MASSES

The relative atomic mass of rubidium is 85.47. The relative isotopic masses of its two isotopes are 84.95 and 86.94. Calculate the relative abundances of the isotopes in naturally occurring rubidium.

Thinking	Working
State the relative abundances of the isotopes in terms of x, where x is the abundance of the lighter isotope. Abundance of lighter isotope = x. The abundance of heavier isotope must equal $100 - x$.	Abundance of 84.95 isotope = x Abundance of 86.94 isotope = $100 - x$
Substitute the relative isotopic masses, relative abundances and relative atomic mass into the formula: $A_r = \frac{(\text{relative isotopic mass} \times \%\ \text{abundance}) + (\text{relative isotopic mass} \times \%\ \text{abundance})}{100}$	$85.47 = \frac{84.95x + (86.94 \times (100 - x))}{100}$
Expand the top line of the equation.	$85.47 = \frac{84.95x + 8694 - 86.94x}{100}$
Solve the equation to find x, the relative abundance of the lightest isotope.	$8547 = 84.95x + 8694 - 86.94x$ $8547 - 8694 = 84.95x - 86.94x$ $-147 = -1.99x$ $x = 73.87\%$
Determine the abundance of the heavier isotope.	Abundance of 86.94 isotope $= 100 - x$ $= 100 - 73.87$ $= 26.13\%$

Worked example: Try yourself 5.1.3

CALCULATING PERCENTAGE ABUNDANCES FROM RELATIVE ATOMIC MASS AND THE RELATIVE ISOTOPIC MASSES

The relative atomic mass of copper is 63.54. The relative isotopic masses of its two isotopes are 62.95 and 64.95. Calculate the relative abundances of the isotopes in naturally occurring copper.

RELATIVE MOLECULAR MASS

Some elements and compounds exist as **molecules**, for example oxygen (O_2), nitrogen (N_2) and carbon dioxide (CO_2). In Chapter 6, you will learn how non-metallic elements bond together to form covalent molecules. For these substances, a **relative molecular mass** can be determined.

The relative molecular mass is the mass of one molecule of that substance relative to the mass of a ^{12}C atom taken as 12 units exactly.

The relative molecular mass, symbol M_r, is equal to the sum of the relative atomic masses of the atoms in the molecule (remember you can obtain relative atomic masses of elements from the periodic table). It is based (like relative atomic mass) on the scale in which the exact mass of an atom of carbon-12 is taken as 12 exactly.

Worked example 5.1.4

CALCULATING THE RELATIVE MOLECULAR MASS OF MOLECULES

Calculate the relative molecular mass of carbon dioxide (CO_2).

Thinking	Working
Use the periodic table to find the relative atomic mass for the elements represented in the formula.	$A_r(C) = 12.0$ $A_r(O) = 16.0$
Determine the number of atoms of each element present, taking into consideration any brackets in the formula.	1 × C atom 2 × O atoms
Determine the relative molecular mass by adding the appropriate relative atomic masses.	$M_r = 1 \times A_r(C) + 2 \times A_r(O)$ $= 1 \times 12.0 + 2 \times 16.0$ $= 44.0$

Worked example: Try yourself 5.1.4

CALCULATING THE RELATIVE MOLECULAR MASS OF MOLECULES

Calculate the relative molecular mass of nitric acid (HNO_3).

RELATIVE FORMULA MASS

You learned in Chapter 4 that some compounds, such as sodium chloride (NaCl) and magnesium oxide (MgO), do not exist as molecules but rather as ionic lattices. For ionic compounds, the term **relative formula mass** is used. Relative formula mass, like relative molecular mass, is calculated by taking the sum of the relative atomic masses of the elements in the formula.

The relative formula mass is the mass of a formula unit relative to the mass of an atom of ^{12}C taken as 12 units exactly. It is numerically equal to the sum of the relative atomic masses of the elements in the formula.

Worked example: 5.1.5

CALCULATING THE RELATIVE FORMULA MASS OF IONIC COMPOUNDS.

Calculate the relative formula mass of magnesium hydroxide ($Mg(OH)_2$).

Thinking	Working
Use the periodic table to find the relative atomic mass for the elements represented in the formula.	$A_r(Mg) = 24.3$ $A_r(O) = 16.0$ $A_r(H) = 1.0$
Determine the number of atoms of each element present, taking into consideration any brackets in the formula.	1 × Mg atom 1 × 2 = 2 O atoms 1 × 2 = 2 H atoms
Determine the relative formula mass by adding the appropriate relative atomic masses.	Relative formula mass $= 1 \times A_r(Mg) + 2 \times A_r(O) + 2 \times A_r(H)$ $= 24.3 + 2 \times 16.0 + 2 \times 1.0$ $= 58.3$

Relative molecular mass and relative formula mass, like relative atomic mass, have no units, because they are based on the masses of atoms of elements compared with the mass of the carbon-12 isotope.

Worked example: Try yourself 5.1.5

CALCULATING THE RELATIVE FORMULA MASS OF IONIC COMPOUNDS

Calculate the relative formula mass of copper(II) nitrate ($Cu(NO_3)_2$).

5.1 Review

SUMMARY

- Most elements consist of a mixture of isotopes.
- The most common isotope of carbon, carbon-12, is used as the reference standard to compare the masses of atoms.
- The carbon-12 isotope is assigned a mass of exactly 12 units.
- The relative isotopic mass of an isotope is the mass of an atom of the isotope relative to the mass of an atom of carbon-12 taken as 12 units exactly.
- The relative isotopic mass and relative abundance of isotopes can be measured using a mass spectrometer.
- The relative atomic mass, A_r, of an element is a weighted average of its isotopic masses.
- The relative molecular mass of molecules, or formula mass of ionic compounds, is calculated from the sum of the relative atomic masses of its constituent elements.

KEY QUESTIONS

1 The isotopic composition of chlorine is shown in Table 5.1.3 on page 112. Select the correct statement about the relative atomic mass of chlorine.

A The precise relative atomic mass of chlorine can be determined by adding the two relative isotopic masses together and dividing by two.

B The relative atomic mass of chlorine is based on the scale where carbon-12 has a mass of exactly 12.

C The lighter isotope is less abundant.

D The reason the isotopes have different masses is because they have different numbers of protons.

2 Use the data in Table 5.1.2 on page 110 to calculate the relative atomic mass of:

a oxygen

b silver

c hydrogen.

3 The element lithium has two isotopes:

- ^{6}Li with a relative isotopic mass of 6.02
- ^{7}Li with a relative isotopic mass of 7.02.

The relative atomic mass of lithium is 6.94. Calculate the percentage abundance of the lighter isotope.

4 The mass spectrum of zirconium is shown in Figure 5.1.9.

a Measure the peak heights to calculate the percentage abundance of each zirconium isotope.

b Use the percentage abundances calculated in part a to determine the relative atomic mass of zirconium. The mass number is a good approximation to the relative isotopic mass.

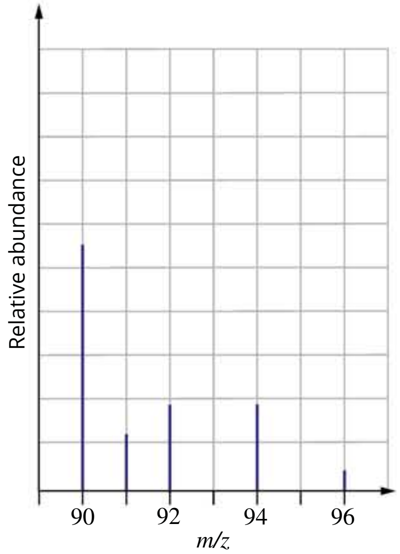


FIGURE 5.1.9 The mass spectrum of zirconium.

5 Calculate the relative molecular masses of:

a sulfuric acid (H_2SO_4)

b ammonia (NH_3)

c ethane (C_2H_6).

6 Calculate the relative formula mass of:

a potassium chloride (KCl)

b sodium carbonate (Na_2CO_3)

c aluminium sulfate ($Al_2(SO_4)_3$).

5.2 Introducing the mole

It is often essential for chemists to be able to measure an exact number of particles of an element or compound. However, the particles in elements and compounds are so small that it would be difficult to count atoms, ions or molecules individually or even by the thousands of millions. If it were possible to count individual particles, the numbers in even very small samples would be huge and very inconvenient to work with.

The ice cubes shown in Figure 5.2.1 each contain more than 10^{23} water molecules (H_2O). As each water molecule is composed of two hydrogen atoms and one oxygen atom, the number of individual atoms in each ice cube is greater than 10^{23}. A quantity that allows chemists to measure accurate amounts of extremely small particles is required.

In this section you will learn about the very convenient quantity used by chemists; the mole.

FIGURE 5.2.1 Each of these ice cubes contains more than 10^{23} water (H_2O) molecules. Molecules and atoms are so small, and the numbers of them in everyday samples are so large, that it would be very inconvenient to always count them individually.

THE CHEMIST'S COUNTING UNIT

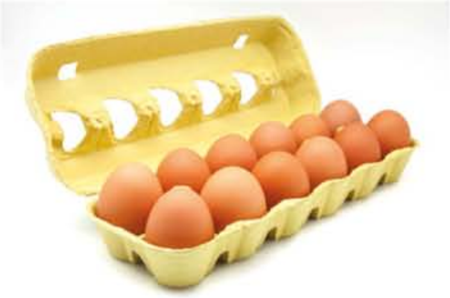


FIGURE 5.2.2 Twelve eggs is one dozen, 24 eggs is two dozen and six eggs is half a dozen.

A dozen is a convenient quantity for buying the eggs shown in Figure 5.2.2. For atoms, ions and molecules that are much smaller than eggs, a quantity that describes a much larger number is needed.

The accepted quantity for chemists is the **mole**. The mole is often referred to as the '**amount** of substance' and is given the symbol *n*, and the unit mol.

So *n*(glucose) = 2 mol is read as 'the amount of glucose molecules is 2 moles'.

Chemists use the mole as a counting measure. Figure 5.2.3 shows some quantities that you would be very familiar with such as pair, dozen and ream. One dozen is equal to 12 and two dozen equals 24, 20 dozen equals 240 and half a dozen equals 6. In the same way, chemists know that one mole is equivalent to a certain number and that 2 moles, 20 moles and half a mole are all multiples of that number.

FIGURE 5.2.3 Convenient quantities that you would be very familiar with. A pair of shoes equals two, a dozen roses equals 12, a ream of paper equals 500 sheets.

Information provided by molecular formulas

When referring to a mole of a substance, it is important to indicate which particle is being specified. In Chapter 6, you will learn that an oxygen molecule contains two oxygen atoms joined by covalent bonding. Figure 5.2.4 shows four different ways that chemists use to represent the oxygen molecule. The oxygen molecule is most commonly described by the **formula** O_2.

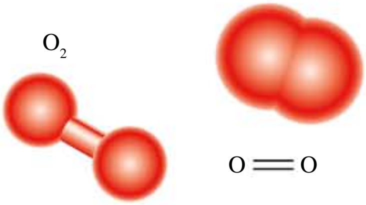


FIGURE 5.2.4 Four different ways chemists represent the oxygen molecule: a formula (O_2), a structural formula (O=O) and two coloured molecular models. Each formula or model shows that one oxygen molecule contains two oxygen atoms.

The expression, 'one mole of oxygen' is ambiguous because it could describe one mole of oxygen atoms (O) or one mole of oxygen molecules (O_2). As there are two atoms in each oxygen molecule, one mole of oxygen molecules will contain two moles of oxygen atoms.

The molecular formula of a substance indicates the number of atoms of each element in one molecule of a substance. For example, in one mole of oxygen gas, there are two moles of oxygen atoms.

Some other examples of the use of the mole as a counting unit are provided in Table 5.2.1.

TABLE 5.2.1 Examples of the use of the mole as a counting unit

Number of moles of element or compound	Information that can be obtained about numbers of particles
1 mole of hydrogen atoms (H)	1 mole of hydrogen atoms (H)
1 mole of hydrogen molecules (H_2)	1 mole of hydrogen molecules (H_2) 2 moles of hydrogen atoms (H)
2 moles of aluminium atoms (Al)	2 moles of aluminium atoms (Al)
2 moles of calcium chloride ($CaCl_2$)	2 moles of Ca^{2+} ions 4 moles of Cl^- ions
10 moles of glucose ($C_6H_{12}O_6$) molecules	10 moles of glucose ($C_6H_{12}O_6$) molecules 60 moles of carbon atoms 120 moles of hydrogen atoms 60 moles of oxygen atoms

AVOGADRO'S NUMBER

One mole of any substance is defined as the same number of particles as there are atoms in exactly 12 grams of carbon-12. This number of atoms has been experimentally determined to be $6.022\,141 \times 10^{23}$ atoms. That's 602 214 100 000 000 000 000 000 atoms!

This number is commonly rounded to 6.02×10^{23} and is referred to as **Avogadro's number** or Avogadro constant. It is given the symbol N_A.

Avogadro's number is written in scientific notation. You can revise your understanding of scientific notation in the Appendix at the end of the book.

ℹ $N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$
Therefore, 1 mol of particles contains 6.02×10^{23} particles.

FIGURE 5.2.5 One mole of sodium chloride and one mole of water contain the same number of particles, 6.02×10^{23}.

Avogadro's number is an enormous number, but the extremely small size of atoms, ions and molecules means that one mole of most elements and compounds does not take up a great deal of mass or volume.

For example, in Figure 5.2.5 you can see that one mole of water, that is 6.02×10^{23} water molecules, has a volume of only 18 mL, whereas, one mole of table salt (NaCl), has a mass of 58.5 grams.

CHEMFILE

Avogadro's number

It is very difficult to imagine just how big Avogadro's number really is, especially when atoms, ions and molecules are so small. Here are some examples to help:

- 6.02×10^{23} grains of sand, placed side by side, would stretch from the Earth to the Sun and back about 7 million times.
- A computer counting 10 billion times every second would take 2 million years to reach 6.02×10^{23}.
- 6.02×10^{23} of the marshmallows shown in Figure 5.2.6 would cover Australia to a depth of 900 km!

FIGURE 5.2.6 One mole or 6.02×10^{23} marshmallows would cover Australia to a depth of 900 km!

If you know that 1 mol of a substance contains 6.02×10^{23} particles, then:

- 2 mol of a substance contains $2 \times (6.02 \times 10^{23}) = 1.204 \times 10^{24}$ particles
- 0.3 mol of a substance contains $0.3 \times (6.02 \times 10^{23}) = 1.81 \times 10^{23}$ particles
- 4.70×10^{23} particles $= \dfrac{4.70 \times 10^{23}}{6.02 \times 10^{23}} = 0.781$ mol
- 7.35×10^{24} particles $= \dfrac{7.35 \times 10^{24}}{6.02 \times 10^{23}} = 12.2$ mol

As you can see from Figure 5.2.7, a mathematical relationship exists between the number of particles, N, and the amount of substance in moles, n. This relationship can be written as:

$$n = \frac{N}{N_A}$$

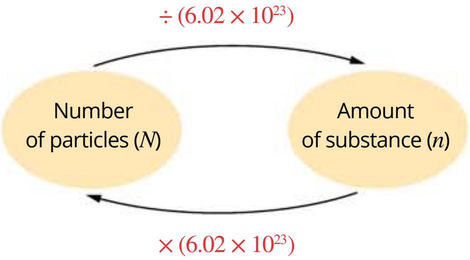


FIGURE 5.2.7 Relationship between number of particles and amount of substance in moles.

Calculations using the mole and Avogadro's number

Three quantities have been introduced so far:

- the mole, which is given the symbol n and the unit mol
- Avogadro's number, which is given the symbol N_A and has the value 6.02×10^{23}
- the actual number of particles (atoms, ions or molecules), which is given the symbol N.

The mathematical relationship that links the three quantities is $n = \dfrac{N}{N_A}$.

Worked example 5.2.1

CALCULATING THE NUMBER OF MOLECULES

Calculate the number of molecules in 3.5 moles of water (H_2O).

Thinking	**Working**
List the data given in the question next to the appropriate symbol. Include units.	The number of water molecules is the unknown, so: $N(H_2O) = ?$ $n(H_2O) = 3.5$ mol $N_A = 6.02 \times 10^{23}$
Rearrange the formula to make the unknown the subject.	$n = \frac{N}{N_A}$ so $N(H_2O) = n \times N_A$
Substitute in data and solve for the answer.	$N(H_2O) = n \times N_A$ $= 3.5 \times 6.02 \times 10^{23}$ $= 2.1 \times 10^{24}$ molecules

Worked example: Try yourself 5.2.1

CALCULATING THE NUMBER OF MOLECULES

Calculate the number of molecules in 1.6 moles of carbon dioxide (CO_2).

Worked example 5.2.2

CALCULATING THE NUMBER OF ATOMS

Calculate the number of oxygen atoms in 2.5 mol of oxygen gas (O_2).

Thinking	**Working**
List the data given in the question next to the appropriate symbol. Include units.	The number of oxygen atoms is the unknown so: $N(O) = ?$ $n(O_2) = 2.5$ mol $N_A = 6.02 \times 10^{23}$
Calculate the amount, in mol, of oxygen atoms from the amount of oxygen molecules and the molecular formula.	$n(O) = n(O_2) \times 2$ $= 2.5 \times 2$ $= 5.0$ mol
Rearrange the formula to make the unknown the subject.	$n = \frac{N}{N_A}$ so $N(O) = n \times N_A$
Substitute in data and solve for the answer.	$N(O) = n \times N_A$ $= 5.0 \times 6.02 \times 10^{23}$ $= 3.0 \times 10^{24}$ atoms

Worked example: Try yourself 5.2.2

CALCULATING THE NUMBER OF ATOMS

Calculate the number of hydrogen atoms in 0.35 mol of methane (CH_4).

Worked example 5.2.3

CALCULATING THE NUMBER OF MOLES OF PARTICLES GIVEN THE NUMBER OF PARTICLES

Calculate the amount, in mol, of ammonia molecules (NH_3) represented by 2.5×10^{22} ammonia molecules.

Thinking	**Working**
List the data given in the question next to the appropriate symbol. Include units.	The number of mol of ammonia molecules is the unknown so: $n(NH_3) = ?$ $N(NH_3) = 2.5 \times 10^{22}$ molecules $N_A = 6.02 \times 10^{23}$
Rearrange the formula to make the unknown the subject.	$n = \frac{N}{N_A}$ *n* is the unknown so rearrangement not required
Substitute in data and solve for the answer.	$n(NH_3) = \frac{N}{N_A}$ $= \frac{2.5 \times 10^{22}}{6.02 \times 10^{23}}$ $= 0.042$ mol

Worked example: Try yourself 5.2.3

CALCULATING THE NUMBER OF MOLES OF PARTICLES GIVEN THE NUMBER OF PARTICLES

Calculate the amount, in mol, of magnesium atoms represented by 8.1×10^{20} magnesium atoms.

Worked example 5.2.4

CALCULATING THE NUMBER OF MOLES OF ATOMS GIVEN THE NUMBER OF MOLES OF MOLECULES

Calculate the amount, in mol, of hydrogen atoms in 3.6 mol of sulfuric acid (H_2SO_4).

Thinking	**Working**
List the data given in the question next to the appropriate symbol. Include units.	The number of mol of hydrogen atoms is the unknown so: $n(H) = ?$ $n(H_2SO_4) = 3.6$ mol
Calculate the amount, in mol, of hydrogen atoms from the amount of sulfuric acid molecules and the molecular formula.	$n(H) = n(H_2SO_4) \times 2$ $= 3.6 \times 2$ $= 7.2$ mol

Worked example: Try yourself 5.2.4

CALCULATING THE NUMBER OF MOLE OF ATOMS GIVEN THE NUMBER OF MOLE OF MOLECULES

Calculate the amount, in mol, of hydrogen atoms in 0.75 mol of water (H_2O).

5.2 Review

SUMMARY

- A mole is a convenient quantity for counting particles. The mole is given the symbol *n* and the unit mol.
- One mole is defined as the amount of substance that contains the same number of 'specified' particles as there are atoms in 12 g of carbon-12.
- The number of particles in 1 mol is given the symbol N_A. This is known as Avogadro's number and has the numerical value of 6.02×10^{23}.
- The formula $n = \frac{N}{N_A}$ can be used or rearranged to calculate the amount or number of specified particles in a sample.

KEY QUESTIONS

1 Calculate the number of:

a atoms in 2.0 mol of sodium atoms (Na)

b molecules in 0.10 mol of nitrogen molecules (N_2)

c atoms in 20.0 mol of carbon atoms (C)

d molecules in 4.2 mol of water molecules (H_2O)

e atoms in 1.0×10^{-2} mol of iron atoms (Fe)

f molecules in 4.62×10^{-5} mol of CO_2 molecules.

2 Calculate the amount of substance, in mol, represented by:

a 3.0×10^{23} molecules of water (H_2O)

b 1.5×10^{23} atoms of neon (Ne)

c 4.2×10^{25} atoms of iron (Fe)

d 4.2×10^{25} molecules of ethanol (C_2H_5OH).

3 Calculate the amount, in mol, of:

a sodium atoms represented by 1.0×10^{20} sodium atoms

b aluminium atoms represented by 1.0×10^{20} aluminium atoms

c chlorine molecules represented by 1.0×10^{20} chlorine molecules.

4 Calculate the amount, in mol, of:

a chlorine atoms in 0.4 mol of chlorine (Cl_2)

b hydrogen atoms in 1.2 mol of methane (CH_4)

c hydrogen atoms in 0.12 mol of ethane (C_2H_6)

d oxygen atoms in 1.5 mol of sodium sulfate (Na_2SO_4).

5.3 Molar mass

Chemical laboratories always contain a simple balance like the one in Figure 5.3.1, which is used for weighing. If a chemist knows that a specific mass of a substance always contains a specific number of particles, it is possible to easily weigh a sample of the substance and calculate the exact number of particles present in the sample.

In this section you will learn about how the amount of a substance, measured in moles, is related to the mass of the substance.

FIGURE 5.3.1 A digital balance is a simple piece of laboratory equipment used for weighing.

MOLAR MASS

Chemists have cleverly defined the mole so that you can determine the number of moles of a substance by simply measuring its mass.

The particles of different elements and compounds have different masses. Therefore, the masses of one mole of different elements or compounds will also be different. This is like saying that the mass of one dozen oranges will be greater than the mass of one dozen mandarins because one orange is heavier than one mandarin. The mass, in grams, of one mole of a particular element or compound is known as its **molar mass**. It is given the symbol M and the unit g mol^{-1}.

Remember that a mole is defined as the amount of substance that contains the same number of specified particles as there are atoms in 12 g of carbon-12. This is a very convenient definition because:

- 1 atom of ^{12}C has a relative atomic mass of 12 exactly
- 1 mole of atoms of ^{12}C has a mass of 12 g exactly.

Naturally occurring carbon is mainly composed of the ^{12}C isotope, so the molar mass of carbon is 12.01 g mol^{-1}.

Consider an atom of ^{12}C and an atom of ^{24}Mg. ^{12}C has been assigned a relative isotopic mass of 12 exactly. On that scale, the relative isotopic mass of ^{24}Mg is approximately 24. Since one mole of ^{12}C atoms weighs exactly 12 g, then one mole of ^{24}Mg must weigh approximately twice as much, 24 g.

In general, the molar mass of an element is the mass of one mole of the element.

The molar mass of a compound is the mass of one mole of the compound. It is equal to the relative molecular or relative formula mass of the compound expressed in grams.

The molar mass is given the symbol, M, and the unit g mol^{-1}.

Table 5.3.1 shows you how to calculate the molar masses of some common substances.

TABLE 5.3.1 Calculating the molar mass of a substance by adding the relative atomic masses for each atom present in the substance based on the molecular or ionic formula

Substance	Relative atomic masses	Molar mass of substance
Na	Na: 23.0	$= 23.0\ \text{g mol}^{-1}$
O_2	O: 16.0	$= 2 \times 16.0$ $= 32.0\ \text{g mol}^{-1}$
H_2O	H: 1.0 O: 16.0	$= (2 \times 1.0) + 16.0$ $= 18.0\ \text{g mol}^{-1}$
CO_2	C: 12.0 O: 16.0	$= 12.0 + (2 \times 16.0)$ $= 44.0\ \text{g mol}^{-1}$
$NaNO_3$	Na: 23.0 N: 14.0 O: 16.0	$= 23.0 + 14.0 + (3 \times 16.0)$ $= 85.0\ \text{g mol}^{-1}$

From the calculations in Table 5.3.1 and the photograph of one mole of some common substances in Figure 5.3.2, you can see that one mole of each substance has a different mass.

FIGURE 5.3.2 One mole of each substance has a different mass.

Counting by weighing

A useful relationship links the amount of a substance (n), in mol, its molar mass (M), in g mol^{-1}, and the given mass of the substance (m), in grams (Figure 5.3.3).

Mass of a given amount of substance (g) = amount of substance (mol) × molar mass (g mol^{-1}).

This can be written as $m = n \times M$ and rearranged to:

Mass in g

Amount in mol $\longrightarrow n = \frac{m}{M}$

Molar mass in g mol^{-1}

FIGURE 5.3.3 The relationship between the amount of substance, n, its molar mass, M, and the given mass of a substance, m.

Worked example 5.3.1

CALCULATING THE MASS OF A SUBSTANCE

Calculate the mass of 0.35 mol of magnesium nitrate ($Mg(NO_3)_2$).

Thinking	Working
List the data given to you in the question. Remember that whenever you are given a formula, you can calculate the molar mass.	$m(Mg(NO_3)_2) = ?$ g $n(Mg(NO_3)_2) = 0.35$ mol $M(Mg(NO_3)_2) = 24.3 + (2 \times 14.0) + (6 \times 16.0)$ $= 148.3$ g mol^{-1}
Calculate the mass of magnesium nitrate using: $n = \frac{m}{M}$	$n = \frac{m}{M}$ so $m = n \times M$ $m(Mg(NO_3)_2) = 0.35 \times 148.3$ $= 52$ g

Worked example: Try yourself 5.3.1

CALCULATING THE MASS OF A SUBSTANCE

Calculate the mass of 4.68 mol of sodium carbonate (Na_2CO_3).

CHEMISTRY IN ACTION

The sting of a bee

The formula for pentyl ethanoate, $C_7H_{14}O_2$, is represented by the structure shown in Figure 5.3.4.

Pentyl ethanoate ($C_7H_{14}O_2$) is the compound that gives bananas their characteristic odour. It is also a pheromone released by bees when they sting. A pheromone is a chemical produced by an animal or insect that changes the behaviour of another animal or insect of the same species. Bees release pentyl ethanoate as an alarm pheromone to alert other bees to danger. The compound is released near the sting shaft and attracts other bees to the area, where the group behaves defensively, charging and stinging. Smoke masks the alarm pheromone, interrupting the defensive response and calming the bees, allowing beekeepers an opportunity to work with the beehive.

Each time a bee stings, one-thousandth of a milligram (1.0×10^{-6} g) of pentyl ethanoate is released. Knowing the mass of pentyl ethanoate released in a bee sting enables chemists to calculate the number of pentyl ethanoate molecules in each sting using the relationship between mass and mole.

As the molar mass of pentyl ethanoate ($C_7H_{14}O_2$) is equal to 130.0 g mol^{-1}, using the formula $n = \frac{m}{M}$, 1.0×10^{-6} g of pentyl ethanoate is equal to 7.7×10^{-9} mol.

FIGURE 5.3.4 Pentyl ethanoate is a compound released when bees sting.

From section 5.2, you know that the number of particles can be calculated using the formula $N = n \times N_A$. The number of pentyl ethanoate molecules in each bee sting is therefore equal to 4.6×10^{15}.

You are now in a position to count atoms by weighing. When you use the mole, you are effectively counting the number of particles in a substance. The number of particles present in a substance is equal to the number of moles of the substance multiplied by 6.02×10^{23}.

Some calculations require you to use both of the formulas $n = \frac{m}{M}$ and $n = \frac{N}{N_A}$. Worked Example 5.3.2 is such a calculation.

Worked example 5.3.2

CALCULATING THE NUMBER OF MOLECULES

Calculate the number of CO_2 molecules present in 22 g of carbon dioxide.

Thinking	**Working**
List the data given to you in the question. Convert mass to grams if required. Remember that whenever you are given a formula you can calculate the molar mass.	$N(CO_2) = ?$ $M(CO_2) = 12.0 + (2 \times 16.0) = 44.0 \text{ g mol}^{-1}$ $m(CO_2) = 22 \text{ g}$
Calculate the amount, in mol, of CO_2 using: $n = \frac{m}{M}$	$n(CO_2) = \frac{m}{M}$ $= \frac{22}{44.0}$ $= 0.50 \text{ mol}$
Calculate the number of CO_2 molecules using: $n = \frac{N}{N_A}$	$n = \frac{N}{N_A}$ so $N = n \times N_A$ $N(CO_2) = 0.50 \times 6.02 \times 10^{23}$ $= 3.0 \times 10^{23}$ molecules

Worked example: Try yourself 5.3.2

CALCULATING THE NUMBER OF MOLECULES

Calculate the number of sucrose molecules in a teaspoon (4.2 g) of sucrose ($C_{12}H_{22}O_{11}$).

5.3 Review

SUMMARY

- The molar mass of an element or compound is the mass, in grams, of one mole of that element or compound. Molar mass is given the symbol *M* and the unit g mol^{-1}.
- The molar mass of an element or compound has the same numerical value as the relative mass of the element or compound.
- The formula $n = \frac{m}{M}$ can be used or rearranged to calculate the mass, amount or molar mass of an element or compound.

KEY QUESTIONS

1 Calculate the molar mass of:
  a nitrogen (N_2)
  b ammonia (NH_3)
  c sulfuric acid (H_2SO_4)
  d iron(III) nitrate ($Fe(NO_3)_3$)
  e ethanoic acid (CH_3COOH)
  f sulfur atoms (S)
  g vitamin C (ascorbic acid, $C_6H_8O_6$)
  h hydrated copper(II) sulfate ($CuSO_4.5H_2O$).

2 Calculate the mass of:
  a 1.0 mol of sodium atoms (Na)
  b 2.0 mol of oxygen molecules (O_2)
  c 0.10 mol of methane molecules (CH_4)
  d 0.25 mol of aluminium oxide (Al_2O_3).

3 Calculate the amount, in mol, of:
  a H_2 molecules in 5 g of hydrogen (H_2)
  b H atoms in 5 g of hydrogen (H_2)
  c Al atoms in 2.7 g of aluminium (Al)
  d CH_4 molecules in 0.4 g of methane (CH_4)
  e O_2 molecules in 0.10 g of oxygen (O_2)
  f O atoms in 0.10 g of oxygen (O_2)
  g P_4 molecules in 1.2×10^{-3} g of phosphorus (P_4)
  h P atoms in 1.2×10^{-3} g of phosphorus (P_4).

4 Calculate the number of atoms in:
  a 23 g of sodium (Na)
  b 4.0 g of argon (Ar)
  c 0.243 g of magnesium (Mg)
  d 10.0 g of gold (Au).

5 Calculate the:
  a number of molecules in:
    i 16 g of oxygen (O_2)
    ii 2.8 g of nitrogen (N_2)
  b number of oxygen atoms in 3.2 g of sulfur dioxide (SO_2)
  c total number of atoms in 288 g of ammonia (NH_3).

5.4 Percentage composition and empirical formulas

Compounds are substances that contain two or more different elements. The relative proportions of each element in a compound can be expressed as a:

- percentage in terms of the mass contributed by each element
- formula, showing either the ratio of atoms contributed by each element in a compound or the actual numbers of atoms in a molecule.

The formulas of compounds are an important part of the language of chemistry. You would be familiar with some of the formulas shown in Figure 5.4.1. Formulas are used to represent chemicals in equations and on numerous other occasions.

In this section you will learn how to calculate percentage composition and a type of formula called an **empirical formula**.

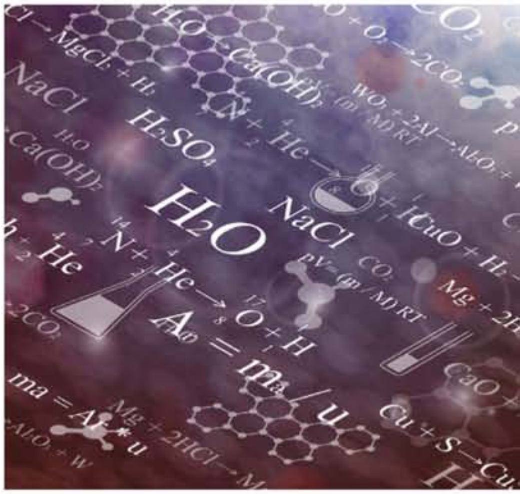


FIGURE 5.4.1 Chemical formulas are part of the language of chemistry.

PERCENTAGE COMPOSITION

The **percentage composition** of a given compound tells you the proportion by mass of the different elements in that compound. The proportion of each element is expressed as a percentage of the total mass of the compound (Figure 5.4.2).

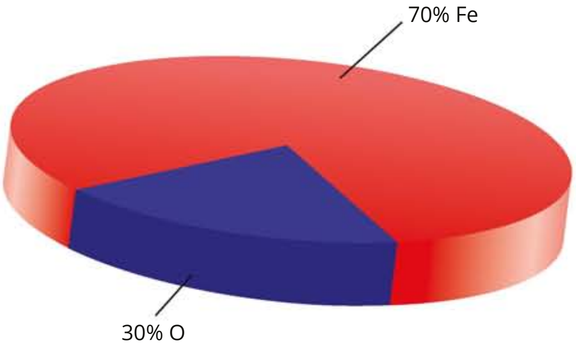


FIGURE 5.4.2 The pie chart shows the percentage composition, by mass, of iron(III) oxide (Fe_2O_3).

Being able to determine percentages by mass is important in chemistry. For example, the iron ore mined in Western Australia is iron(III) oxide, and has the formula Fe_2O_3. A company that is producing iron from this iron ore will want to know the mass of iron that can be extracted from a given quantity of iron ore. The pie chart in Figure 5.4.2 shows that the percentage of iron in iron(III) oxide is 70%. This means that the company can extract a maximum of 70 g iron per 100 g of iron ore.

If the chemical formula of a compound is known, the percentage composition can be determined using the molar masses of the elements and compound. In general, we can write:

$$\text{\% by mass of an element in a compound} = \frac{\text{mass of the element in 1 mol of the compound}}{\text{molar mass of the compound}} \times 100$$

CHEMFILE

Elemental analysis of magnetite

If the chemical formula of a compound is unknown, the percentage composition by mass may be found using elemental analysis in a laboratory. An example is the analysis of the mineral magnetite, one of the three most commonly occurring oxides of iron. The most magnetic of all naturally occurring minerals on Earth, magnetite was used by the Chinese to make the first magnetic compass.

Found in many different types of igneous and metamorphic rocks, large deposits are located in the Pilbara region of Western Australia. Elemental analysis allowed chemists to determine the percentage composition of magnetite as 72.4% iron and 27.6% oxygen (Figure 5.4.3). The percentage composition can then be used to determine the chemical formula, which is Fe_3O_4. This type of calculation is described on page 129.

FIGURE 5.4.3 Elemental analysis of the mineral magnetite has allowed chemists to determine the percentage composition to be 72.4 % iron and 27.6% oxygen.

Worked example 5.4.1

CALCULATING PERCENTAGE COMPOSITION

Calculate the percentage by mass of aluminium in alumina (Al_2O_3).

Thinking	Working
Find the molar mass of the compound.	$M(Al_2O_3) = (2 \times 27.0) + (3 \times 16.0)$ $= 102.0 \text{ g mol}^{-1}$
Find the total mass of the element in one mole of the compound.	mass of Al in 1 mol $= 2 \times M(Al)$ $= 2 \times 27.0$ $= 54.0$ g
Find the percentage by mass of the element in the compound.	% by mass of Al in Al_2O_3 $= \dfrac{\text{mass of Al in 1 mol of } Al_2O_3}{\text{molar mass of } Al_2O_3} \times 100$ $= \dfrac{54.0}{102.0} \times 100$ $= 52.9\%$

Worked example: Try yourself 5.4.1

CALCULATING PERCENTAGE COMPOSITION

Calculate the percentage by mass of nitrogen in ammonium nitrate (NH_4NO_3).

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. See Table 5.4.1 for some examples.

TABLE 5.4.1 Empirical formulas of some common compounds

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 formula

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 5.4.4 are followed to convert these masses to a mole ratio, that is, a ratio by number of atoms, and then to an empirical formula.

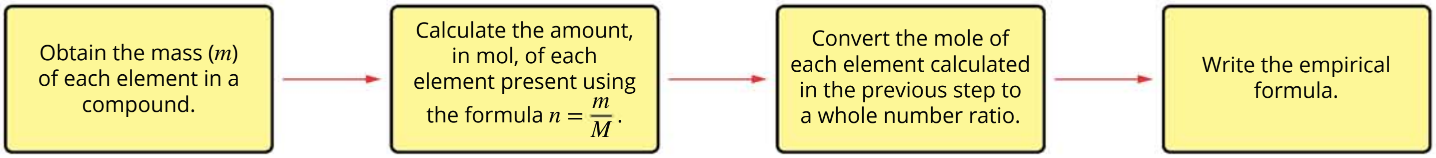


FIGURE 5.4.4 Follow these steps to calculate an empirical formula.

Worked example 5.4.2

DETERMINING THE EMPIRICAL FORMULA

A compound of carbon and oxygen contains 27.3% carbon and 72.7% oxygen by mass. Calculate the empirical formula of the compound.

Thinking	Working
Write down the mass, in g, of all elements present in the compound. If masses are given as percentages, assume that the sample weighs 100 g, then the percentages become masses in grams.	$m(\text{C}) = 27.3$ g $m(\text{O}) = 72.7$ g
Calculate the amount, in mol, of each element in the compound using: $n = \frac{m}{M}$	$n(\text{C}) = \frac{27.3}{12.0}$ $n(\text{O}) = \frac{72.7}{16.0}$ $= 2.28$ mol $= 4.54$ mol
Simplify the ratio by dividing each number of moles by the smallest number of moles calculated in the previous step. This gives you a ratio of the number of atoms of each element.	$\frac{2.28}{2.28}$ $\frac{4.54}{2.28}$ $= 1$ $= 2$
Find the simplest whole number ratio.	1:2
Write the empirical formula.	CO_2

Worked example: Try yourself 5.4.2

DETERMINING THE EMPIRICAL FORMULA

0.50 g of magnesium is heated and allowed to completely react with chlorine. 1.96 g of white powder is formed. Determine the empirical formula of the compound.

MOLECULAR FORMULA

Molecular compounds have a **molecular formula** in addition to an empirical formula. The molecular formula gives the actual number of atoms of each element present in a molecule, rather than the simplest whole number ratio.

The molecular formula can be the same as or different from the empirical formula.

The empirical and molecular formulas of some common molecular compounds are shown in Table 5.4.2.

TABLE 5.4.2 Empirical and molecular formulas of some common molecular compounds

Molecule	Molecular formula	Empirical formula
Water	H_2O	H_2O
Ethane	C_2H_6	CH_3
Carbon dioxide	CO_2	CO_2
Glucose	$C_6H_{12}O_2$	CH_2O

Ionic compounds do not have molecular formulas because they do not exist as molecules. However, they do have empirical formulas that describe the fixed ratio of ions that exist in their lattices. The formula for calcium chloride ($CaCl_2$) is an example of an empirical formula of an ionic compound.

Determining molecular formula

A molecular formula can be determined from the empirical formula of a compound if the molar mass of the compound is also known.

The molecular formula of a molecule is always a whole number multiple of the empirical formula. The number of the multiple is determined by the following formula.

$$\text{Number of empirical formula units in a molecule} = \frac{\text{molar mass of the compound}}{\text{molar mass of one empirical formula unit}}$$

The general steps in the determination of a molecular formula are shown in Figure 5.4.5.

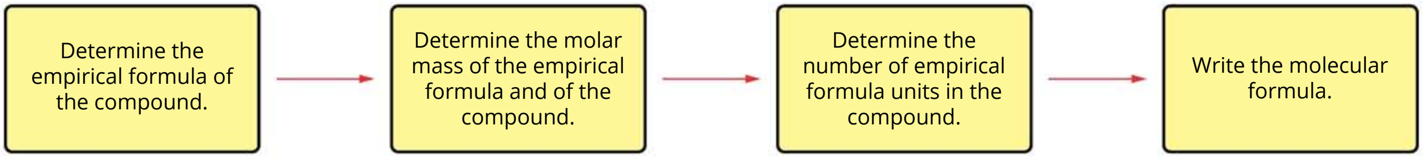


FIGURE 5.4.5 Steps for calculating a molecular formula.

Worked example 5.4.3

DETERMINING MOLECULAR FORMULA

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?

Thinking	Working
Calculate the molar mass of one unit of the empirical formula.	Molar mass of a CH unit = 12.0 + 1.0 = 13.0 g mol^{-1}
Determine the number of empirical formula units in the molecular formula.	Number of CH units = $\frac{78}{13.0}$ = 6
Determine the molecular formula of the compound.	Molecular formula = 6 × CH = C_6H_6

Worked example: Try yourself 5.4.3

DETERMINING MOLECULAR FORMULA

A compound has the empirical formula C_2H_5. The molar mass of this compound was determined to be 58 g mol^{-1}. What is the molecular formula of the compound?

CHEMFILE

Caffeine

Many of the chemicals you use in daily life are large molecules with molecular formulas that are different from their empirical formulas. Caffeine is a molecule found in tea, coffee, cola drinks and chocolate. The structure of the caffeine molecule is shown in Figure 5.4.6. Caffeine is found naturally in the leaves and seeds of many plant species, of which coffee beans, cocoa beans and tea leaves are the most well known. The molecular formula for caffeine is $C_8H_{10}N_4O_2$ and its empirical formula is $C_4H_5N_2O$.

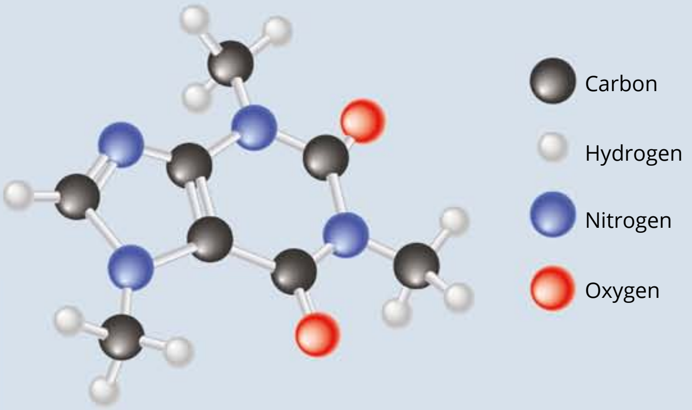


FIGURE 5.4.6 The seed of the coffee cherry is one source of the chemical caffeine. The molecular formula for caffeine is $C_8H_{10}N_4O_2$and its empirical formula is $C_4H_5N_2O$.

5.4 Review

SUMMARY

- The percentage, by mass, of an element in a compound can be calculated from the mass of the element in 1 mol of the compound and the molar mass of the compound.
- The empirical formula of a compound gives the simplest whole number ratio of atoms or ions in the compound.
- Ionic compounds only have an empirical formula.
- Molecular compounds have a molecular formula that gives the actual number of atoms of each element in the molecule. It may be the same as, or different from, the empirical formula.

KEY QUESTIONS

1 Calculate the percentage by mass of:
  a iron in iron(III) oxide (Fe_2O_3)
  b uranium in uranium oxide (U_3O_8)
  c nitrogen in ammonium chloride (NH_4Cl)
  d oxygen in copper(II) nitrate ($Cu(NO_3)_2$).

2 Determine the empirical formulas of the compounds with the following compositions:
  a 2.74% hydrogen, 97.26% chlorine
  b 42.9% carbon, 57.1% oxygen
  c 10.0 g of a compound of magnesium and oxygen that contains 6.03 g of magnesium
  d 3.2 g of a hydrocarbon that contains 2.4 g of carbon.

3 Determine the molecular formula of the following compounds.

	Empirical formula	**Relative molecular mass**
a	CH	78
b	HO	34
c	CH_2O	90
d	NO_2	46
e	CH_2	154

4 A hydrocarbon contains 85.7% carbon. Its relative molecular mass is 70. Determine the hydrocarbon's:
  a empirical formula
  b molecular formula.

5 A sample of the carbohydrate glucose contains 1.8 g carbon, 0.3 g hydrogen and 2.4 g oxygen.
  a Calculate the empirical formula of the compound.
  b Deduce its molecular formula given that its relative molecular mass is 180.

Chapter review

05

KEY TERMS

amount
Avogadro's number
carbon-12
empirical formula
formula
ionise
isotope
mass spectrometer
mass spectrum
molar mass
mole
molecular formula
molecule
percentage composition
relative atomic mass
relative formula mass
relative isotopic abundance
relative isotopic mass
relative molecular mass

Masses of particles

1 The standard on which all relative masses are based is the ^{12}C isotope, which is given a mass of 12 exactly. Explain why in the table of relative atomic masses in the Appendix at the end of the book, the relative atomic mass of carbon is listed as 12.011.

2 When a sample of palladium is placed in a mass spectrometer, the following peaks are recorded as the relative isotopic masses and corresponding percentage abundances given in Table 5.5.1.

TABLE 5.5.1

Relative isotopic mass	Abundance (%)
101.9049	0.9600
103.9036	10.97
104.9046	22.23
105.9032	27.33
107.9039	26.71
109.9044	11.80

Calculate the relative atomic mass of palladium.

3 Table 5.5.2 gives isotopic composition data for argon and potassium.

TABLE 5.5.2

Element	Atomic number	Relative isotopic mass	Relative abundance (%)
Argon	18	35.978	0.307
		37.974	0.060
		39.974	99.633
Potassium	19	38.975	93.3
		39.976	0.011
		40.974	6.69

a Determine the relative atomic masses of argon and potassium.

b Explain why the relative atomic mass of argon is greater than that of potassium, even though potassium has a larger atomic number.

4 The mass spectrum of chromium is shown in Figure 5.5.1.

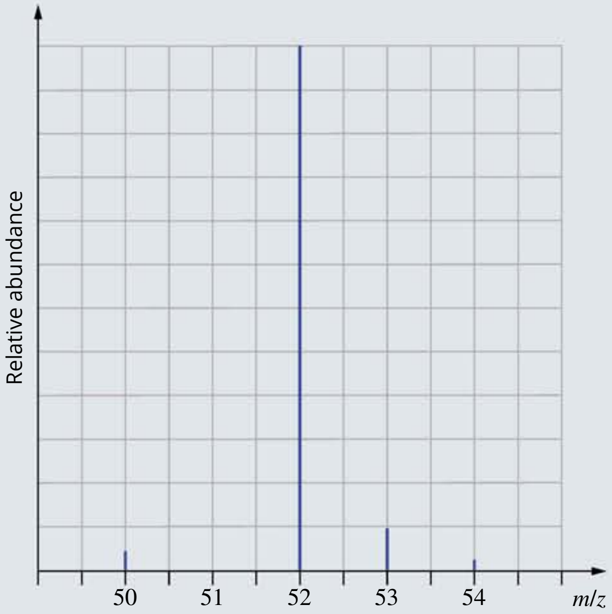


FIGURE 5.5.1 Mass spectrum of chromium.

a Measure the peak heights to calculate the percentage abundance of each chromium isotope.

b Use the percentage abundances calculated in part **a** to determine the relative atomic mass for chromium. The mass number is a good approximation to the relative isotopic mass.

5 The relative atomic mass of europium is 151.96. The relative isotopic masses of its two isotopes are 150.92 and 152.92. Calculate the relative abundances of the isotopes in naturally occurring europium.

6 Determine the percentage abundance of the lighter isotope of each of the following elements.

a Gallium: relative isotopic masses 68.95 and 70.95 respectively; A_r = 69.72

b Boron: relative isotopic masses 10.02 and 11.01 respectively; A_r = 10.81

7 Determine the relative molecular mass (M_r) of:

a water (H_2O)

b white phosphorus (P_4)

c carbon monoxide (CO).

8 Determine the relative formula mass of:

a zinc bromide ($ZnBr_2$)
b barium hydroxide ($Ba(OH)_2$)
c iron(III) carbonate ($Fe_2(CO_3)_3$).

Introducing the mole

9 For each of the following numbers of molecules, calculate the amount of substance, in mol.

a 4.50×10^{23} molecules of water (H_2O)
b 9.00×10^{24} molecules of methane (CH_4)
c 2.3×10^{28} molecules of chlorine (Cl_2)
d 1 molecule of sucrose ($C_{12}H_{22}O_{11}$)

10 For each of the following amounts of molecular substances calculate the:

i number of molecules
ii total number of atoms.

a 1.45 mol of ammonia (NH_3)
b 0.576 mol of hydrogen sulfide (H_2S)
c 0.0153 mol of hydrogen nitrate (HNO_3)
d 2.5 mol of sucrose ($C_{12}H_{22}O_{11}$)

Molar mass

11 How would the molar mass (M) of a compound differ from its relative molecular mass (M_r)?

12 What is the molar mass (M) of each of the following?

a Iron (Fe)
b Sulfuric acid (H_2SO_4)
c Sodium oxide (Na_2O)
d Zinc nitrate ($Zn(NO_3)_2$)
e Glycine (H_2NCH_2COOH)
f Aluminium sulfate ($Al_2(SO_4)_3$)
g Hydrated iron(III) chloride ($FeCl_3.6H_2O$)

13 What is the mass of each of the following?

a 0.060 mol of ethane (C_2H_6)
b 0.32 mol of glucose ($C_6H_{12}O_6$)
c 6.8×10^{-3} mol of urea ($(NH_2)_2CO$)
d 6.12 mol of copper atoms (Cu)

14 What is the amount, in mol, of each of the following?

a Carbon atoms in 1.201 g carbon
b Sulfur molecules (S_8) in 10.0 g sulfur
c Methane molecules (CH_4) in 20.0 g methane
d Aspirin molecules ($C_6H_4(OCOCH_3)COOH$) in 300 mg aspirin
e Aluminium oxide (Al_2O_3) in 3.5 tonnes of aluminium oxide (1 tonne = 1000 kg)

15 **a** If 6.0×10^{23} atoms of calcium have a mass of 40.1 g, what is the mass of one calcium atom?
b If 1 mol of water molecules has a mass of 18 g, what is the mass of one water molecule?
c What is the mass of one molecule of carbon dioxide?

16 For each of the following molecular substances calculate the:

i amount of substance in moles
ii number of molecules
iii total number of atoms.

a 4.2 g of phosphorus (P_4)
b 75.0 g of sulfur (S_8)
c 0.32 g of hydrogen chloride (HCl)
d 2.2×10^{-2} g of glucose ($C_6H_{12}O_6$)

17 What mass of iron (Fe) would contain as many iron atoms as there are molecules in 20.0 g water (H_2O)?

18 For each of the following ionic substances calculate the amount of:

i substance, in moles
ii each ion, in moles.

a 5.85 g of NaCl
b 45.0 g of $CaCl_2$
c 1.68 g of $Fe_2(SO_4)_3$

19 **a** If 0.50 mol of a substance has a mass of 72 g, what is the mass of 1.0 mol of the substance?
b If 6.0×10^{22} molecules of a substance have a mass of 10 g, what is the molar mass of the substance?

20 Calculate the molar mass of a substance if:

a 2.0 mol of the substance has a mass of 80 g
b 0.1 mol of the substance has a mass of 9.8 g
c 1.7 mol of the substance has a mass of 74.8 g
d 3.5 mol of the substance has a mass of 371 g.

21 Which of the following metal samples has the greatest mass?

A 100 g copper
B 4.0 mol of iron atoms
C 1.2×10^{24} atoms of silver

22 A new antibiotic has been isolated and only 2.0 mg is available. The molar mass is found to be 12.5 kg mol^{-1}.

a Express the molar mass in g mol^{-1}.
b Calculate the amount of antibiotic, in mol.
c How many molecules of antibiotic have been isolated?

Percentage composition and empirical formulas

23 Calculate the percentage by mass of each element in:

a Al_2O_3
b $Cu(OH)_2$
c $MgCl_2.6H_2O$
d $Fe_2(SO_4)_3$
e perchloric acid ($HClO_4$).

24 Determine the percentage by mass of carbon in:

a naphthalene ($C_{10}H_8$)
b ethanoic acid (CH_3COOH)
c urea (NH_2CONH_2)
d aspirin ($C_6H_4(OCOCH_3)COOH$).

25 Determine the empirical formulas of the compounds with the following compositions.

- **a** 42.9% carbon, 57.1% oxygen
- **b** 27.2% carbon, 72.8% oxygen
- **c** 54.5% carbon, 9.1% hydrogen, 36.4% oxygen
- **d** 1.72 g iron, 1.48 g sulfur, 3.02 g oxygen
- **e** 9.6 g carbon, 0.67 g hydrogen, 4.7 g chlorine
- **f** 4.42 g carbon, 0.842 g hydrogen

26 A compound used as a solvent for dyes has the following composition by mass: 32.0% carbon, 6.7% hydrogen, 18.7% nitrogen and 42.6% oxygen. Find the empirical formula of the compound.

27 A compound of tungsten and sulfur is a useful solid lubricant. Deduce the empirical formula of this compound if a particular sample is formed when 1.84 g of tungsten reacts exactly with 0.64 g of sulfur.

28 A clear liquid extracted from fermented lemons was found to consist of carbon, hydrogen and oxygen. Analysis showed it to be 52.2% carbon and 34.8% oxygen.

- **a** Find the empirical formula of the substance.
- **b** If 2.17 mol of the compound has a mass of 100 g, find the molecular formula of the compound.

29 When 0.200 g of white phosphorus is burnt in oxygen, 0.456 g of an oxide of phosphorus is formed. Deduce the empirical formula of this oxide.

30 A hydrocarbon is a compound that contains carbon and hydrogen only. Determine the empirical formula of a hydrocarbon that is used as a specialty fuel and contains 90.0% carbon.

31 Find the relative atomic mass of nickel if 3.370 g nickel was obtained by reduction of 4.286 g of the oxide (NiO).

32 4.150 g tungsten was burned in chlorine and 8.950 g tungsten chloride (WCl_6) was formed. Find the relative atomic mass of tungsten.

33 3.72 g of element X exactly reacts with 4.80 g of oxygen to form a compound whose molecular formula is shown, from other experiments, to be X_4O_{10}. What is the relative atomic mass of X?

34 Determine the molecular formulas of compounds with the following compositions and relative molecular masses.

- **a** 82.75% carbon, 17.25% hydrogen; $M_r = 58$
- **b** 43.66% phosphorus, 56.34% oxygen; $M_r = 284$
- **c** 40.0% carbon, 6.7% hydrogen, 53.3% oxygen; $M_r = 180$
- **d** 0.164 g hydrogen, 5.25 g sulfur, 9.18 g oxygen; $M_r = 178$

Connecting the main ideas

35 Using suitable examples, clearly distinguish between:

- **a** relative isotopic mass
- **b** relative atomic mass
- **c** relative molecular mass
- **d** relative formula mass
- **e** molar mass.

36 Caffeine contains 49.48% carbon, 5.15% hydrogen, 28.87% nitrogen and the rest oxygen.

- **a** Determine the empirical formula of caffeine.
- **b** If 0.20 mol of caffeine has a mass of 38.8 g, what is the molar mass of a caffeine molecule?
- **c** Determine the molecular formula of caffeine.
- **d** How many moles of caffeine molecules are in 1.00 g caffeine?
- **e** How many molecules of caffeine are in 1.00 g caffeine?
- **f** How many atoms altogether are in 1.00 g caffeine?

37 The empirical formula of a metal oxide can be found by experimentation as shown in Figure 5.5.2. The mass of the metal and the mass of the oxygen that reacts with it must be determined. Steps A–F form the experimental method.

- **A** Ignite a burner and heat the metal.
- **B** Allow the crucible to cool, then weigh it.
- **C** Continue the reaction until no further change occurs.
- **D** Clean a piece of metal with emery paper to remove any oxide layer.
- **E** Place the metal in a clean, weighed crucible and cover with a lid.
- **F** Weigh the metal and record its mass.

- **a** Place the steps in the correct order by letter.
- **b** Wan and Eric collected the following data:

Mass of the metal = 0.542 g
Mass of the empty crucible = 20.310 g
Mass of the crucible and metal oxide = 21.068 g

They found from this data that the metal oxide had a 1 : 1 formula, i.e. MO, where M = metal. Copy and complete table 5.5.3, using the data given.

TABLE 5.5.3

	Metal	Oxygen
Mass (g)		
Relative atomic mass		16.0
Moles		
Ratio		

- **c** What metal was used in the experiment?

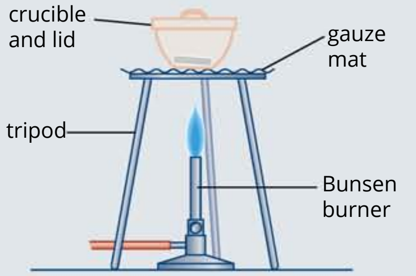


FIGURE 5.5.2 Equipment for finding the empirical formula of a metal oxide.

UNIT 1 • Area of Study 1

REVIEW QUESTIONS

How can knowledge of elements explain the properties of matter?

Multiple-choice questions

1 Consider the following electrostatic forces.

I Attraction between oppositely charged particles
II Repulsion between positively charged particles
III Repulsion between negatively charged particles

The electrostatic forces operating in an atom are:

A I only
B I and II only
C I and III only
D I, II and III.

2 Zinc is an element. Therefore:

A zinc has no isotopes
B all zinc atoms are identical
C zinc atoms always contain the same number of protons
D zinc atoms contain equal numbers of protons and neutrons.

3 Copper has two isotopes, ^{63}Cu and ^{65}Cu. It has a relative atomic mass of 63.55. So, any one particular copper atom would:

A contain either 63 or 65 protons
B contain either 34 or 36 neutrons
C have a mass number of 63.55
D have an atomic number of 29 or 31.

4 Which pair of elements are chemically most similar to each other?

A Li and Be
B Cl and Ar
C N and P
D Ne and Na

5 An ion that contains 11 protons, 12 neutrons and 10 electrons will have a mass number and charge corresponding to:

	Mass number	Charge
A	11	–1
B	11	+1
C	23	–1
D	23	+1

6 Main group elements are placed into groups on the periodic table according to each element's:

A mass number
B atomic number
C number of occupied electron shells
D number of electrons in the outer shell.

7 The electronic configuration of an atom of chromium, Cr, in its ground state is:

A $1s^2\,2s^22p^63s^23p^63d^6$
B $1s^22s^22p^63s^23p^64s^24p^4$
C $1s^22s^22p^63s^23p^63d^44s^2$
D $1s^22s^22p^63s^23p^63d^54s^1$

8 The ground state electronic configuration for an ion of sulfur, S^{2-} is:

A $1s^22s^22p^63s^23p^4$
B $1s^22s^22p^63s^23p^5$
C $1s^22s^22p^63s^23p^6$
D $1s^22s^22p^63s^23p^44s^2$

9 The 3d subshell has:

A 3 orbitals and can hold up to 3 electrons
B 3 orbitals and can hold up to 6 electrons
C 5 orbitals and can hold up to 10 electrons
D 5 orbitals and can hold up to 15 electrons.

The following information relates to questions 10 and 11.

The atomic number, mass number and electron configuration of four particles, W, X, Y and Z, are given below:

	Atomic number	Mass number	Electron configuration
W	17	37	$1s^22s^22p^63s^23p^6$
X	19	39	$1s^22s^22p^63s^23p^6$
Y	20	40	$1s^22s^22p^63s^23p^64s^2$
Z	19	40	$1s^22s^22p^63s^23p^64s^1$

10 Which one of the following alternatives lists particles that are isotopes of the same element?

A W and X only
B X and Z only
C Y and Z only
D W, X and Y only

11 Which one of the following statements about particles W, X, Y and Z is correct?

A W is a noble gas.
B X is a positively charged ion.
C Y is in group 4 of the periodic table.
D Z is a negatively charged ion.

12 Which one of the following metals reacts most readily with oxygen?

A Na
B K
C Mg
D Ca

13 Which one of the following properties is not typical of transition metals?

A They are softer and more malleable than main group metals.
B Their ions can have more than one valency.
C Their compounds are often coloured.
D They are often used as catalysts.

14 Predict which one of the following ionic compounds will have the highest melting point.

A MgO
B $MgCl_2$
C Na_2O
D NaCl

15 Which one of the following statements about ionic bonding is not correct?

A When molten, ionic compounds are conductors of electricity.
B An ionic lattice contains both cations and anions in fixed positions.
C Ionic bonding involves the sharing of electrons between two different atoms.
D Compounds held together by ionic bonding generally have high melting temperatures.

16 Which one of the following quantities contains the same number of ions as in 1 mol of NaOH?

A 1 mol Na_2S
B 0.5 mol K_3PO_4
C 1 mol $MgCl_2$
D 1.5 mol MgO

17 The study of the emission spectrum of hydrogen led the Danish physicist Niels Bohr to propose a model for an atom. An emission spectrum is produced when electrons in an atom:

A release energy as they move from higher to lower energy levels
B absorb energy as they move from higher to lower energy levels
C release energy as they move from lower to higher energy levels
D absorb energy as they move from lower to higher energy levels.

18 The mass, in grams, of one molecule of carbon dioxide is closest to:

A 7.3×10^{-23}
B 44
C 6.02×10^{23}
D $44 \times 6.02 \times 10^{23}$

19 A particular brand of plant fertiliser contains 58.5% urea ($CO(NH_2)_2$), as the only nitrogen-containing compound.

The mass of nitrogen, in g, in 125 g of this fertiliser is:

A 34.1
B 40.0
C 50.0
D 73.1

20 The mass, in g, of calcium chloride that contains 6.02×10^{23} chloride ions is:

A 35.5
B 55.6
C 75.6
D 111

Short-answer questions

21 Write the formula of each of these compounds.

a Potassium phosphate
b Aluminium oxide
c Sodium nitrate
d Iron(III) sulfide

22 Write the name of each of the compounds listed.

a $Ca(NO_3)_2$
b $CuCO_3$
c $Mg(OH)_2$
d Cr_2O_3

23 Ionic compounds have a variety of uses in everyday life.

a Give the formula, and a use, of one ionic compound.
b Use the ionic bonding model to explain the following properties of ionic compounds.
  i Solid ionic compounds cannot conduct electricity.
  ii Ionic compounds are generally brittle.
  iii Ionic compounds have high melting temperatures.

24 Iridium has two naturally occurring isotopes. Their relative abundances and masses are shown in the table below.

Isotope	Relative isotopic mass	Percentage abundance
^{191}Ir	190.97	37.30%
^{193}Ir	192.97	62.70%

a What is the name of the instrument that is commonly used to experimentally obtain the abundances and relative isotopic masses data?

b Using the information in the table, determine the relative atomic mass of iridium. Show your working and give your answer to the appropriate number of significant figures.

25 **a** Several methods are used to extract metals from their ores. The method chosen for the extraction of a particular metal depends on the reactivity of the metal. Describe one method of extraction of a named metal and state one relevant environmental or economic issue associated with this extraction.

b The properties of metals can be modified by changing the crystal structure of a metal by heat treatment.

Describe the properties of a metal that has undergone:

i quenching

ii tempering

iii annealing.

c Describe the difference between the processes of quenching and tempering.

d Describe the different changes in the crystal structure of the metal that occur in the processes of annealing and quenching.

26 Magnesium is a commonly used structural metal.

a Write the electronic configuration of a magnesium atom, using subshell notation.

b **i** The radius of a magnesium atom is 160 pm (1 pm = 10^{-12} m). What is the radius of the magnesium atom in nanometres?

ii Would you predict the radius of a sodium atom to be smaller or larger than 160 pm? Explain your answer.

c **i** Describe the model commonly used to describe the structure of metals such as magnesium and the nature of the bonding between its particles. You may include a labelled diagram in your answer.

ii Use the metallic bonding model to explain why magnesium is a good conductor of electricity.

iii The metallic bonding model is useful to explain many of the properties of metals. However, like most models, it has some limitations. Give one example of the limitations of the metallic bonding model.

d **i** Magnesium reacts readily with dilute hydrochloric acid. What would you observe if a small piece of magnesium was added to some hydrochloric acid? Write a chemical equation for this reaction.

ii Give the symbol for one metal that would be expected to react more vigorously with hydrochloric acid than magnesium.

e Magnesium is classified as a main group metal and not as a transition metal.

How does the electronic configuration of a transition metal differ from that of a main group metal?

f Magnesium is most commonly used as an alloy for structural purposes. What is an alloy? Give one example of how alloying affects the properties of a metal.

27 **a** Describe how Bohr used evidence from spectral analysis to propose his model of the atom.

b Give two specific limitations of Bohr's model of the atom.

c Describe one way in which the Schrodinger model of the atom differs from that of Bohr.

28 **a** Using an atom of sodium as an example, clearly explain the difference between an electron shell, a subshell and an orbital.

b Consider the following electronic configuration:
$1s^22s^22p^63s^23p^63d^1$.

Does this electronic configuration represent a ground state or excited atom? Give a reason for your answer.

29 **a** With the aid of a periodic table, identify the correct chemical symbol for each of the following.

i The element that is in group 2 and period 4

ii A noble gas with exactly three occupied electron shells

iii An element from group 14 that is a non-metal

iv An element that has exactly three occupied electron shells and is in the s-block

v The element in period 2 that has the largest atomic radius

vi The element in group 15 that has the highest first ionisation energy

vii The element in period 2 with the highest electronegativity

b Describe the trend in chemical reactivity of elements going down group 1 of the periodic table and give a brief explanation for this trend.

30 Give brief definitions of the following terms.

- **a** Mass number
- **b** Atomic number
- **c** Relative isotopic mass
- **d** Avogadro's constant
- **e** Ion

31 Give a concise explanation for each of the following.

- **a** The atomic radius of chlorine is smaller than that of sodium.
- **b** The first ionisation energy of fluorine is higher than that of lithium.
- **c** The reactivity of Be is less than that of Ba.
- **d** There are two groups in the s-block of the periodic table.

32 A sample of aluminium nitrate ($Al(NO_3)_3$), has a mass of 30.5 g.

- **a** Calculate the amount, in mol, of aluminium nitrate in the sample.
- **b** Calculate the amount, in mol, of nitrogen atoms present.
- **c** Calculate the total number of atoms present in the sample.
- **d** Determine the percentage by mass of oxygen in aluminium nitrate.

33 Copper forms two oxides, copper(I) oxide (Cu_2O) and copper(II) oxide (CuO). The following experiment was carried out to determine whether a particular oxide of copper was Cu_2O or CuO.

A sample of the oxide was dissolved in sulfuric acid. An excess of zinc powder was added to precipitate the copper as copper metal. The copper metal was collected, washed, thoroughly dried and then weighed. The results are given below:

m(oxide) = 2.127 g
m(dried copper) = 1.704 g

- **a** Determine the empirical formula of this oxide of copper.
- **b** If the sample analysed was a mixture of the two oxides instead of one of the oxides only, would the mass of copper obtained be greater than or less than 1.704 g? Explain your answer.

34 Metal X burns in air and forms a compound with the empirical formula MO_2.

When 0.753 g of the metal burns completely, 1.368 g of XO_2 forms.

- **a** Calculate the molar mass of X.
- **b** Identify metal M.

35 Potassium nitrate (KNO_3), and ammonium sulfate ($(NH_4)_2SO_4$), can both be used in fertilisers as a source of nitrogen for plants.

What mass of ammonium sulfate contains the same amount of nitrogen as 65.0 g of potassium nitrate?

CHAPTER

06

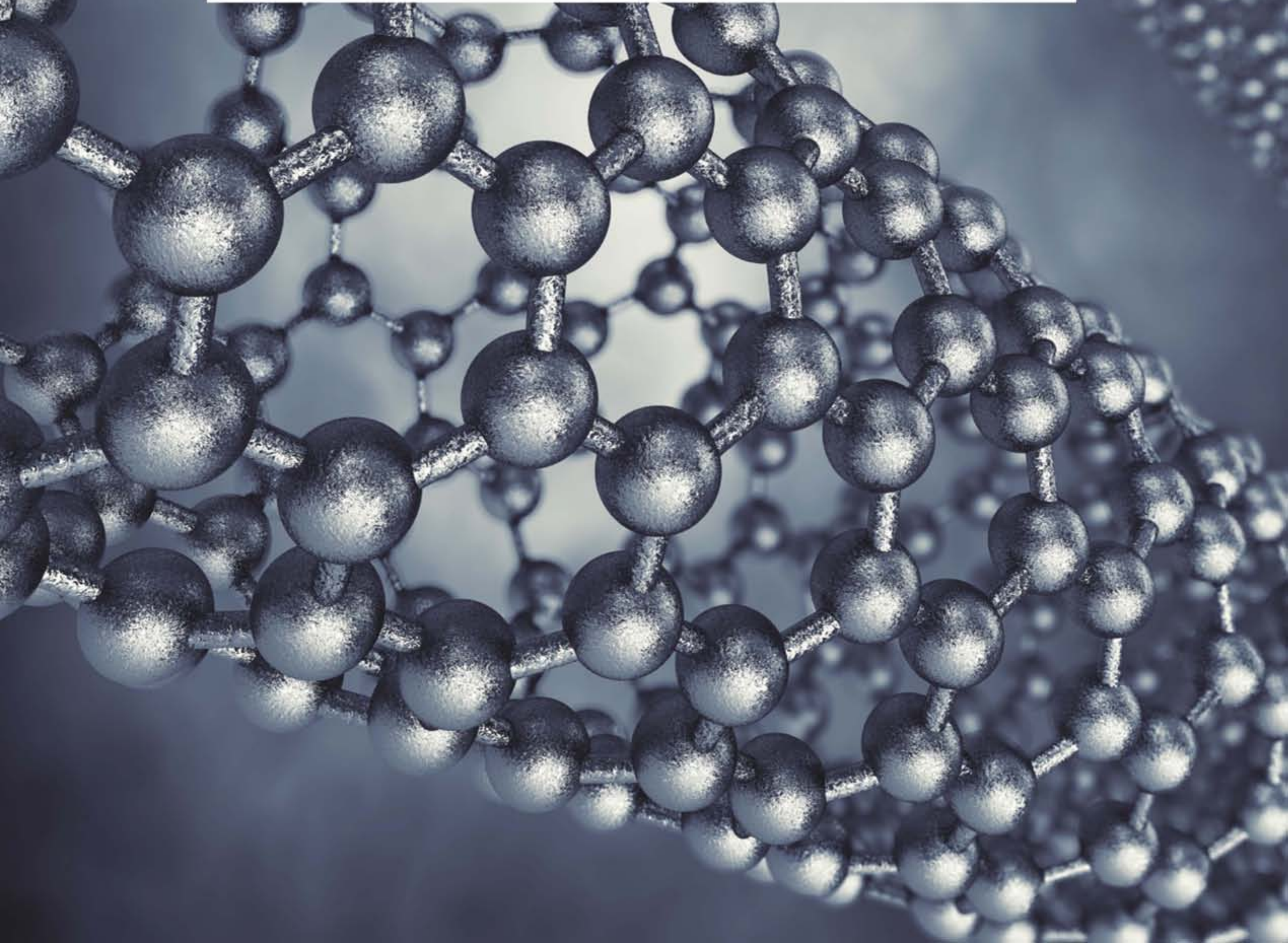
Materials made of molecules

At the end of this chapter, you will have an understanding of the bonding in compounds formed by the reaction of two or more non-metals. When non-metals bond, their atoms share electrons to gain stable outer shells.

Most substances formed from non-metallic elements have relatively low melting and boiling temperatures and are composed of small molecules.

Key knowledge

- Explanation of properties of molecular substances (including low melting point and boiling point, softness and non-conduction of electricity) with reference to their structure, intramolecular bonding and intermolecular forces
- Representations of molecular substances (electron dot formulas, structural formulas, valence structures, ball-and-stick models, space-filling models)
- Limitations of representations of molecules



6.1 Properties of non-metallic substances

In Chapter 3, you saw that the bonding between atoms in metallic elements is called metallic bonding. When metal atoms combine with atoms of non-metallic elements, the compounds contain another form of bonding, ionic bonding. In this chapter, you will look at the chemical bonding that occurs when atoms of non-metals combine with each other.

EXAMPLES OF NON-METAL COMPOUNDS

Although there are fewer non-metals than metals in the periodic table, the atoms of non-metals form a much larger number of compounds than metals. Water, carbon dioxide, caffeine, sugar and cooking oil are just a few examples of common compounds formed from non-metals.

PROPERTIES OF NON-METALLIC ELEMENTS AND COMPOUNDS

The properties of compounds formed by non-metallic elements can tell you a lot about their chemical structures. Table 6.1.1 lists some of the properties of a range of common substances. The substances chosen include a metal, ionic compounds and non-metal compounds. The information in Table 6.1.1 is useful because it allows you to:

- identify the characteristic properties of each category of substances. For example, metals conduct electricity as solids and liquids
- deduce information about the chemical structures of these substances. If a substance has a high melting point, the bonding between particles must be strong. If a substance conducts electricity, it must contain charged particles that are free to move.

TABLE 6.1.1 Properties of some common metals, ionic compounds and non-metal compounds

Substance	Formula	Melting point (°C)	Boiling point (°C)	Conducts electricity as a solid?	Conducts electricity as a liquid?
Ammonia	NH_3	–77	–33	No	No
Copper	Cu	1084	2562	Yes	Yes
Copper(II) chloride	$CuCl_2$	498	993	No	Yes
Laughing gas	N_2O	–90	–88	No	No
Table salt	NaCl	801	1413	No	Yes
Water	H_2O	0	100	No	No

From Table 6.1.1, you can see that:

- metals such as copper have high melting points and conduct electricity both as solids and as liquids. As you saw in Chapter 3, this indicates that strong bonds exist in metals and that they contain charged particles (delocalised electrons) that are free to move
- the ionic compounds copper(II) chloride and sodium chloride have high melting points and conduct electricity as liquids but not as solids. In Chapter 4, you learned that ionic solids have strong bonds and that they contain charged particles (ions) that are free to move in a liquid form but not in a solid form
- the non-metal compounds ammonia, laughing gas and water have low melting points and do not conduct electricity. Non-metal compounds can be soft in the solid state. Two conclusions about bonding in non-metal compounds that can be drawn from these properties are shown in Figure 6.1.1.

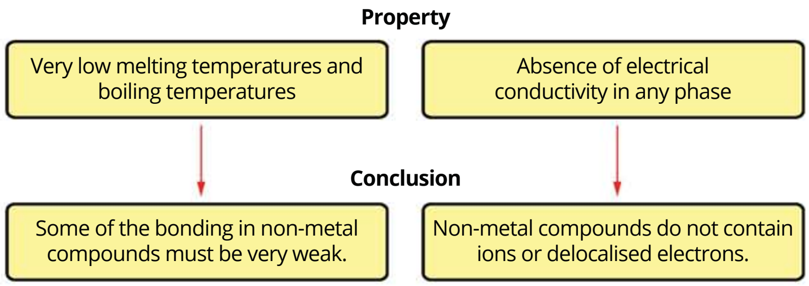
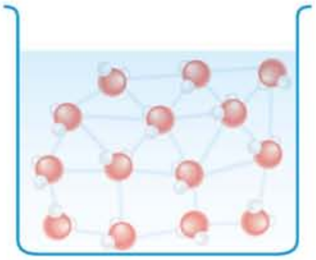


FIGURE 6.1.1 These conclusions can be drawn from the properties of non-metallic substances.

MOLECULES

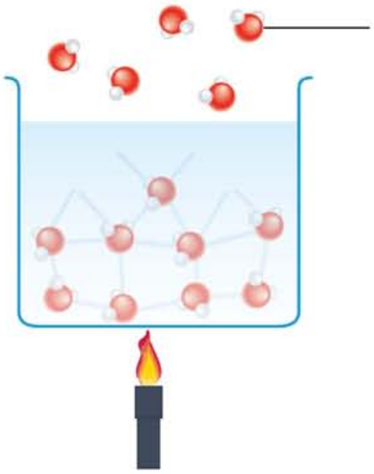
You gain further insight into the chemical structure of non-metallic substances by considering what happens when you boil water in a beaker. Figure 6.1.2 shows that each water particle contains two hydrogen atoms bonded to one oxygen atom. In between the particles are weak bonds holding the particles to each other.



Water in a beaker contains two types of bonds:
1. the bonds between hydrogen and oxygen atoms within each water particle
2. the bonds holding one particle of water to another.

FIGURE 6.1.2 This representation shows the bonds between particles of water in a beaker.

When water boils (Figure 6.1.3), the weak bonds between particles must break. However, the water particles do not separate into hydrogen and oxygen. Rather, the water vapour that is formed still contains particles in which two hydrogen atoms are bonded to one oxygen atom. This indicates that liquid water must contain more than one form of bonding.



Water particles in steam are still H_2O and not hydrogen and oxygen gas. Therefore the bonds in the particle are unchanged.

When water boils, the bonds between one H_2O particle and its neighbouring H_2O particles are broken.

FIGURE 6.1.3 Changes occur to the bonding in water when water starts to boil.

The particles of water shown in Figure 6.1.3 are examples of a **molecule**. A molecule is a discrete (individually separate) group of atoms of known formula, bonded together.

Molecules can be found in some elements as well as in some compounds. The element oxygen, for example, forms O_2 molecules. Water can be referred to as a molecular compound with a **molecular formula** of H_2O. The bonds between the hydrogen and oxygen atoms within water molecules are referred to as **intramolecular bonds** and the bonds between water molecules are referred to as **intermolecular bonds**.

The intramolecular bonds between the hydrogen and oxygen atoms in water molecules are strong compared to the intermolecular bonds between the water molecules. It is the intermolecular bonds that are broken when molecular substances such as water boil or melt. This allows the molecules to separate from each other while the atoms within the molecules remain bound to one another.

CHEMFILE

Helium

The Sun is made up of about 24% helium and 75% hydrogen (Figure 6.1.4).

Helium is an interesting case study of bonding because there are almost no bonds between its atoms. Helium atoms are small and they have two electrons in their outer shells. The first shell can only hold two electrons, so this means the outer shell is full and the atoms are very stable. As a consequence, helium atoms do not form molecules.

The forces of attraction between helium atoms are almost non-existent. Helium has to be cooled to –269°C before it turns to a liquid. As a liquid, it can climb up the sides of its container and escape!

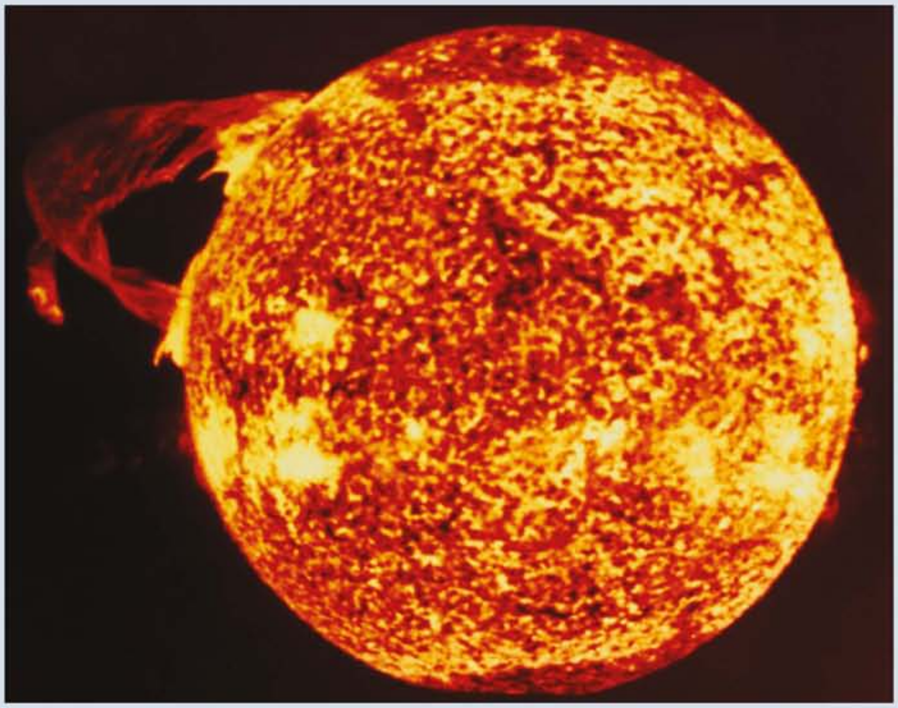


FIGURE 6.1.4 The Sun is made up of about 24% helium and 75% hydrogen. The first evidence for the existence of helium came from a spectral line observed in sunlight during a solar eclipse in 1868.

6.1 Review

SUMMARY

- Many substances contain only non-metal atoms. Some of these substances are elements, while others are compounds.
- Non-metallic elements and compounds usually have low boiling temperatures and do not conduct electricity.
- Many non-metallic elements and compounds are composed of molecules. Molecules are discrete groups of atoms of known formula, bonded together.
- There are two important types of bonds in molecular compounds—the bonds within the molecules (intramolecular bonds) and the bonds between molecules (intermolecular bonds).
- The melting and boiling temperatures of non-metallic elements and compounds depend on the bonding between molecules. Generally, molecular substances have low melting and boiling temperatures. This indicates they have weak bonds between molecules. The weak bonds mean that solid compounds of non-metallic elements can be soft.
- In general, non-metallic elements and compounds do not conduct electricity because they do not contain free-moving charged particles (neither delocalised electrons nor ions).

KEY QUESTIONS

1 Identify the non-metallic elements and compounds from this list: $MgSO_4$, NO_2, H_2, Ni, $CaCl_2$, Br_2.

2 Write the definition of a molecule.

3 Explain the following general properties of non-metals.
- **a** Non-metals do not conduct electricity.
- **b** Non-metals have low melting and boiling temperatures.

4 Identify whether the following statements about methane (CH_4) are true or false.
- **a** Methane is a molecular compound.
- **b** A molecule of methane contains four atoms.
- **c** There are 20 atoms in four molecules of methane.
- **d** The bonds between the carbon and hydrogen atoms in methane are intermolecular bonds.

5 When sugar is gently heated, it turns into a clear liquid. If the liquid is heated strongly, it turns black and a gas is produced. Explain what is happening to the bonds in sugar when it is heated. Use the terms ‘intermolecular bonds’ and ‘intramolecular bonds’ in your answer.

6.2 Covalent bonding

This section examines a series of simple molecules to help you to understand the concept of a **covalent bond**, which is formed when non-metallic atoms share electrons. Using your knowledge of the valence shell electron arrangements of non-metallic atoms, you will be able to predict the molecules that different elements can form.

COVALENT BONDS

In Chapter 1, you saw that many atoms become more stable if they gain an outer shell of eight electrons by combining with other atoms (the **octet rule**).

Commonly, when atoms of non-metals combine, electrons are shared so that each atom has eight electrons in its outer shell. Molecules formed in this way are more stable than the separate atoms.

Non-metallic atoms have a relatively high number of electrons in their outer shells and they tend to share rather than to transfer electrons. Covalent bonding occurs when electrons are shared between atoms.

Single covalent bonds

When atoms share two electrons, one from each atom, the covalent bond formed is called a **single covalent bond**. Two examples of substances that contain single bonds are hydrogen and chlorine.

Example 1: Hydrogen

Hydrogen atoms have one electron. The valence shell for a hydrogen atom can hold a maximum of two electrons. A hydrogen atom can bond to another hydrogen atom to form a molecule of H_2, as shown in Figure 6.2.1.

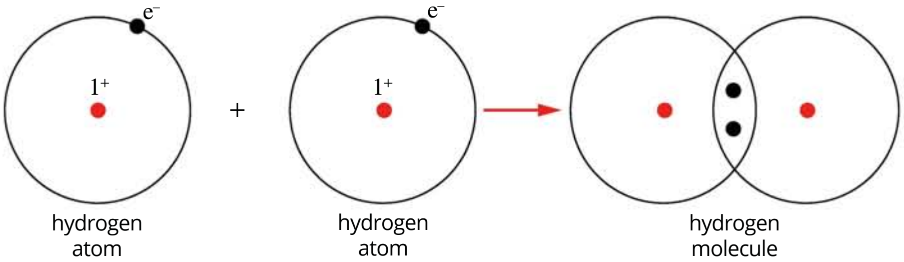


FIGURE 6.2.1 A covalent bond is formed when two hydrogen atoms share two electrons, one from each atom.

CHEMFILE

Hydrogen airships

Hydrogen has a low density. This was once thought to make it suitable for use in airships. Zeppelins were a type of rigid airship that was used as a mode of transport during the early 1900s. However, their popularity as a way of travel decreased after the hydrogen gas in the zeppelin *Hindenburg* (Figure 6.2.3) caught fire in 1937, killing many on board.

FIGURE 6.2.3 The German passenger zeppelin *Hindenburg* exploded during its attempt to dock at the Lakehurst Naval Air Station in the United States.

In the molecule that is formed:

- two hydrogen atoms share two electrons, one from each atom, to form a single covalent bond
- the atoms of hydrogen are now strongly bonded together by two electrons (an electron pair) in their outer shells.

The hydrogen molecule can be represented as H_2. Molecules that contain two atoms are called **diatomic molecules**.

Two alternative ways of representing a hydrogen molecule are shown in Figure 6.2.2.

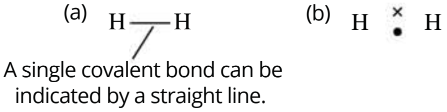


FIGURE 6.2.2 A hydrogen molecule can be represented by (a) a valence structure or (b) an electron dot formula (or diagram) (Lewis structure).

In a hydrogen molecule, the electron in each atom is attracted to the proton within the neighbouring atom, as well as to their own proton. This means the two electrons will spend most of their time between the two nuclei instead of orbiting their own proton within its nuclei. Even though the protons in the two nuclei still repel each other (remember, like charges repel), the electrostatic attraction to the electrons (which are closer) keeps the molecule held together.

This model of a hydrogen molecule is consistent with the observed properties of hydrogen gas. The covalent bonds in the molecules are strong, but the intermolecular forces in hydrogen (the attractions between one molecule and the surrounding molecules) are weak. This explains the low melting temperature of –259°C for hydrogen. Hydrogen does not conduct electricity as it does not contain ions or delocalised electrons.

Hydrogen is an example of a covalent molecular substance.

Example 2: Chlorine

A chlorine atom has an electronic configuration of 2,8,7. It requires one more electron to achieve eight electrons in its outer shell. (Note: Throughout this chapter we will use shell-model electronic configurations and diagrams to represent the electron arrangement in atoms as simply as possible.)

One chlorine atom can share an electron with another chlorine atom to form a molecule of chlorine with a single covalent bond. As a result, both atoms gain outer shells of eight electrons as shown in Figure 6.2.4. This is an example of the application of the octet rule.

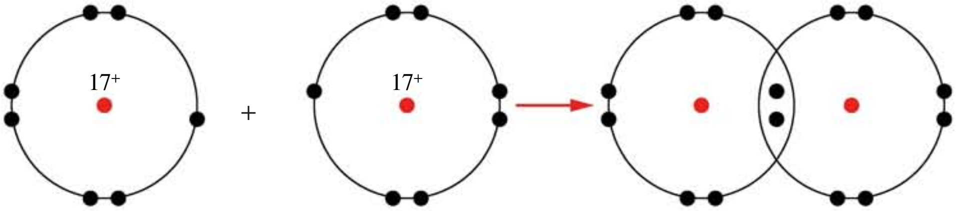


FIGURE 6.2.4 Two chlorine atoms share one electron each to form a chlorine molecule. Note that only outer-shell electrons are usually shown in these diagrams.

Electron dot diagrams

Chemists often use **electron dot diagrams** (also known as electron dot formulas or Lewis structures) and **valence structures** to simplify the drawing of molecules.

Electron dot diagrams show the valence shell electrons of an atom, as only electrons in the valence shells of atoms are involved in bonding. In a valence structure, lines are used to represent the two electrons in a covalent bond. One line represents one pair of electrons.

The electron dot diagram also allows you to distinguish between bonding electrons and non-bonding electrons. A chlorine molecule has one pair of bonding electrons. The outer-shell electrons that are not involved in bonding are called the **non-bonding electrons**. Each chlorine atom has six non-bonding electrons, present as three pairs of electrons. Pairs of non-bonding electrons are known as **lone pairs**.

Figure 6.2.5 shows the electron dot diagram and valence structure for a molecule of chlorine. It is easy to see that each chlorine atom in the molecule has eight electrons in its outer shell.

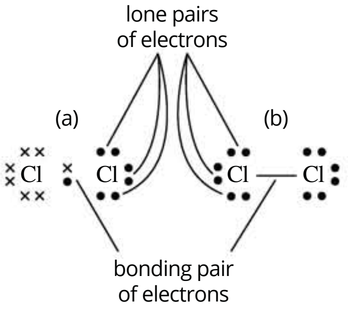


FIGURE 6.2.5 Two different ways of representing the chlorine molecule. They show the outer-shell electrons only. (a) Electron dot diagrams are also called Lewis structures. The electrons can be represented by either dots or crosses. (b) In a valence structure, lines are used to represent pairs of electrons.

Double covalent bonds

In a **double covalent bond**, two pairs of electrons (four electrons in total) are shared between the atoms, rather than just one pair.

The oxygen molecule contains a double covalent bond. The electronic configuration of an oxygen atom is 2,6. Each oxygen atom requires two electrons to gain a stable outer shell containing eight electrons. Therefore, when one oxygen atom bonds to another one, each atom shares two electrons.

As you can see in Figure 6.2.6, each oxygen atom in the molecule now has eight outer-shell electrons, four of these are bonding electrons and four are non-bonding electrons.

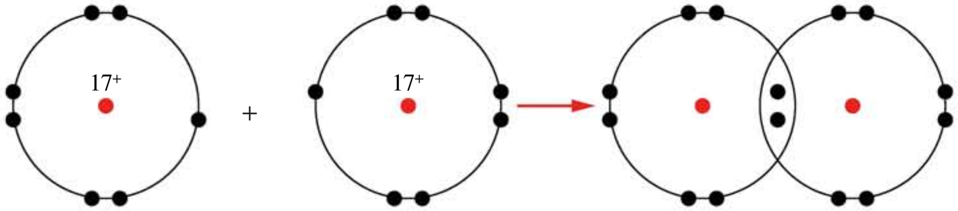


FIGURE 6.2.6 In oxygen molecules, each oxygen atom contributes two electrons to the bond between the atoms.

In Figure 6.2.7, you can see both the electron dot diagram and the valence structure of an oxygen molecule, two different ways of representing the oxygen molecule.

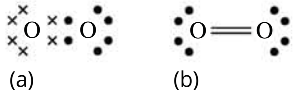


FIGURE 6.2.7 (a) The electron dot diagram shows that O_2 has a double covalent bond. Four electrons are shared and each oxygen has two non-bonding electron pairs. (b) The valence structure shows the double bond as two parallel lines.

Triple covalent bonds

A **triple covalent bond** occurs when three electron pairs are shared between two atoms. The nitrogen molecule contains a triple bond. The electronic configuration of nitrogen is 2,5. A nitrogen atom requires three electrons to achieve eight electrons in its outer shell. When it bonds to another nitrogen atom, each atom contributes three electrons to the bond that forms, as shown in Figure 6.2.8. The valence structure of the nitrogen molecule is shown in Figure 6.2.9.

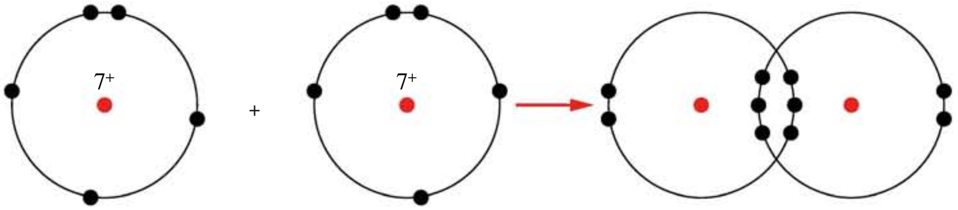


FIGURE 6.2.8 Nitrogen atoms contribute three electrons each to form a triple covalent bond in a molecule of N_2.

FIGURE 6.2.9 The triple covalent bond in a nitrogen molecule can be shown as three parallel lines.

CHEMFILE

The strong triple covalent bond in N_2

The triple covalent bond in nitrogen gas (N_2) is relatively strong and not easily broken. This means that nitrogen gas is relatively unreactive. Nitrogen is an essential element in living organisms because it is a major component of proteins and other biological molecules. Even though 78% of air is nitrogen gas, very few organisms can make use of the nitrogen because it is so unreactive. Only nitrogen-fixing microorganisms are able to convert nitrogen gas into soluble nitrogen-containing compounds. These compounds are then absorbed by plants, allowing nitrogen to then be passed up the food chain.

In the early 20th century, German chemist Fritz Haber invented a process for converting nitrogen gas and hydrogen gas into ammonia, which is used to make synthetic fertilisers. This allowed humans to grow more food to feed a growing world population.

MOLECULAR COMPOUNDS

A diatomic molecule contains two atoms. The molecules discussed so far have been diatomic molecules that contain atoms of the same elements.

Covalent bonds can also form between atoms of different elements. Hydrogen chloride (HCl) is a simple example (Figure 6.2.10). A hydrogen atom requires one electron to gain a stable outer shell, as does a chlorine atom. They can share an electron each and form a single covalent bond.

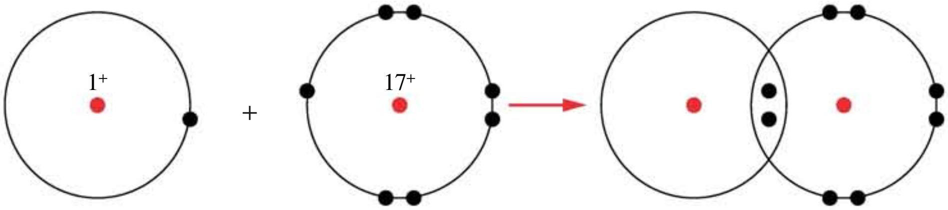


FIGURE 6.2.10 A pair of electrons is shared in the formation of a molecule of HCl.

Polyatomic molecules

If the atoms of one element have a different number of valence electrons from the atoms of the element it is bonding with, the molecule that is formed may not be a simple diatomic molecule. Molecules made up of more than two atoms are called **polyatomic molecules**. Two examples of polyatomic molecules are water and methane.

Example 1: Water

When a compound forms between hydrogen and oxygen, an oxygen atom shares two electrons and a hydrogen atom shares one. To resolve this imbalance, two hydrogen atoms each share one electron with an oxygen atom.

As you can see in the electron dot diagram (Figure 6.2.11), a water molecule contains:

- two single covalent bonds, each containing a shared electron pair
- four non-bonding electrons on the oxygen atom.

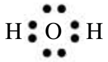


FIGURE 6.2.11 A water molecule has two single covalent bonds. Electrons can be represented as dots and crosses, or simply, as here, by dots.

Example 2: Methane

When a compound forms between carbon and hydrogen, four hydrogen atoms are needed to provide the four electrons required in order to have eight electrons in the outer shell of a carbon atom (Figure 6.2.12). The molecule formed has a chemical formula of CH_4 and is called methane.

FIGURE 6.2.12 In a methane molecule, a carbon atom shares one electron with each of four hydrogen atoms to gain eight electrons in its outer shell.

SHAPES OF MOLECULES

The shapes of diatomic molecules such as H_2 and HCl are simple. With two atoms only, a diatomic molecule is linear, as you can see in Figure 6.2.13.

FIGURE 6.2.13 H_2 and HCl both contain only one bond, so they are linear in shape.

Electron dot diagrams can be used as a starting point in determining the shape of molecules. These diagrams show the outer-shell electron pairs in the molecule. Electron pairs have a negative charge and they repel each other. The electron pairs arrange themselves as far away from each other as possible.

In the case of methane, the electron dot diagram (Figure 6.2.14) shows four outer-shell electron pairs around the carbon atom. Repulsion between the electron pairs means that the hydrogen atoms form a **tetrahedral shape** around the carbon atom (Figure 6.2.15). In this molecule, the bonds between the carbon and hydrogen atoms are at an angle of 109.5° to each other.

You will have a more detailed look at the shapes of molecules and intermolecular bonding in Chapter 7.

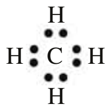


FIGURE 6.2.14 The carbon atom in methane has four pairs of electrons in its outer shell. These electron pairs repel each other.

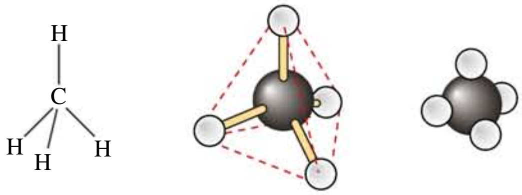


FIGURE 6.2.15 A valence structure and two models of a methane molecule show that hydrogen atoms form a tetrahedron around the central carbon atom.

Representations of molecules

An electron dot diagram does not show the shape of a molecule but there are several other accepted styles for representing molecules that do. A **ball-and-stick model**, as shown in Figure 6.2.16, displays the shape and the type of bonds (single, double or triple) in a molecule. The atoms are represented by spheres that are connected by rods, representing the bonds. The spheres represent the centre of the atom, not the whole space the atom occupies.

A **space-filling model** (Figure 6.2.17) also uses spheres but this time the spheres represent the whole atom, including its electron charge cloud. Different coloured spheres are used in both types of models to identify the different elements.

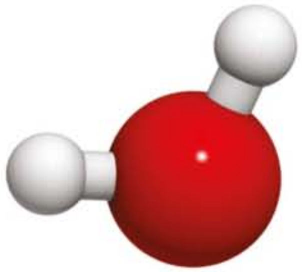
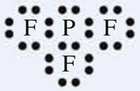
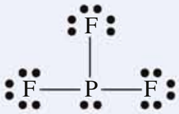


FIGURE 6.2.16 Ball-and-stick model of a water molecule.

FIGURE 6.2.17 Space-filling model of a water molecule.

Each different representation of a molecule has its advantages. An electron dot diagram is often drawn before the shape of the molecule is determined and can be used to determine the bonds present. A valence structure simplifies the electron dot diagram while the ball-and-stick and space filling models show the shape of the molecule and the position of atoms. Table 6.2.1 compares different representations of a PF_3 molecule.

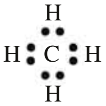
TABLE 6.2.1 Comparison of different representations of phosphorus fluoride, PF_3

	Electron dot	Valence	Ball-and-stick	Space-filling
Diagram				
Model best used for	Determining the formula of the molecule and the type of bonds	Simplifying the electron dot diagram	Displaying the molecule shape	Showing the relative size and position of the atoms in the molecule
Limitation of model	Does not show the relative size of atoms or shape of the molecule	Does not show the relative size of atoms or shape of the molecule	Shows the shape but not the relative sizes of the atoms	Shows the relative size and position of the atoms but does not show bond angles or types of bonds

Worked example 6.2.1

ELECTRON DOT DIAGRAMS

Draw an electron dot diagram of methane (CH_4).

Thinking	Working
Write the electronic configuration of the atoms in the molecule.	C electronic configuration: 2,4 H electronic configuration: 1
Determine how many electrons each atom requires for a stable outer shell.	C requires 4 electrons. H requires 1 electron.
Draw an electron dot diagram of the likely molecule, ensuring that each atom has a stable outer shell. Electrons not involved in bonding will be in non-bonding (lone) pairs.	Draw an electron dot diagram of the molecule. 

Worked example: Try yourself 6.2.1

ELECTRON DOT DIAGRAMS

Draw an electron dot diagram of ammonia (NH_3).

EXTENSION

The octet rule for covalent bonding

In the examples considered, the maximum number of electron pairs in the outer shell of an atom was four pairs or eight electrons. For elements in period 2, such as C, N, O and F, this completes the outer shell. This led G.N. Lewis to describe the octet rule: the maximum number of covalent single bonds formed by an atom is such that the atoms share electrons to obtain just eight electrons in their outer shells. Hydrogen (two electrons) is the one exception to the rule. However, the problem with this rule was the discovery of compounds such as SF_6 and PF_5, which contain six and five pairs of electrons respectively, and BF_3 with only three pairs of electrons.

Sulfur and phosphorus, in period 3, have their outer-shell electrons in the third shell, which can hold up to 18 electrons. This means that atoms of those elements can have more than four electron pairs (that is, more than eight valence electrons). This explains the formation of compounds such as SF_6 and PF_5 (Figure 6.2.18). In those compounds, phosphorus and sulfur are said to have an expanded octet. However, it must be remembered that the noble gas electronic configuration of s^2p^6, with eight valence electrons, is particularly stable and so the octet rule still applies for many elements beyond period 2.

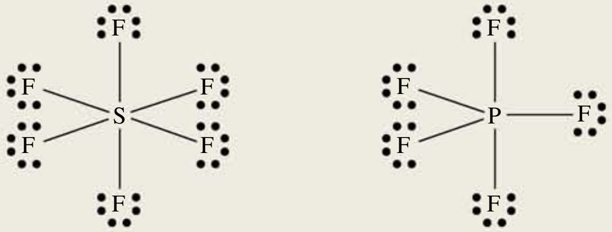


FIGURE 6.2.18 Valence structures of SF_6 and PF_5.

For BF_3, each fluorine atom (electronic configuration 2,7) forms one covalent bond. Boron has an electronic configuration of 2,3. There are only three electrons in the outer shell of boron. Each of these is shared with one of three fluorine atoms to form covalent bonds. This results in only three pairs of electrons (six electrons) around the boron atom in BF_3 (Figure 6.2.19). Boron is said to have an incomplete octet.

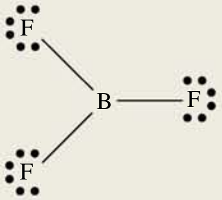


FIGURE 6.2.19 Valence structure of BF_3.

Size also affects the formula of molecules. As previously discussed, nitrogen forms a diatomic molecule with a triple covalent bond. Phosphorus, a period 3 element, in the same group of the periodic table as nitrogen, forms the diatomic molecule P_2 only at high temperatures. The P_4 molecule, known as white phosphorus, is much more stable. This is because the larger size of the phosphorus atom means that it is not as easy, and hence less stable, for the electron shells to overlap and allow three pairs of electrons to be shared. Instead, a more stable arrangement is achieved with the tetrahedral P_4 molecule created with single covalent bonds.

6.2 Review

SUMMARY

- The atoms in non-metallic molecules are held together by covalent bonds.
- A covalent bond involves the sharing of electrons.
- Covalent bonds form between non-metallic atoms, often enabling the atoms to gain outer shells containing eight electrons (except hydrogen which gains an outer shell containing two electrons).
- A single covalent bond forms when two atoms share a pair of electrons.
- A double covalent bond forms when two atoms share four electrons.
- A triple covalent bond forms when two atoms share six electrons.
- Outer-shell electrons that are not involved in bonding are called lone pairs.
- Electron dot diagrams show the valence electron arrangements of atoms in a molecule.

KEY QUESTIONS

1 How many covalent bonds are formed between atoms in these diatomic molecules?

a H_2
b N_2
c O_2
d F_2

2 Draw electron dot and valence structures for each of the following molecules: fluorine (F_2), hydrogen fluoride (HF), water (H_2O), tetrachloromethane (CCl_4), phosphine (PH_3), butane (C_4H_{10}), carbon dioxide (CO_2).

3 What is the maximum number of covalent bonds an atom of each of the following elements can form?

a F
b O
c N
d C
e H
f Ne

4 When oxygen forms covalent molecular compounds with other non-metals, the valence structures that represent the molecules of these compounds all show each oxygen atom with two lone pairs of electrons. Why are there always two lone pairs?

5 Suggest the most likely formula of the compound formed between the following pairs of elements.

a C, Cl
b N, Br
c Si, O
d H, F
e P, F

6 Identify the type of representation of a molecule that best fits the following descriptions.

a Shows the shape of the molecule and type of atoms present
b Shows the arrangement of valence electrons between atoms in a molecule as dots
c Shows the relative size and position of atoms and the shape of molecule

Chapter review

06

KEY TERMS

ball-and-stick model
covalent bond
diatomic molecule
double covalent bond
electron dot diagram
intermolecular bond
intramolecular bond
lone pair
molecular formula
molecule
non-bonding electron
octet rule
polyatomic molecule
single covalent bond
space-filling model
tetrahedral shape
triple covalent bond
valence structure

Properties of non-metallic substances

1 Hydrogen chloride (HCl) exists as a gas at room temperature. What can you conclude about the strength of the intermolecular bonding in pure hydrogen chloride?

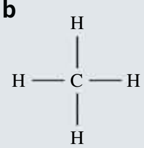
2 Non-metallic substances generally do not contain free-moving charged particles. What does this indicate about the general physical properties of non-metallic substances?

3 Solid carbon dioxide sublimes when it is heated; that is, it goes straight from a solid to a gas. Explain what happens to the bonds in carbon dioxide when it sublimes. Use the terms 'intermolecular bonds' and 'intramolecular bonds' in your answer.

4 Identify each type of molecular representation of CH_4.

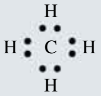
a

b



c

d



Covalent bonding

5 Select the statement that best describes the way hydrogen atoms bond to each other.

A One hydrogen atom donates an electron to another hydrogen atom to form a molecule.
B Hydrogen atoms form a lattice with delocalised electrons.
C Hydrogen atoms share electrons to obtain a complete outer shell of eight electrons.
D Two hydrogen atoms share an electron each to form a hydrogen molecule.

6 In a molecule of nitrogen (N_2), how many of the following are there?

a Bonding electrons
b Covalent bonds
c Non-bonding electrons

7 The formula of a molecule is XY_4. Select the alternative that could match this formula.

A OH_4 **B** CH_4 **C** HBr_4 **D** CO_4

8 Atom X has an electronic configuration of 2,6. Atom Y has a configuration of 2,7. What is the likely molecular formula of the compound that will form between X and Y?

9 Explain why neon atoms do not form covalent bonds.

10 How many lone pairs are in each of the following molecules?

a H_2
b NH_3
c HCl
d O_2

11 Draw electron dot diagrams for each of the following molecules and identify the number of bonding and non-bonding electrons in each molecule.

a HBr
b H_2O
c CF_4
d C_2H_6
e PF_3
f Cl_2O
g CH_4
h H_2S

12 The atoms in molecules of nitrogen, oxygen and fluorine are held together by covalent bonds. How are the bonds in these molecules:

a similar?
b different?

13 Experimental evidence shows that the double bond between the two oxygen atoms in O_2 is much stronger than a single bond between two oxygen atoms in a compound such as hydrogen peroxide (H_2O_2).

a Draw electron dot diagrams and structural formulas for O_2 and H_2O_2.
b Explain why the oxygen double bond is stronger than the oxygen single bond.
c Why does oxygen not form a triple bond or three single covalent bonds?

Connecting the main ideas

14 Classify the following substances as metallic, ionic or molecular: $CuCl_2$, Ag, HCl, H_2O, Cu, CaS, NH_3.

15 Identify whether the following statements about carbon dioxide (CO_2) are true or false.

a Carbon dioxide is a molecular compound.
b A molecule of carbon dioxide contains three atoms.
c There are 99 oxygen atoms in 33 molecules of carbon dioxide.
d The bonds between the carbon and oxygen atoms in carbon dioxide are intramolecular bonds.
e There are two single covalent bonds in a molecule of carbon dioxide.
f There are four lone pairs of electrons in a molecule of carbon dioxide.

CHAPTER

07

Intermolecular forces

Covalent molecular substances have a much greater range of properties than ionic or metallic substances. Covalent molecular substances are the only substances that can be solids, liquids or gases at room temperature. They can be hard or soft, flexible or brittle, sticky or oily—almost any consistency. This broad range of properties makes molecular substances very useful materials.

The properties of covalent molecular substances are the result of two main types of bonding. These are the strong covalent bonds inside the molecules and much weaker bonds between molecules.

At the end of this chapter, you will know how intermolecular forces determine many of the physical properties of covalent molecular substances. You will become familiar with the valence shell electron pair repulsion (VSEPR) theory and use the theory to predict the shape and polarity of molecules. You will then use these predictions to infer information about the nature of the bonding between molecules.

In addition, you will learn to identify intermolecular forces, including dipole–dipole forces, hydrogen bonding and dispersion forces. Finally, you will examine the factors that influence the strength of these intermolecular forces.

Key knowledge

- Shapes of molecules and an explanation of their polar or non-polar character with reference to the electronegativities of their atoms and electron pair repulsion theory
- Explanation of properties of molecular substances (including low melting point and boiling point, softness and non-conduction of electricity) with reference to their structure, intramolecular bonding and intermolecular forces
- The relative strengths of bonds (covalent bonding, dispersion forces, dipole–dipole attraction and hydrogen bonding) and evidence and factors that determine bond strength, including explanations for the floating of ice and expansion of water at higher temperatures

7.1 Shapes of molecules

FIGURE 7.1.1 Water (H_2O) molecules have a distinctive shape that is responsible for many of its properties. The valence shell electron pair repulsion theory accurately predicts the shape of water molecules.

The shapes of molecules are critical in determining many physical properties of covalent molecular substances. In particular, molecular shape affects melting point, boiling point, hardness and solubility. This is because the shape of a molecule determines how it interacts with other molecules.

For very large molecules, such as DNA, proteins and enzymes, shape plays a key role in how they behave chemically and biologically. For example, the twisted double helix of DNA allows the molecule to coil up tightly so that it fits inside the nucleus of a cell.

To understand the shape of large molecules like DNA, scientists use complex techniques such as X-ray crystallography or powerful computer simulations. However, the shape of small molecules can be predicted using a relatively simple model known as the **valence shell electron pair repulsion (VSEPR) theory**. In this section, you will see how VSEPR theory can be used to predict the shape of molecules such as the water molecule shown in Figure 7.1.1.

VALENCE SHELL ELECTRON PAIR REPULSION THEORY

As the name suggests, the VSEPR theory uses our knowledge of the **valence electrons** in the atoms of a molecule to predict the shape of the molecule. The VSEPR theory is based on the principle that negatively charged electron pairs in the outer shell of an atom repel each other. As a consequence, these electron pairs are arranged as far away from each other as possible.

Electron pair repulsion

In general, atoms in covalent molecules are most stable when they have eight electrons in their valence shell. This is known as the **octet rule**. These eight electrons are arranged into four pairs of electrons.

For example, the carbon atom in methane is covalently bonded to four hydrogen atoms. In this arrangement, the carbon atom shares a pair of electrons with each hydrogen atom. The four pairs of electrons give the carbon atom a stable octet as shown in Figure 7.1.2. In this diagram, the dots represent electrons donated to the **single covalent bond** by the carbon atom. The crosses represent electrons donated to the single covalent bond by the hydrogen atoms. (Note that dots and crosses are used here to distinguish the electrons of the hydrogen atoms from the electrons in the carbon atom valence shell. It is also correct to use dots or crosses only.)

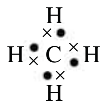


FIGURE 7.1.2 This electron dot diagram (Lewis structure) of a methane (CH_4) molecule shows the four electron pairs surrounding the central carbon.

Hydrogen atoms are an exception to the octet rule. Hydrogen atoms are stable with just two electrons because this gives them the stable electronic configuration of a helium atom.

The VSEPR theory states that the electron pairs in methane repel each other so that they are as far apart as possible. This repulsion between the electron pairs results in a tetrahedral shape as shown in the ball and stick model in Figure 7.1.3. The tetrahedral shape ensures that the electron pairs are as far from each other as possible with angles of 109.5° between all of the single bonds.

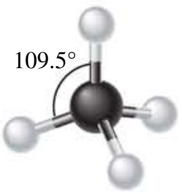


FIGURE 7.1.3 In a methane molecule (CH_4), the electron pairs in the single covalent bonds repel each other. The repulsion forces the bonds as far apart as possible, arranging the hydrogen atoms into a tetrahedral shape at an angle of 109.5° to each other.

Lone pairs of electrons

Not all electron pairs in molecules exist as covalent bonds. Some electrons form a non-bonding pair of electrons known as a **lone pair** of electrons. In the VSEPR theory, lone pairs of electrons are treated in the same way as electron pairs in covalent bonds in order to determine the shape of a molecule.

In the ammonia molecule shown in Figure 7.1.4, the nitrogen atom has a stable octet made up of one lone pair of electrons and three single bonds. The four electron pairs repel each other to form a tetrahedral arrangement. However, the lone pair is ignored when determining the shape of the molecule. Instead, the three hydrogen atoms are described as forming a pyramidal arrangement with the nitrogen atom. The lone pair occupies slightly more space than the bonding electrons, so the three single covalent bonds are pushed closer together. The bond angle is therefore now slightly less than 109.5°.

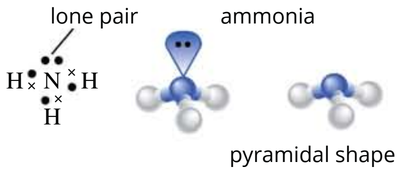


FIGURE 7.1.4 The electron dot diagram of an ammonia (NH_3) molecule shows that the nitrogen atom has one lone pair of electrons and three covalent bonds. These four electron pairs form a tetrahedral arrangement around the atom due to the repulsion of the electron pairs. The result is a pyramidal molecule.

In water molecules, the oxygen atom has a stable octet made up of two lone pairs and two single bonds. The four electron pairs repel each other to form a tetrahedral arrangement. This causes the two hydrogen atoms to form a V-shape or bent arrangement with the oxygen atom as shown in Figure 7.1.6. With two lone pairs in the molecule, the two single covalent bonds are pushed closer together. In this case, the bond angle around the central atom is also slightly less than 109.5°.

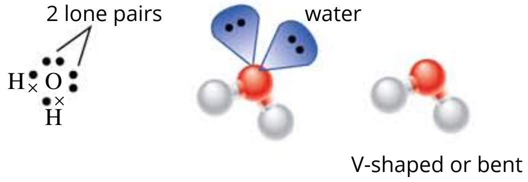


FIGURE 7.1.6 The electron dot diagram of a water (H_2O) molecule shows that the oxygen atom has two lone pairs of electrons and two covalent bonds. These four electron pairs form a tetrahedral arrangement around the atom due to the repulsion of the electron pairs. The result is a V-shaped or bent molecule.

In a hydrogen fluoride molecule, the fluorine atom has a stable octet made up of three lone pairs and one single bond. The four electron pairs repel each other to form a tetrahedral arrangement. Therefore, the hydrogen and fluorine atoms form a linear molecule, as you can see in Figure 7.1.7.

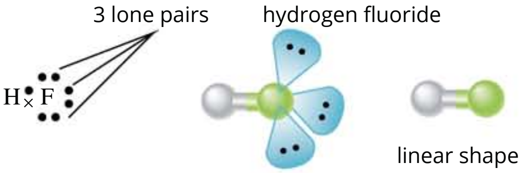


FIGURE 7.1.7 The electron dot diagram of a hydrogen fluoride (HF) molecule shows that the fluorine atom has three lone pairs of electrons and one covalent bond. These four electron pairs form a tetrahedral arrangement around the atom due to the mutual repulsion of the electron pairs. The result is a linear molecule.

Lone pairs of electrons influence a molecule's shape but are not considered a part of the shape.

CHEMFILE

That's a-maser-ing!

Ammonia is not just a useful household cleaning product; it can also be used to create microwave lasers—'masers'. A pyramidal ammonia molecule with its hydrogen atoms pointing down can suddenly flip so that the hydrogen atoms are pointing up. This is a bit like an umbrella flipping inside-out on a windy day. When the ammonia molecule flips, it can release microwave radiation.

Charles Hard Townes and James Power Gordon used this property of ammonia to create the first maser, as shown in Figure 7.1.5. Their work laid the foundation for other types of masers, which are now used in radio telescopes to study the far reaches of the universe. Charles Hard Townes was awarded the Nobel Prize in Physics in 1964 for this work.

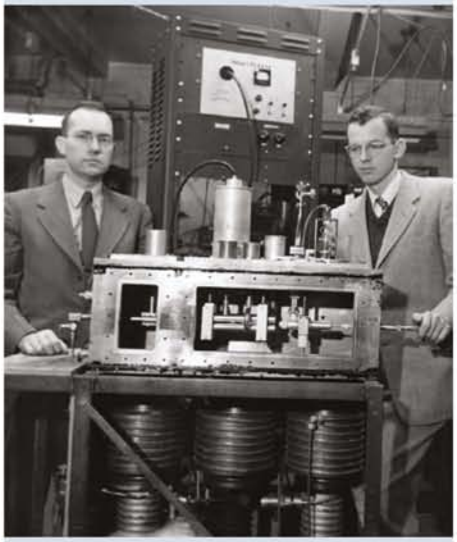
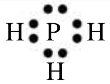


FIGURE 7.1.5 Charles Hard Townes and James Power Gordon invented the first maser using ammonia gas.

Worked example 7.1.1

PREDICTING THE SHAPE OF MOLECULES

Predict the shape of a molecule of phosphine (PH_3).

Thinking	Working
Draw the electron dot diagram for the molecule.	
Count the number of bonds and lone pairs on the central atom.	There are three bonds and one lone pair.
Determine how the groups of electrons will be arranged to get maximum separation.	Because there are four electron pairs, the groups will be arranged in a tetrahedral arrangement.
Deduce the shape of the molecule by considering the arrangement of just the atoms.	The phosphorus and hydrogen atoms are arranged in a pyramidal shape.

Worked example: Try yourself 7.1.1

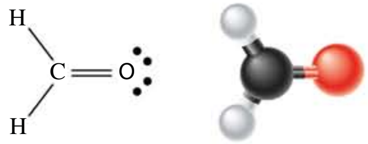
PREDICTING THE SHAPE OF MOLECULES

Predict the shape of a molecule of hydrogen sulfide (H_2S).

Double bonds, triple bonds and valence shell electron pair repulsion theory

A double bond contains two pairs of electrons. A triple bond contains three pairs of electrons. The VSEPR theory treats double and triple bonds in the same way that it treats single bonds and lone pair electrons.

For example, if a central atom has two single bonds and one double bond, then the three sets of bonds will repel each other to get maximum separation. This results in a molecular shape known as trigonal planar because the atoms form a triangle in one plane. An example of this structure is the methanal (CH_2O) molecule shown in Figure 7.1.8. Trigonal planar molecules have bond angles of 120°.



methanal, CH_2O
(trigonal planar)

FIGURE 7.1.8 Methanal has a central carbon atom that forms a double bond with an oxygen atom and single bonds with two hydrogen atoms. The bonds repel each other to form a trigonal planar arrangement.

If the central atom has two double bonds, then the two double bonds repel each other. This results in a linear molecule like carbon dioxide (CO_2), shown in Figure 7.1.9. A linear molecule has a bond angle of 180°.

carbon dioxide, CO_2
(linear)

FIGURE 7.1.9 In a carbon dioxide molecule, the carbon atom forms double bonds with two oxygen atoms. The two double bonds repel each other. This results in a linear molecule.

Finally, if the central atom has a single bond and a triple bond, as in hydrogen cyanide (HCN), then the molecule is also linear (Figure 7.1.10).

hydrogen cyanide, HCN
(linear)

FIGURE 7.1.10 The hydrogen cyanide molecule is linear. In this case, the central carbon atom forms a triple bond with the nitrogen atom and a single bond with the hydrogen atom.

EXTENSION

Molecules that do not obey the octet rule

Not all atoms obey the octet rule. Boron forms stable molecules with just three electron pairs in its valence shell. In borane (BH_3), the central boron atom is bonded to three hydrogen atoms, but has no lone pairs. There are only three pairs of electrons in this molecule. These three pairs repel each other to form a trigonal planar molecule (Figure 7.1.11).

borane, BH_3 trigonal planar shape

FIGURE 7.1.11 Borane (BH_3) has a central boron atom attached to three hydrogen atoms.

The VSEPR theory can be used to predict the shape of these molecules. The VSEPR theory predicts that the three electron pairs will move as far away from each other as possible into a trigonal planar shape.

Boron trichloride has a similar arrangement. The three chlorine atoms are located 120° from each other around the central boron atom, as can be seen in Figure 7.1.12.

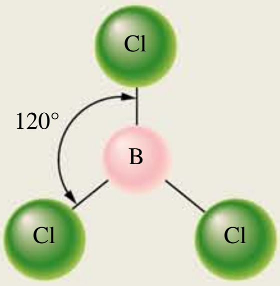


FIGURE 7.1.12 Boron trichloride (BCl_3) has a trigonal planar shape.

Beryllium forms stable molecules with just two electron pairs in its valence shell. In beryllium hydride (BeH_2), the central beryllium atom forms single bonds with two hydrogen atoms, but has no lone pairs of electrons. The two single bonds repel each other to form a linear molecule, as shown in Figure 7.1.13.

beryllium hydride, BeH_2 linear shape

FIGURE 7.1.13 Beryllium hydride has a central beryllium atom attached to two hydrogen atoms. There are only two pairs of electrons in this molecule. These two pairs repel each other to form a linear molecule.

Sulfur hexafluoride (SF_6) is made up of a central atom of sulfur with six valence electrons. This sulfur atom bonds to six fluorine atoms. These six pairs of electrons repel each other to form an octahedral shape. The bond angle between the fluorine atoms is 90°, the maximum angle possible for six electron pairs (Figure 7.1.14).

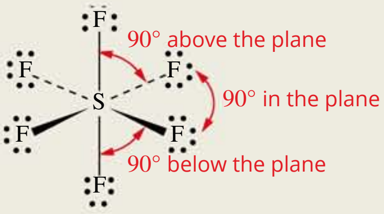


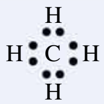
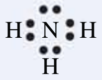
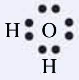
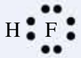
FIGURE 7.1.14 Bond angles in SF_6.

7.1 Review

SUMMARY

- The shapes of molecules play an important role in determining the intermolecular forces between molecules and are related to the physical properties of substances.
- The shapes of simple molecules can be predicted by the valence shell electron pair repulsion (VSEPR) theory.
- The VSEPR theory is based on the principle that electron pairs in the outer shell of an atom repel each other. As a consequence, these electron pairs are arranged as far away from each other as possible.
- Electron pairs can exist in covalent bonds or as lone pairs of electrons. Lone pairs and covalent bonds repel each other.
- Lone pairs influence a molecule's shape but are not considered a part of the shape.

TABLE 7.1.1 Summary of shapes of molecules

Example	Methane, CH_4	Ammonia, NH_3	Water, H_2O	Hydrogen fluoride, HF
Electron dot diagram				
Number of single bonds	4	3	2	1
Number of lone pairs	0	1	2	3
Ball-and-stick model				
Shape	Tetrahedral	Pyramidal	V-shaped or bent	Linear

KEY QUESTIONS

1 Explain VSEPR theory and how it is used to determine the shape of molecules.

2 How many electron pairs are there in the valence shell of the fluorine atom in a hydrogen fluoride molecule?

3 Draw the valence structure for each of the following molecules.

a H_2S
b HI
c CCl_4
d PH_3
e CS_2

4 Describe the shape of each of the molecules in Question 3.

5 Copy and complete the Table 7.1.2, determining the shape of each of the molecules with the specific number of bonds listed.

TABLE 7.1.2

Molecule	Number of single bonds on the central atom	Number of lone pairs of electrons on the central atom	Shape of the molecule
a	4	0	
b	3	1	
c	2	2	

7.2 Properties of covalent molecular substances

The physical properties of covalent molecular substances are primarily determined by the strength of the forces between the molecules. These forces are known as **intermolecular forces**. The shape of a molecule is one factor that determines the strength of intermolecular forces. However, the covalent bonds inside the molecules also play an important role.

Both the shape of a molecule and the nature of its covalent bonds must be taken into account when predicting the strength of intermolecular forces. This section examines how these factors determine the strength of intermolecular forces and therefore determine important physical properties such as melting point, boiling point, hardness and conductivity.

INTERMOLECULAR FORCES

Intermolecular forces exist between molecules, and their effects are seen everywhere. If you have ever struggled to flatten out a sheet of cling wrap, then you've experienced the effects of intermolecular forces. Glue is an example of how intermolecular forces can be used to stick things together. The bubbles shown in Figure 7.2.1 are also held together by intermolecular forces.

If you take a closer look at liquids, you will notice further evidence of intermolecular bonding. Intermolecular bonds create the **surface tension** that allows insects to walk on water, as shown in Figure 7.2.2.

FIGURE 7.2.1 These bubbles are held together by intermolecular forces.

FIGURE 7.2.2 The surface tension created by intermolecular forces allows insects to walk on water.

Strength of intermolecular forces

Intermolecular forces are 100 times weaker than strong forms of bonding such as ionic, metallic and covalent bonds. For example, diamond is made up of a lattice of carbon atoms that are bonded with strong covalent bonds. This extremely strong lattice is the reason why diamond has a very high melting point and is the hardest natural substance on Earth.

Ruby is also a very hard substance made of the ionic compound aluminium oxide (Al_2O_3). Ruby is not quite as hard as diamond because the ionic bonds in Al_2O_3 are not as strong as the carbon–carbon covalent bonds in diamond. However, ruby is still much harder than most covalent molecular substances. This is because the ionic bonds in ruby are much stronger than the intermolecular forces in covalent molecular substances.

The atoms in covalent molecules such as water (H_2O) and carbon dioxide (CO_2) are also held together by strong covalent bonds. However, covalent molecular substances tend to have much lower melting and boiling points than ionic, metallic and covalent network substances. This is because the forces between the molecules are much weaker. It is the weak intermolecular forces that are broken when a covalent molecular substance is converted from a solid to a liquid or a liquid to a gas.

When liquids change to gases, the intermolecular bonds are broken. For example, when liquid water changes to gaseous water, the intermolecular bonds holding the water molecules to other water molecules are broken, not the covalent bonds between the hydrogen and oxygen atoms.

Hardness of covalent molecular substances

In general, covalent molecular substances tend to be softer than ionic or metallic substances. Wax, putty and butter are typical examples of soft, covalent molecular substances. These substances are soft because the intermolecular forces holding the molecules together are weak. Therefore, the bonds between the molecules can be readily broken and the substances can be easily moulded, scratched or crushed.

Despite having weak intermolecular forces, covalent molecular substances can still form crystals. For example, sugar is a covalent molecular substance that forms crystals. Water also forms crystals of ice. However, most covalent molecular crystals are softer than typical metals and ionic crystals.

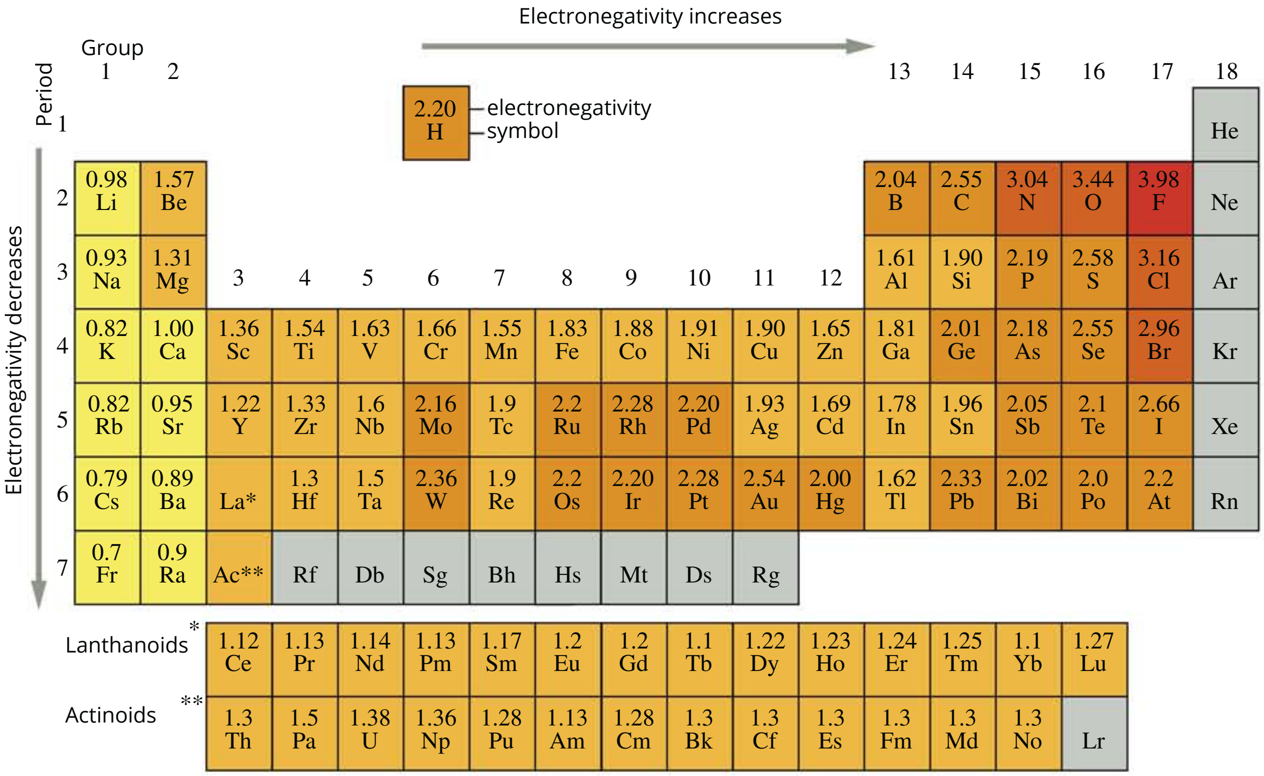
ELECTRONEGATIVITY AND POLARITY

Intermolecular forces are an example of electrostatic forces. You have already seen many other examples of how electrostatic forces form bonds at the atomic level. The attractions between positive and negative ions in an ionic crystal lattice (Chapter 4) and the attraction of shared electrons and nuclei in a covalent bond (Chapter 6) are all examples of electrostatic forces.

The electrostatic attraction between molecules works in a similar way. In intermolecular forces, the electrostatic attraction is between positive and negative charges in the molecules. These charges appear as a result of uneven electron distributions within the molecules. The following sections examine how the shape of the molecule and the electronegativity of its atoms can cause these uneven electron distributions.

Polarity of diatomic molecules

Electronegativity is the key factor that determines the electron distribution in diatomic molecules. Electronegativity is the tendency of an atom in a covalent bond to attract electrons. Electronegativity increases from left to right across the periods of the periodic table and decreases down the groups of the table, as shown in Figure 7.2.3. You will remember seeing these patterns in Chapter 2, page 44.



Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1																		He
2	0.98 Li	1.57 Be											2.04 B	2.55 C	3.04 N	3.44 O	3.98 F	Ne
3	0.93 Na	1.31 Mg											1.61 Al	1.90 Si	2.19 P	2.58 S	3.16 Cl	Ar
4	0.82 K	1.00 Ca	1.36 Sc	1.54 Ti	1.63 V	1.66 Cr	1.55 Mn	1.83 Fe	1.88 Co	1.91 Ni	1.90 Cu	1.65 Zn	1.81 Ga	2.01 Ge	2.18 As	2.55 Se	2.96 Br	Kr
5	0.82 Rb	0.95 Sr	1.22 Y	1.33 Zr	1.6 Nb	2.16 Mo	1.9 Tc	2.2 Ru	2.28 Rh	2.20 Pd	1.93 Ag	1.69 Cd	1.78 In	1.96 Sn	2.05 Sb	2.1 Te	2.66 I	Xe
6	0.79 Cs	0.89 Ba	La*	1.3 Hf	1.5 Ta	2.36 W	1.9 Re	2.2 Os	2.20 Ir	2.28 Pt	2.54 Au	2.00 Hg	1.62 Tl	2.33 Pb	2.02 Bi	2.0 Po	2.2 At	Rn
7	0.7 Fr	0.9 Ra	Ac**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

Lanthanoids *	1.12 Ce	1.13 Pr	1.14 Nd	1.13 Pm	1.17 Sm	1.2 Eu	1.2 Gd	1.1 Tb	1.22 Dy	1.23 Ho	1.24 Er	1.25 Tm	1.1 Yb	1.27 Lu
Actinoids **	1.3 Th	1.5 Pa	1.38 U	1.36 Np	1.28 Pu	1.13 Am	1.28 Cm	1.3 Bk	1.3 Cf	1.3 Es	1.3 Fm	1.3 Md	1.3 No	Lr

FIGURE 7.2.3 Table of electronegativity values. This periodic table shows the electronegativities of the atoms of each element. The electronegativities increase from left to right across the periods and decrease down the groups.

Non-polar diatomic molecules

When two atoms form a covalent bond, you can regard the atoms as competing for the electrons being shared between them. If the two atoms in a covalent bond are the same (i.e. have identical electronegativities), then the electrons are shared equally between the two atoms. This is the case for diatomic molecules such as chlorine (Cl_2), oxygen (O_2), hydrogen (H_2), and nitrogen (N_2).

Bonds with an equal distribution of valence (outer shell) electrons are said to be **non-polar** because there is no charge on either end of the molecule.

Electron density is the measure of the probability of an electron being present at a particular location within an atom. In molecules, areas of electron density are commonly found around the atom, and its bonds.

Figure 7.2.4 shows the electron distribution in the non-polar fluorine molecule (F_2). The molecule has a high **electron density** between the two fluorine atoms, forming the covalent bond. However, the valence electrons are distributed evenly between the two atoms, making the bond non-polar.

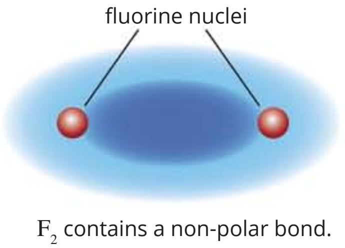


FIGURE 7.2.4 Fluorine molecules have a symmetric distribution of electrons and are therefore non-polar.

Polar diatomic molecules

If the covalent bond is between atoms of two different elements, then the electrons will stay closer to the most electronegative atom as it has a stronger pull on the electrons in the bond. An example is the hydrogen fluoride (HF) molecule, shown in Figure 7.2.5. Molecules with an imbalanced electron distribution are said to be **polar**.

A fluorine atom is more electronegative than a hydrogen atom. Therefore, in a hydrogen fluoride molecule the electrons tend to stay closer to the fluorine atom. This imbalance in the electron distribution means the fluorine atom is negatively charged and the hydrogen atom is positively charged. A molecule with two oppositely charged poles is said to be polar. The fluorine atom is described as having a partial negative charge, which is represented with the Greek letter delta as $\delta-$. The hydrogen atom is described as having a partial positive charge, $\delta+$. The separation of the positive and negative charges is known as an **electric dipole**, or simply as a **dipole** as they have two oppositely charged poles at each end of the molecule.

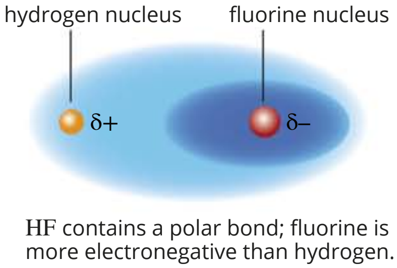


FIGURE 7.2.5 The electron distribution in hydrogen fluoride is asymmetric because of the different electronegativities of the hydrogen and fluorine atoms. Hydrogen fluoride is an example of a polar molecule.

Hydrogen fluoride is polar because it has a permanent electric dipole created by the different electronegativities of the two atoms. All diatomic molecules that are made up of atoms with different electronegativities are polar to some extent. The level of **polarity** will depend on the difference between the electronegativities of the two atoms. The greater the difference between the electronegativities, the greater the polarity of the molecule.

The partial charges on polar molecules are different from the charges on ions. The partial charges on a polar molecule will always add to give a total charge of zero, since the charges on polar molecules are due to the unequal sharing of electrons between atoms. However, ions do have an overall charge. The partial charges on a polar molecule are also a lot smaller than the charges on ions. That is why intermolecular bonds are much weaker than ionic bonds.

It is not just the covalent bonds in diatomic molecules that can be polar. Covalent bonds in larger molecules can have some degree of polarity. The polarity of any covalent bond can be compared by examining the difference in the electronegativities of the atoms involved in the bond.

As the difference in electronegativities of two atoms increases, the covalent bond formed between them increases in polarity. In other words, it becomes more like an ionic bond.

Worked example 7.2.1

COMPARING THE POLARITY OF COVALENT BONDS

Compare the polarity of the covalent bonds in hydrogen fluoride (HF) and carbon monoxide (CO).

Thinking	Working
Use the table of electronegativity values in Figure 7.2.3 on page 163 to find the electronegativities of the atoms in each molecule.	HF: hydrogen 2.20; fluorine 3.98 CO: carbon 2.55; oxygen 3.44
For each molecule, subtract the lowest electronegativity value from the highest value.	HF: 3.98 – 2.20 = 1.78 CO: 3.44 – 2.55 = 0.89
Determine which molecule has the biggest difference in electronegativity in order to determine the more polar bond.	HF is more polar than CO.

Worked example: Try yourself 7.2.1

COMPARING THE POLARITY OF COVALENT BONDS

Compare the polarity of the covalent bonds in nitrogen monoxide (NO) and hydrogen chloride (HCl).

Polarity of polyatomic molecules

Determining the polarity of molecules with more than two atoms is a little more complicated. This is because the polarity of **polyatomic molecules** depends on the shape of the molecule as well as the polarity of the covalent bonds. As a general rule:

- **symmetrical molecules** are non-polar
- **asymmetrical molecules** are polar.

Non-polar molecules

Even molecules with polar covalent bonds can be non-polar if the molecule is symmetrical.

In methane, the carbon atom is slightly more electronegative than the hydrogen atoms. Therefore, the carbon atom attracts the electrons more strongly than each hydrogen atom and has a partial negative charge, leaving hydrogen with a partial positive charge. However, the methane molecule is a perfect tetrahedron and is therefore symmetrical. The symmetry of the molecule means that the individual dipoles of the covalent bonds cancel each other perfectly (Figure 7.2.6). The result is a molecule with no overall dipole. It is non-polar.

The methane molecule shown in Figure 7.2.6 is an example of a non-polar molecule with polar covalent bonds.

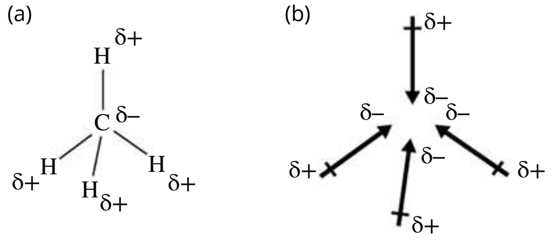


FIGURE 7.2.6 (a) Structure of a methane molecule showing the partial charges on the atoms. (b) The individual dipoles are distributed symmetrically around the molecule.

Polar molecules

In asymmetrical molecules, the individual dipoles of the covalent bonds do not cancel each other. This results in a net dipole, making the overall molecule polar.

The chloromethane molecule shown in Figure 7.2.7 is an example of an asymmetric molecule. The chlorine atom is more electronegative than the carbon atom. Therefore, the chlorine atom attracts electrons from the carbon atom while the carbon atom attracts electrons from the hydrogen atoms. The individual dipoles of the covalent bonds are shown in the central image in Figure 7.2.7. These add to give the molecule a net dipole.

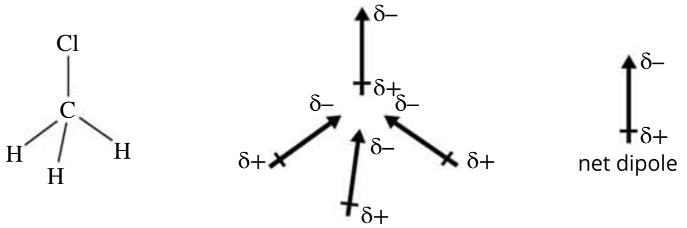
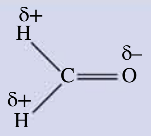
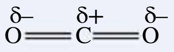
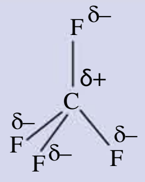
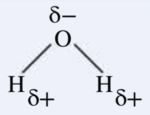
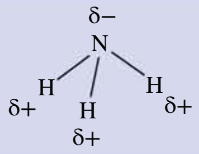


FIGURE 7.2.7 Chloromethane is a polar molecule because the individual dipoles of the covalent bonds add to give a net dipole.

Table 7.2.1 shows some more examples of how symmetry determines the polarity of covalent molecules.

TABLE 7.2.1 Examples of polar and non-polar covalent molecules

Molecule	Valence structure	Symmetrical/ asymmetrical	Polar/ non-polar
Formaldehyde (methanal)		Asymmetrical	Polar
Carbon dioxide	 $\overset{\delta-}{O}=\overset{\delta+}{C}=\overset{\delta-}{O}$	Symmetrical	Non-polar
Tetrafluoromethane		Symmetrical	Non-polar
Water		Asymmetrical	Polar
Ammonia		Asymmetrical	Polar

The polarity of a molecular substance has a significant impact on its solubility. In general, substances that are polar tend to dissolve in polar solvents. Non-polar substances tend to dissolve in non-polar solvents. You can remember this with the saying 'like dissolves like'.

CHEMFILE

How a microwave oven works

Microwave ovens use the polarity of molecules (especially water molecules) to heat food. The microwave oven irradiates the food with microwaves. The microwaves produce an electric field that interacts with the dipolar molecules. The electric field causes the molecules to rotate up and down billions of times per second. This gives the molecules extra kinetic energy. As the kinetic energy of the molecules increases, the temperature increases. Therefore, the molecules heat and cook the food.

7.2 Review

SUMMARY

- Many of the physical properties of covalent molecular substances are determined by intermolecular forces. These properties include melting point, boiling point, hardness and electrical conductivity.
- Intermolecular forces are 100 times weaker than strong chemical bonds such as ionic, covalent and metallic bonds.
- Shape and polarity of molecules are factors in determining the strength of intermolecular forces.
- As the difference in electronegativities of two atoms increases, a covalent bond increases in polarity.
- Diatomic molecules containing the same type of atom are non-polar.
- In general, symmetrical molecules are non-polar and asymmetrical molecules are polar.

KEY QUESTIONS

1 Covalent bonds can form between the following pairs of elements in a variety of compounds. Use the electronegativity values given in Figure 7.2.3 on page 162 to identify the atom in each pair that would have the largest share of bonding electrons.

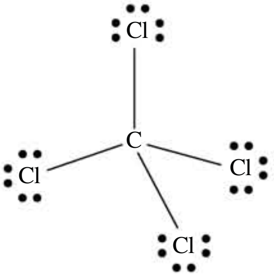
   a S and O
   b C and H
   c C and N
   d N and H
   e F and O
   f P and F

2 The greater the differences in electronegativity between two atoms, the more polar is the bond formed between them.

   a Which of the examples in Question 1 would be the most polar bond?
   b Which of the examples in Question 1 would be the least polar bond?

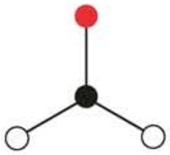
3 Use the electronegativity values in Figure 7.2.3 on page 162 to order the polarity of the covalent bonds between the following atoms from highest to lowest: carbon–nitrogen, nitrogen–nitrogen, hydrogen–nitrogen, sulfur–nitrogen, oxygen–nitrogen.

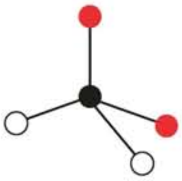
4 Label the following diagram of a tetrachloromethane molecule to show the dipoles between the atoms.



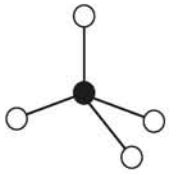
5 Examine the symmetry of each of these general diagrams of molecular structures, and determine if the molecules are likely to be polar or non-polar. The white, black and red circles represent atoms with different electronegativities.

a


b


c


d


e


7.3 Types of intermolecular forces

Many factors determine the strength of intermolecular forces, including the size, shape and polarity of molecules. These factors not only determine the strength of the intermolecular forces in a substance, they also determine the types of intermolecular forces.

There are three main types of intermolecular forces:

- dipole–dipole forces
- hydrogen bonding
- dispersion forces.

In this section, you will examine the nature of these three types of intermolecular forces and their role in determining the physical properties of covalent molecular substances.

DIPOLE—DIPOLE FORCES

Dipole–dipole forces only occur in polar molecules. These forces result from the attraction between the positive and negative ends of the polar molecules, as shown in Figure 7.3.1.

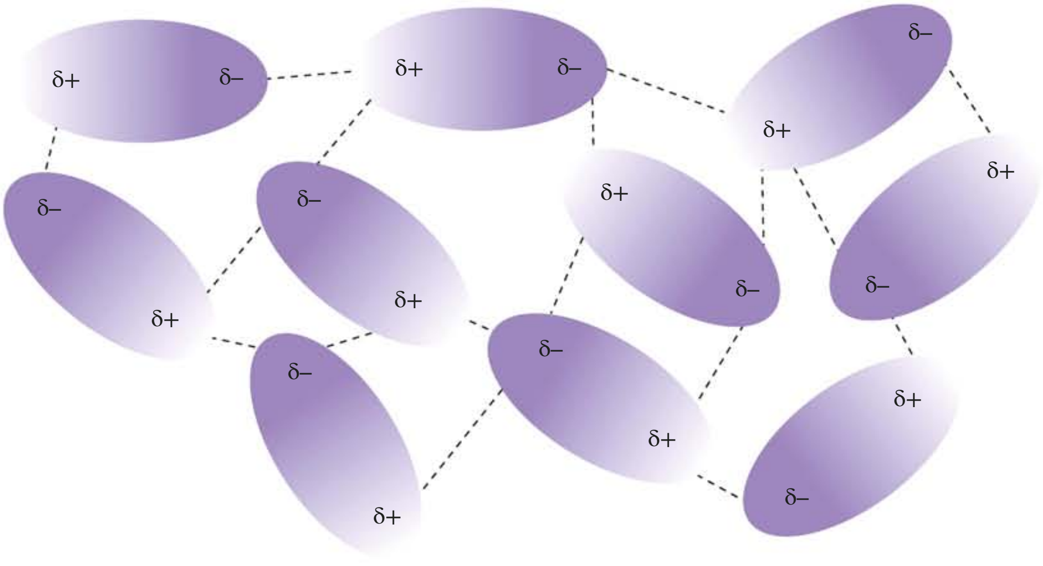


FIGURE 7.3.1 The positive and negative ends of polar molecules attract each other.

Dipole–dipole forces are relatively weak since the partial charges (the δ+ and δ–) on the molecules are small. However, the more polar a molecule is, the stronger the dipole–dipole forces are. The polarity will be larger when there is a large difference in the electronegativities of the atoms or a large asymmetry in the shape of the molecule.

Molecules are more polar when there is a greater difference in electronegativities of the atoms or a large asymmetry in the shape of the molecule. Molecules that are more polar have stronger dipole–dipole forces between them.

The strength of the dipole–dipole forces in molecules is directly related to the melting and boiling points of the substance. The stronger the dipole–dipole forces, the higher the melting and boiling points. This is because dipole–dipole forces bond the molecules together in the solid or liquid. Stronger dipole–dipole forces require more energy (i.e. higher temperatures) to break these bonds and change the solid to a liquid or the liquid to a gas.

For example, compare methanal (CH_2O) and ethane (CH_3CH_3), shown in Figure 7.3.2. Methanal is asymmetrical and therefore a polar molecule. This results in dipole–dipole forces between the molecules. Methanal's boiling point is −19°C. On the other hand, the ethane molecule is symmetrical and therefore non-polar. This means there are no dipole–dipole forces and its boiling point is much lower at −88.5°C.

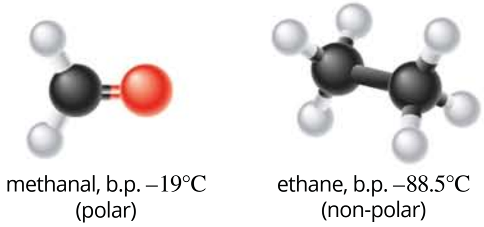


FIGURE 7.3.2 Molecular structures of methanal and ethane.

Hydrogen bonding

Hydrogen bonding is a special form of dipole–dipole force. Hydrogen bonding only occurs between molecules in which a hydrogen atom is covalently bonded to an oxygen, a nitrogen or a fluorine atom.

Oxygen, nitrogen and fluorine atoms are small and highly electronegative. Therefore, they strongly attract the electrons in a covalent bond. This creates a significant partial positive charge on a hydrogen atom bonded to these atoms. The partial positively charged hydrogen atom is then attracted to lone pairs of electrons in the nitrogen, oxygen and fluorine atoms of neighbouring molecules, as shown in Figure 7.3.3. Remember that hydrogen only has one electron and this electron is strongly attracted to the N, O or F atom in the covalent bond. The exposed positively charged hydrogen (proton) is attracted to a lone pair on a nitrogen, oxygen or fluorine atom in another molecule.

The result is a relatively strong intermolecular bond that is approximately ten times stronger than a dipole–dipole bond but about one-tenth the strength of an ionic or a covalent bond.

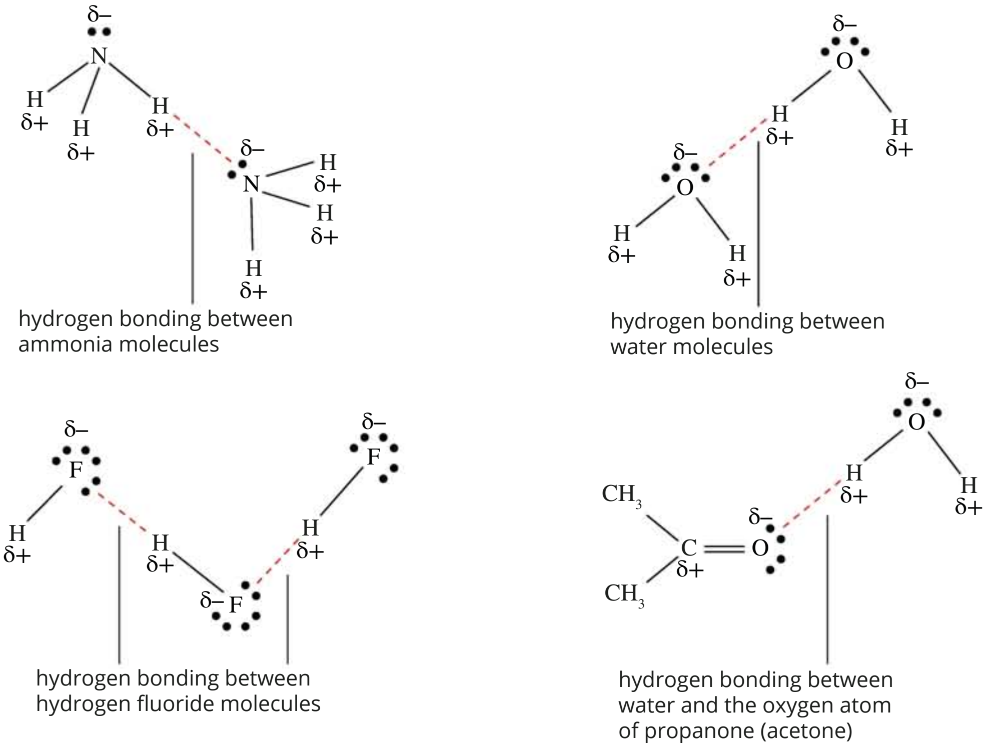


FIGURE 7.3.3 Examples of polar hydrogen bonding between molecules.

The presence of hydrogen bonds results in higher melting and boiling points. Figure 7.3.4 demonstrates the effect of hydrogen bonding on boiling point by comparing methanol to ethane and methanal. Recall that ethane is non-polar so it has no dipole–dipole forces between molecules. Methanal has dipole–dipole forces but does not have hydrogen bonding. Methanol has hydrogen bonding between molecules because of the hydrogen atom attached to the oxygen atom. As a result, the boiling point of methanol (64.7°C) is significantly higher than the boiling point of methanal (–19°C) and ethane (–88.5°C).

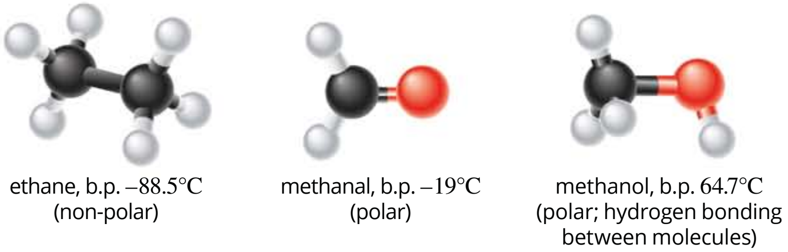


FIGURE 7.3.4 Molecular structures of ethane, methanal and methanol.

The two key requirements for hydrogen bonding are a:

1 hydrogen atom covalently bonded to an oxygen, a nitrogen or a fluorine atom
2 lone pair of electrons on the nitrogen, oxygen or fluorine atoms of neighbouring molecules.

It is both the very high electronegativities and small atomic radii of oxygen, nitrogen and fluorine atoms that cause the formation of the hydrogen bonds. Chlorine atoms also have a very high electronegativity but do not form hydrogen bonds because of their larger atomic radius, which reduces the concentration of negative charge around the atom.

Hydrogen bonding occurs in molecules where a hydrogen atom is bonded to an oxygen, a nitrogen or a fluorine atom.

Hydrogen bonding in water

Water is a very common substance but it has some unusual properties. One unusual property of water is that ice floats. Ice floats because ice is less dense than liquid water. For most other substances, the solid form is denser than the liquid.

The fact that ice is less dense than liquid water can be explained by hydrogen bonding. Water has two hydrogen atoms attached to an oxygen atom in a V-shape. Therefore, the hydrogen atoms can form hydrogen bonds with the lone pairs of electrons on the oxygen atoms of neighbouring molecules as shown in Figure 7.3.5. In this way, a water molecule can form hydrogen bonds with four other water molecules.

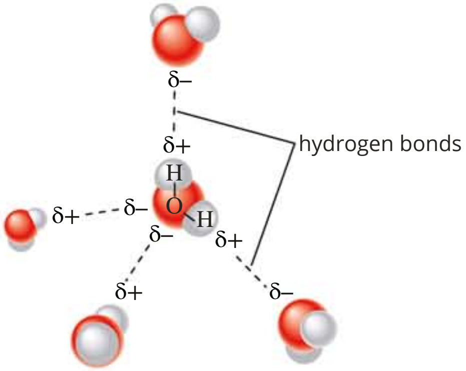


FIGURE 7.3.5 Each water molecule can form hydrogen bonds with four other water molecules. The two lone pairs of electrons on the molecule bond to hydrogen atoms on two neighbouring molecules. In addition, the two hydrogen atoms on the molecule form bonds with lone pairs of electrons in two neighbouring molecules.

The hydrogen bonding holds the water molecules in ice in a regular crystal lattice. In this lattice, the molecules are held further apart than in liquid water as shown in Figure 7.3.6. As a result, ice is less dense and therefore floats in liquid water.

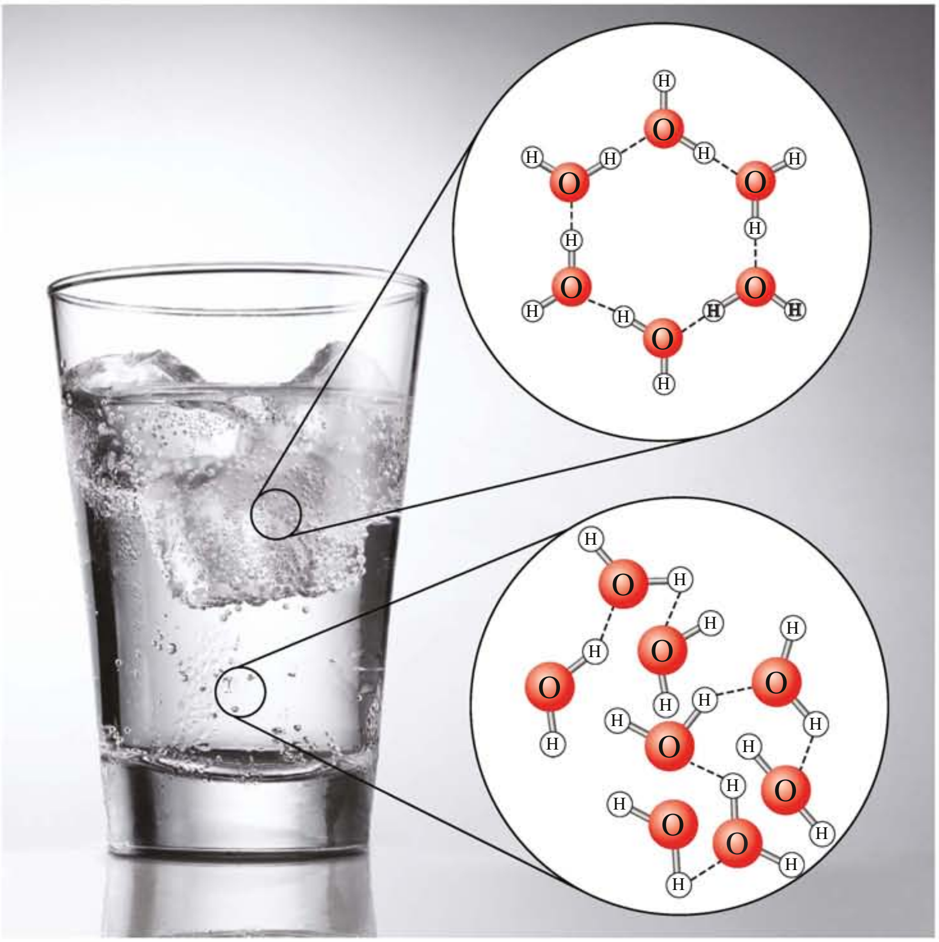


FIGURE 7.3.6 Ice floats because the water molecules form a crystal lattice in which the molecules are spaced more widely apart than in liquid water. This arrangement means ice is less dense than liquid water.

When ice melts and forms liquid water, the density of the water increases rapidly. This is because the open crystal lattice collapses and the water molecules pack together more tightly.

However, as the temperature of the water increases further, water molecules in the liquid move and vibrate more rapidly. The movement causes the molecules to spread further apart. As the molecules move further apart, the liquid becomes less dense.

CHEMFILE

Snowflake symmetry

No two snowflakes are exactly alike but all snowflakes have something in common. Every snowflake has six symmetrical arms. This phenomenon is the result of hydrogen bonding. The hydrogen bonding between the water molecules creates a crystal lattice with hexagonal symmetry (Figure 7.3.7). As a result, snowflakes show the same hexagonal symmetry as the crystal lattice.

FIGURE 7.3.7 A snowflake with hexagonal symmetry.

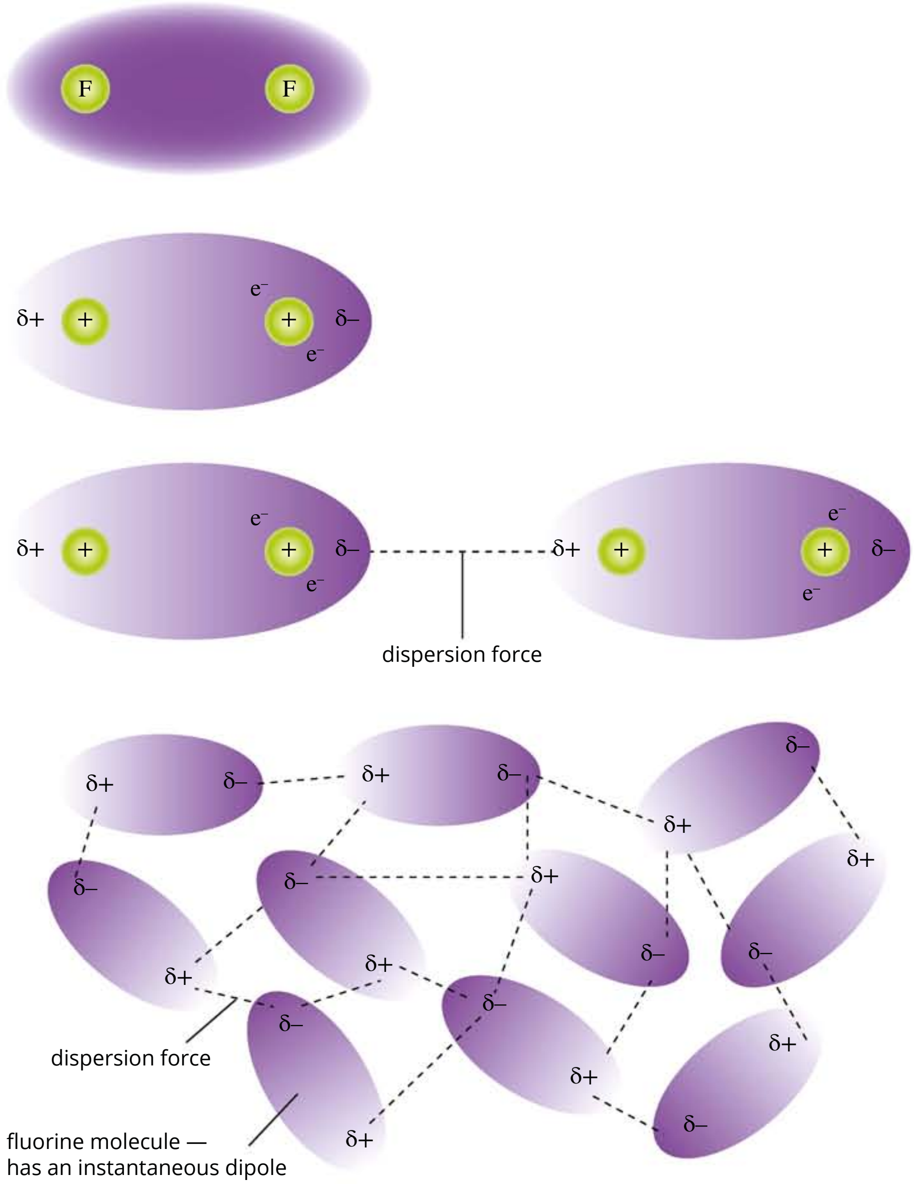
Dispersion forces

Dipole–dipole forces and hydrogen bonding explain the intermolecular forces in polar substances. However, they do not explain the existence of intermolecular forces in non-polar substances.

We know that intermolecular forces are present in non-polar substances because non-polar substances form liquids and solids. Without intermolecular forces, there would be nothing to hold the molecules together and non-polar substances would only exist as gases. However, there are many non-polar compounds that are liquids at room temperature (such as vegetable oil) and even non-polar solids, such as candle wax. In fact, all non-polar substances form liquids or solids if cooled to a low enough temperature. Even hydrogen liquefies below –259°C.

The forces of attraction between non-polar molecules are known as **dispersion forces**. Dispersion forces are caused by **temporary dipoles** in the molecules that are the result of random movement of the electrons surrounding the molecule. These temporary dipoles are also known as **instantaneous dipoles**.

Dispersion forces are always present between molecules, no matter whether they are polar or non-polar as electrons are constantly in motion within atoms (Figure 7.3.8).



(a) In a molecule, the electrons are constantly moving. In the case of a non-polar molecule, such as fluorine, the electrons spend an equal amount of time around each atom.

(b) Occasionally, the electrons gather more closely together at one end of the molecule, causing one end of the molecule to become negative and the other end to become positive. This is known as a temporary dipole.

(c) These temporary dipoles can then induce (create) dipoles in the neighbouring molecules.

(d) The neighbouring molecules then induce dipoles in their neighbours and so on. The temporary dipoles attract each other to create the intermolecular forces known as dispersion forces.

FIGURE 7.3.8 How dispersion forces form within non-polar substances.

Strength of dispersion forces

The strength of dispersion forces increases as the size of the molecule increases. Larger molecules have a larger number of electrons. Therefore, it is easier to produce temporary dipoles in molecules with large numbers of electrons. Since larger molecules have stronger dispersion forces, they have higher melting and boiling points.

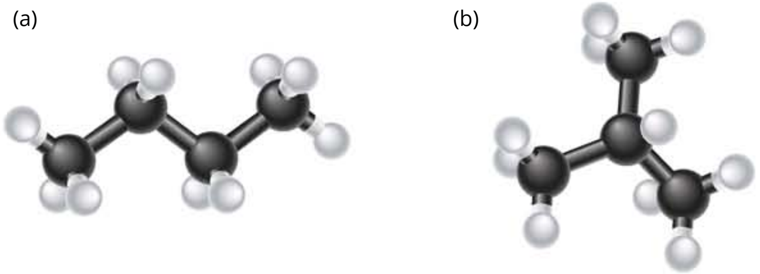
Table 7.3.1 shows the boiling points of the halogens (group 17), which all form non-polar, diatomic molecules. The only forces between their molecules are dispersion forces. You can see that as the molecules increase in size and the dispersion forces become stronger, the boiling points of the substances increase.

TABLE 7.3.1 The effect of dispersion forces and the size of atoms on the boiling points of some molecules

Molecule	Molecular mass	Number of electrons	Boiling point (°C)
Fluorine (F_2)	38.0	18	–188
Chlorine (Cl_2)	70.9	34	–35
Bromine (Br_2)	159.8	70	59
Iodine (I_2)	253.8	106	184

The shape of a molecule also influences the strength of the dispersion forces. Molecules that form long chains will tend to have stronger dispersion forces than more compact molecules with similar numbers of electrons.

For example, butane and methylpropane (Figure 7.3.9) both contain four carbon atoms and 10 hydrogen atoms. The boiling point of butane is –0.5°C, while the boiling point of methylpropane is –11°C. The higher boiling point of butane is because of the different shapes of the two molecules; butane is a long molecule while methylpropane is compact. Being less compact and long means butane has more contact area to interact with its neighbouring molecules to form stronger dispersion forces.



butane, C_4H_{10} (b.p. –0.5°C)   methylpropane, C_4H_{10} (b.p. –11°C)

FIGURE 7.3.9 Butane and methylpropane have different boiling points because their molecules are different shapes.

It is important to remember that dispersion forces occur in both polar and non-polar molecules. In large molecules, the dispersion forces can even dominate over the dipole–dipole forces and hydrogen bonding.

Table 7.3.2 shows the boiling points of three polar molecules: hydrogen chloride (HCl), hydrogen bromide (HBr) and hydrogen iodide (HI). Hydrogen chloride is the most polar of these molecules and therefore has the strongest dipole–dipole forces. However, hydrogen iodide has the highest boiling point because it is a larger molecule and therefore has stronger dispersion forces.

TABLE 7.3.2 Comparison of the boiling points of three polar molecules

Substance	Molecular mass	Number of electrons	Boiling point (°C)
Hydrogen chloride (HCl)	36.5	18	–85.1
Hydrogen bromide (HBr)	81.0	36	–66.8
Hydrogen iodide (HI)	127.9	54	–35.4

The boiling point of hydrogen fluoride (19.5°C) is much higher than any of these other compounds. This is because the hydrogen bonding between hydrogen fluoride molecules is much stronger than both the dispersion forces and the dipole–dipole forces between the other molecules listed in Table 7.3.2.

7.3 Review

SUMMARY

- The melting and boiling points of covalent molecular substances increase as the strength of the intermolecular bonding increases.
- There are three main types of intermolecular bonds: dipole–dipole forces, hydrogen bonds and dispersion forces.
- Dipole–dipole forces are only present between polar molecules and are the result of the attraction between the positive and negative ends of the molecules.
- The polarity of polyatomic molecules depends on the electronegativity of the atoms in the molecule and the symmetry of the molecule.
- The greater the polarity of a molecule, the stronger the dipole–dipole forces.
- Hydrogen bonding occurs between highly polar molecules in which hydrogen atoms are covalently bonded to an oxygen, a nitrogen or a fluorine atom.
- A hydrogen bond is formed between the hydrogen atom in one molecule and lone pairs of electrons in an oxygen, a nitrogen or a fluorine atom in another molecule.
- Hydrogen bonding is the reason why ice floats in liquid water. As a consequence of the hydrogen bonds between the water molecules, ice forms a crystal lattice in which the molecules are spaced further apart than in liquid water. The greater spacing of molecules makes ice less dense then liquid water and so it floats on water.
- Dispersion forces occur between polar and non-polar molecules.
- Dispersion forces are the result of attraction between temporary dipoles that form in molecules.
- Temporary dipoles are due to random fluctuations in the distribution of electrons in molecules.
- Dispersion forces are stronger between larger molecules because it is easier to create temporary dipoles in molecules with a larger number of electrons.
- Hydrogen bonds are the strongest of the three main types of intermolecular forces.

KEY QUESTIONS

1 Identify which of the following substances would contain dipole–dipole forces between the molecules: bromine (Br_2), hydrogen chloride (HCl), methane (CH_4), tetrachloromethane (CCl_4), chloromethane (CH_3Cl).

2 Refer to Figure 7.2.3 on page 162 for electronegativity values and select which one of the following substances would have the strongest dipole–dipole forces between the molecules in the liquid state.

A Fluorine (F_2)
B Carbon monoxide (CO)
C Hydrogen chloride (HCl)
D Methane (CH_4)

3 Consider the following substances. Identify whether the molecules are attracted to one another by dipole–dipole forces or hydrogen bonds.

a NH_3
b $CHCl_3$
c CH_3Cl
d F_2O
e HBr
f H_2S
g HF
h H_2O
i H_2

4 In ice, each water molecule is surrounded, at equal distances, by four other water molecules. In each case, there is an attraction between the positive hydrogen atom on one water molecule and a lone pair associated with the oxygen atom of another water molecule. Draw a diagram to show the arrangement of four water molecules around another water molecule.

5 ‘Cloudy ammonia’ is often used as a cleaning solution in bathrooms. This solution contains ammonia (NH_3) dissolved in water. Draw a diagram to represent hydrogen bonding between a water molecule and an ammonia molecule.

6 Identify the types of bonding in the following substances.

a Methane (CH_4)
b Methanol (CH_3OH)
c Chloromethane (CH_3Cl)
d Methylamine (CH_3NH_2)
e Propane ($CH_3CH_2CH_3$)

Chapter review

KEY TERMS

asymmetrical molecule
dipole
dipole–dipole force
dispersion force
electric dipole
electron density
electronegativity
hydrogen bonding
instantaneous dipole
intermolecular force
lone pair
non-polar
octet rule
polar
polarity
polyatomic molecule
single covalent bond
surface tension
symmetrical molecule
temporary dipole
valence electrons
valence shell electron pair repulsion (VSEPR) theory

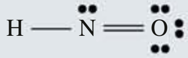
Shapes of molecules

1 Match the molecular formula to the correct molecular shape.

Molecular formula	**Molecular shape**
Phosphorus trichloride (PCl_3)	Tetrahedral
Hypochlorous acid (HOCl)	Linear
Trichloromethane ($CHCl_3$)	V-shaped
Hydrogen fluoride (HF)	Pyramidal

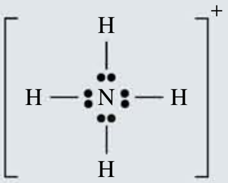
2 Examine the following valence structure and use the VSEPR theory to predict the shape of the molecule.

3 How many electrons are involved in the bonding in a molecule of beryllium fluoride?

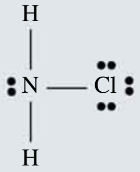


4 All of the following molecules have four pairs of electrons around the central atom. Classify the molecular shapes as tetrahedral, pyramidal or V-shaped.

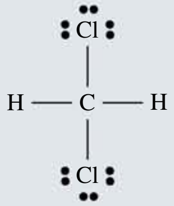
a



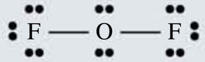
b



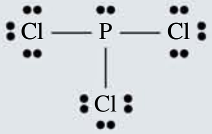
c



d



e



Properties of covalent molecular substances

5 Are the following molecules polar or non-polar? Draw structural formulas to help you decide.

a CS_2
b Cl2O
c SiH_4
d CH_3Cl
e CH_3CH_3
f CCl_4

6 Use the electronegativities from Figure 7.2.3 on page 162 to determine which of the following molecules contains the most polar bond.

a CO_2
b H_2O
c H_2
d H_2S
e NH_3

7 For each of the molecules listed in Question 6, state whether they are polar or non-polar.

8 Order the following covalent bonds from most polar to least polar.

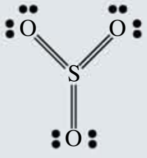
Si–O, N–O, F–F, H–Br, O–Cl

Types of intermolecular forces

9 For each of the following structures, state whether the:

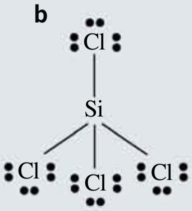
i molecule is polar or non-polar
ii strongest intermolecular forces of attraction between molecules of each type would be dispersion forces, hydrogen bonding or dipole–dipole forces.

a



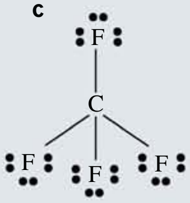
SO_3

b



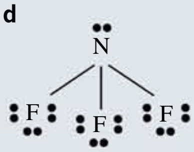
$SiCl_4$

c



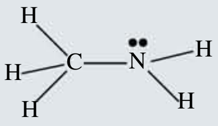
CF_4

d



NF_3

e



CH_3NH_2

10 Consider solid samples of the following compounds. In which cases will the only forces between molecules in the samples be dispersion forces? (You should first ascertain whether molecules of these compounds are polar or non-polar. You can do this by drawing a structural formula for each one.)

A Tetrachloromethane (CCl_4)
B Sulfur dioxide (SO_2)
C Carbon dioxide (CO_2)
D Hydrogen sulfide (H_2S)

11 The melting points of four halogens are given in Table 7.4.1. Describe and explain the trend in melting points of these elements.

TABLE 7.4.1 Melting points of four halogens

Halogen	Melting point (°C)
Fluorine (F_2)	–220
Chlorine (Cl_2)	–101
Bromine (Br_2)	–7
Iodine (I_2)	114

12 Consider the two compounds OF_2 and CF_4. OF_2 has a boiling point of –145°C and CF_4 has a boiling point of –128°C. Between molecules of which compound would the intermolecular forces of attraction be greater? Explain your answer.

13 The mass of a hydrogen fluoride molecule is similar to the mass of a neon atom. However, the boiling points of these substances are very different. The boiling point of hydrogen fluoride is 19.5°C whereas that of neon is −246°C. Explain the difference in this property of the two substances.

14 At room temperature, CCl_4 is a liquid whereas CH_4 is a gas.

a Which substance has the stronger intermolecular attractions?
b Explain the difference in the strengths of the intermolecular attractions.

15 Fluorine (F_2) is a gas at room temperature whereas iodine (I_2) is a solid. With respect to intermolecular forces, what factor best explains this difference?

16 Explain the difference between a permanent dipole and a temporary dipole. Your explanation should describe how the dipoles are formed and the type of intermolecular bonding that results.

Connecting the main ideas

17 Consider the following list of molecules:

N_2, Cl_2, O_2, NH_3, HCl, CH_4, H_2O, CO_2, CCl_4, $CHCl_3$

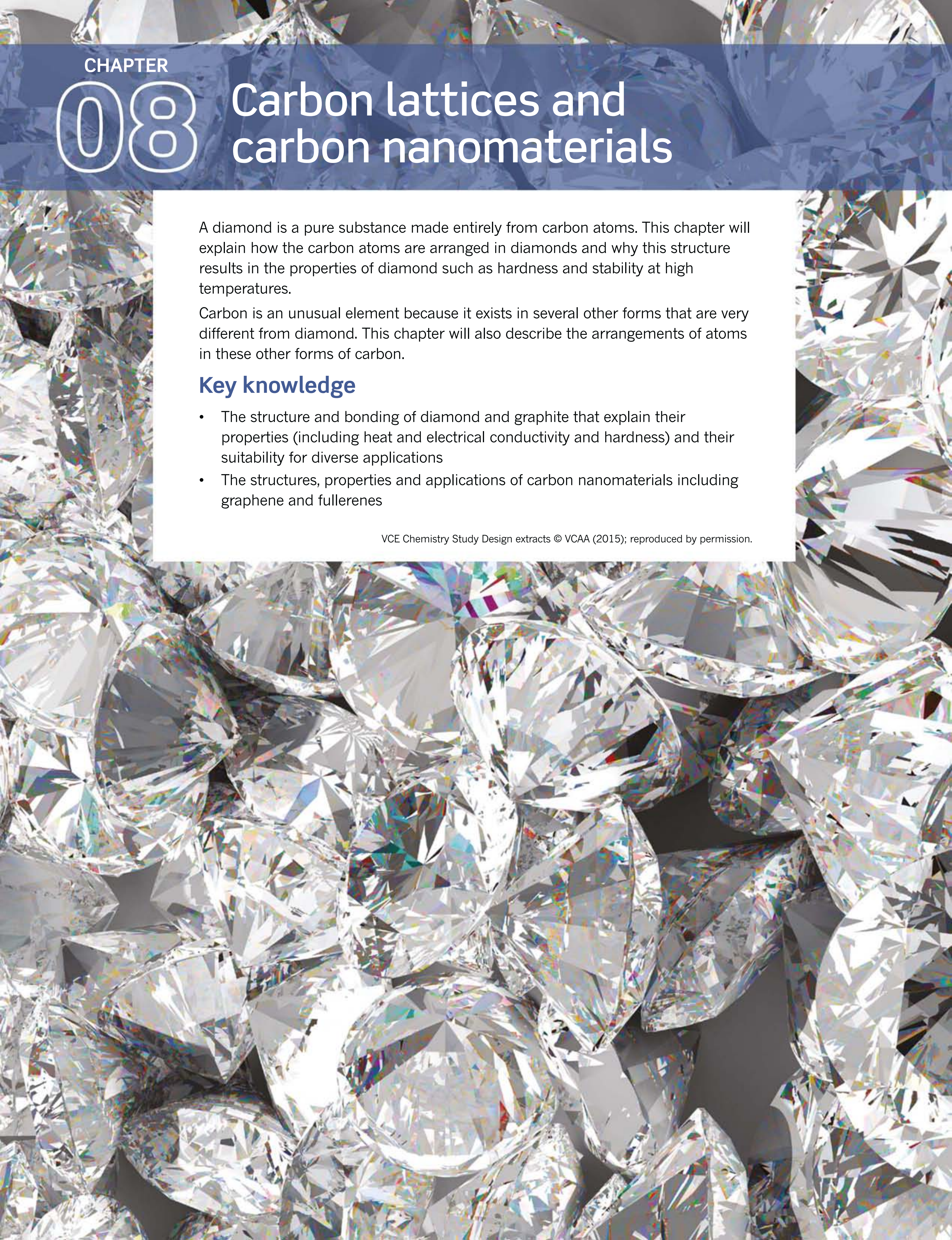
a Draw a valence structure for each of the following from the list, showing bonding and non-bonding electron pairs.
  i A molecule that contains one triple bond
  ii A molecule that contains one double bond
  iii A molecule that contains two double bonds
b From the list, which substances contain:
  i polar molecules?
  ii symmetrical molecules?
  Iii molecules with hydrogen bonding between them?

18 Water is a polar molecule. Explain how this fact shows that water is not a linear molecule.

19 Explain why covalent molecular substances generally have lower melting and boiling points than ionic and metallic substances.

CHAPTER

08 Carbon lattices and carbon nanomaterials



A diamond is a pure substance made entirely from carbon atoms. This chapter will explain how the carbon atoms are arranged in diamonds and why this structure results in the properties of diamond such as hardness and stability at high temperatures.

Carbon is an unusual element because it exists in several other forms that are very different from diamond. This chapter will also describe the arrangements of atoms in these other forms of carbon.

Key knowledge

- The structure and bonding of diamond and graphite that explain their properties (including heat and electrical conductivity and hardness) and their suitability for diverse applications
- The structures, properties and applications of carbon nanomaterials including graphene and fullerenes

8.1 Carbon lattices

Diamonds are highly valued in our society. Diamonds are a form of pure carbon, but they are not the only form that carbon can take. **Graphite**, charcoal, **graphene** and **fullerenes** are also made entirely from carbon but their properties are very different from those of diamond. Scientists have found many exciting uses for these other forms of carbon. As the properties of these forms of carbon are quite different, it is not surprising that their chemical structures are also different.

ABUNDANCE AND PROPERTIES OF CARBON

Carbon is a fascinating element for many reasons. Carbon:

- is a vital component of all living systems
- is the 11th most abundant element in the universe
- has three isotopes: ^{12}C (98.9% abundant), ^{13}C (1.1% abundant) and ^{14}C (traces)
- has one of the highest melting points of any element. It undergoes **sublimation**, changing from a solid state directly to a gas state at temperatures above 3550°C
- is a non-metal, but a number of forms can conduct electricity
- can form single, double and triple covalent bonds with several other elements
- can form large molecules and lattice structures by bonding to itself.

ALLOTROPES

Some elements can exist with their atoms in several different structural arrangements called **allotropes**, that give them different physical forms. In different allotropes, the atoms are bonded to each other in different, specific ways. This gives them significantly different properties from other allotropes of the same element.

Oxygen forms allotropes. Oxygen gas consists of diatomic molecules with the formula O_2. Each oxygen atom in this arrangement is bound to one other oxygen atom. Ozone is another molecule containing only oxygen. Ozone molecules have the formula O_3 and consist of a central oxygen atom bound to two other oxygen atoms. Figure 8.1.1 shows the structure of these two molecules. As both contain only oxygen atoms, they are both allotropes of oxygen. The rest of this section will focus on the different allotropes of carbon.

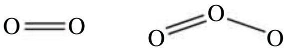


FIGURE 8.1.1 Oxygen and ozone are two molecules that contain only oxygen atoms.

FIGURE 8.1.2 Diamond is the hardest naturally occurring substance.

Allotropes are different forms of the same element.

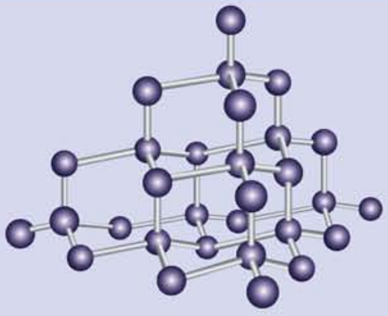
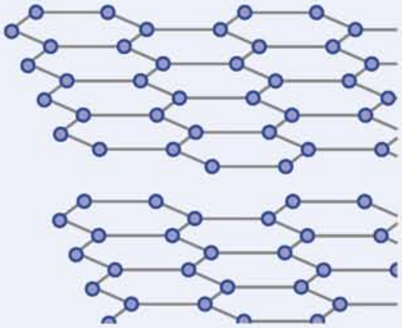
ALLOTROPES OF CARBON

Diamonds (Figure 8.1.2) might be a 'girl's best friend' but it is unlikely that graphite (Figure 8.1.3) will ever be held in the same esteem. Both of these minerals are made of the same single element—carbon. Graphene and fullerenes are new materials that are also allotropes of carbon.

Table 8.1.1 summarises some information about the structure, properties and uses of the three most common allotropes of carbon: diamond, graphite and amorphous carbon.

FIGURE 8.1.3 Natural graphite is soft and black.

TABLE 8.1.1 Comparison of properties of some of the allotropes of carbon

Allotrope	Structure	Properties	Uses
Diamond	 Covalent network lattice, each carbon surrounded by four other carbon atoms in a tetrahedral arrangement	• Very hard • Sublimes • Non-conductive • Brittle	• Jewellery • Cutting tools • Drills
Graphite	 Covalent layer lattice, each carbon bonded to three other carbons, one delocalised electron per carbon atom	• Conductive • Slippery • Soft • Greasy material	• Lubricant • Pencils • Electrodes • Reinforcing fibres
Amorphous carbon	Irregular structure of carbon atoms. Many varieties exist with many different, non-continuous packing arrangements	• Conductive • Non-crystalline • Cheap	• Printing ink • Carbon black filler • Activated charcoal • Photocopying

Diamond

Diamond is the hardest naturally occurring substance known.

Diamond does not contain small, discrete (individual) molecules. Instead, the carbon atoms bond to each other to form a continuous three-dimensional structure called a **covalent network lattice**. There are no weak intermolecular forces present, only strong covalent bonds. This is what gives diamond its strength.

Diamond is made up of carbon atoms that bond with four neighbouring carbon atoms forming a covalent network lattice. This structure makes diamond extremely hard.

In general, substances that have a network lattice structure have very high melting points or decomposition temperatures. They are also very hard because the atoms are held firmly in fixed positions in the lattice.

As you saw in Chapter 7, when an atom has four electron pairs in its outer shell, the electron pairs position themselves as far away from each other as possible in a tetrahedral shape. In the covalent network lattice for diamond shown in Figure 8.1.4, you can also see that individual atoms within diamond form single covalent bonds to four other carbon atoms in a tetrahedral arrangement.

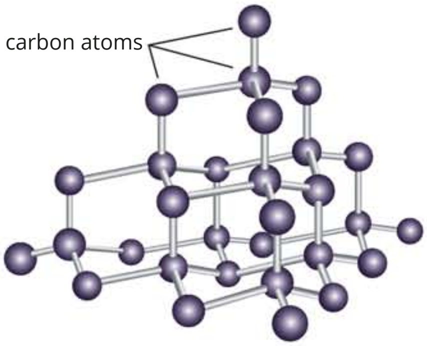


FIGURE 8.1.4 The structure of diamond showing each carbon atom with four single covalent bonds to neighbouring atoms.

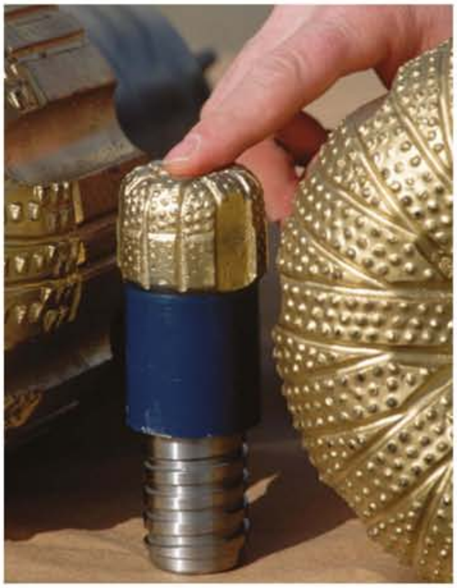


FIGURE 8.1.5 Diamond-tipped drills used to drill through rock in the fracking industry.

The structure of diamond is directly related to its properties.

- Single covalent bonds between carbon atoms are strong bonds. The entire structure of a diamond consists of a continuous network of these bonds, making diamond very hard and rigid.
- There are no small molecules in diamond, so there are no weak forces between the atoms. There are only strong covalent bonds between carbon atoms and this makes the sublimation point very high (about 3500°C).
- The rigidity means that diamonds are brittle and break rather than bend.
- Diamond does not conduct electricity because it does not contain any charged particles that are free to move.
- Because the atoms in diamonds are held together very strongly, the thermal conductivity is extremely high. It is five times greater than that of copper, leading to some specialty electronic uses where diamond is used to transfer heat away from some important electrical components.

The crystalline appearance of diamonds and their high refractive index make them sparkle and has made them extremely popular as jewellery, but the hardness of diamond also lends itself to industrial uses. Many industrial cutting and drilling tools for working with tough materials are diamond tipped. The drill tips in Figure 8.1.5 are used to drill through rock in the fracking industry. They contain small pieces of diamond that improve the hardness and durability of the tool.

CHEMFILE

Impact diamonds

'We are speaking about trillions of carats', trumpeted the 2012 headline from the British *Daily Mail*. It was in reference to a 100 km meteorite crater, the Popigai Crater, in Russia that could supply world markets with diamonds for 3000 years. The now closed Mirny mine, shown in Figure 8.1.6, is also in Russia. This open-cut mine is over 500 metres deep and has yielded diamonds worth more than $20 billion since 1951.

It is thought that the impact of a large meteorite created enough heat and pressure in the Popigai Crater to make diamonds. Russian scientists are reported to have known of this deposit since 1971, but kept details hidden until supplies from other sources began to run out. Diamonds formed from a meteorite strike, like those in Figure 8.1.7, are referred to as 'impact diamonds'. They can be almost as large as a 20-cent coin, and are prized for their extreme hardness.

FIGURE 8.1.6 The Mirny diamond mine is over 500 metres deep.

FIGURE 8.1.7 High-quality 'impact diamonds' can be almost the size of a 20-cent coin.

Graphite

Graphite is a very different form of carbon. As you can see in Figure 8.1.8, the carbon atoms in graphite are in layers. There are strong covalent bonds between the carbon atoms in each layer. However, there are weak dispersion forces between the layers. As a consequence, it is hard in one direction but quite slippery and soft in another direction. The structure of graphite is referred to as a **covalent layer lattice**.

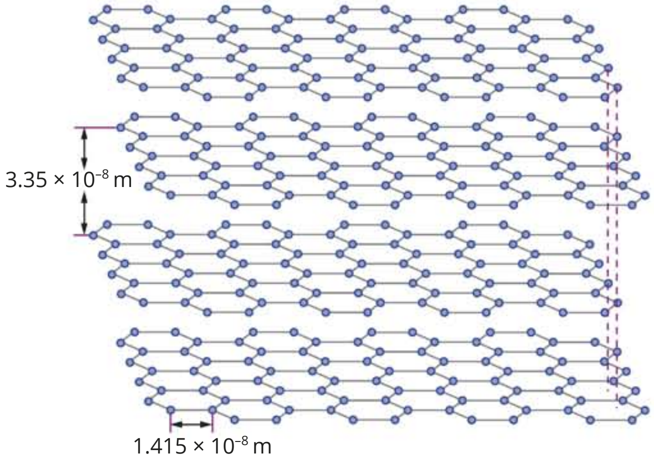


FIGURE 8.1.8 Graphite has a covalent layer lattice structure. The carbon atoms within each layer are covalently bonded to each other. Weak dispersion forces exist between the layers.

The covalent layer lattice structure of graphite also explains some of its other properties.

- The strong covalent bonds between the atoms in each layer explain graphite's resistance to heat. Graphite sublimes at a temperature of about 3600°C.
- Each carbon atom is bonded to three other carbon atoms. The fourth valence electron from each atom is able to move within the layer. The electrical conductivity of graphite is due to these delocalised electrons.

The conductivity of graphite makes it suitable for applications such as battery electrodes where conductivity is required but a metal is not suitable.

In graphite, each carbon atom is covalently bonded to three other carbon atoms. The layered network structure contains delocalised electrons. Bonds within the layers are strong but bonds between layers are weak dispersion forces.

CHEMFILE

Black-lead pencils

In 1564, a very pure deposit of graphite was discovered in England. The graphite was so stable that it could be cut into thin, square sticks that could be used for writing. String was wrapped around the graphite to make the first pencils. Later the string was replaced with wood (Figure 8.1.10).

The pencils were so effective that during the Napoleonic Wars, the English were considered to have a technological advantage, because their pencil-written communications were far more effective than the French equivalents. Napoleon commissioned a French inventor, Nicholas-Jacques Conte, to develop an alternative to pure graphite. The mixtures of clay and powdered graphite that he designed are the basis for the 'lead' in modern pencils.

FIGURE 8.1.10 An early pencil that consisted of a strip of graphite placed between pieces of wood.

Graphite can also be used as a lubricant. The weak dispersion forces between layers allow these layers to slide over each other and to reduce the friction between moving parts, such as in locks or machinery.

Graphite is also used as an additive to improve the properties of rubber products and it can be woven into a fibre. This helps to reinforce plastics. Figure 8.1.9 shows spun graphite fibre, which can be used to make strong composite materials such as those used in tennis racquets, fishing rods and racing car shells.

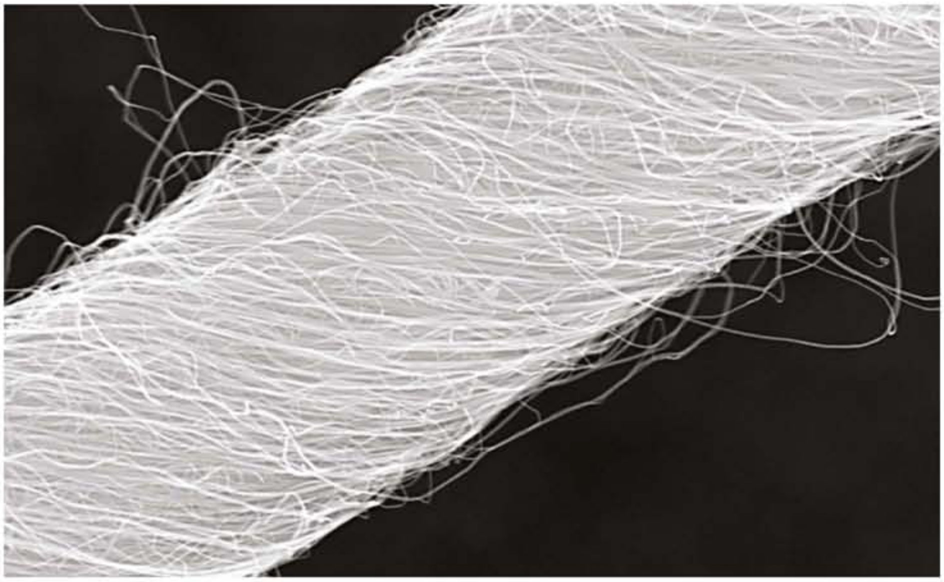


FIGURE 8.1.9 Graphite fibre can be used to reinforce plastics.

Amorphous forms of carbon

Charcoal (Figure 8.1.11) and carbon black (Figure 8.1.12) are examples of **amorphous** carbon that has no consistent structure. It contains irregularly packed, tiny crystals of graphite and other non-uniform arrangements. Lumps of charcoal are produced for use as a fuel, while carbon black is used to make printer toner ink.

FIGURE 8.1.11 Lumps of charcoal are produced for use as a fuel.

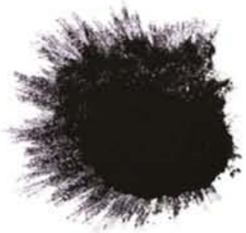


FIGURE 8.1.12 Carbon black is used in printer toner ink.

Amorphous carbon can be formed from the **combustion** of wood and other plant matter when there is a limited supply of air. There are several other types of amorphous carbon, including soot, which can be seen in Figure 8.1.13, being emitted from an industrial chimney. The distinctions between the different forms of amorphous carbon are blurred.

FIGURE 8.1.13 Soot is emitted from an industrial chimney.

Each form of amorphous carbon has its uses and some have been used by society for centuries. Since the Middle Ages it has been common to produce charcoal in ovens. Figure 8.1.14 shows a number of beehive-shaped ovens that were used to produce charcoal from timber. These ovens were built between 1876 and 1879.

FIGURE 8.1.14 These ovens in Nevada, USA, were built between 1876 to 1879 to make charcoal.

Uses of carbon black

Carbon black is a refined type of amorphous carbon in which the particle size is more uniform. Most carbon black is used to reinforce rubber products such as tyres and hoses, causing their black appearance. The surface interaction between the fine carbon particles and the rubber molecules increases the strength and toughness of the product.

Many printer and photocopier toners contain carbon black particles mixed with a binder polymer and other additives. More than 9 million tonnes of carbon black is used annually worldwide.

Uses of activated charcoal

Charcoal can be 'activated' by heating it to high temperatures in the presence of an inert gas. Activated charcoal particles are so porous that it is estimated that a 1-gram sample has a surface area similar to that of an Australian Rules football oval. Figure 8.1.15 shows a microscope image of activated charcoal.

FIGURE 8.1.15 A microscope image of activated charcoal shows that it contains many pores and hollows.

Activated charcoal can adsorb impurities onto its porous surface. The impurities are trapped in the pores of the activated charcoal particles by weak attractive forces, such as dispersion forces. This makes activated charcoal useful as:

- water filters
- 'odour-eater' inserts in shoes
- a treatment for a drug overdose. Activated charcoal is pumped into the victim's stomach to adsorb the harmful drug molecules.

CHEMFILE

Production of biochar

Most scientists agree that rising levels of carbon dioxide in the atmosphere, which are a result of human activities, are causing global warming. One area of research at the CSIRO to help combat rising carbon dioxide levels is the production of **biochar**.

Biochar is a high-carbon, porous and fine-grained residue produced by placing biomass (plant and forest waste) in a trench and covering it with soil. The biomass is allowed to smoulder, burning very slowly in the absence of oxygen. The product of this process is carbon and not carbon dioxide.

Biochar can increase the fertility of soils and agricultural production, using waste that would otherwise have become carbon dioxide. Figure 8.1.16 shows farmers adding biochar to the soil in a field.

FIGURE 8.1.16 Biochar added to soil improves the soil by supplying carbon and trapping nutrients.

8.1 Review

SUMMARY

- Carbon can be found in the Earth's crust in the form of diamond, graphite or charcoal. The structures and properties of these allotropes are very different.
- In diamond, each carbon atom is covalently bonded to another four carbon atoms in a tetrahedral shape, forming a covalent network lattice structure. Diamond sublimes at a high temperature, is extremely hard and has a sparkling, crystalline appearance.
- In graphite, each carbon atom is covalently bonded to three other carbon atoms. The layered network structure contains delocalised electrons. Bonds within the layers are strong but bonds between layers are weak dispersion forces. Graphite is slippery, conducts electricity and sublimes at a high temperature.
- Amorphous carbon products, such as carbon black, soot and charcoal, are formed from the combustion of plant and animal matter in a limited supply of air. Amorphous carbon has no consistent structure.

KEY QUESTIONS

1 Why can carbon form so many different compounds?

2 **a** What is meant by the word *sublime*?

b Explain why diamond and graphite only sublime at temperatures over 3500°C.

3 Explain the following properties of diamond and graphite in terms of their respective structures.

a Hardness or softness

b Ability or inability to conduct electricity

4 Explain the following in terms of the structures of graphite and diamond.

a Graphite is used as a lubricant.

b Diamond is often used as an edge on saws and a tip on drills.

8.2 Carbon nanomaterials

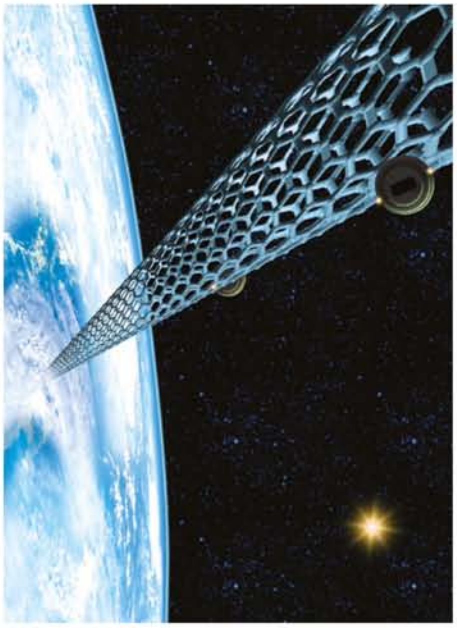


FIGURE 8.2.1 Artist's impression of a space elevator made of a carbon nanotube.

Imagine an elevator with a difference, an elevator into space. Rockets are costly and dangerous. Why not take an elevator ride instead? While this concept might sound like science fiction, scientists are considering this idea very seriously. Japanese company Obayashi has announced that they will have a space elevator up and running by the year 2050. The elevator would reach 96 000 km into space and use robotic cars powered by magnetic linear motors. The concept is only possible because of the properties of a recently discovered allotrope of carbon—carbon **nanotubes**. Figure 8.2.1 is an artist's impression of a space elevator, made of a carbon nanotube.

Diamond, graphite and amorphous carbon have long been recognised as allotropes of carbon. However, since the 1970s, scientists have discovered how to make a new range of carbon allotropes that are examples of **nanomaterials**.

You will remember from Chapter 1 that nanomaterials are particularly interesting because they have a very high surface area to volume ratio, leading to some unique or enhanced properties.

Fullerenes

In the late 1970s, while working at the Australian National University in Canberra, Dr Bill Burch discovered a new allotrope of carbon. This allotrope was made up of molecules containing a roughly spherical group of carbon atoms arranged in a series of pentagons and hexagons, similar to the shape of a soccer ball, as you can see in Figure 8.2.2.

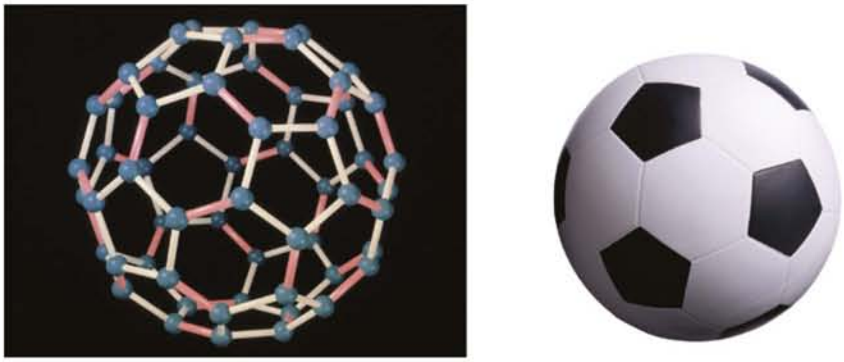


FIGURE 8.2.2 The structure of a fullerene has a similar pattern to the surface of some soccer balls.

Fullerenes are an allotrope of carbon where the atoms are arranged in a series of pentagons and hexagons.

FIGURE 8.2.3 The Biosphere in Montreal, Canada, is a museum designed by Buckminster Fuller.

Scientists have since found further variations of this molecule. These molecules have similar structures to the geodesic designs of architect Richard Buckminster 'Bucky' Fuller. They are called fullerenes, although they are more commonly referred to as **buckyballs**. Figure 8.2.3 shows the Biosphere in Montreal, Canada—a museum designed by Buckminster Fuller.

Fullerenes have three covalent bonds to each carbon atom and in some ways appear to be similar to graphite. This leaves delocalised electrons in the structure and the possibility of electrical conductivity. Although fullerenes were initially just a curiosity, scientists predict that they have significant potential in a number of fields such as composite materials and **photovoltaic cells** (solar panels). The most stable fullerene molecule involves 60 carbon atoms bonded into an approximately spherical shape that is known as buckminsterfullerene or C_{60}.

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Fullerenes in flexible photovoltaic cells

Traditional photovoltaic cells (the solar panels you see on many rooftops) are made from highly refined and purified silicon crystals. Manufacturing these crystals is complex and the cells produced are rigid and brittle.

Research into fullerenes has led to alternative types of photovoltaic cells, known as polymer solar cells. Polymer solar cells (Figure 8.2.4) use alternate layers of fullerene molecules instead of silicon. The cell produced is lighter than conventional cells and offers the advantage of being flexible. A flexible cell could match the curved shape of a caravan roof or the cabin of a boat. The initial problem with these cells was their low efficiency. Research into fullerenes and other aspects of the cells continues to improve their efficiency.

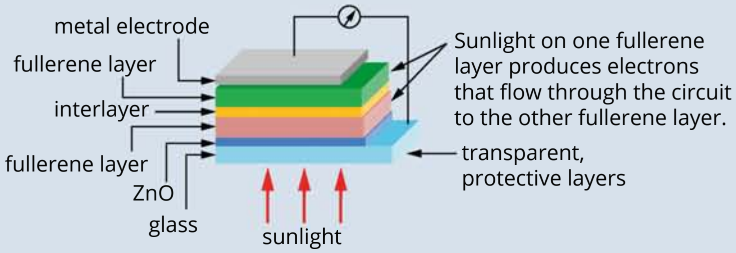


FIGURE 8.2.4 Polymer solar cells are constructed from transparent covering layers and alternate layers of fullerenes.

Graphene and nanotubes

Two other allotropes of carbon that are being heavily researched are nanotubes, which are regarded as being part of the fullerene family, and graphene.

Graphene

You have seen that graphite has a layered structure. Graphene is best described as a single layer of graphite (Figure 8.2.5). Graphene is a single layer sheet with the same arrangement as those stacked in graphite. It is a very new material and was first isolated in 2004.

Graphite is soft, due to the weak dispersion forces between its layers. Graphene is only a single layer and retains the electrical conductivity of graphite but it is an extremely strong and tough material.

Graphene has many potential uses. Graphene could:

- replace silicon as the basis for computer chips and circuits due to its high electrical conductivity
- be used in desalination plants. Water under pressure can pass through the thin layer but dissolved impurities cannot
- be used to construct electrodes where it is an advantage for an electrode to be a non-metal
- be used in organic photovoltaic cells
- be used to reinforce composite materials because of its strength.

An interesting feature of graphene is that, because it is a single layer, every carbon atom is available for reaction from two sides at any instant during a chemical reaction.

FIGURE 8.2.5 Graphene is a single layer sheet with the same arrangement as those stacked in graphite.

Nanotubes

'Nanotubes' are closely related to graphene. They are called nanotubes because they have a long, hollow structure with walls formed from graphene. The diameter of these cylinders is very small, around 1 nanometre (10^{-9} metre) wide, while they can be millions of times longer. They can be capped on the end of each cylinder by a half fullerene molecule as shown in Figure 8.2.6.

Nanotubes can be single-walled or multi-walled. A multi-walled nanotube has smaller tubes sitting inside larger tubes.

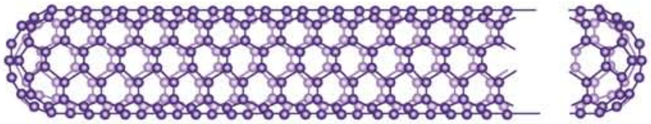


FIGURE 8.2.6 A carbon nanotube can be regarded as a sheet of graphene rolled into a cylinder and capped on the ends by half a fullerene molecule.

Scientists are interested in nanotubes because of their:

- unique strength
- electrical conductivity
- thermal conductivity
- strong forces of attraction to each other.

Nanotubes hold great promise in fields such as optics, nanotechnology and electronics. Their extraordinary strength and thermal and electrical conductivity suggest they may be useful as additives in various structural materials.

POTENTIAL OF CARBON NANOMATERIALS

Carbon nanomaterials offer huge gains in performance and properties over some other materials in current use and have a broad range of potential applications. The carbon–carbon bonds in these structures are very strong and there are no weak points in a single layer of graphene or a nanotube.

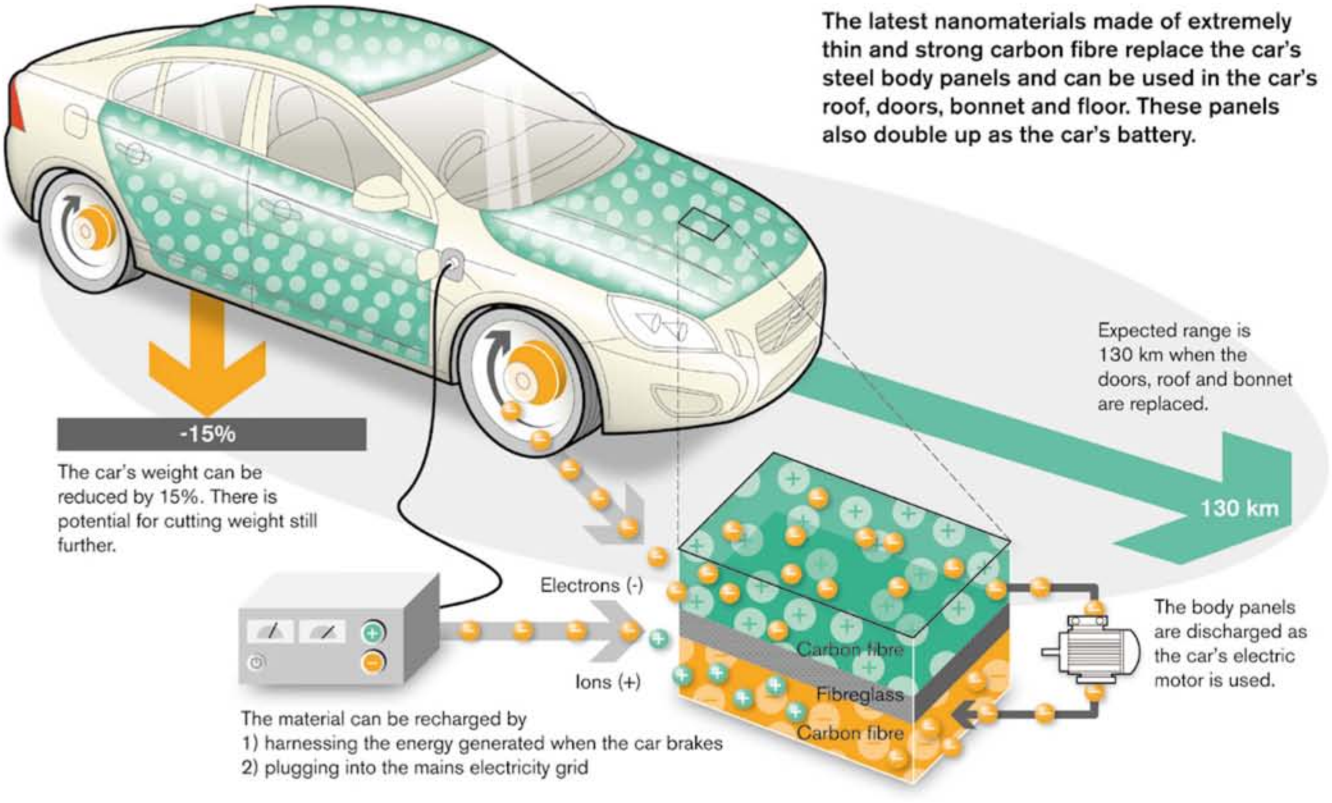
Carbon nanotubes are:

- up to 300 times stronger than steel. Rope made from nanotubes with a diameter of 1 cm could support a weight of over 1000 tonnes. Nanotubes are already being used in high-performance sporting equipment
- better conductors of electricity than silver. Since nanotubes are essentially 'wires' that are much narrower in diameter than metal wire, they offer the possibility for extreme miniaturisation of electrical circuits
- better thermal conductors than diamond. Nanotubes could be used to transfer heat away from electrical components
- stronger than Kevlar fibres. Stain-resistant nanofabrics that never require washing are already available. You could even carry water in the pockets of a vest made from this material
- capable of adsorbing more gas or impurities than activated charcoal.

Perhaps the best way to highlight the potential of nanomaterials is with two exciting examples.

Example 1. Volvo concept car

Volvo has embarked on a radical new design for an electric car that aims to harness the properties of nanomaterials. As shown in Figure 8.2.7, most of the steel in the car has been replaced with carbon nanotube sheets. These sheets have the advantage of lightweight strength but they can also serve as a giant battery for the car. Fullerenes are incorporated in the carbon sheets, allowing them to act as photovoltaic cells, supplying the energy needed to recharge and power the car.


The latest nanomaterials made of extremely thin and strong carbon fibre replace the car's steel body panels and can be used in the car's roof, doors, bonnet and floor. These panels also double up as the car's battery.

Expected range is 130 km when the doors, roof and bonnet are replaced.

The car's weight can be reduced by 15%. There is potential for cutting weight still further.

The body panels are discharged as the car's electric motor is used.

The material can be recharged by
1) harnessing the energy generated when the car brakes
2) plugging into the mains electricity grid

FIGURE 8.2.7 The Volvo concept car.

Example 2. Solar aircraft

In 2015, the Swiss-designed plane Solar Impulse-2 (Figure 8.2.8) set off to become the first solar-powered aeroplane to circumnavigate the globe. The plane is powered by solar cells and the lightweight strength for the structure comes from an assortment of carbon nanomaterials and composites.

FIGURE 8.2.8 The Solar Impulse-2.

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Nanofabrics

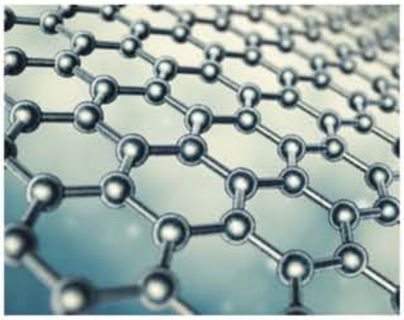
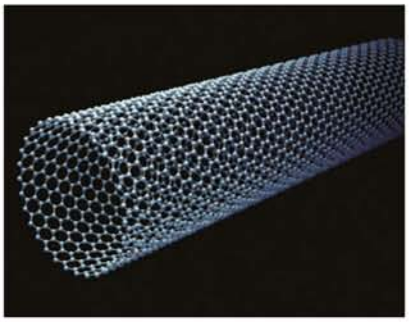
Workers at textile manufacturer Garrison Bespoke received an unusual offer at work one day—they were given a hunting knife and invited to stab their boss! However, the boss remained unscathed after several attempted stabbings because of the wonder suit he was wearing. Garrison Bespoke manufactures hi-tech protective clothing from materials such as carbon nanotube fibres. The suit outperforms regular Kevlar, yet is only half the weight and thickness. The fabric is so tough it has to be cut with a bandsaw.

8.2 Review

SUMMARY

- Over the past 40 years, scientists have developed a range of new carbon allotropes called fullerenes.
- Fullerenes are examples of nanomaterials and are of interest to scientists because of the enhanced properties that their high surface area to volume ratio offers. Their high tensile strength and high electrical and heat conductivity are of particular interest.
- Spherical fullerenes are known as buckyballs. Fullerenes can also be tubular, as in nanotubes. Graphene is a single-layered form of graphite. In all these allotropic forms, the carbon atoms are bonded to three other carbon atoms as shown in Table 8.2.1.
- Potential applications of fullerenes include fibres and fabrics, electrical circuits, photovoltaic cells and filtration systems.

TABLE 8.2.1 Types of carbon nanomaterials

Buckyball	Graphene	Nanotube
		

KEY QUESTIONS

1 Describe how the structures and properties of fullerenes are both similar to and different from those of graphite.

2 Describe the bonding within a C_{60} buckyball.

3 Describe the bonding within a graphene sheet.

4 Explain why carbon nanotubes are being considered for use in the construction of a space elevator.

Chapter review

KEY TERMS

allotrope
amorphous
biochar
buckyball
combustion
covalent layer lattice
covalent network lattice
diamond
fullerene
graphene
graphite
nanomaterial
nanotube
photovoltaic cell
sublimation

Carbon lattices

1. ‘Carbon forms several allotropes.’ Explain the meaning of this statement.
2. Graphite has unusual properties. It sublimes at a high temperature, it conducts electricity and it can be used as a lubricant. Use a diagram to explain why graphite has these properties.
3. Charcoal is often used by chemists to decolourise solutions. Explain how the structure of charcoal removes compounds from solution.
4. Why does diamond have such a high sublimation point?
5. The structures of methane and diamond are shown in Figure 8.3.1. Each carbon atom in methane (CH_4) has a tetrahedral arrangement of atoms around it. A carbon atom in diamond also has a tetrahedral arrangement. However, the two substances have very different properties.

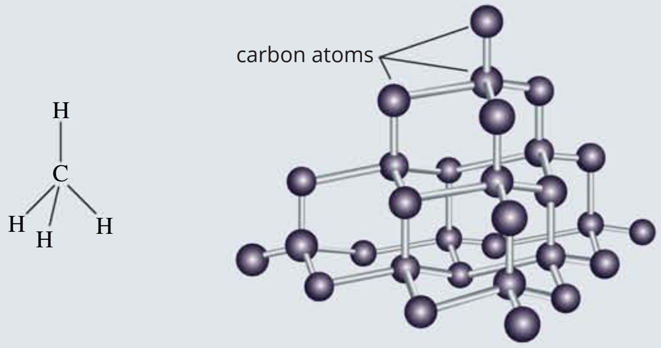


FIGURE 8.3.1 Structures of methane and diamond.

   a. Describe all of the types of bonding that would be present in each substance.
   b. Use the types of bonding present in each substance to explain the different properties you would expect each to have.

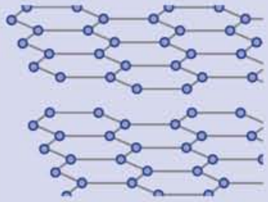
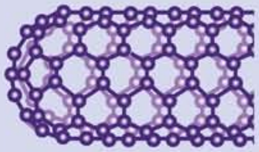
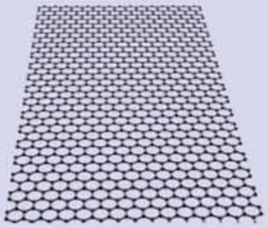
Carbon nanomaterials

6. Describe the geometry of the bonds around carbon atoms in diamond and graphene.
7. In terms of the bonding between the carbon atoms, explain why graphene is so strong.
8. Describe the structure of a carbon nanotube.

Connecting the main ideas

9 Copy and complete Table 8.3.1.

TABLE 8.3.1

				
Allotrope name				
Bonding feature				
Properties				

10 Compare and contrast the structure and properties of graphite and graphene.

11 Figure 8.3.2 shows an experiment to determine the electrical conductivity of diamond.

FIGURE 8.3.2 Electrical conductivity testing equipment.

a Explain briefly how this test works and what is required for a substance to conduct electricity.

b Classify each allotrope of carbon as either conductive or non-conductive of electricity.

CHAPTER

09 Organic compounds

At the end of this chapter, you will appreciate the significance of the compounds that are formed between carbon, hydrogen and other elements. Carbon is only the eleventh most abundant element in the universe, yet it forms more compounds than all other elements except hydrogen. Carbon is present in living things and many non-living things.

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 telephone to the pasta that you may eat for dinner tonight.

In this chapter, you will start to explore some of the many families of carbon compounds. However, you will only scratch the surface of a varied and fascinating area of chemistry.

Key knowledge

- The origin of crude oil and its use as a source of hydrocarbon raw materials
- The grouping of hydrocarbon compounds into families (alkanes, alkenes, alkynes, alcohols, carboxylic acids and non-branched esters) according to similarities in their physical and chemical properties, including general formulas
- Representing these families of organic compounds (structural formulas, condensed formulas, Lewis structures)
- Naming according to IUPAC systematic nomenclature (limited to non-cyclic compounds up to C10, and structural isomers up to C7) and uses based upon properties
- Determination of empirical and molecular formulas of organic compounds from percentage composition by mass and molar mass

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9.1 Crude oil as a source of raw materials

Carbon forms more compounds than all other elements combined. This is because:

- carbon has four valence electrons so carbon can potentially form covalent bonds with four different atoms
- carbon atoms can form strong covalent bonds with other carbon atoms
- the covalent bonds formed can be a combination of 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 produced by the effects of heat and pressure on dead animals, plants and microorganisms trapped in the Earth's crust, buried beneath sediment formed over millions of years. The branch of chemistry that studies the chemistry of carbon compounds is known as organic chemistry. This section focuses on crude oil as a source of carbon compounds and on compounds formed between carbon and hydrogen: the **hydrocarbons**.

CHEMFILE

The original idea of organic chemistry

The term 'organic chemistry' was introduced by the chemist Jöns Jacob Berzelius, who believed that a wide range of carbon compounds only occurred in living systems. Friedrich Wohler disproved this idea in 1828 when he produced urea ($CO(NH_2)_2$) in the laboratory.

CHEMFILE

Carbon-containing inorganic compounds

Organic chemistry studies the chemistry of carbon-containing compounds. However, some carbon-containing compounds such as carbon monoxide (CO), carbon dioxide (CO_2), carbonic acid (H_2CO_3) and carbonates (e.g. Na_2CO_3) are considered to be inorganic compounds. This historical distinction goes back to Berzelius who defined inorganic compounds as originating from non-living systems.

CRUDE OIL

The amount of carbon on Earth is essentially fixed, with most of the carbon atoms on Earth having been here for billions of years. It is the location of these carbon atoms that changes over time. Whether they are currently part of a sunflower seed, a molecule of carbon dioxide, a human being or a plastic chair, you can be certain that the carbon atoms have been in a different compound previously.

Origin of crude oil

Fossil fuels, such as coal, oil and natural gas, come from the remains of plants and animals. When prehistoric marine microorganisms, such as bacteria and plankton, died and were buried by sands millions of years ago, these organisms accumulated as organic sediment and gradually became part of the Earth's crust. Over millions of years, this organic material was affected by high temperatures and pressures, causing the oils and fats to be converted into hydrocarbons. This mixture of hydrocarbons is crude oil.

Crude oil has a low density, which means it could migrate upwards through the crust, where it often became trapped beneath impervious (unable to be passed through) rock (Figure 9.1.1). Accumulation of oil and gas under the rock creates an oil field.

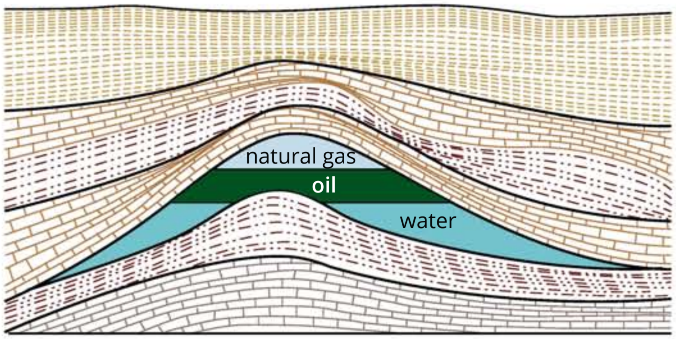
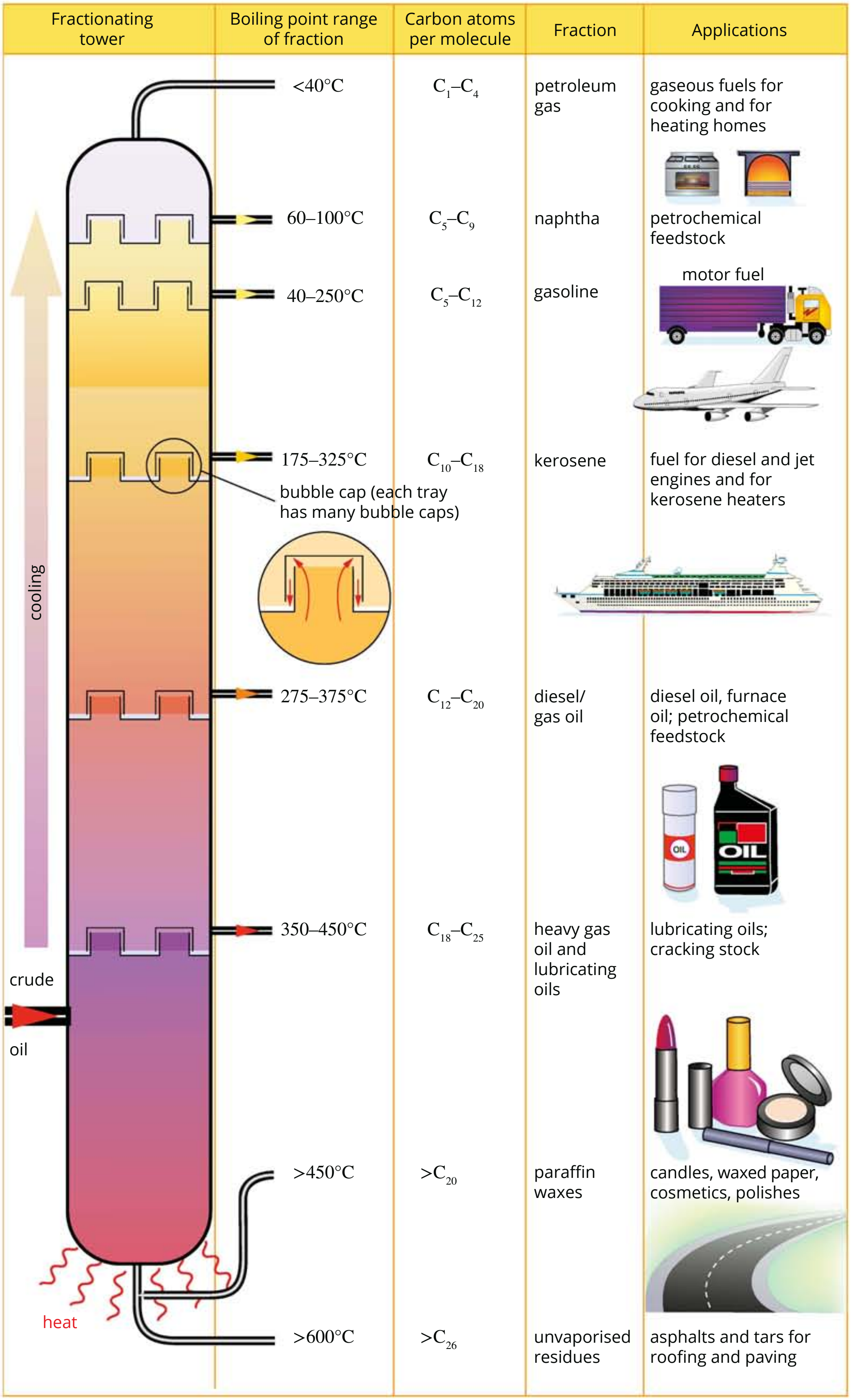


FIGURE 9.1.1 Typical structure of the impervious rock that traps oil and natural gas underground and creates an oil field.

Crude oil is not used in its raw state. It is transported from oil fields to oil refineries where it undergoes **fractional distillation** in a fractionating tower as shown in Figure 9.1.2. In this process, the crude oil is separated into its various components, or fractions. Each fraction is made up of a range of hydrocarbons with similar boiling points and hence molecular masses. The components of crude oil that are obtained by fractional distillation are used for a wide range of purposes, but presently over 90% of them are used for fuels.

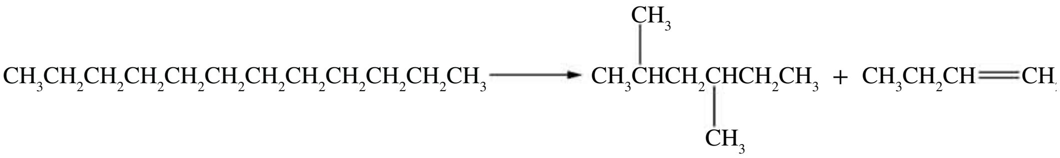


Boiling point range of fraction	Carbon atoms per molecule	Fraction	Applications
<40°C	C_1–C_4	petroleum gas	gaseous fuels for cooking and for heating homes
60–100°C	C_5–C_9	naphtha	petrochemical feedstock
40–250°C	C_5–C_{12}	gasoline	motor fuel
175–325°C	C_{10}–C_{18}	kerosene	fuel for diesel and jet engines and for kerosene heaters
275–375°C	C_{12}–C_{20}	diesel/ gas oil	diesel oil, furnace oil; petrochemical feedstock
350–450°C	C_{18}–C_{25}	heavy gas oil and lubricating oils	lubricating oils; cracking stock
>450°C	$>C_{20}$	paraffin waxes	candles, waxed paper, cosmetics, polishes
>600°C	$>C_{26}$	unvaporised residues	asphalts and tars for roofing and paving

FIGURE 9.1.2 Fractions found in crude oil.

Further processing of the crude oil fractions is needed to make these components even more useful.

Heavier fractions undergo a process called **cracking**, which is shown in Figure 9.1.3. This process breaks the larger hydrocarbon molecules into smaller molecules using heat and a **catalyst**. The smaller molecules and especially those with carbon–carbon double bonds are needed by the petrochemical industry.



$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \longrightarrow CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3 + CH_3CH_2CH{=}CH$$

FIGURE 9.1.3 Cracking of a larger hydrocarbon molecule results in two smaller molecules, one of which has a carbon–carbon double bond.

ALKANES

Hydrocarbons are composed only of carbon and hydrogen. The simplest hydrocarbon is methane. In methane, one carbon atom is covalently bonded with four hydrogen atoms to form a molecule with the formula CH_4.

Methane is a colourless, odourless gas that is very flammable. It is the main component of natural gas, which is used in many Australian homes for heating and cooking.

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. A series of molecules in which each member differs by $-CH_2-$ from the previous member is known as a **homologous series**.

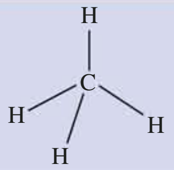
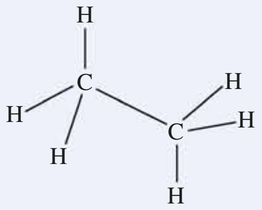
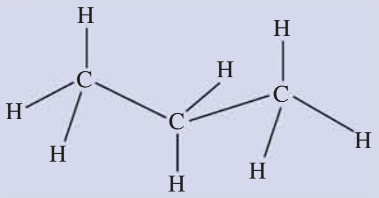
Compounds that are members of the same homologous series have:

- a similar structure
- a pattern to their physical properties
- similar chemical properties
- the same general formula.

Alkanes are non-polar molecules. As a result, they are insoluble in water and the only attractive force between the molecules is dispersion forces. As the number of carbons and the size of the molecules increase within this homologous series, the strength of the dispersion forces increases, so the melting and boiling points of the alkanes increase.

Table 9.1.1 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 9.1.1 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)

The naming of the members of each homologous series follows set conventions. The **stem name**, or parent name, in propane (prop-) indicates there are three carbon atoms in the molecule. This same stem name is used in other series for the member that contains three carbon atoms. The stem names used for molecules with between one and ten carbon atoms are listed in Table 9.1.2.

TABLE 9.1.2 Stem names used for molecules with between one and ten 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
non-	9
dec-	10

Alkanes are named by adding -ane after the stem name. For example, an alkane that contains eight carbon atoms is called octane. The **molecular formula** of octane is C_8H_{18}. The alkanes have the general formula C_nH_{2n+2}, where n stands for the number of carbon atoms. If an alkane molecule has 12 carbon atoms, the number of hydrogen atoms is $2n + 2 = 2 \times 12 + 2 = 26$. The molecular formula is $C_{12}H_{26}$.

The name of an alkane ends in -ane and alkanes have the general formula C_nH_{2n+2}.

Reactions of alkanes

Alkanes tend to be relatively unreactive, although like most hydrocarbons, they can be used as a fuel. The reaction between a fuel and oxygen is known as **combustion**. The burning of petrol in a car engine and the use of natural gas for cooking are examples of combustion reactions.

If the supply of oxygen is plentiful, the products of combustion will be carbon dioxide and water. This is known as **complete combustion**. The complete combustion of an alkane releases significant amounts of energy, which is why alkanes are used as fuels. For example, Figure 9.1.4 shows methane undergoing complete combustion in a Bunsen burner when the air holes are open. The equation for the complete combustion of methane is:

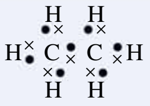
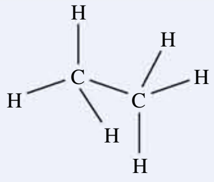
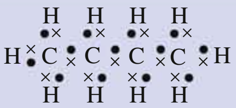
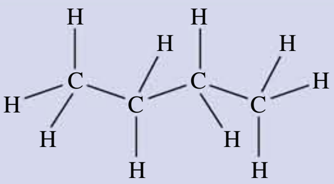
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

FIGURE 9.1.4 Methane undergoes complete combustion in a Bunsen burner when the air holes are open.

Writing formulas of alkanes

Sometimes we want to show more information about a molecule than just its overall composition. You can use a variety of ways to write the formulas of carbon compounds. Table 9.1.3 shows different ways of representing ethane and butane.

TABLE 9.1.3 Different ways of representing alkanes

Alkane	Molecular formula	Electron dot diagram (Lewis structure)	Condensed structural formula (semistructural formula)	Structural formula
Ethane	C_2H_6		CH_3CH_3	
Butane	C_4H_{10}		$CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$	

Structural formulas are very similar to the valence structures that you learned about in Chapter 6. They show all the bonds in a molecule, but lone pairs can be omitted. **Condensed structural formulas** are also known as semistructural formulas and show the atoms that are connected to each carbon atom, but do not show the bonds.

Representing three-dimensional molecules on a two-dimensional computer screen or page is a challenge for chemists. For example, each carbon in an alkane has four bonds in a tetrahedral arrangement. When the shape of the molecule is not important, it is often drawn in a simplified two-dimensional format as shown in Figure 9.1.5.

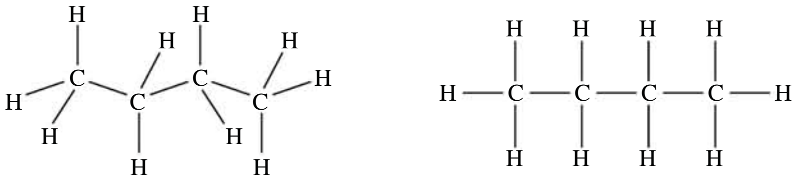
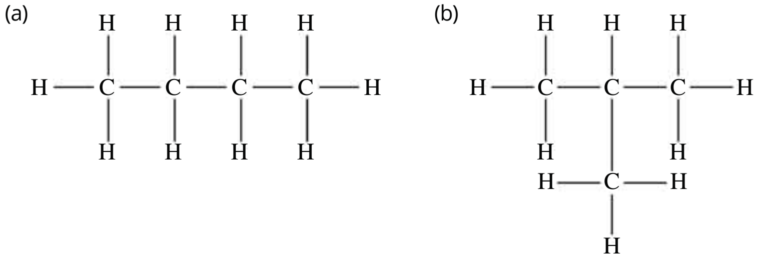


FIGURE 9.1.5 Molecules such as butane are often drawn in two dimensions for simplicity.

Structural isomers of alkanes

There is only one molecule that can be formed with the molecular formula of methane (CH_4). This is also the case for ethane (C_2H_6) and propane (C_3H_8). However, alkanes that have four or more carbon atoms have more than one possible structure.

Figure 9.1.6 shows two different molecules that have the molecular formula C_4H_{10}. Molecules that have the same molecular formula but have different arrangements of atoms are said to be **structural isomers** of each other. The more atoms in the molecule, the more possible isomers there are.



$CH_3(CH_2)_2CH_3$

$(CH_3)_3CH$ or $CH_3CH(CH_3)_2$

FIGURE 9.1.6 There are two structural isomers that have the molecular formula C_4H_{10}.

Figure 9.1.6a shows the straight-chain isomer of butane, so named because the four carbon atoms are bonded in a continuous chain. Figure 9.1.6b is the branched isomer because you could consider it as a straight-chain alkane with a $-CH_3$ side group attached. A $-CH_3$ side group is called a methyl group, as its structure is similar to that of methane with one less hydrogen. A $-CH_2CH_3$ side group is called an ethyl group.

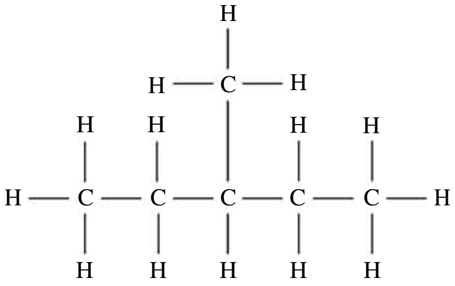
Therefore, Figure 9.1.6b is named methylpropane, as it can be regarded as a propane molecule with a methyl group attached. Methyl and ethyl groups are examples of **alkyl groups**. Alkyl groups have one less hydrogen atom than the corresponding alkane of the same name, so the general formula of an alkyl group is $-C_nH_{2n+1}$.

Table 9.1.4 lists the names of the alkyl groups with 1–5 carbon atoms.

TABLE 9.1.4 Names of the alkyl groups with 1–5 carbons

Alkyl group	Corresponding alkane	Name of alkyl group
$-CH_3$	methane	methyl
$-CH_2CH_3$	ethane	ethyl
$-CH_2CH_2CH_3$	propane	propyl
$-CH_2CH_2CH_2CH_3$	butane	butyl
$-CH_2CH_2CH_2CH_2CH_3$	pentane	pentyl

When writing the condensed structural formula of a branched alkane, alkyl groups are written in brackets (Figure 9.1.7).

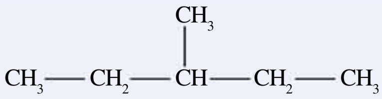
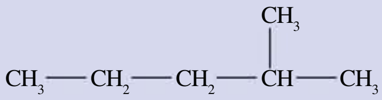
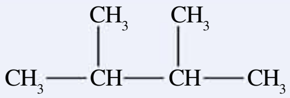
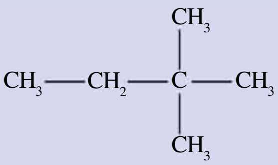


$CH_3CH_2CH(CH_3)CH_2CH_3$

FIGURE 9.1.7 The structural and condensed structural formula of a branched alkane.

Structural isomers are different compounds with different physical and chemical properties. Table 9.1.5 shows the isomers of hexane and their respective melting points and boiling points.

TABLE 9.1.5 Melting and boiling points of the isomers of hexane

Isomer	Melting point (°C)	Boiling point (°C)
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$ hexane	–95.3	68.7
 $CH_3-CH_2-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-CH_3$ 3-methylpentane	–118.0	63.3
 $CH_3-CH_2-CH_2-\overset{\overset{CH_3}{\vert}}{CH}-CH_3$ 2-methylpentane	–153.7	60.3
 $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-\overset{\overset{CH_3}{\vert}}{CH}-CH_3$ 2,3-dimethylbutane	–128.6	58
 $CH_3-CH_2-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_3$ 2,2-dimethylbutane	–99.8	49.7

NAMING ALKANES

The systematic naming of carbon compounds is controlled by the International Union of Pure and Applied Chemists (IUPAC). Under the IUPAC system, the name of the compound provides details of its structure. 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 are alkyl side chains of different lengths on the molecule, list them in alphabetical order at the start of the name, with their numbers to indicate their respective positions.

ℹ Carefully check that you have identified the longest unbranched carbon chain. Sometimes the longest carbon chain is not drawn in a straight line.

The following steps show the process of naming the isomer of hexane shown in Figure 9.1.8.

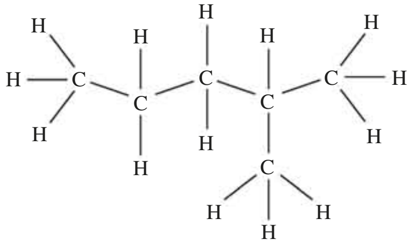
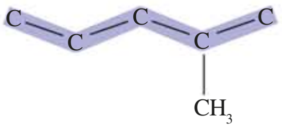
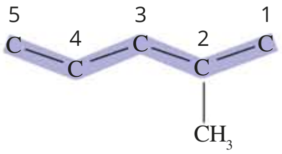


FIGURE 9.1.8 The IUPAC system will be used to name this isomer of hexane.

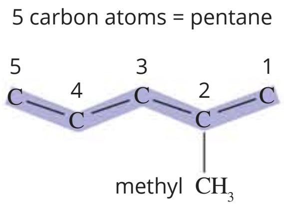
1 Identify the longest unbranched carbon chain.



2 Number the carbons, starting from the end closest to the branch.

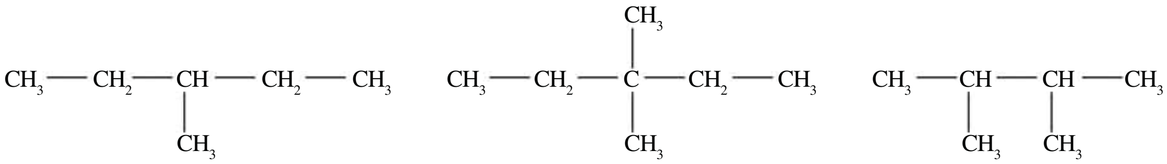


3 Name the side branches and main chain.



4 Combine all components to write the full name:
2-methylpentane

Figure 9.1.9 shows examples of applications of these rules. 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 come off the third carbon atom).



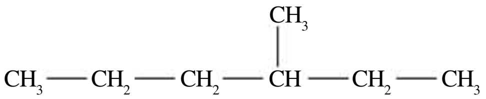
3-methylpentane 3,3-dimethylpentane 2,3-dimethylbutane

FIGURE 9.1.9 IUPAC systematic names for three alkanes. Note that there are no spaces in the names of these compounds.

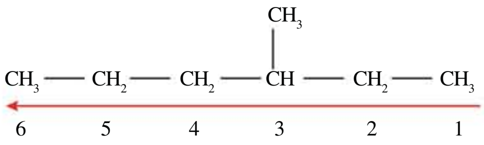
Worked example 9.1.1

IUPAC NAMING SYSTEM FOR ALKANES

Write the systematic name for the following molecule.



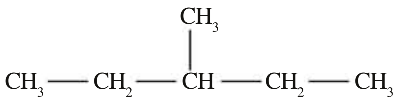
$$CH_3-CH_2-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-CH_3$$

Thinking	Working
Identify the longest carbon chain in the molecule. The stem name of the molecule is based on this longest chain.	There are 6 carbons in the longest chain. The stem name is based on hexane.
Number the carbon atoms starting from the end closest to the branch.	 $CH_3-CH_2-CH_2-\overset{\displaystyle CH_3}{\overset{\vert}{CH}}-CH_2-CH_3$
Identify the branch.	The side chain is a methyl group.
Combine all components.	The name of the molecule is 3-methylhexane.

Worked example: Try yourself 9.1.1

IUPAC NAMING SYSTEM FOR ALKANES

Write the systematic name for the following molecule.



$$CH_3-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-CH_3$$

9.1 Review

SUMMARY

- Hydrocarbons are compounds containing carbon and hydrogen only.
- Crude oil is the source of many hydrocarbons. These hydrocarbons are separated from one another by fractional distillation.
- 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}.
- Alkanes are relatively unreactive, although they do undergo combustion reactions.
- Structural isomers are molecules with the same molecular formula but different arrangements of atoms.
- Hydrocarbon molecules can be drawn using structural formulas or condensed structural formulas.
- The IUPAC naming system is used to provide systematic names for hydrocarbon molecules. Names are based on the longest unbranched carbon chain.

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.

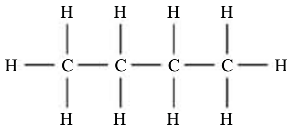
a What is the name of this hydrocarbon?
b Write a balanced chemical equation for the complete combustion of this hydrocarbon. This hydrocarbon exists as a gas at room temperature.
c Draw the structural formula of this hydrocarbon.
d Write the condensed structural formula of this hydrocarbon.

4 Write the systematic names of these alkanes based on their condensed structural formulas.

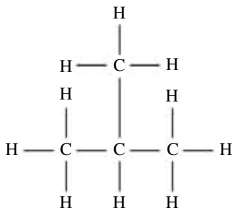
a $CH_3CH_2CH_2CH_3$
b $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
c $CH_3CH_2CH_2CH(CH_3)_2$
d $CH_3CH(CH_3)CH_2CH_3$
e $CH_3CH(CH_3)CH_2CH(CH_3)_2$

5 Write the systematic names of the alkanes shown here based on their structural formulas.

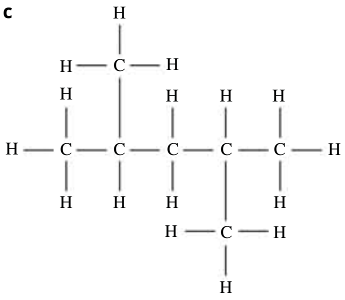
a



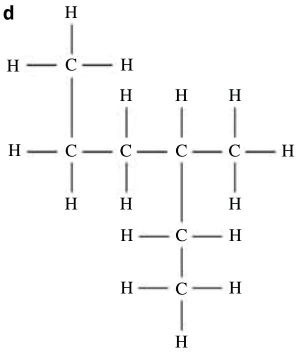
b



c



d



6 Draw the structural formulas of these alkanes based on their systematic names.

a Hexane
b 3-Methylhexane
c 3,3-Dimethylpentane
d 3-Ethyl-2-methylpentane

9.2 Unsaturated hydrocarbons

Carbon forms many compounds with hydrogen in which there are double or even triple bonds between the carbon atoms. These compounds are called **unsaturated** hydrocarbons. A double bond is formed when two pairs of electrons are shared and a triple bond is formed when three pairs of electrons are shared. Some of the most useful carbon compounds are unsaturated. This section focuses on the structures and naming of hydrocarbon compounds with carbon–carbon double bonds and triple bonds.

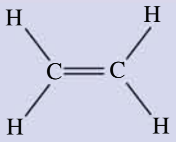
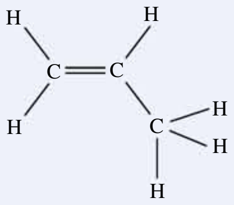
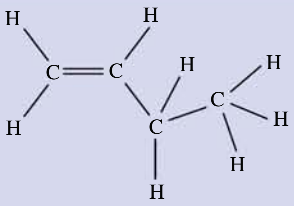
ALKENES

Alkenes are a homologous series of hydrocarbons with at least one carbon–carbon double bond. The general formula for the alkenes with one double bond is C_nH_{2n}. The presence of a carbon–carbon double bond means the alkenes are described as unsaturated molecules. Alkenes are more reactive than alkanes, which do not have any carbon–carbon double bonds.

The name of an alkene ends in -ene and alkenes have the general formula C_nH_{2n}.

The simplest alkene is ethene (C_2H_4). The next member in the series is propene (C_3H_6), which has an additional $–CH_2–$ unit. The first three members of the alkene homologous series are shown in Table 9.2.1. Note that the H–C–H bond angle around a carbon atom with a double bond is 120°. All alkenes are non-polar and hence do not dissolve in water.

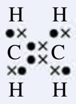
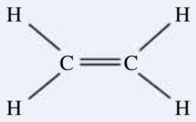
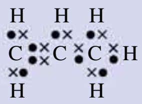
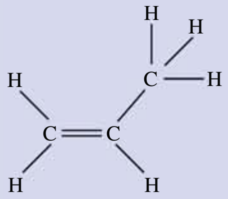
TABLE 9.2.1 Structure, properties and some uses of the first three alkenes

Name and molecular formula	Structural formula	Properties	Uses
Ethene, C_2H_4		Non-polar, gas, boiling point (BP) –78.4°C	In the manufacture of a wide range of chemicals
Propene, C_3H_6		Non-polar, gas, BP –47.7°C	In the manufacture of propene oxide and polymers
Butene, C_4H_8		Non-polar, gas, BP –6.3°C	In the manufacture of butanol and polymers

Writing formulas of alkenes

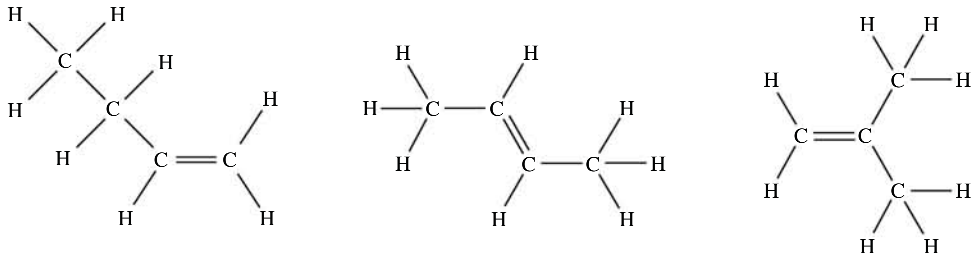
Like alkanes, there are a variety of ways for writing the formulas of alkenes. Table 9.2.2 shows different ways of representing ethene and propene.

TABLE 9.2.2 Different ways of representing alkenes

Alkene	Molecular formula	Electron dot diagram (Lewis structure)	Condensed structural formula (semistructural formula)	Structural formula
Ethene	C_2H_4		CH_2CH_2	
Propene	C_3H_6		CH_2CHCH_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 9.2.1, 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 9.2.1 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 9.2.1, 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.

Reactions of alkenes

Like alkanes, all alkenes undergo complete combustion in a plentiful supply of oxygen. For example, ethene can undergo complete combustion according to the following equation:

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$$

The greater reactivity of a carbon–carbon double bond compared with a single bond enables alkenes to also take part in **addition reactions**. In addition reactions, part of a reactant becomes bonded to one carbon in the double bond and the other part of the reactant becomes bonded to the other carbon atom in the double bond. The double bond is broken and a single C–C bond is formed.

CHEMFILE

Benzene

In 1825, Michael Faraday isolated a new hydrocarbon, named benzene (C_6H_6). The structure and properties of benzene puzzled scientists for 40 years.

August Kekulé made a major contribution to the puzzle in 1865. He proposed a ring structure in which alternate carbon atoms were joined by double bonds. The idea of a ring structure came to him in a dream.

It is now known that benzene has a ring structure, but it does not have alternating double and single bonds (Figure 9.2.2).

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 the molecule is more stable than would be expected of an unsaturated molecule.

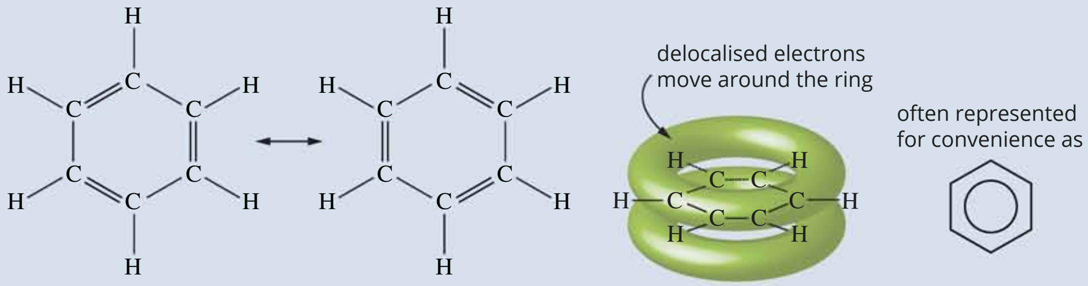


FIGURE 9.2.2
Representations of benzene. All six carbon atoms and six hydrogen atoms in the benzene molecule are in the same plane. There are no double bonds in benzene: the electrons are delocalised.

Table 9.2.3 lists some of the more important addition reactions of ethene. The first reaction shown in the table describes the reaction of an alkene with bromine solution (Br_2 dissolved in an organic solvent). Bromine solution is orange and when it reacts with an alkene in an addition reaction, the bromine solution loses its colour. This is often used as a test to determine if an organic compound is unsaturated (Figure 9.2.3 on page 204).

TABLE 9.2.3 Addition reactions of ethene

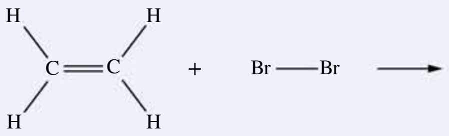
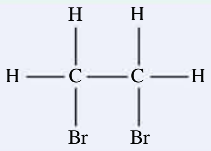
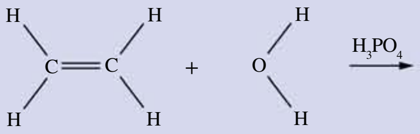
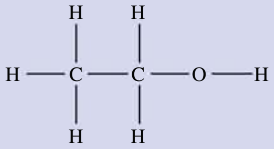
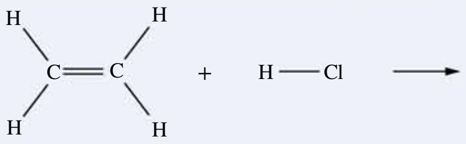
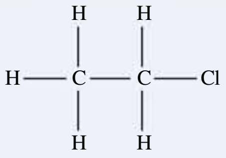
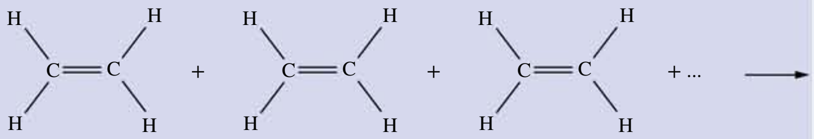
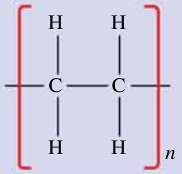
Reactants	Products	Name and uses of products
		1,2-Dibromoethane: reaction can be used as to test for unsaturation of organic compounds
		Ethanol: solvent, ink, cleaning agent
		Chloroethane: once used as a refrigerant and aerosol spray propellant
		Polyethene: common plastic

FIGURE 9.2.3 Test for unsaturation. Adding a few drops of orange-coloured bromine solution to hexane (right) produces no reaction. In sunflower oil (left), the colour of the bromine solution disappears almost immediately because molecules in the sunflower oil contain carbon–carbon double bonds, which undergo addition reactions with bromine (Br_2).

Polyethene, which is shown in Table 9.2.3 on page 203, is an example of a **polymer**. Polymers are very long molecules formed from the linking of a large number of small molecules, called **monomers**. Polyethene is formed from the reaction of thousands of ethene monomer molecules. The different types of polymers and how they are formed will be discussed in greater detail in Chapter 10.

ALKYNES

Alkynes are a homologous series of hydrocarbons with one carbon–carbon triple bond.

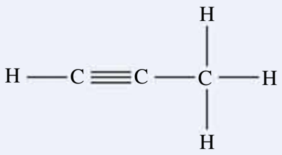
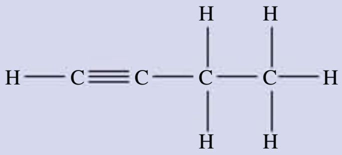
The general formula for the alkynes with one triple bond is C_nH_{2n-2}. The presence of a carbon–carbon triple bond means the alkynes can also be described as unsaturated molecules. The names of alkynes end with -yne. The arrangement of the atoms around the C–C triple bond is linear.

The name of an alkyne ends in -yne and alkynes have the general formula C_nH_{2n-2}.

The simplest alkyne is ethyne (C_2H_2) (also known as acetylene). The next member in the series is propyne, which has an additional $-CH_2-$ unit.

The first three members of the alkyne homologous series are shown in Table 9.2.4.

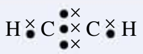
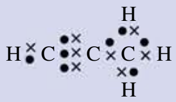
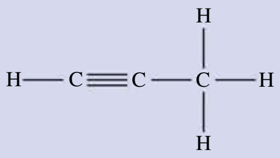
TABLE 9.2.4 Structure, properties and some uses of the first three alkynes

Name	Molecular formula	Structural formula	Properties	Uses
Ethyne	C_2H_2	$H-C\equiv C-H$	Colourless gas, slightly soluble in water, boiling point (BP) –84°C	Welding: an oxy-acetylene (ethyne is also known as acetylene) flame has a temperature of about 3000°C.
Propyne	C_3H_4	 $H-C\equiv C-\overset{H}{\underset{H}{C}}-H$	Colourless gas, slightly soluble in water, BP –23.2°C	Possible rocket fuel
Butyne	C_4H_6	 $H-C\equiv C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	But-1-yne: colourless gas, BP 81°C But-2-yne: colourless liquid, BP 27°C	As a reactant in the synthesis of other organic compounds

Writing formulas of alkynes

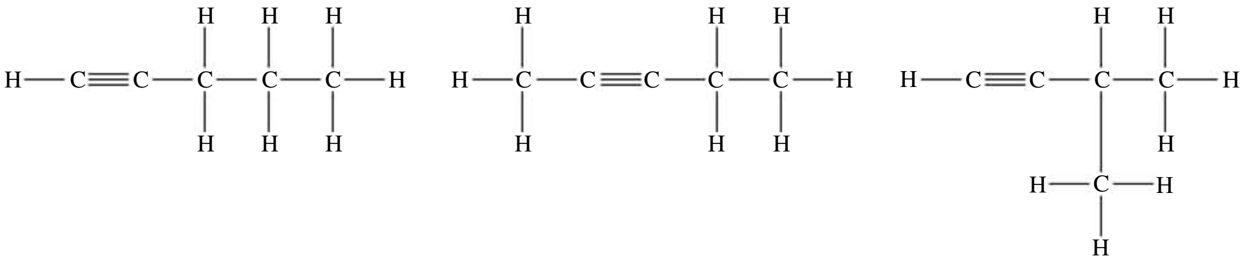
In Table 9.2.5, ethyne and propyne are used as examples to show different ways of representing alkynes.

TABLE 9.2.5 Different ways of representing alkynes

Name	Molecular formula	Electron dot diagram (Lewis structure)	Condensed structural formula	Structural formula
Ethyne	C_2H_2		CHCH	
Propyne	C_3H_4		$CHCCH_3$	

Structural isomers of alkynes

Structural isomers exist for alkyne molecules that contain more than three carbon atoms. As you can see in Figure 9.2.4, some isomers have branches on the carbon chain, while, in other isomers, the carbon–carbon triple bond is in different positions. The position of the triple bond can make a significant difference to the boiling point.



pent-1-yne
Boiling point 40.2°C

pent-2-yne
Boiling point 56°C

3-methylbut-1-yne
Boiling point 30°C

FIGURE 9.2.4 Structural isomers of pentyne. Isomers of alkynes can include molecules with branches in the carbon chain and molecules with the triple bond at different points in the carbon chain.

NAMING ALKENES AND ALKYNES

The following rules apply when naming alkenes and alkynes.

1. Identify the longest unbranched carbon chain. For alkenes, the chain must include the double bond and for alkynes the chain must include the triple bond.
2. Number the carbon atoms in the chain from the end of the chain that will give the smallest numbers to double-bonded or triple-bonded carbon atoms and to branching groups.
3. Name the alkyl groups after the alkane from which they are derived.
4. Identify the position of the double bond or triple bond by the number of the first carbon atom involved in the bond. Use the suffix '-ene' to indicate the presence of a double bond, e.g. hex-2-ene. Use the suffix '-yne' to show the presence of a triple bond, e.g. hex-2-yne.
5. List the number and position of each of the alkyl groups at the beginning of the compound's name in alphabetical order.
6. If two identical side chains are present, use 'di-' as a prefix; for three use 'tri-'.

The following steps show the process of naming the isomer of hexene shown in Figure 9.2.5.

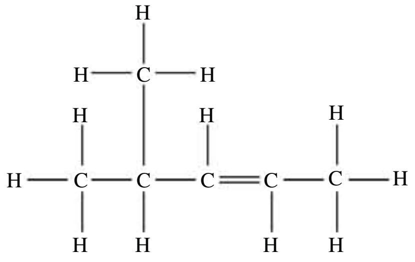
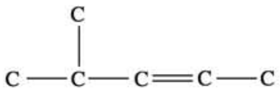
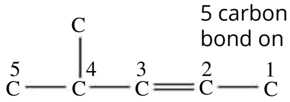


FIGURE 9.2.5 The IUPAC system will be used to name this isomer of hexene.

1 Identify the longest carbon chain that contains the double or triple bond. The name of the molecule is based on this chain.



2 Number the carbons, starting from the end closest to the double or triple bond. Note the position of the double or triple bond.

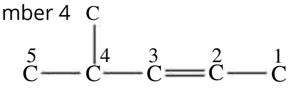


5 carbon chain with double bond on C number 2

- It is a 5-carbon chain with double bond starting at C number 2.

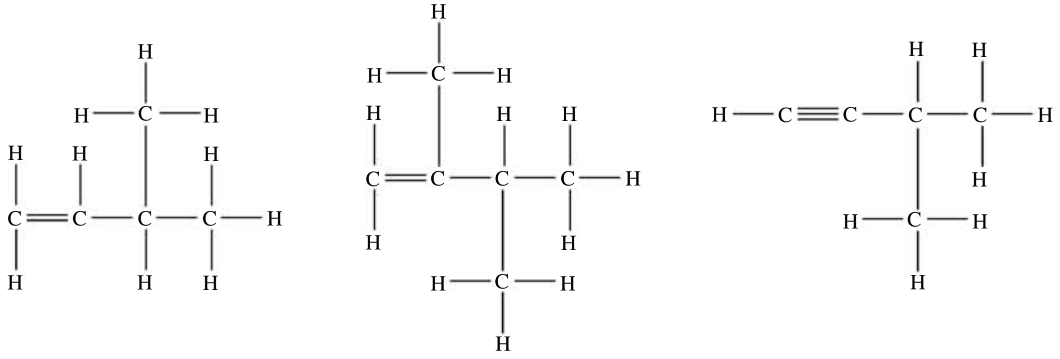
3 Name each side branch and the number of the carbon that it is on.

methyl on C number 4



- There is a methyl group on C number 4.

4 Combine all components to write the full name.
4-methylpent-2-ene
Figure 9.2.6 shows examples of applications of these rules.



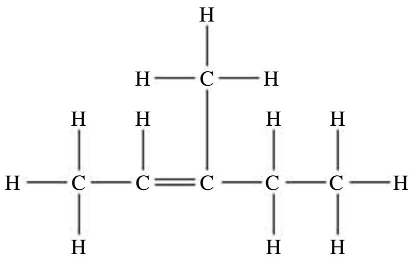
3-methylbut-1-ene 2,3-dimethylbut-1-ene 3-methylbut-1-yne

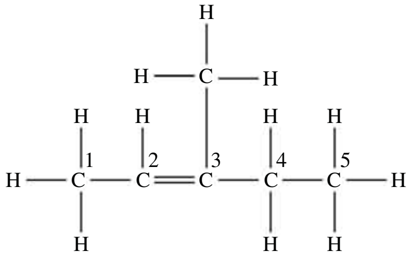
FIGURE 9.2.6 IUPAC systematic names for three unsaturated hydrocarbons.

Worked example 9.2.1

IUPAC NAMING SYSTEM FOR UNSATURATED HYDROCARBONS

Write the systematic name for the following molecule.

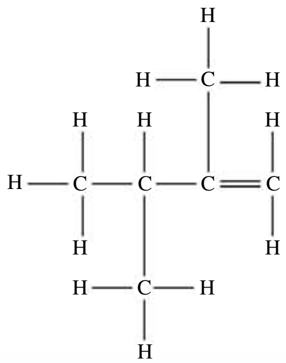


Thinking	Working
Identify the longest carbon chain in the molecule that contains the double or triple bond. The name of the molecule is based on this longest chain.	There are 5 carbons in the longest chain. The name is based on pentene.
Number the carbon atoms starting from the end closest to the double or triple bond. Note the position of any double or triple bond.	 There is a double bond on carbon number 2, so the longest chain is pent-2-ene.
Identify each branch and the number carbon that it is on.	The side chain is a methyl group and it is on carbon number 3.
Combine all components.	The name of the molecule is 3-methylpent-2-ene.

Worked example: Try yourself 9.2.1

IUPAC NAMING SYSTEM FOR UNSATURATED HYDROCARBONS

Write the systematic name for the following molecule.



9.2 Review

SUMMARY

- Unsaturated hydrocarbons are compounds containing carbon and hydrogen only, with a carbon–carbon double or triple bond.
- Alkenes and alkynes are more reactive than alkanes.
- Alkenes undergo addition reactions, where part of the reactant bonds to one carbon in the double bond and the other part of the reactant bonds to the other carbon in the double bond. The double bond breaks and a single C–C bond is formed.
- Alkenes have the general formula C_nH_{2n}. Alkynes have the general formula C_nH_{2n-2}.
- Names are based on the longest unbranched carbon chain. The position of the double or triple bond determines which end to start numbering from.

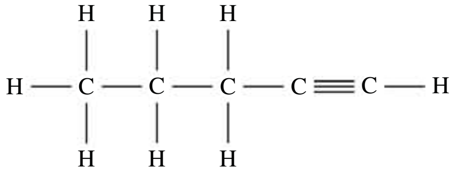
KEY QUESTIONS

1 List the following alkenes in order from lowest to highest number of atoms: pentene, ethene, methylpropene, octene, propene.

2 **a** How many carbon atoms are in methylpropene?
  b How many hydrogen atoms are in methylpropene?
  c Of which alkene is methylpropene an isomer?

3 Which of the following is the correct condensed structural formula of pent-1-yne?

A C_5H_8
B $CH_3CH_2CH_2CCH$
C $CH_3CH_2CH_2CHCH_2$
D



$\mathrm{H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-C\equiv C-H}$

4 **a** How many carbon atoms are in 3-methylbut-1-yne?
  b How many hydrogen atoms are in 3-methylbut-1-yne?
  c Of which straight-chain alkyne is 3-methylbut-1-yne an isomer?

5 Write the systematic names of the unsaturated hydrocarbons shown in Figure 9.2.7, based on their structural formulas.

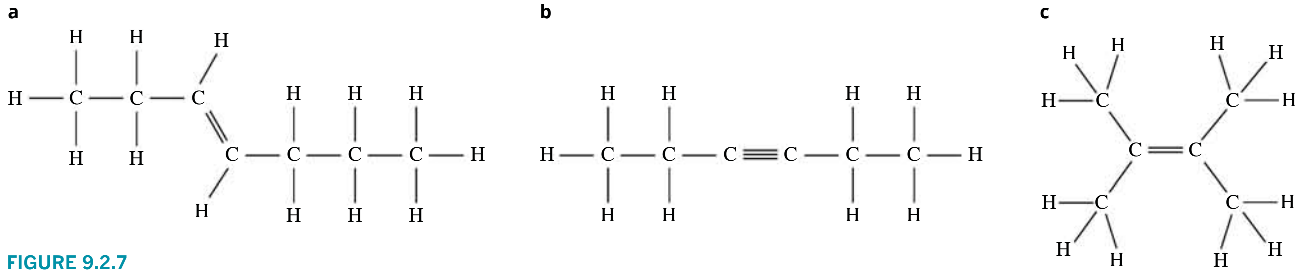


FIGURE 9.2.7

6 Draw the structural formulas of these unsaturated hydrocarbons based on their systematic names.

a But-2-ene
b Hex-1-yne
c 4-Methylpent-1-ene
d 4,4-Dimethylpent-1-yne

9.3 Alcohols

A vast range of organic molecules contain other atoms as well as carbon and hydrogen. The presence of different atoms in organic compounds increases their chemical reactivities compared to that of alkanes. It explains why different functions can be performed by carbon-based compounds.

For example, the presence of an –OH group in a molecule can enable the compound to dissolve in water and changes its boiling point. Such compounds are called **alcohols**. In this section you will learn about the properties, uses and structures of the homologous series of alcohols.

FUNCTIONAL GROUPS

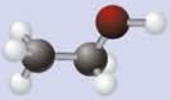
While carbon atoms are covalently bonded only to other carbon and hydrogen atoms in alkanes, alkenes and alkynes, it is possible for carbon to form covalent bonds with other atoms or groups of atoms called **functional groups**.

A functional group is an atom or a group of atoms that gives a characteristic set of chemical properties to a molecule containing those atoms.

Homologous series, such as alkenes, alkynes, alcohols, carboxylic acids and esters, are characterised by the presence of a particular functional group. In section 9.2, you saw that the carbon–carbon double bond characterises alkenes and the carbon–carbon triple bond distinguishes alkynes.

Some examples of compounds that contain two carbon atoms and a particular functional group are shown in Table 9.3.1. Although all have two carbon atoms, they have different physical and chemical properties and are members of different homologous series. The alkane ethane is shown first for comparison.

TABLE 9.3.1 Examples of two-carbon compounds with different functional groups

Homologous series	Name and molecular formula	Ball and stick model	Additional information
Alkanes	Ethane, C_2H_6		Ethane is found in natural gas and is used commercially to produce ethene, from which many plastics are made.
Alkenes	Ethene, $CH_2{=}CH_2$		Ethene is a gas which is an important natural plant hormone. It is used in agriculture to force fruit to ripen.
Alkynes	Ethyne, $CH{\equiv}CH$		Ethyne is a gas used with oxygen for welding.
Alcohols	Ethanol, C_2H_5OH		Ethanol is the alcohol found in alcoholic drinks.
Carboxylic acids	Ethanoic acid, CH_3COOH		Ethanoic acid dissolves in water to from vinegar, giving its distinctive sour taste and pungent smell.
Esters	Methyl methanoate, $HCOOCH_3$		Methyl methanoate is a clear liquid with a strong, pleasant odour.

Members of the same homologous series contain the same functional group. The presence of the same functional group in these molecules means that they have similar, although not identical, physical and chemical properties.

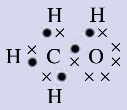
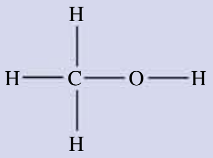
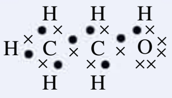
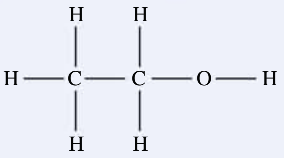
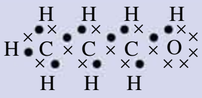
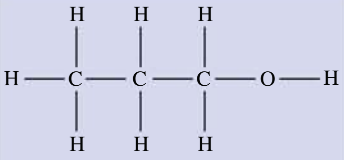
ALCOHOLS

Formulas 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, alkenes and alkynes 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 9.3.2 shows different ways to represent alcohols.

TABLE 9.3.2 The first three members of the homologous series of alcohols

Alcohol	Molecular formula	Electron dot formula (Lewis structure)	Structural formula	Condensed structural formula (semistructural formula)
Methanol	CH_3OH			CH_3OH
Ethanol	C_2H_5OH			CH_3CH_2OH
Propanol	C_3H_7OH			$CH_3CH_2CH_2OH$

Properties and uses of alcohols

Many of the 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 can be seen in Figure 9.3.1.

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.

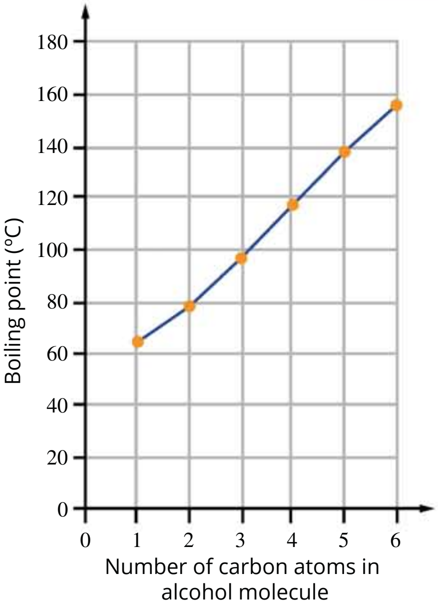


FIGURE 9.3.1 As the number of carbon atoms in an alcohol molecule increases, the boiling point increases.

Hydrogen bonding also influences the solubility of the alcohols. The presence of the –OH group allows hydrogen bonds to form between water molecules and alcohol molecules (Figure 9.3.2). For the 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.

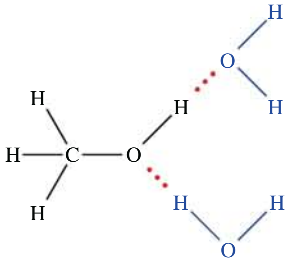


FIGURE 9.3.2 Hydrogen bonds form between the hydroxyl group of a methanol molecule and water.

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 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 dissolve 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 9.3.3). The stopper and yeast are then removed quickly and the stopper is replaced.

FIGURE 9.3.3 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.

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. 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.

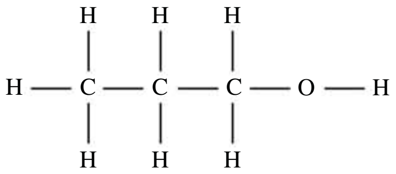
Naming alcohols

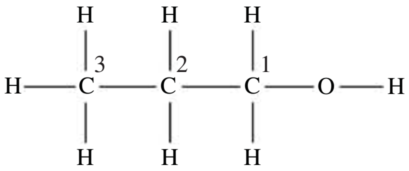
To name an alcohol, start with the name of the parent alkane, remove the 'e' from the end and add the suffix '-ol'. The atoms in the longest carbon chain are numbered from the end that is closest to the functional group. The number of the carbon atom to that the hydroxyl group is bonded is shown before the -ol ending and is separated by hyphens.

Worked example 9.3.1

IUPAC NAMING SYSTEM FOR ALCOHOLS

Write the systematic name for the following molecule.

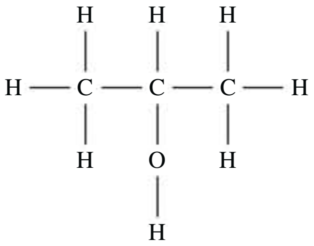


Thinking	Working
Identify the longest carbon chain in the molecule. The name of the molecule is based on this longest chain.	There are 3 carbons in the longest chain. The name is based on propane.
Identify the functional group that is present.	There is a hydroxyl group present.
Number the carbon atoms 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 9.3.1

IUPAC NAMING SYSTEM FOR ALCOHOLS

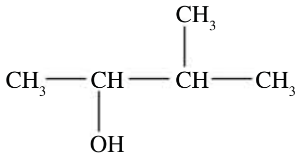
Write the systematic name for the following molecule.



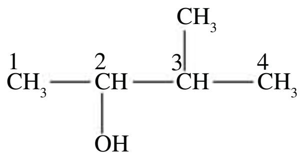
Worked example 9.3.2

IUPAC NAMING SYSTEM FOR ALCOHOLS

Write the systematic name for the following molecule.



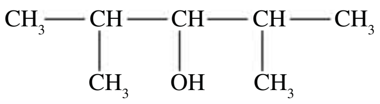
$CH_3-\underset{\underset{OH}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3$

Thinking	**Working**
Identify the longest carbon chain in the molecule. The name of the molecule is based on this longest chain.	There are 4 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.	 $\overset{1}{CH_3}-\underset{\underset{OH}{|}}{\overset{2}{CH}}-\overset{\overset{CH_3}{|}}{\overset{3}{CH}}-\overset{4}{CH_3}$
Identify the position(s) and the type(s) of branches.	There is a methyl (–CH_3) group on C3 so the prefix 'methyl' will be 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 9.3.2

IUPAC NAMING SYSTEM FOR ALCOHOLS

Write the systematic name for the following molecule.



$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

9.3 Review

SUMMARY

- A functional group is an atom or group of atoms that gives a characteristic set of chemical properties to a molecule.
- The uses of alcohols relate to the properties of the alcohols, such as their ability to dissolve in water.
- All alcohols have a hydroxyl (–OH) functional group.
- Alcohols can dissolve in water because the hydroxyl group can form hydrogen bonds with water molecules. However, the solubility of alcohols decreases as the length of the carbon chain attached to the hydroxyl group increases.
- When naming an alcohol:
  - identify the longest carbon chain to give the stem name of the molecule
  - number the carbons from the end nearest to the hydroxyl group and use the same set of numbers for any branches that occur
  - indicate the presence of the hydroxyl functional group with the suffix '-ol'.

KEY QUESTIONS

1 Which of the following alcohol molecules is most soluble in water?

A C_3H_7OH
B C_2H_5OH
C CH_3OH
D C_4H_9OH

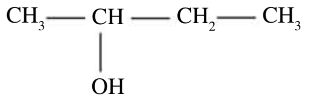
2 Which one of the following best defines a functional group?

A An atom or group of atoms that is substituted into an alkane molecule in place of a hydrogen atom
B An atom or group of atoms that changes the physical properties of a molecule
C An atom or group of atoms that changes the chemical and physical properties of a molecule
D An atom or group of atoms that does not contain a hydrogen atom

3 Which of the following organic compounds belongs to the same homologous series as ethanol (C_2H_5OH)?
CH_3OH, C_4H_9OH, $C_2H_5NH_2$, C_3H_5COOH, $C_5H_{11}OH$, C_2H_4, $C_{25}H_{52}$, C_6H_6

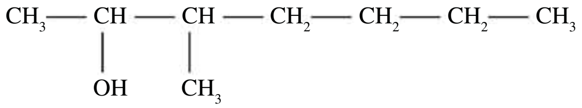
4 Write the systematic names of the alcohols shown in Figure 9.3.4, based on their structural formulas.

a



$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_3$

b



$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_2-CH_3$

c

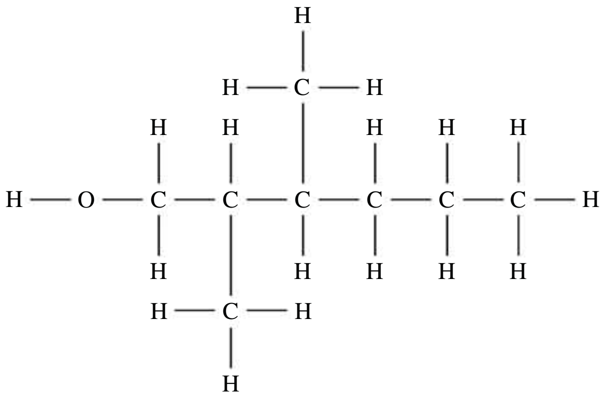


FIGURE 9.3.4

5 Draw the structural formulas of these alcohols based on their systematic names.

a Pentan-3-ol
b 3-Methylpentan-1-ol
c 2,5-Dimethylhexan-3-ol

6 Draw and give the correct systematic names of the alcohols based on these incorrect systematic names.

a Butan-4-ol
b 1,2-Dimethylhexan-2-ol
c 2,3-Dimethylbutan-3-ol

9.4 Carboxylic acids

The **carboxylic acids** are an important class of organic compounds. These compounds are **weak acids** that are often present in food, giving it a sour taste. As shown in Figure 9.4.1, carboxylic acids are also found in some insect venoms. At other times they are formed when food deteriorates, such as when wine becomes sour on exposure to air.

In this section you will learn about the structures, properties and uses of the carboxylic acid homologous series.

FIGURE 9.4.1 These ants are attacking the intruder from another colony by spraying it with a jet of methanoic (formic) acid from their abdomens. Methanoic acid is the smallest carboxylic acid molecule.

CARBOXYLIC ACIDS

Formulas and structure of carboxylic acids

Carboxylic acids are identified by the presence of a **carboxyl group** (–COOH). The structure of the carboxyl functional group is shown in Figure 9.4.2.

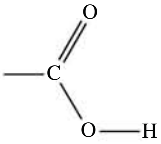


FIGURE 9.4.2 The structure of a carboxyl functional group.

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 9.4.3.

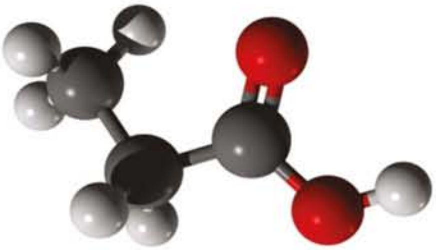


FIGURE 9.4.3 A carboxylic acid has a tetrahedral arrangement of atoms in the hydrocarbon part of the molecule, but there is a trigonal planar arrangement of atoms in the carboxyl functional group.

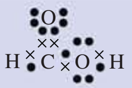
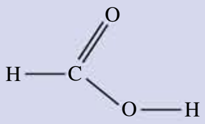
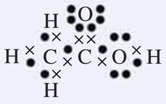
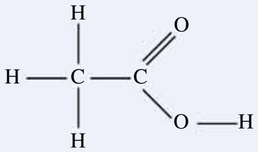
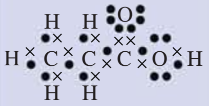
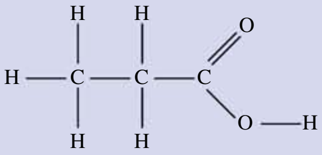
Naming carboxylic acids

The prefixes that are used to indicate the number of carbon atoms in alkanes are also used with carboxylic acids. Other features of carboxylic acid nomenclature are listed below:

- Names of carboxylic acids end with the suffix '-oic acid'.
- The carbon in the functional group is counted in the chain used to name the carboxylic acid. For example, C_2H_7COOH has three carbons and is called propanoic acid.
- The carboxyl carbon is always carbon 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 9.4.1. Successive members of the series differ by a $-CH_2-$ unit.

TABLE 9.4.1 The first four members of the homologous series of carboxylic acids

Name	Molecular formula	Electron dot formula (Lewis structure)	Structural formula	Condensed structural formula (semistructural formula)
Methanoic acid	HCOOH			HCOOH
Ethanoic acid	CH_3COOH			CH_3COOH
Propanoic acid	C_2H_5COOH			CH_3CH_2COOH

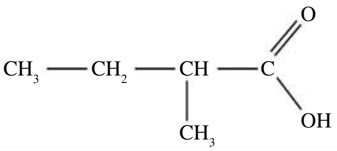
Structural isomers of carboxylic acids

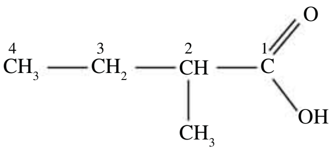
The carboxyl group can only occur on the end of a molecule because the carbon atom in the carboxyl group has a double bond to one oxygen and a single bond to another oxygen. Carboxylic acids can form isomers with different branches, but the carbon atom in the carboxyl group is always carbon number 1.

Worked example 9.4.1

IUPAC NAMING SYSTEM FOR CARBOXYLIC ACIDS

Write the systematic name for the following molecule.

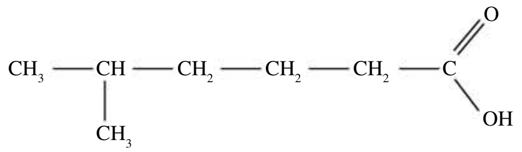


Thinking	Working
Identify the functional group that is present.	There is a carboxyl group present.
Identify the longest carbon chain that includes the carboxyl carbon. This atom will be C1. The stem name of the molecule is based on this longest chain.	There are four carbons in the longest chain, so the 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 9.4.1

IUPAC NAMING SYSTEM FOR CARBOXYLIC ACIDS

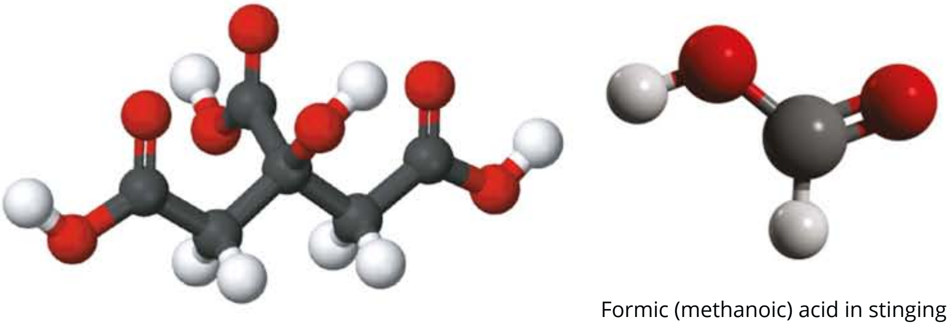
Write the systematic name for the following molecule.



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_2-CH_2-C\overset{\displaystyle O}{\underset{\displaystyle OH}{\lessgtr}}$$

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 (see Figure 9.4.4 for the structures of these carboxylic acids).



Citric acid in lemon juice

Formic (methanoic) acid in stinging nettles and ant stings

FIGURE 9.4.4 Lemons, stinging nettles and ants all provide a source of carboxylic acids in nature.

As shown in Figure 9.4.5, 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 (the nature of acids will be discussed in more detail in Chapter 15).

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.

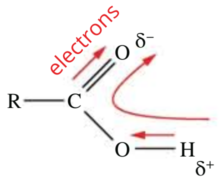


FIGURE 9.4.5 Electrons are drawn away from the hydrogen of the carboxyl functional group, allowing the hydrogen to be donated as a H^+ ion in an acid–base reaction.

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 9.4.6). 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 9.4.6 Sea Shepherd crew members throw butanoic acid in the form of rancid butter onto a Japanese whaling ship.

Carboxylic acids have higher boiling points than you might expect from their molecular masses (see Figure 9.4.7 for a comparison between the boiling points of carboxylic acids and alcohols). The high boiling points are a direct result of the presence of hydrogen bonds between carboxylic acid molecules.

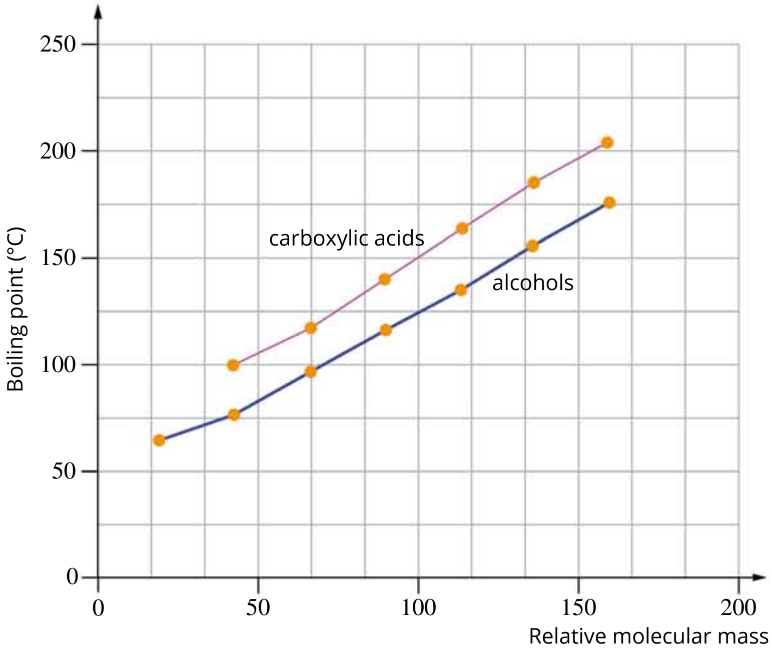


FIGURE 9.4.7 Carboxylic acids have higher boiling points than alcohols with similar relative molecular masses.

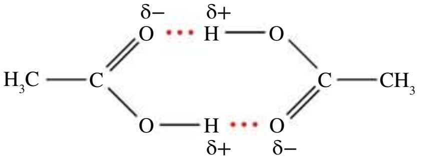


FIGURE 9.4.8 Hydrogen bonding between two ethanoic acid molecules results in the formation of a dimer.

Hydrogen bonding between two carboxylic molecules results in the two molecules forming a **dimer** (two identical molecules bonded together). You can see this in Figure 9.4.8. The formation of dimers between two carboxylic acids is one of the reasons carboxylic acids have higher boiling points.

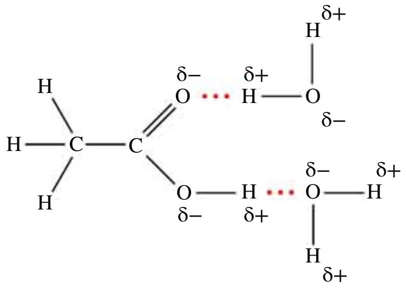


FIGURE 9.4.9 Hydrogen bonds form between carboxylic acid molecules and water molecules.

As shown in Figure 9.4.9, when dissolved in water, hydrogen bonding occurs between the carboxyl group of carboxylic acids and water molecules, making carboxylic acids more soluble than alcohols in water. The high solubility of carboxylic acids explains why they are frequently found in solutions such as citric acid in orange and lemon juice.

The solubility of the carboxylic acids decreases as they increase in size. A longer carbon chain means that more of the molecule is non-polar. This is shown in Table 9.4.2.

TABLE 9.4.2 Solubility of carboxylic acids with 1–10 carbon atoms

Name	Formula	Number of carbon atoms	Solubility (g per 100 g H_2O)
Methanoic acid	$HCOOH$	1	unlimited
Ethanoic acid	CH_3COOH	2	unlimited
Propanoic acid	CH_3CH_2COOH	3	unlimited
Butanoic acid	$CH_3(CH_2)_2COOH$	4	unlimited
Pentanoic acid	$CH_3(CH_2)_3COOH$	5	5.0
Hexanoic acid	$CH_3(CH_2)_4COOH$	6	1.1
Heptanoic acid	$CH_3(CH_2)_5COOH$	7	0.25
Octanoic acid	$CH_3(CH_2)_6COOH$	8	0.07
Nonanoic acid	$CH_3(CH_2)_7COOH$	9	0.03
Decanoic acid	$CH_3(CH_2)_8COOH$	10	0.015

9.4 Review

SUMMARY

- Carboxylic acid molecules contain the functional group –COOH.
- The –COOH group is called a carboxyl functional group and its presence is shown in the name of carboxylic acids with the suffix '-oic acid'.
- Carboxylic acids are weak acids with relatively high boiling points.
- Hydrogen bonds exist between carboxylic acid molecules, resulting in the formation of dimers.
- Smaller carboxylic acids are soluble in water because they can form hydrogen bonds with water molecules and less of the molecule is non-polar.
- When naming a carboxylic acid:
  - identify the longest carbon chain containing the carboxyl group to determine the stem name of the molecule
  - number from the carboxyl group and assign appropriate numbers to branches.

KEY QUESTIONS

1 Small carboxylic acids, such as ethanoic acid, are very soluble in water. Which one of the following is the strongest type of intermolecular bonding that occurs between carboxylic acid molecules and water molecules?

A Dipole–dipole attraction
B Dispersion forces
C Ion–dipole attraction
D Hydrogen bonding

2 Which one of the following best describes why carboxylic acids have higher boiling points than the alcohols with the same number of carbon atoms?

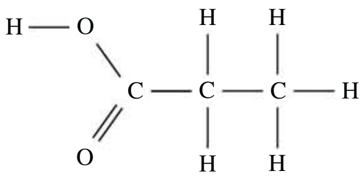
A Carboxylic acid molecules form dimers.
B Carboxylic acid molecules are able to form hydrogen bonds.
C The extra oxygen in a carboxylic acid molecule increases the boiling point.
D Carboxylic acids are all solids at room temperature.

3 Write condensed structural formulas of the carboxylic acids based on their systematic names.

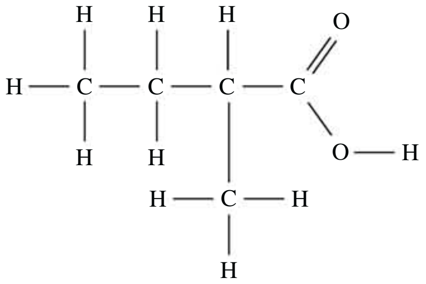
a Butanoic acid
b Methylpropanoic acid
c 2,3-Dimethylpentanoic acid
d 3,3-Dimethylbutanoic acid

4 Write the systematic names of the carboxylic acids shown here, based on their structural formulas.

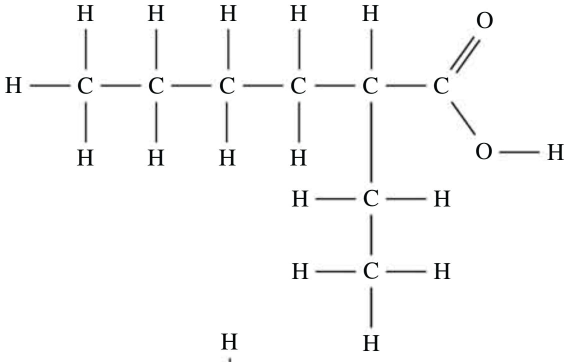
a



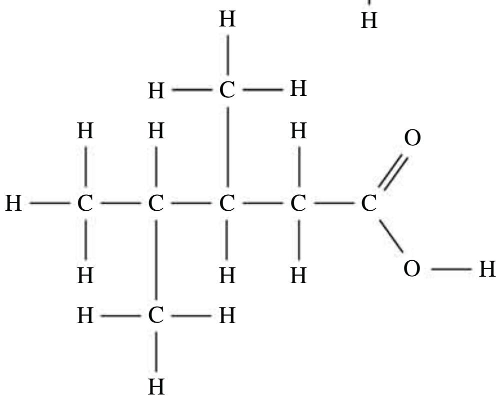
b



c



d



5 Draw the structural formulas of these carboxylic acids based on their systematic names.

a Heptanoic acid
b 3-Methylbutanoic acid
c 2,3-Dimethylpentanoic acid
d 3-Methyl-2-ethylpentanoic acid

9.5 Esters

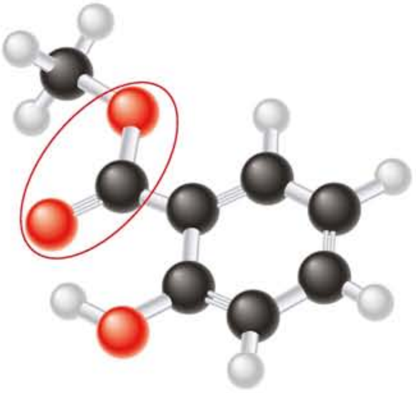


FIGURE 9.5.1 This molecule is methyl salicylate, which is also known as oil of wintergreen. The smell of methyl salicylate is often associated with creams used to rub down sore muscles. The ester functional group is circled.

Esters form another homologous series. The chemicals in this class of organic compounds are responsible for many of natural odours and flavours. Many esters have a fruity smell, while others such as methyl salicylate (Figure 9.5.1) will remind you of creams used to rub down sore muscles.

In this section you will learn about the structures, nomenclature, properties and uses of this homologous series.

ESTERS

Formulas and structure of esters

An **ester** functional group consists of a carbonyl (C=O) group with a second oxygen bonded to the carbon atom to form –COO–. The structural formula is shown in Figure 9.5.2.

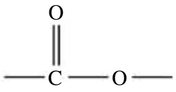


FIGURE 9.5.2 Structural formula of an ester functional group.

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 as it increases the rate of reaction, but is not consumed by the reaction.

In Figure 9.5.3, 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. Since water is also formed during this reaction, it is also called a **condensation reaction**.

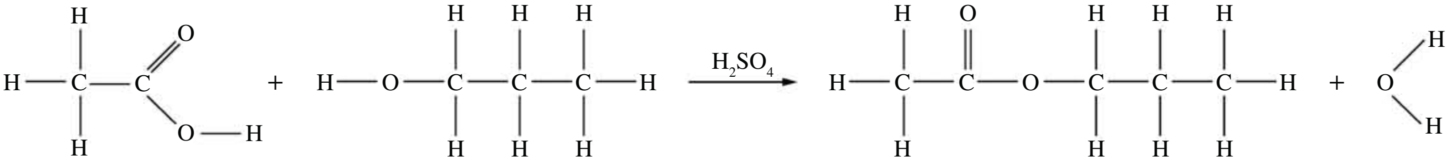


FIGURE 9.5.3 Reaction of a carboxylic acid and an alcohol to form an ester.

Naming esters

The naming of esters tends to be a little more complex than the naming of compounds in the other homologous series that have been discussed so far. 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 9.5.4.

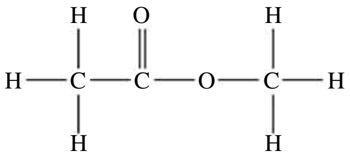


FIGURE 9.5.4 Methyl ethanoate is an ester formed by the reaction of methanol with ethanoic acid.

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.
- The alkyl group bonded to the singly bonded oxygen atom is then added in front of the name. This portion of the ester is derived from the alcohol.

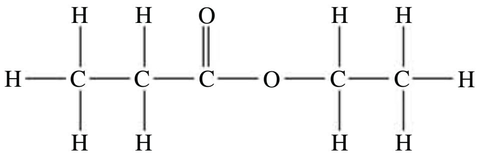
The name of the ester can easily be determined if you know the names of the carboxylic acid and alcohol that it is made from. The alkyl group name is derived from the name of the alcohol; for example, methanol becomes methyl. The -oic acid portion of the carboxylic acid name is replaced with -oate; for example, ethanoic acid becomes ethanoate. The name of the example ester would be methyl ethanoate.

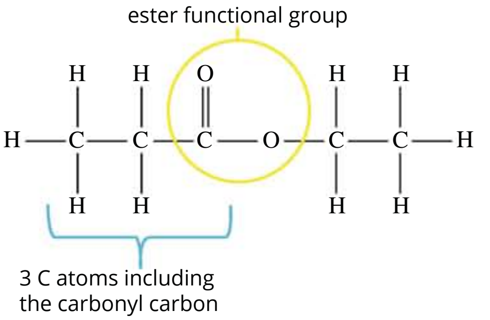
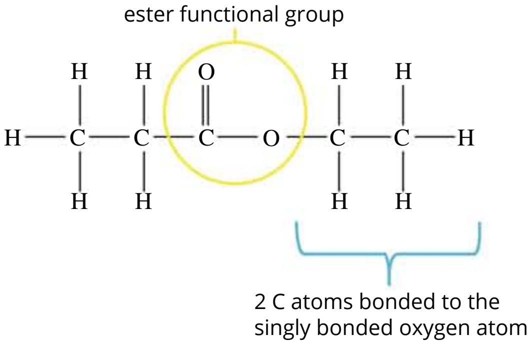
Use Worked Example 9.5.1 to develop your skills in naming esters.

Worked example 9.5.1

IUPAC NAMING SYSTEM FOR ESTERS

Write the systematic name for the following molecule.

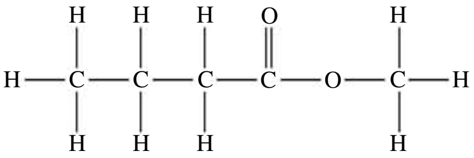


Thinking	Working
Locate the ester functional group. Starting from the carbonyl carbon, determine the number of carbon atoms in the chain attached to it and name according to the stem name, adding the suffix '-oate'.	 ester functional group 3 C atoms including the carbonyl carbon There are three carbons in the chain including the carbonyl carbon, so the last part of the molecule'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.	 ester functional group 2 C atoms bonded to the singly bonded oxygen atom 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.

Worked example: Try yourself 9.5.1

IUPAC NAMING SYSTEM FOR ESTERS

Write the systematic name for the following molecule.



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 9.5.5).

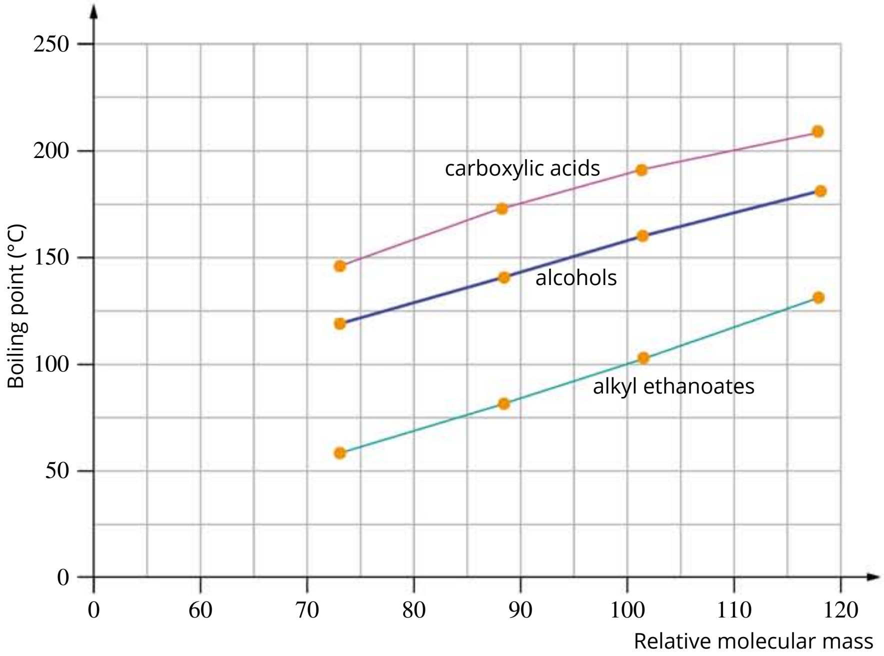


FIGURE 9.5.5 Boiling points of alkyl ethanoates (a series of esters) compared to carboxylic acids and alcohols of similar relative molecular mass.

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 9.5.6).

FIGURE 9.5.6 Beeswax is largely composed of an ester called triacontanyl palmitate.

CHEMFILE

Creating tastes

Manufacturers of products such as soft drinks, toppings and ice cream like their products to smell and taste as natural as possible. Using extracts from natural foods may achieve this, but the extracts are often expensive and so the use of artificial flavourings is common (Figure 9.5.7).

In practice, it would be much more expensive to synthesise the exact mixture of compounds found in a natural food, such as an apple, rather than using the natural extract. Fortunately, manufacturers have found that they can add only one or a few compounds, usually esters, to achieve the desired taste and smell economically.

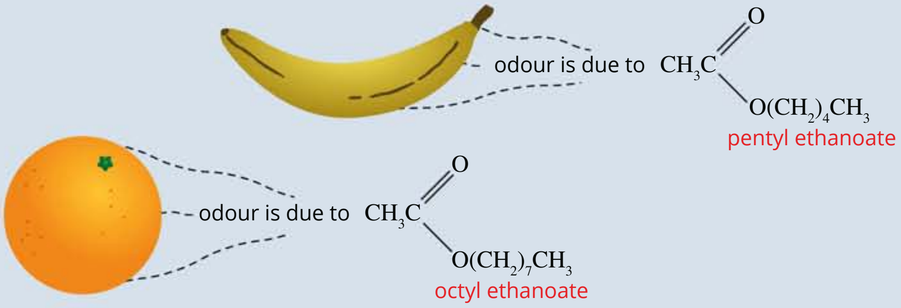
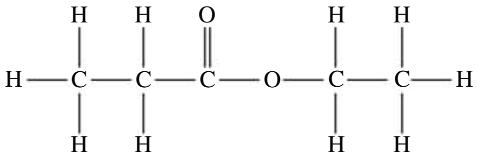


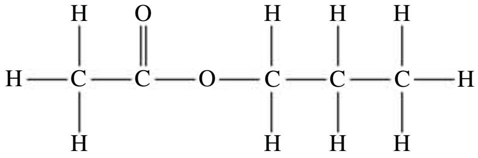
FIGURE 9.5.7 Small esters are volatile and have distinctive odours and flavours. The odour of oranges is largely due to octyl ethanoate, whereas pentyl ethanoate has the odour of banana.

Structural isomers of esters

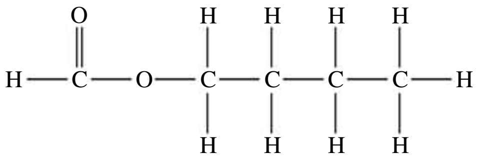
The position of the ester group can vary within a molecule and create structural isomers. Figure 9.5.8 shows three esters that are structural isomers with the molecular formula, $C_5H_{10}O_2$. The position of the ester functional group is shown by the naming of the ester, rather than by using numbers. A series of carboxylic acids also has the same molecular formula.



ethyl propanoate



propyl ethanoate



butyl methanoate

FIGURE 9.5.8 Three esters which are structural isomers with the molecular formula $C_5H_{10}O_2$.

9.5 Review

SUMMARY

- Ester molecules contain the functional group –COO–.
- The names of esters are derived from the names of the alcohol and carboxylic acid that react to form them.
- When naming an ester, determine the number of carbon atoms in the:
  - carbon chain that is bonded to the singly bonded oxygen atom. This gives the stem name the ending '-yl'
  - carbon chain, beginning at the carboxyl carbon. This gives the stem name with the suffix '-oate'.
- Esters often have characteristic sweet, fruity odours. They have lower boiling points than alcohols and carboxylic acids of a similar size.

KEY QUESTIONS

1 Which one of the following is a property of esters?

A They have no odour.

B They are non-polar.

C They are have a lower boiling point than alcohols of similar size.

D They form hydrogen bonds between the molecules.

2 Which one of the following is a structural isomer of methyl propanoate?

A Butyl methanoate

B Propyl ethanoate

C Ethyl ethanoate

D Ethyl propanoate

3 List the total number of carbon atoms in the following esters.

a Methyl methanoate

b Ethyl propanoate

c Propyl methanoate

d Pentyl butanoate

e Butyl propanoate

4 Write condensed structural formulas of the following esters based on their systematic names.

a Methyl ethanoate

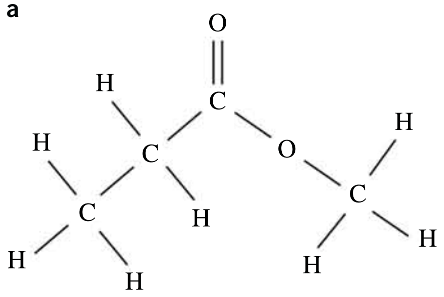
b Ethyl propanoate

c Ethyl ethanoate

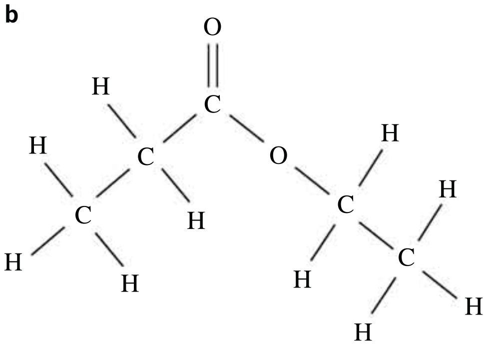
d Propyl butanoate

5 Write the systematic names of the following esters, based on their structural formulas.

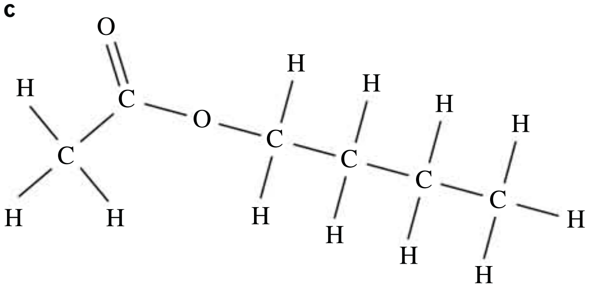
a



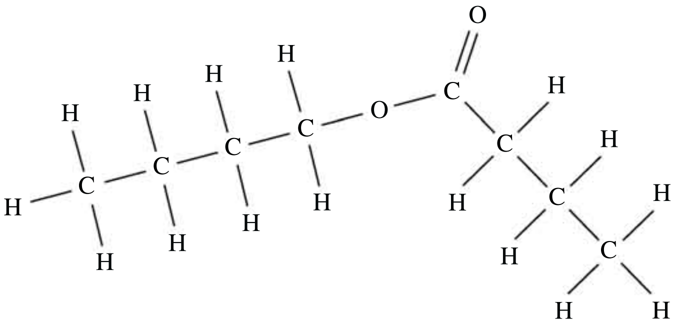
b



c



d



9.6 Determining formulas 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 9.6.1 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 it operates in the body.

In this section, you will learn about ways in which the chemical formulas of compounds can be determined.

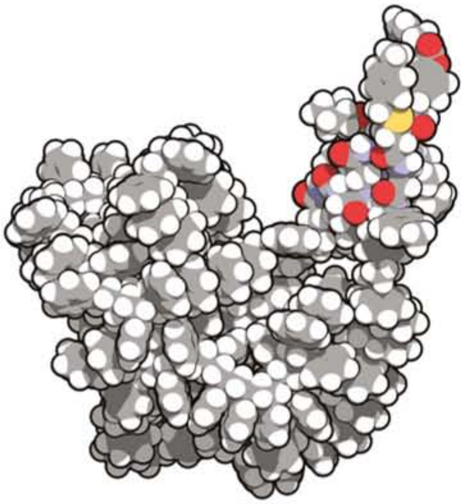


FIGURE 9.6.1 A representation of the chemical structure of the hormone insulin.

CALCULATING PERCENTAGE COMPOSITION OF ORGANIC COMPOUNDS

As you saw in Chapter 5, 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 9.6.1

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.	$\text{\% carbon} = \frac{\text{mass of the element present}}{\text{total mass of the compound}} \times 100$ $= \frac{1.52}{2.85} \times 100$ $= 53.3\%$
Divide the mass of the second element by the total mass of the compound and multiply by 100.	$\text{\% hydrogen} = \frac{\text{mass of the element present}}{\text{total mass of the compound}} \times 100$ $= \frac{0.45}{2.85} \times 100$ $= 15.8\%$
Repeat the previous step for any further elements in the compound.	$\text{\% nitrogen} = \frac{\text{mass of the element present}}{\text{total mass of the compound}} \times 100$ $= \frac{0.88}{2.85} \times 100$ $= 30.9\%$
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 9.6.1

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 FORMULAS

Determining empirical formulas

Finding the chemical formula of an unknown compound is a vital step in determining its chemical structure. Remember that an **empirical formula** gives the simplest whole number ratio of each kind of element in a compound. For example, the molecular formula of glucose is $C_6H_{12}O_6$ and its empirical formula is CH_2O.

Calculations of empirical formulas were introduced in Chapter 5, on page 130.

Worked Example 9.6.2 shows how to calculate the empirical formula of an unknown organic compound.

Worked example 9.6.2

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: $n = \frac{m}{M}$	$n(C) = \frac{52.2}{12.0}$ $= 4.35$ $n(H) = \frac{13.0}{1.0}$ $= 13.0$ $n(O) = \frac{34.8}{16.0}$ $= 2.18$
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.	$C = \frac{4.35}{2.18}$ $= 2.0$ $H = \frac{13.0}{2.18}$ $= 6.0$ $O = \frac{2.18}{2.18}$ $= 1.0$
Find the simplest whole number ratio.	C : H : O 2 6 1
Write the empirical formula.	C_2H_6O

Worked example: Try yourself 9.6.2

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.

EXTENSION

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**.

For example, elemental analysis of an an organic compound can be performed by burning the compound in air and the combustion products, carbon dioxide and water, absorbed by chemicals that have been previously weighed.

- 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 9.6.2.

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:

$$n(CO_2) = \frac{m}{M} = \frac{m}{44.0}$$

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:

$$m(C) = n \times M = n \times 12.0$$

Determining the mass of hydrogen in the organic compound

From the mass of water produced, calculate the amount of water produced, in mol:

$$n(H_2O) = \frac{m}{M} = \frac{m}{18.0}$$

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:

$$m(H) = n \times M = n \times 1.0$$

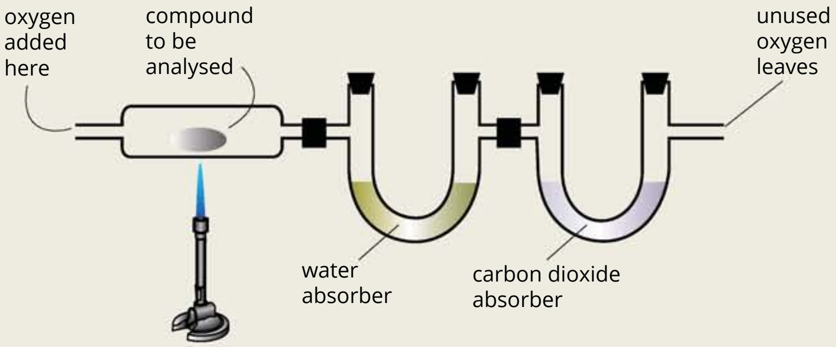


FIGURE 9.6.2 Experimental set-up for the elemental analysis of an organic compound.

continued >

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 9.6.3).

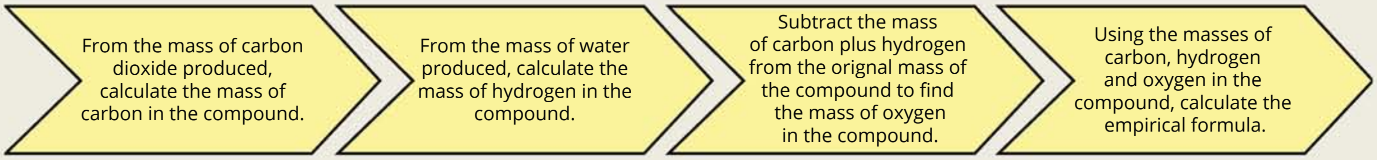


FIGURE 9.6.3 The steps taken to determine the empirical formula from data obtained by elemental analysis.

Determining molecular formulas

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 g mol^{-1}. Figure 9.6.4 summarises the steps taken to determine the molecular formula from the empirical formula.

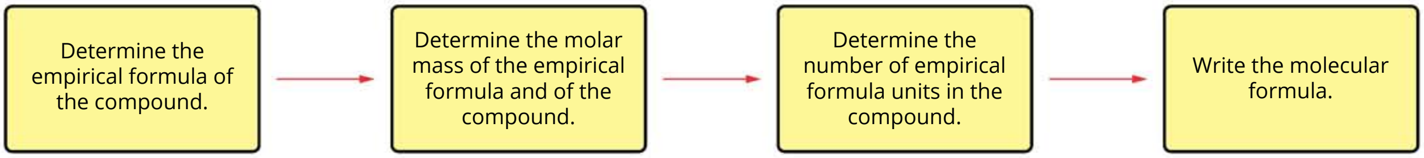


FIGURE 9.6.4 Follow these steps to calculate the molecular formula from the empirical formula.

Worked Example 9.6.3 shows how to calculate a molecular formula.

Worked example 9.6.3

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.	$M(CH_3) = 12.0 + (3 \times 1.0)$ $= 15.0$
Determine the number of empirical formula units in the molecular formula.	Number of empirical formula units $= \dfrac{\text{molar mass}}{\text{molar mass of empirical formula unit}}$ $= \dfrac{30}{15.0}$ $= 2.0$
Multiply the empirical formula by this factor to determine the molecular formula of the compound.	The molecular formula is 2 × CH_3 i.e. C_2H_6

Worked example: Try yourself 9.6.3

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?

9.6 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.

Chapter review

KEY TERMS

addition reaction
alcohol
alkane
alkene
alkyl group
alkyne
carbonyl group
carboxyl group
carboxylic acid
catalyst
combustion
complete combustion
condensation reaction
condensed structural formula
cracking
crude oil
dimer
elemental analysis
empirical formula
ester
esterification reaction
fossil fuels
fractional distillation
functional group
homologous series
hydrocarbon
hydroxyl group
molecular formula
monomer
percentage composition
polymer
saturated
stem name
structural formula
structural isomer
unsaturated
weak acid

Crude oil as a source of raw materials

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 Write a balanced chemical equation for the complete combustion of the following alkanes. Remember to include the states of the reactants and products.
- **a** Gaseous methane
- **b** Liquid hexane
- **c** Gaseous methylpropane
- **d** Solid $C_{31}H_{64}$

5 Draw the structural formulas 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** $CH_3(CH_2)_3CH_3$

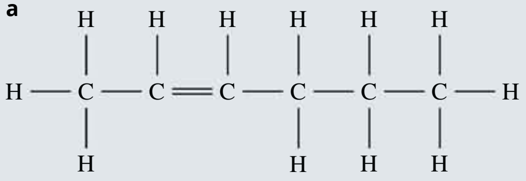
Unsaturated hydrocarbons

6 Classify each of the following hydrocarbons as alkanes, alkenes or alkynes.
- **a** C_2H_6
- **b** C_3H_6
- **c** $C_{20}H_{42}$
- **d** C_2H_2
- **e** C_5H_{10}
- **f** C_5H_{12}
- **g** C_8H_{14}

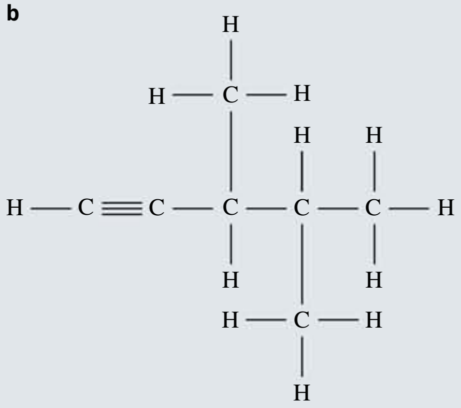
7 Draw the structural formulas and give the systematic names of all the isomers of butene.

8 Write the systematic names of the following unsaturated hydrocarbons, based on their structural formulas.

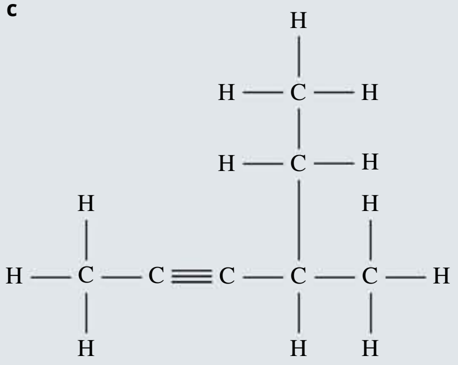
a



b



c



9 Write a balanced chemical equation for each of the following reactions.

- **a** Complete combustion of ethyne gas
- **b** Gaseous propene bubbled into bromine solution
- **c** Gaseous butene reacted with steam in the presence of a phosphoric acid catalyst
- **d** Gaseous ethene reacted with gaseous hydrogen chloride

Alcohols

10 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.

11 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.

12 Table 9.7.1 lists the boiling points of the first five alkanes and alcohols (hydroxyl group on carbon number 1).

TABLE 9.7.1 Boiling points of the first five alkanes and alcohols

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.

13 Explain why:

- **a** butan-1-ol has a higher boiling point than methanol
- **b** a '1' needs to be included in the name of butan-1-ol but not in methanol.

Carboxylic acids

14 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

15 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

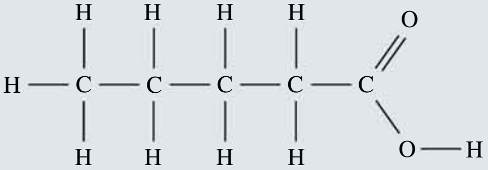
C Dispersion forces

D Carbon–oxygen bonding

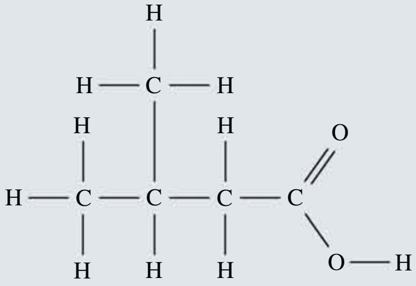
16 Explain why the solubilities of carboxylic acids in water decrease as the length of their carbon chain increases.

17 Write the systematic names of these carboxylic acids, based on their structural formulas.

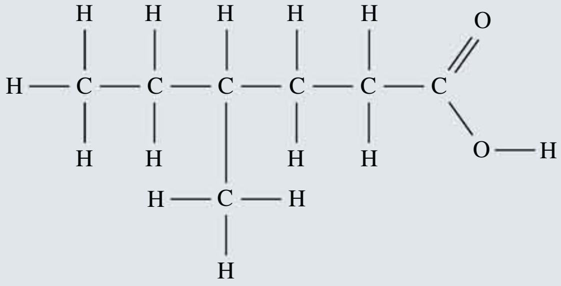
a



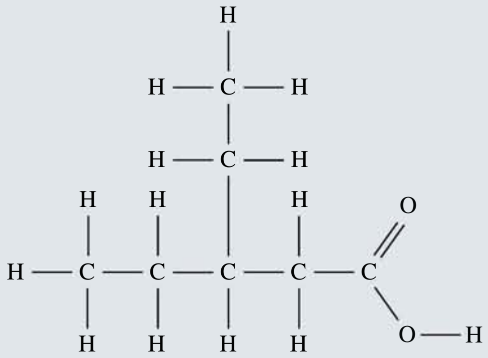
b



c



d



Esters

18 Draw the structural formulas of the following esters and then name them.

- **a** CH_3COOCH_3
- **b** $CH_3COOCH_2CH_3$
- **c** $CH_3CH_2COOCH_2CH_3$

19 **a** Write a chemical equation to describe the preparation of propyl ethanoate from an alcohol and a carboxylic acid.

- **b** What name is given to this type of reaction?
- **c** Sulfuric acid would be present in the reaction mixture. Why?

20 Figure 9.7.1 shows the structure of aspirin (acetylsalicylic acid).

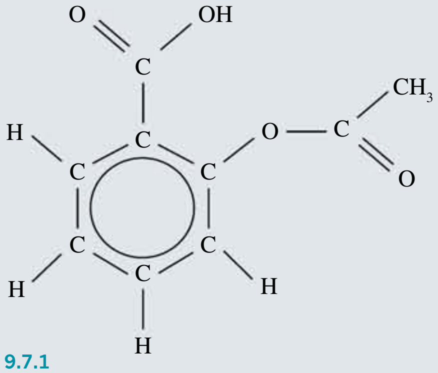


FIGURE 9.7.1

- **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.

Determining formulas 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 present in the sample.

22 Using the empirical formula and the relative molecular mass, determine the molecular formulas of the following compounds.

Empirical formula	Relative molecular mass	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}.

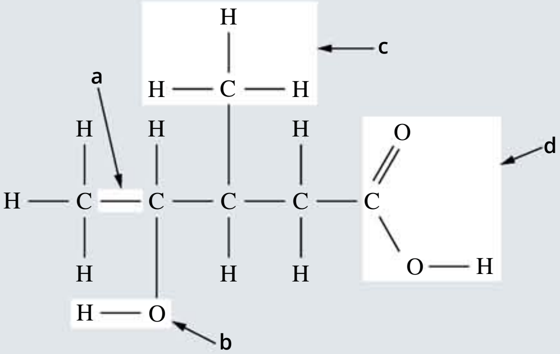
- **a** Calculate the empirical formula of the hydrocarbon.
- **b** Determine its molecular formula.
- **c** To which homologous series does the compound belong?

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.

Connecting the main ideas

25 Identify the structures or functional groups labelled a, b, c and d.



26 Prepare a poster that summarises the rules for the systematic naming of carbon compounds.

27 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.

28 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.

CHAPTER

10 Polymers

Polymers (commonly called plastics) offer an almost limitless variety of properties, enabling them to be used for many different purposes.

In this chapter, you will learn about the formation of addition polymers. The characteristics of the molecules used to make these very large molecules will be considered, as will the unique properties of the different polymers they form.

Starting with the most widely used synthetic polymer, polyethene, you will learn how the properties of polymers can be modified for different applications.

Finally, you will examine the relative merits and disadvantages of the widespread use of polymers.

Key knowledge

- The formation of polymers from monomers, including addition polymerisation of alkenes
- The distinction between linear (thermoplastic) and cross-linked (thermosetting) polymers with reference to structure, bonding and properties, including capacity to be recycled
- The features of linear polymers designed for a particular purpose, including the selection of a suitable monomer (structure and properties), chain length, degree of branching, percentage crystalline areas and addition of plasticisers
- The advantages and disadvantages of the use of polymer materials

10.1 Types of polymers

Polymers are often referred to by the general term **plastics**. You can probably identify many items that are made of polymers. Polymers are used in the construction of many different objects because they are cheap, versatile and easy to manufacture.

Many products such as combs, pen casings and rulers do not require special properties. They don't have to withstand high temperatures or highly corrosive environments. These products can be made from cheap, lightweight polymer materials.

In Figure 10.1.1, you can see a range of familiar polymers. The polymers that make up these objects are selected for their strength or flexibility or other properties. In this chapter you will learn that scientists have developed very sophisticated polymers with high performance properties.

FIGURE 10.1.1 (a) The polymer used to make the toy soccer players in this game was selected for its strength and how easy it is to mould. (b) The polymer bank notes used in Australia are strong and flexible. (c) The polymers in the helmet, gloves and bottle are similar, but differences in processing have given them very different properties.

POLYMER STRUCTURE

Polymers are covalent molecular substances composed of many small molecules all joined together. The word is made up of two parts, which come from Greek words. *Poly* means 'many', and *mer* means 'part'. They are formed by joining together thousands of smaller molecules, called **monomers** (*mono* means 'one') through a process called **polymerisation**, as shown in Figure 10.1.2.

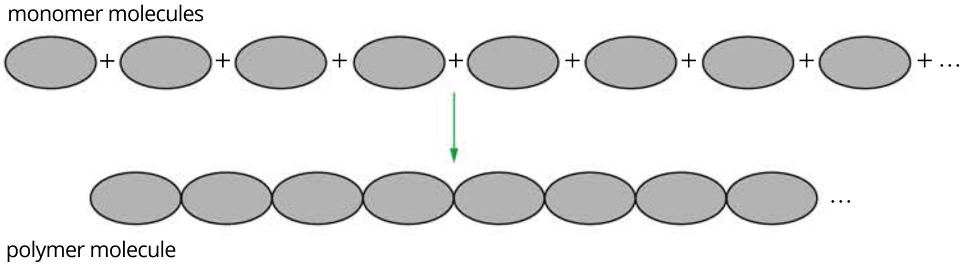


FIGURE 10.1.2 Monomers join to each other to form polymers.

Plastics and polymers

The word 'plastic' is frequently used to describe many items such as cling wrap and detergent bottles. For chemists the word 'plastic' describes a property of a material, not the material itself. A substance is described as being plastic if it can be moulded into different shapes readily. This is because the material from which it is made is a plastic material. Figure 10.1.3 shows two examples of objects made from polymers. The polymer used to make the crate has plastic properties because upon heating, the polymer would melt, allowing it to be reshaped. However, the saucepan handle is hard and brittle and will not melt when heated.

FIGURE 10.1.3 A plastic basket has plastic properties, whereas a polymer frying pan handle does not.

ADDITION POLYMERISATION

As you saw in section 9.2, addition reactions involve the reaction of an alkene with another molecule. All of the atoms of both molecules are present in the final molecule. Under some conditions, alkenes undergo an addition reaction with themselves to produce long chains. The reaction of the monomer ethene with itself to form polyethene, shown in Figure 10.1.4, is an example of the **addition polymerisation** process. Several thousand ethene monomers usually react to make one molecule of polyethene.

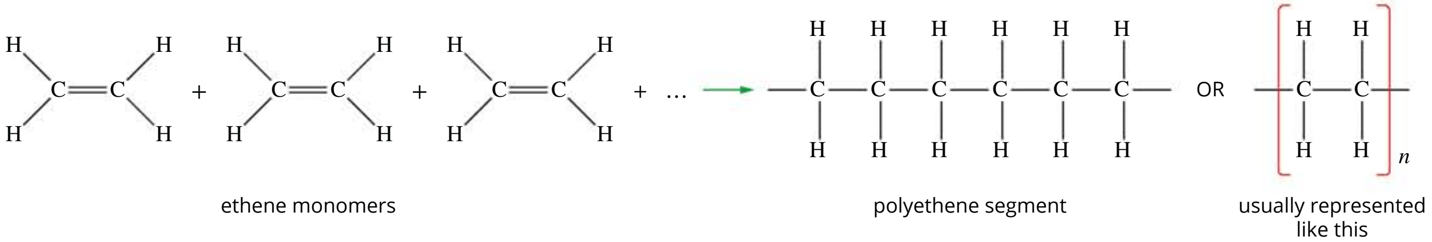


FIGURE 10.1.4 Thousands of ethene monomers join together to make one chain of polyethene. The standard notation shown simplifies the drawing of such a large chain.

Large square brackets, and the subscript *n*, are used to simplify the drawing of long polymer molecules. The value of *n* may vary within each polymer molecule, but the average molecular chain formed might contain as many as 20 000 carbon atoms. Polymers really are very large molecules!

Since all the atoms of the monomers are present in an **addition polymer**, the empirical formula of the monomer is the same as that of the polymer. Figure 10.1.5 provides an alternative representation of a polyethene chain segment, called a ball-and-stick model.

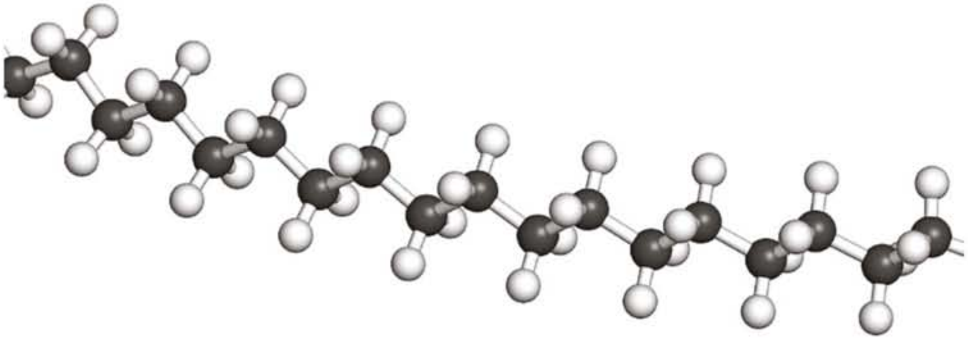


FIGURE 10.1.5 A ball-and-stick representation of a segment of polyethene.

Ethene is an **unsaturated** molecule because it contains a carbon–carbon double bond. When ethene polymerises, the double bonds break and new covalent bonds are formed between carbon atoms on nearby monomers. The polyethene formed does not contain any double bonds. The name of a polymer formed through addition polymerisation will often include the monomer that was used to make it. The names of three common addition polymers and their monomers are listed in Table 10.1.1.

TABLE 10.1.1 Monomer and polymer names

Monomer	Polymer
Ethene	Polyethene
Propene	Polypropene
Tetrafluoroethene	Polytetrafluoroethene

Polymer properties

It is the length of polymer molecules that gives them many of their useful properties. Polyethene is essentially an extremely long alkane. You know from section 7.2 that, as the size of molecules increases, the melting point of a substance increases. The weak dispersion forces (as shown in Figure 10.1.6) between the long polymer chains are sufficiently strong to cause polyethene to be a solid at room temperature.

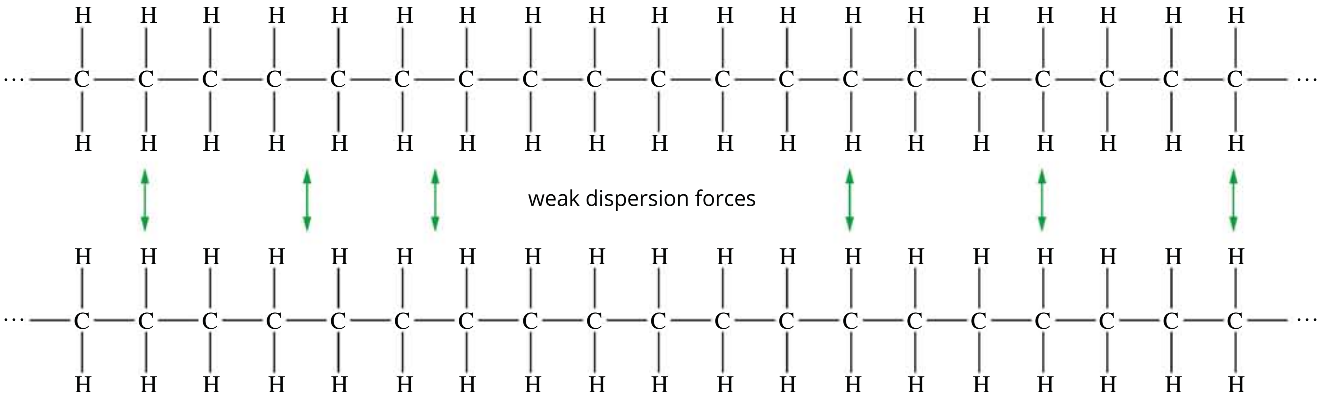


FIGURE 10.1.6 Dispersion forces between polyethene molecules are sufficiently strong to make it a solid at room temperature.

There are thousands of different polymers, many with specialised properties. However, in general, polymers are:

- lightweight
- non-conductors of electricity
- durable
- versatile
- acid-resistant
- flammable.

EXTENSION

History of polymers

Wool, cellulose and proteins are naturally occurring polymers. However, most commercial polymers are synthetic and it is only in the last 100 years or so that their use has become widespread. It is said that Native Americans were playing with crude rubber balls when European settlers first arrived in North America. These balls were made from the sap of rubber trees.

American Charles Goodyear introduced large-scale production of rubber in 1839 when he invented the process of **vulcanisation**. He realised that the properties of rubber are improved when it is heated with a small amount of sulfur. Goodyear is still a famous name in tyres.

The first completely synthetic polymer was released in 1909 by Leo Baekeland, a Belgian-born American chemist. He reacted the chemicals phenol and formaldehyde to form a hard material that he called Bakelite. Bakelite continues to be used to make bowling balls and saucepan handles. Table 10.1.2 shows a number of significant milestones in the history of polymers.

TABLE 10.1.2 Timeline for the development of some early polymers

Year	Polymer	Significance
1869	Celluloid (cellulose nitrate)	Billiard balls, photographic film and table-tennis balls
1907	Bakelite (phenol formaldehyde)	Light switches, saucepan handles
1927	Nylon	Created a shopping frenzy when used to make stockings in 1939
1927	PVC (polyvinyl chloride)	Low flammability and low electrical conductivity
1933	Perspex (polymethyl methacrylate)	Transparency enabled it to take the place of glass during World War II
1937	Polyurethane	Invented in Germany by Professor Otto Bayer. First used to replace rubber
1938	Teflon (polytetrafluoroethene)	Extremely difficult to handle due to its lack of 'stickiness'
1951	Polypropene	Second-most used polymer in the world
1972	Kevlar	Very strong and lightweight polymer. Flame proof
1980	Polyacetylene	Conductive polymer
1990	Polylactic acid	Biodegradable polymer

The two contrasting photos of cyclists in Figure 10.1.7 highlight the rapid developments made by the polymer industry over the last 100 years. Not only have the materials that the bicycles are made from changed but so has the attire of the two cyclists. However, in both cases their clothing is made of polymers.

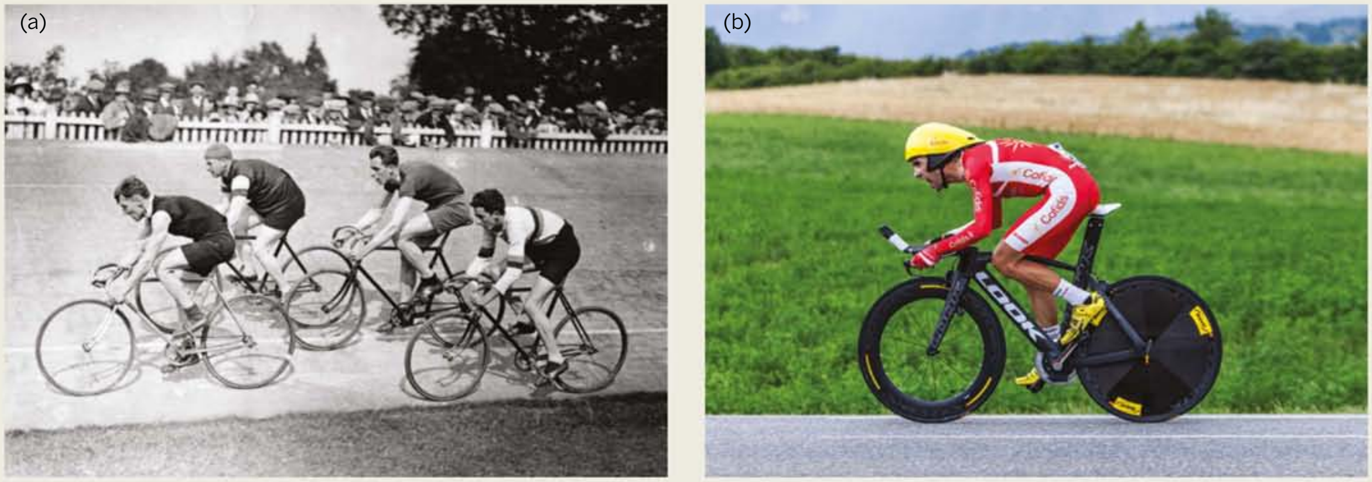


FIGURE 10.1.7 (a) Cyclists and metal bicycles from around 1920. (b) Cyclist pedals during Le Tour de France 2013.

CHEMFILE

The discovery of polyethene

The first practical method for the synthesis of polyethene was discovered by accident in 1933 in the laboratory of 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.

His colleagues went to lunch and he continued to top up the reaction vessel with more ethene. After they 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.

Low density polyethene

The earliest method of producing polyethene involved high temperatures (around 300°C) and extremely high pressures. Under these harsh conditions, the polymer is formed too rapidly for the molecules to be neat and symmetrical. Figure 10.1.8 shows that the product contains many small chains that divide off from the main polymer, called branches.

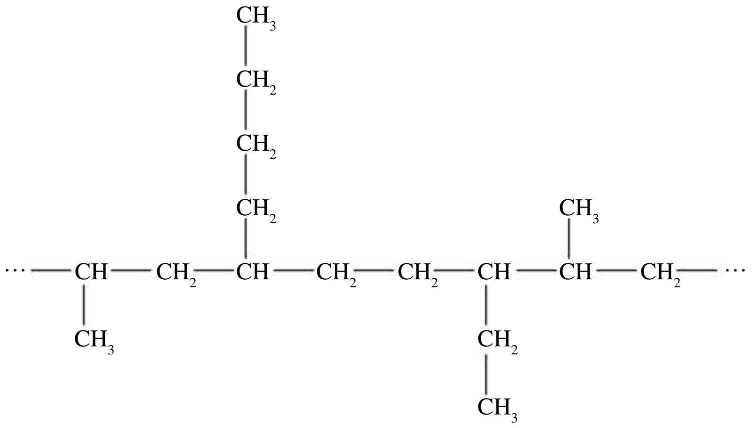
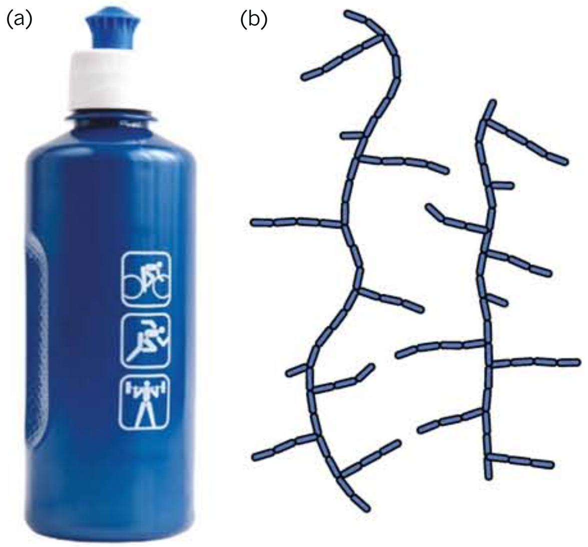


FIGURE 10.1.8 Polyethene made under high pressure and at high temperatures has short branches off the main chain.

The presence of these branches impacts upon the properties of the polymer as the molecules cannot pack closely together. The dispersion forces between molecules are weaker when the molecules are further apart. The arrangement of the polymer molecules can be described as disordered or non-crystalline. This form of polyethene is known as **low density polyethene** or LDPE. Its structure and properties are described in Figure 10.1.9.



Properties

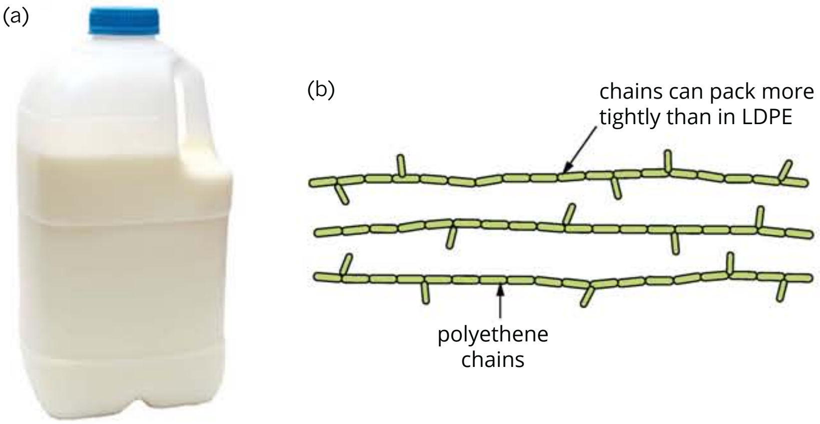
- Low density
- Relatively soft
- Low melting point
- Non-crystalline
- Opaque
- Non-conductor of electricity

FIGURE 10.1.9 Low density polyethene. (a) A bottle made from LDPE. (b) LDPE branched structure.

High density polyethene

A low-pressure method of producing polyethene was developed by Union Carbide in the late 1960s. Highly specialised transition metal catalysts, known as **Ziegler–Natta catalysts**, are used to avoid the need for high pressures. The polymer molecules are produced under much milder conditions and there are very few branches.

The lack of branches allows the molecules to pack together tightly, increasing the density and the hardness of the polymer formed. The arrangement of the polymer molecules is more ordered, resulting in crystalline sections. This form of polyethene is known as **high density polyethene** or HDPE. Its properties and uses are summarised in Figure 10.1.10.



Properties

- High density
- Hard
- Relatively high melting point
- Crystalline sections
- Non-conductor of electricity

FIGURE 10.1.10 Properties and structure of HDPE. (a) A bottle made from HDPE. (b) HDPE structure.

OTHER ADDITION POLYMERS

Many applications require polymers with more specialised properties than polyethene. For example, low flammability is essential for electrical wiring and a baby's bottle needs a polymer with a higher melting point. As you will see in section 10.2, one way to improve the properties of polyethene is to replace one or more of the hydrogen atoms on the monomer with more electronegative atoms or with a larger group of atoms.

As can be seen in Figure 10.1.11, when a chlorine atom replaces a hydrogen atom on ethene, the polymer polyvinylchloride, PVC, is formed.

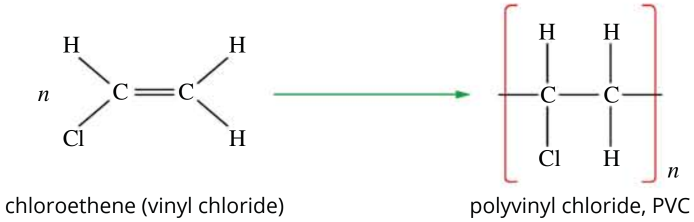
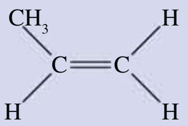
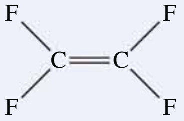
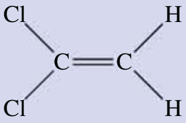
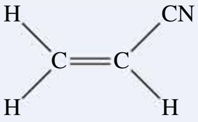
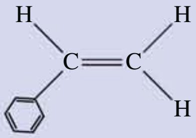
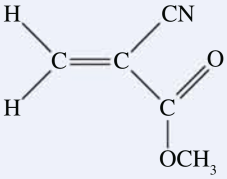
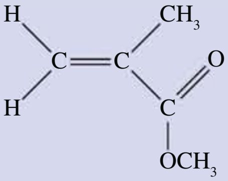


FIGURE 10.1.11 Polyvinylchloride is made from the monomer chloroethene.

The chlorine atoms introduce dipoles into the long molecules. This increases the strength of the forces between polymer molecules, which leads to a higher melting point. PVC offers other advantages over polyethene: it has a low electrical conductivity and a low flammability. A PVC item burning in a flame will extinguish itself when it is removed from the flame. PVC is used in conveyor belts, cordial bottles, water pipes and the covering of electrical wiring.

There are thousands of commercial addition polymers. Table 10.1.3 shows a number of other polymers that may be familiar to you. Each of these polymers offers a unique property or properties that make them of commercial interest.

TABLE 10.1.3 Commercial addition polymers

Monomer	Poylmer	Properties	Examples	Application
 Propene	Polypropene (polypropylene)	Durable, cheap	Artificial grass, dishwasher-safe plastic, ice-cream containers, rope	
 Tetrafluoroethene	Polytetrafluoroethene (PTFE, Teflon)	Non-stick, high melting point	Frying pan and iron coatings, plumber's tape, Gore-Tex fabric	
 Dichloroethene	Polyvinylidene chloride (PVDC)	Sticks to self, transparent, stretchy	Food wrap	
 Propenenitrile	Polypropenenitrile (acrylic)	Strong, able to form fibres	Acrylic fibres, fabrics	
 Phenylethene (styrene)	Polyphenylethene (polystyrene)	Hard, brittle, low melting point	Toys, packaging, expanded foams	
 Methylcyanoacrylate	Polymethylcyanoacrylate	Polymerises on contact with water	Super glue	
 Methyl 2-methylpropenoate	Polymethyl methacrylate (Perspex)	Transparent, strong	Perspex (a glass substitute)	

EXTENSION

Condensation polymerisation

Another method for producing polymers is to use monomers with functional groups on each end of the molecule. The monomers join when the functional groups react with each other. Polymers formed in this way are called **condensation polymers**. Nylon is a condensation polymer. The polymer is formed when two different monomers meet and join together through a condensation reaction, as shown in Figure 10.1.12.

This form of nylon is described as a **copolymer** as it is formed from a reaction between two different monomers. A feature of condensation polymerisation is that small molecules, usually water, are also produced each time the monomer molecules join.

Bakelite, polyester and Kevlar are other common condensation polymers.

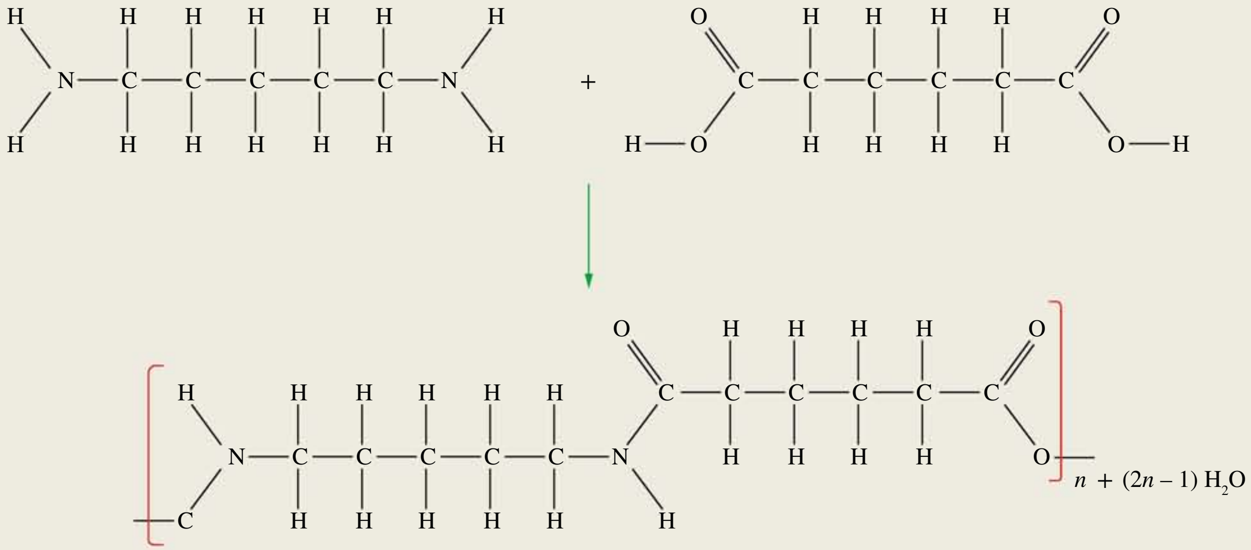


FIGURE 10.1.12 Production of nylon from the condensation reaction between two types of monomers.

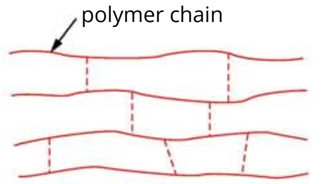
THERMOPLASTIC AND THERMOSETTING POLYMERS

Polymers can be classified into two groups on the basis of their behaviour when heated:

- **thermoplastic** polymers
- **thermosetting** (or thermoset) polymers.

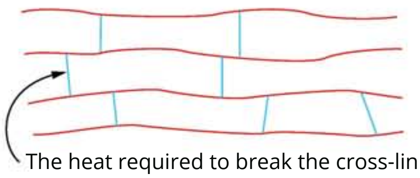
Thermoplastic polymers soften when heated, which means they can be remoulded or recycled. Polymers are only thermoplastic if the bonds between the long polymer chains are hydrogen bonds, dipole–dipole bonds or weak dispersion forces (Figure 10.1.13). When heated, the molecules in thermoplastic materials have enough energy to overcome the intermolecular forces and become free to move and slip past one another. If the polymer can be remoulded, then it can probably be recycled easily, a desirable property in modern society.

Thermosetting polymers decompose or burn when heated. They do not soften because the bonds between the chains are very strong (Figure 10.1.14). If the temperature becomes high enough to break the covalent bonds, the breaks may be at any point, causing the polymer to decompose. It is difficult to recycle thermosetting polymers as they cannot be remoulded into new shapes.



Heat causes the molecules to move enough to overcome the weak forces between molecules.

FIGURE 10.1.13 A thermoplastic polymer has weak bonds between the chains.



The heat required to break the cross-links is also sufficient to break the bonds within the molecules themselves.

FIGURE 10.1.14 A thermosetting polymer has strong covalent bonds between the chains.

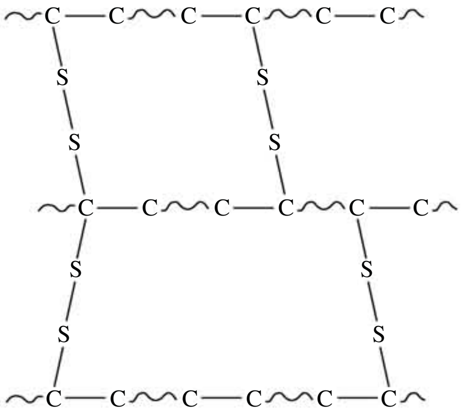


FIGURE 10.1.15 The elastomer chains in rubber car tyres are cross-linked by sulfur atoms.

Covalent bonds between polymer molecules are called **cross-links**. Cross-links limit movement between the polymer molecules and make the polymer rigid, hard and heat resistant. Thermosetting polymers are used to make items such as saucepan handles, bowling balls and shatterproof crockery.

Elastomers are an interesting class of polymers that are formed when only occasional cross-links are present. The chains in these polymers can still move past each other when stretched but the cross-links return the chains to their original positions once the force causing the stretching is released. Elastic bands and other rubber items are made of elastomers. The cross-links stop elastomers from completely melting when heated and makes recycling difficult. For example, the sulfur cross-links in the polymer in car tyres (Figure 10.1.15) make the tyres non-recyclable.

10.1 Review

SUMMARY

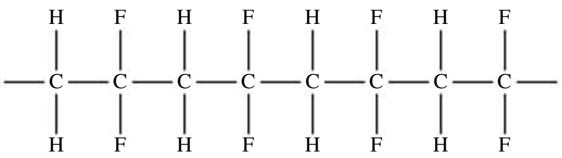
- Polymers are long molecules formed by the reaction of thousands of monomer units.
- Addition polymers are formed from the reactions of monomers containing carbon–carbon double bonds.
- In general, polymers are durable and have relatively low densities. They are non-conductors of electricity and have relatively low melting points.
- The most common polymer used is polyethene. It can be manufactured in two different ways to make two different products: high density polyethene (HDPE) and low density polyethene (LDPE).
- A polymer is thermoplastic if it will soften when heated, allowing it to be reshaped. A thermoplastic polymer can be recycled by moulding it into a new shape. Thermoplastic materials have no strong bonds between polymer chains.
- Some polymers have covalent bonds, or cross-links, between polymer chains. Such thermosetting materials do not melt and they cannot be reshaped. If they cannot be reshaped, recycling is limited.
- Elastomers are polymers with special cross-links that allow them to stretch.

KEY QUESTIONS

1 What is the empirical formula of the following monomers?
  - **a** Ethene
  - **b** Propene
  - **c** Phenylethene
  - **d** Chloroethene

2 What would be the molecular formula for a molecule of:
  - **a** polypropene made from three monomer units?
  - **b** polyvinyl chloride made from six monomer units?
  - **c** polyethene made from 65 monomer units?

3 How many repeating monomer units does the following polymer segment contain?



$-\mathrm{CH_2{-}CF_2{-}CH_2{-}CF_2{-}CH_2{-}CF_2{-}CH_2{-}CF_2}-$

4 Explain why a molecule containing 18 repeating units from the monomer phenylethene would not be considered a polymer.

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?

6 Refer to Table 10.1.3 on page 240 and draw diagrams to represent the formation of:
  - **a** polypropene
  - **b** Teflon
  - **c** polypropenenitrile.

10.2 Designing polymers for a purpose

The development of new polymers has been motivated by the need to replace existing materials that are in short supply and to produce materials with improved physical and chemical properties. The widespread use of polymers brings many advantages, as well as challenges. A very important issue is the reduction of polymer waste, through either **biodegradable** polymers or recyclable polymers. Figure 10.2.1 shows apples packaged in biodegradable plastic and waste plastic waiting to be recycled.

In this section, you will explore how changes in monomer structure, the length of polymer chains, amount of branching, and the addition of other substances to the polymer can modify polymer properties.

FIGURE 10.2.1 (a) Apples packaged in biodegradable plastic. (b) Waste plastic waiting to be recycled.

SELECTING A MONOMER

Non-polar monomers

In section 10.1, you learned that polyethene is the addition polymer manufactured in greatest amounts. The properties of a polymer depend largely on the monomer used to make them. Tetrafluoroethene ($CF_2=CF_2$) (shown in Figure 10.2.2) is formed when all of the hydrogen atoms in ethene are replaced by highly electronegative fluorine atoms.

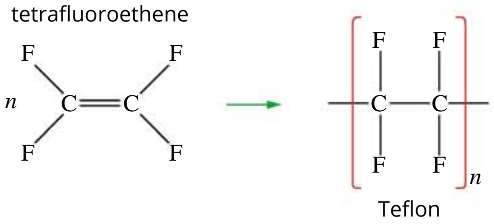


FIGURE 10.2.2 Addition polymerisation of tetrafluoroethene makes the polymer Teflon.

Molecules of tetrafluoroethene react with themselves to form the polymer polytetrafluoroethene, known as Teflon. Teflon has quite exceptional properties that are very different from those of polyethene. Teflon can be used to make non-stick frying pans, medical implants, gears and Gore-Tex clothing. The electronegative fluorine atoms reduce the strength of intermolecular bonds with other substances. The properties of Teflon are summarised in Table 10.2.1.

TABLE 10.2.1 A summary of the properties of Teflon

Property	Description
Non-stick	Teflon repels all other substances, both hydrophobic (oil, fat) and hydrophilic (water).
Heat resistant	The melting point of Teflon is 335°C and the upper operating temperature for this polymer is 260°C.
Chemical resistant	The polymer is extremely resistant to all known chemicals. It is not attacked by strong acids and bases and is inert towards all organic solvents.
Good mechanical properties	Teflon is strong and durable, but not as hard as PVC.
Low friction coefficient	Teflon is slippery to the touch. The friction coefficient between two pieces of Teflon is very low.
Flame resistant	Teflon is non-flammable.

CHEMFILE

Teflon—a wonder material

American polymer company DuPont first manufactured Teflon in 1938. It was used during World War II as part of the process of isolating uranium for the first atomic bomb. After the war, its uses spread to plumber's tape, non-stick cookware and artificial hips and vocal chords as manufacturers sought to take advantage of its heat resistance and low coefficient of friction.

The non-stick nature of Teflon has the disadvantage of making it difficult to apply to a surface such as a clothes iron. The metal surface has to be sand blasted and the Teflon applied in several layers, starting with a type of primer.

Another innovative application of Teflon is in Gore-Tex (Figure 10.2.3). 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.

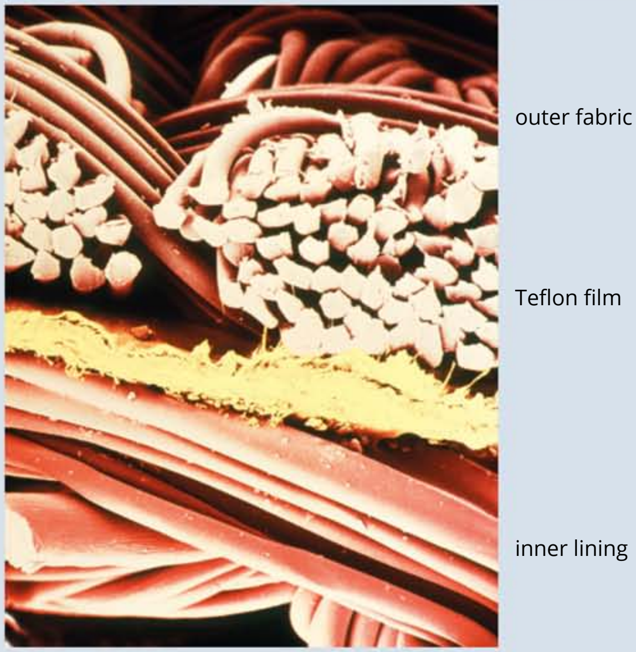


FIGURE 10.2.3 Scanning electron micrograph of Gore-Tex fabric. The small yellow and white particles are Teflon. The small holes between these particles allow vapour to pass through the fabric but not liquid.

Polar monomers

Ethene and tetrafluoroethene molecules are non-polar, meaning that the intermolecular forces present between polyethene and Teflon molecules are weak dispersion forces. When a polymer is made from polar monomers, the chains will be held together by stronger polar attractions, such as dipole–dipole interactions or hydrogen bonds.

Polyvinyl chloride (PVC) is made from the polymerisation of chloroethene ($CHCl{=}CH_2$) as shown in Figure 10.2.4.

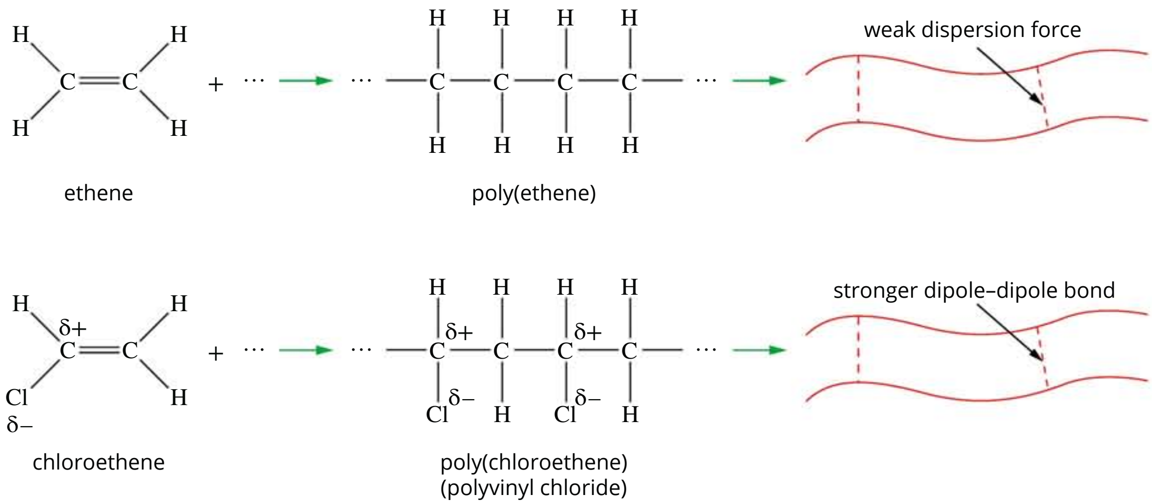


FIGURE 10.2.4 Polyvinyl chloride is formed from polymerisation of polar chloroethene monomers, and has dipole–dipole attractions between chains.

The carbon–chlorine bonds in a PVC molecule are polar and allow dipole–dipole attractions to occur between polymer chains. Because of this, PVC is harder and more rigid than polyethene and Teflon. One of the main applications of PVC is in drain pipes. Incorporating additives, which is discussed later in this section, allows even more widespread use of PVC.

Copolymers

In recent years, a new generation of versatile materials has been developed by combining two or more monomers together into one polymer. A copolymer is a polymer made from at least two different monomers.

The Water Cube Stadium built for the 2008 Beijing Olympic Games (Figure 10.2.5) 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% 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 10.2.5 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 10.2.6) is formed from styrene ($CH_2{=}CH(C_6H_5)$) and butadiene ($CH_2{=}CHCH{=}CH_2$). Pure polybutadiene is an elastomer used in the production of synthetic rubbers for applications such as tyres and golf balls.

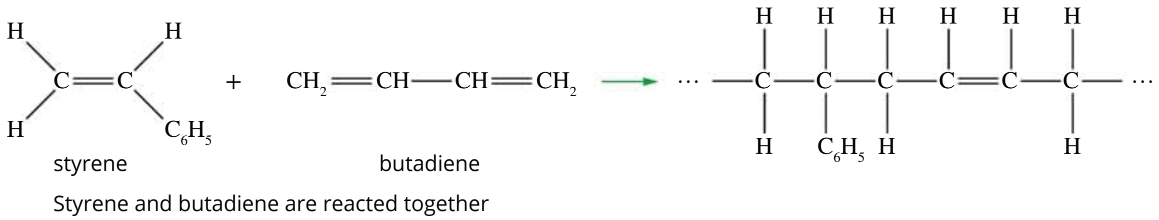


FIGURE 10.2.6 Formation of the SBR copolymer chain from two monomers.

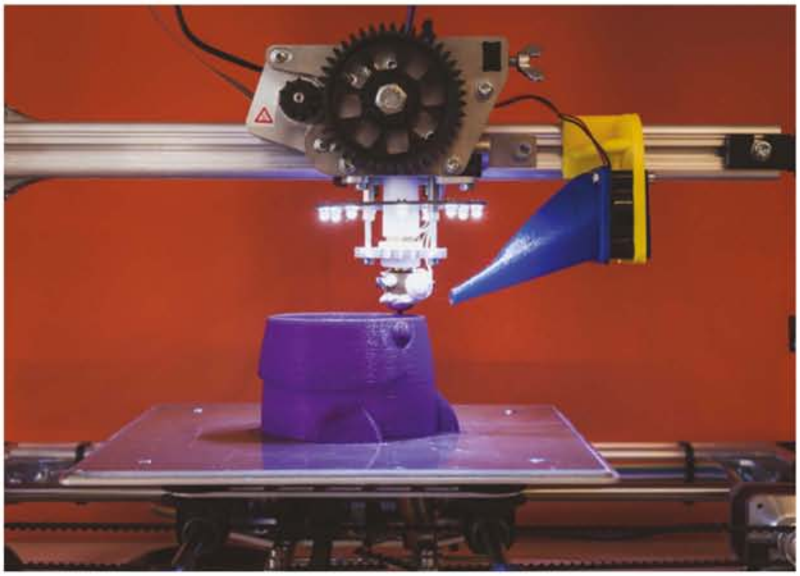


FIGURE 10.2.7 This 3D printer uses an ABS copolymer filament to make an object.

A variety of polymers with different properties can be produced simply by altering the ratio of the monomers. For example, an elastomer similar to natural rubber is produced when the two monomers are present in close to equal amounts. The styrene monomers increase the abrasion resistance of the polymer and make it suited for use in car tyres, its main application.

Addition of a third monomer, acrylonitrile ($CH_2{=}CHC{\equiv}N$), 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 10.2.7, 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.

Conductive polymers

Polymers are usually known for their insulating properties. In 2000, the Nobel Prize in Chemistry was awarded to Alan MacDiarmid (born in New Zealand), Hideki Shirakawa (Japan) and Alan Heegar (USA) for the discovery of electrically conducting polymers. These groundbreaking **conductive polymers** have opened the way to lighter, polymer-based circuits that are being used now 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, shown in Figure 10.2.8.

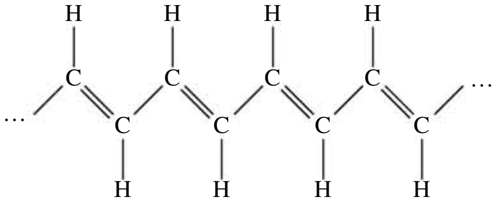


FIGURE 10.2.8 The structure of polyethyne, a polymer which becomes conductive under some conditions.

When ethyne ($CH{\equiv}CH$) polymerises, one of the carbon–carbon bonds is rearranged to bond to neighbouring monomers. As you can see in Figure 10.2.9, each repeating monomer unit in polyethyne retains a carbon–carbon double bond.

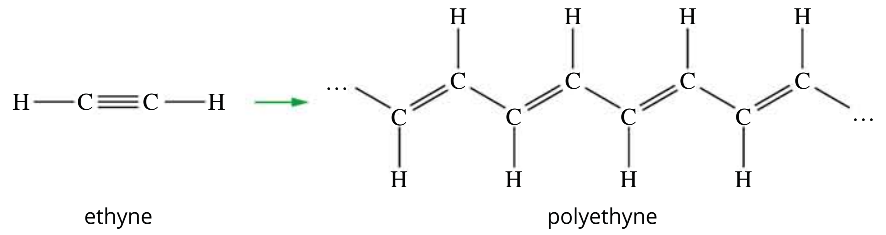
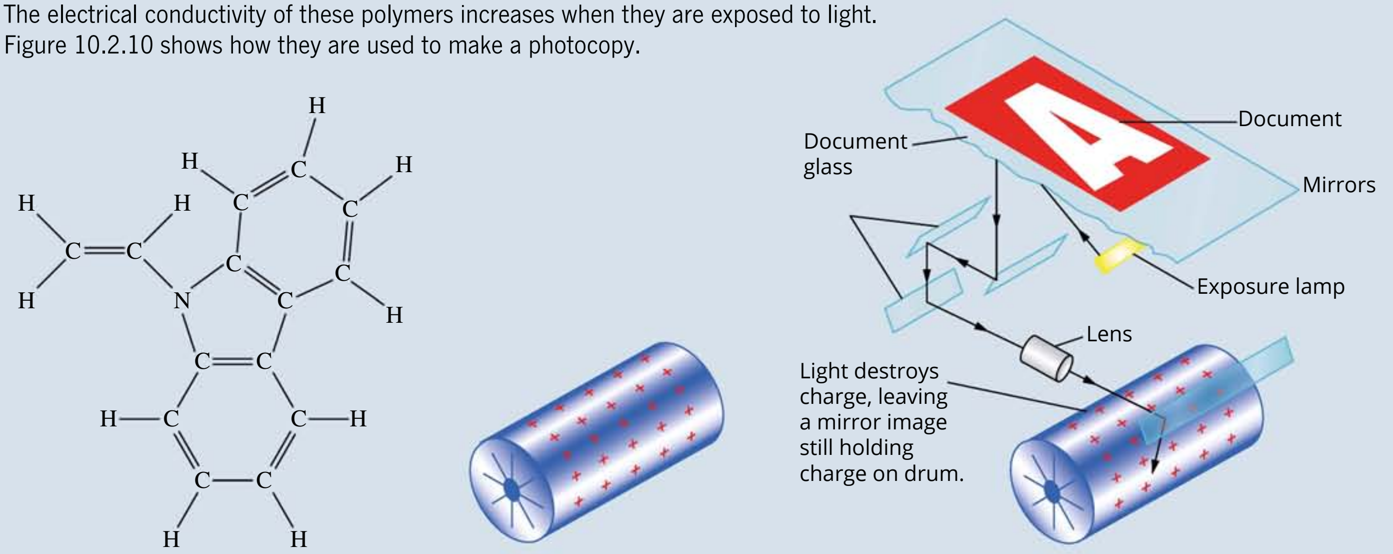


FIGURE 10.2.9 Addition polymerisation of ethyne produces polyethyne with alternating double and single carbon–carbon bonds.

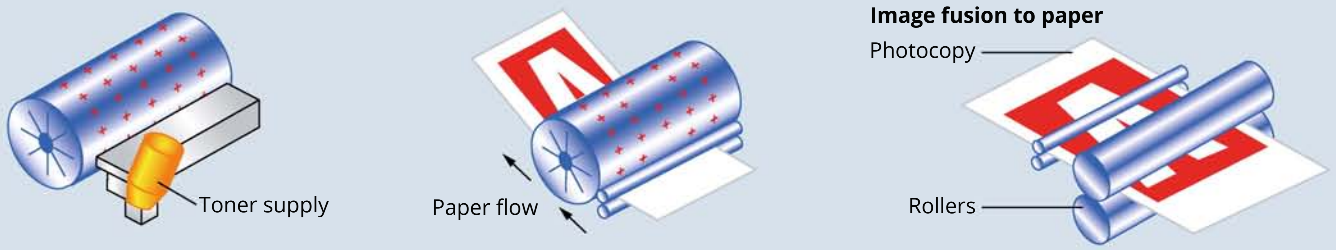
CHEMFILE

Photoconductive polymers

The process of making a photocopy relies on polymers that are **photoconductive**. The electrical conductivity of these polymers increases when they are exposed to light. Figure 10.2.10 shows how they are used to make a photocopy.



1. The light-sensitive monomer vinyl carbazole is used to make the photoconducting polymer, polyvinyl carbazole.
2. The drum surface of the photocopier, coated with a very thin layer of polyvinyl carbazole, is charged.
3. A document is placed on the document glass of the copier and light scans over the document so that its image is projected onto the drum surface.



4. The drum is coated with a fine layer of ink powder or toner that is attracted to the charged areas on the drum surface.
5. A sheet of paper now passes across the drum and toner is attracted to the paper.
6. Hot rollers fuse the image with the paper, resulting in an exact photocopy of the original document.

FIGURE 10.2.10 The process of producing a photocopy.

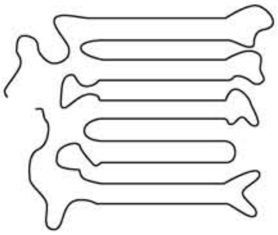


FIGURE 10.2.11 A crystalline region of a polymer material forms where the polymer chains are arranged in an ordered fashion.

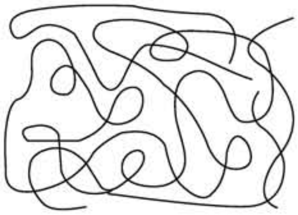


FIGURE 10.2.12 An amorphous region forms when polymer chains are disordered.

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 10.2.11.

Being regularly arranged brings the polymer chains closer together. The intermolecular forces between the closely packed chains are stronger and the presence of crystalline regions strengthens the material overall. Crystalline regions in a polymer prevent the transmission of light through the material, making it appear opaque (cloudy), so that light does not pass directly through it.

An amorphous region is an arrangement where the polymer chains are randomly tangled and unable to pack very closely. The polymer chains shown in Figure 10.2.12 are amorphous because they have no orderly arrangement.

In some polymer materials, the entire solid is amorphous. Amorphous polymers are usually less rigid, weaker and often transparent (see-through).

The percentage of the polymer that is crystalline, rather than being amorphous, influences the properties of the polymer. Increasing the percentage crystallinity of a material makes it stronger and less flexible. This also makes the material less transparent as the crystalline regions scatter light.

POLYETHENE: POLYMER CHAIN LENGTH AND BRANCHING

Polyethene exists in several different forms that provide good examples of the effects of polymer chain length and branching on polymer properties.

Chain length

Ultra-high molecular weight polyethene (UHMWPE) consists of extremely long polymer molecules. As a consequence, dispersion forces between chains are much stronger than in shorter chains of polyethene. Because of this, UHMWPE is such a tough a polymer that it can be used to make artificial hip joints, safety helmets and even bulletproof vests.

Extent of branching

As you learned in section 10.1, the amount of branching in polyethene can be varied by changing the process used for its manufacture.

When the monomers join in long chains with very few, short branches, the polymer molecules can pack together closely and the polymer material is called high density polyethene (HDPE) (Figure 10.2.13). 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. Many cars have a fuel tank made from HDPE.

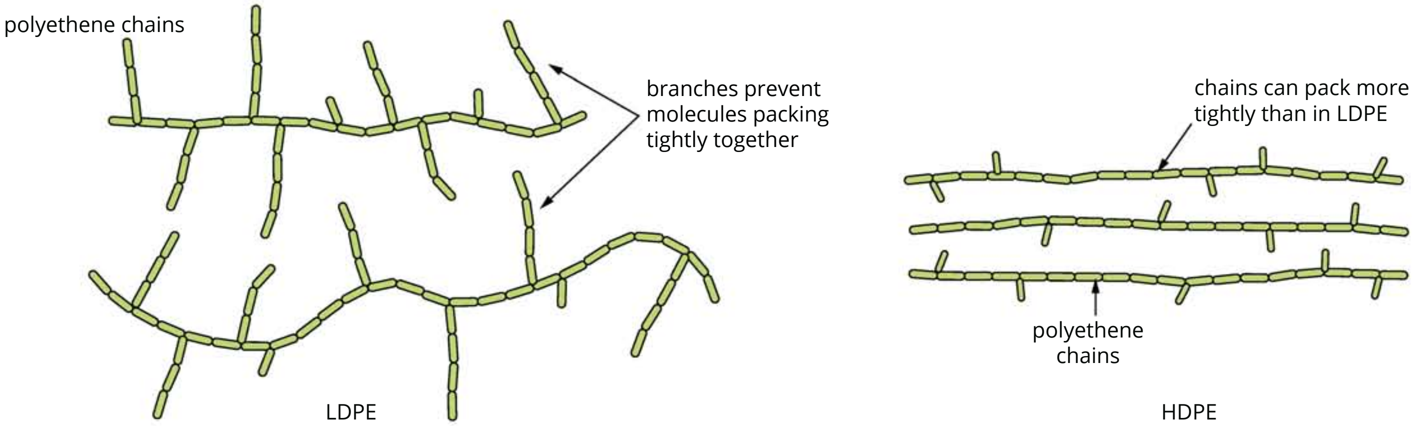


FIGURE 10.2.13 The arrangement of polymer molecules in low density polyethene (LDPE) and high density polyethene (HDPE).

Polyethene chains formed under high-pressure reaction conditions have a high degree of branching. These longer, more frequent and random branches prevent the polymer molecules from forming extensive crystalline regions. This polymer material is LDPE and its percentage crystallinity is only 65% (Figure 10.2.13). LDPE is softer and more flexible and is used in cling wrap, squeeze bottles and insulating cables.

POLYPROPENE: THE ARRANGEMENT OF SIDE GROUPS

Polypropene (PP) is an addition polymer made from the monomer propene ($CH_2{=}CHCH_3$), as shown in Figure 10.2.14.

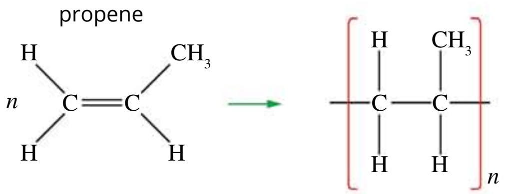


FIGURE 10.2.14 Propene undergoes addition polymerisation to form polypropene.

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 10.2.15 shows the three different structural forms of polypropene.

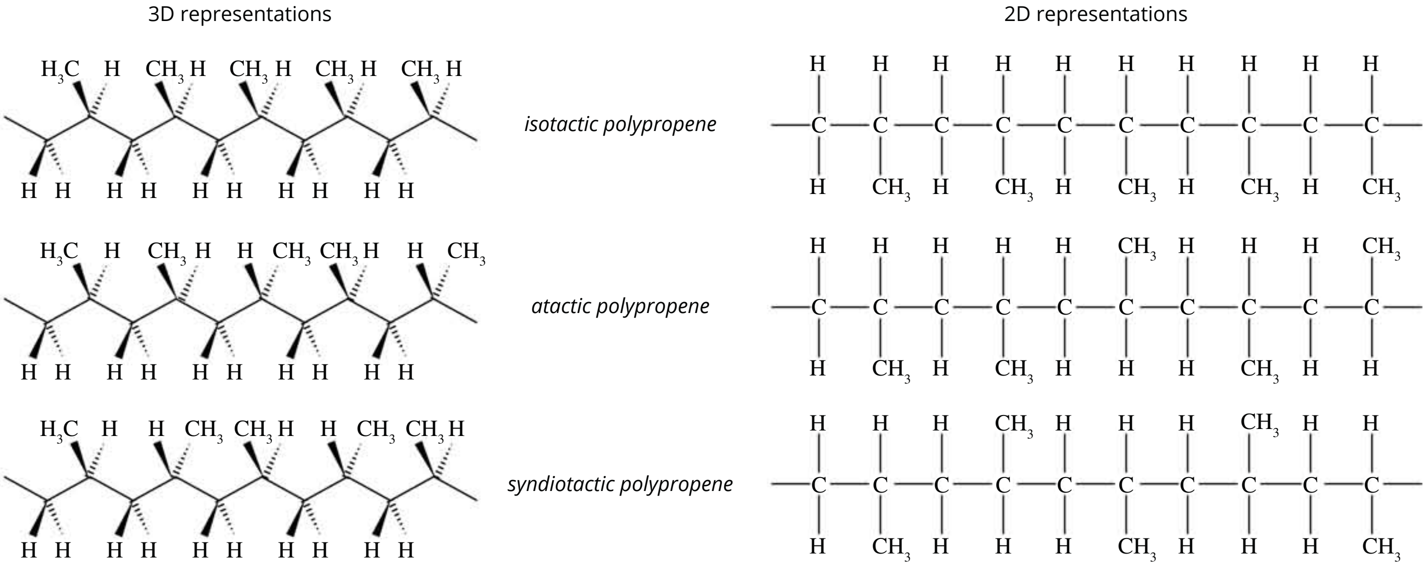


FIGURE 10.2.15 Sections of three different structural forms of polypropene.

- **Isotactic** polypropene has all the side groups on one side of the polymer chain. This allows crystalline regions to form, and significant attractive forces between the chains.

  This polymer material is used in many applications. For example, it is used to make babies' bottles that can be sterilised in boiling water without softening, Australian banknotes, very strong fibres and ropes, thermal underwear and fleece jackets.
- **Atactic** polypropene has the side groups randomly distributed. This prevents the chains from stacking together well and forming crystalline regions. Atactic polypropene is very soft and has limited usefulness.
- **Syndiotactic** polypropene has the side groups on regularly alternating sides of the polymer chain. This allows for good packing and the material is highly crystalline. It is a relatively new form of polypropylene and many new applications for it are currently being explored.

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 been traditionally used.

Polystyrene

The side group in styrene is a flat ring of six carbon atoms, often called a benzene ring, as shown in Figure 10.2.16.

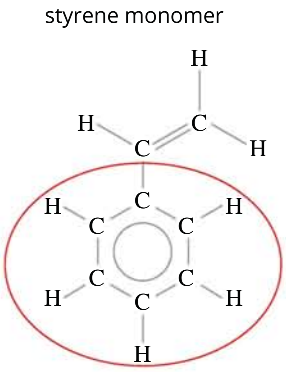


FIGURE 10.2.16 The chemical structure of the styrene monomer showing the bulky side group circled in red.

Styrene polymerises as shown in Figure 10.2.17, where benzene rings are covalently bonded to every second carbon atom in the polymer chain. This causes polystyrene to be a hard but quite brittle plastic with a low density. It is used to make food containers, picnic sets, refrigerator parts, and CD and DVD cases.

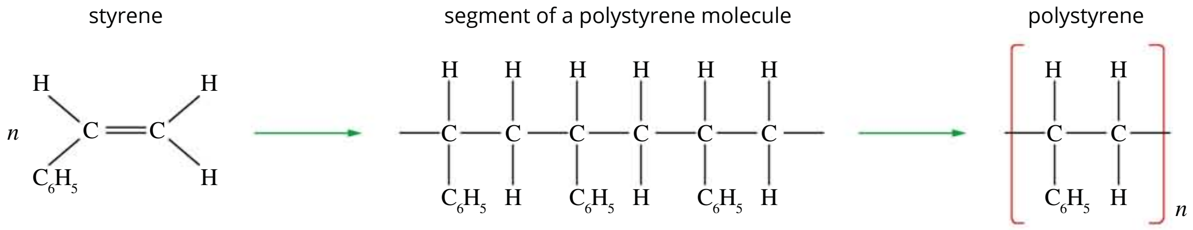


FIGURE 10.2.17 The polymerisation of styrene to form polystyrene.

Polymethyl methacrylate

Polymethyl methacrylate (PMMA) also has large side groups, as you can see in the structure of its monomer in Figure 10.2.18. Due to the absence of crystalline regions that refract light, PMMA is transparent like polystyrene.

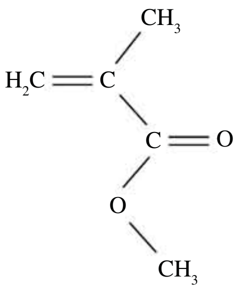


FIGURE 10.2.18 The bulky methyl and ester side groups of methyl methacrylate prevent the polymer chains from forming compact crystalline structures.

Polymethyl methacrylate is much lighter than glass, more malleable and less prone to shattering. It is the ideal polymer for car headlamps, safety glasses and safety shields used by riot police (Figure 10.2.19).

FIGURE 10.2.19 Polymethyl methacrylate is an amorphous material that is used in safety glasses and shields used by riot police.

ADDITIVES

Very few polymers are used in their pure form. Most include additives that improve or extend the properties of the polymer. They include pigments (to add colour), UV stabilisers (to prevent deterioration in sunlight), flame retardants and **plasticisers**.

Plasticisers

Plasticisers are small molecules that can be added to polymers during their manufacture. The polymer molecules are forced slightly further apart, weakening the forces between the chains and making the material softer and more flexible.

Because of the polar carbon–chlorine bond in polyvinyl chloride (PVC), the polymer chains are held together strongly by dipole–dipole attractions. Pure PVC is quite rigid at room temperature.

When a plasticiser is introduced between the chains, the chains can slide past each other, making the polymer softer and more flexible. By varying the amount of plasticiser used, PVC can be produced with a wide range of flexibilities. You can see the difference between the packing of PVC without and with plasticiser in Figure 10.2.20. Diisononyl phthalate is a plasticiser that is used to make PVC into vinyl floor coverings.

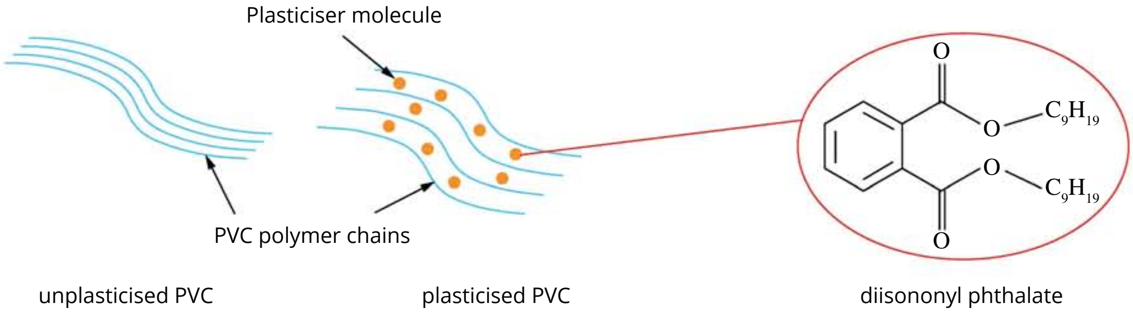


FIGURE 10.2.20 The presence of a plasticiser between the polymer chains weakens the attractive forces.

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 10.2.21. 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 10.2.21 A model plane made of rigid polystyrene sitting on a block of foamed polystyrene.

ADVANTAGES AND DISADVANTAGES OF POLYMERS

Polymers have become the dominant material used in our society. There are many reasons why this has occurred and it is wise to be aware of potential drawbacks that arise from their use. Some of these advantages and disadvantages are shown in Table 10.2.2.

TABLE 10.2.2 Some advantages and disadvantages of using polymers

Advantages	Disadvantages
Available in an enormous variety of different forms, with distinctive properties	Many are derived from petroleum, a non-renewable resource
Generally biologically inert, chemical resistant, corrosion resistant	Microorganisms cannot break down most synthetic polymers (they are not biodegradable)
Easy to process by moulding	Thermoplastic polymers have a limited thermal stability
Low density	Some plastic products crack, scratch or break easily
Good mechanical strength	Many plastics produce toxic gases, such as hydrogen chloride, hydrogen cyanide and dioxins, when burned
Properties can be modified, e.g. by foaming or adding plasticisers	Some plasticisers can leach out of containers or wraps and pose a health risk
Many can be recycled	Thermosetting polymers are currently difficult to recycle

Plastic waste

Australians consume more than 1.5 million tonnes (1.5 billion kilograms) of polymer materials every year, which includes many different plastics. The disposal of the waste polymer material is a serious issue in our society.

Plastics are durable, chemically resistant and lightweight. These properties make plastics very useful, but they also have a serious environmental impact. The biodegradation of plastics is very slow. Once discarded, plastics persist for a very long time, possibly hundreds of years. Because synthetic polymers have low density, waste plastic takes up more volume than other kinds of waste. They occupy the limited space available in landfills and litter the environment (Figure 10.2.22). Burning plastics raises concerns about pollution from harmful combustion by-products. One of these is hydrogen chloride, which is formed by the combustion of waste containing PVC.

FIGURE 10.2.22 Plastic persists for a very long time in the environment.

Biodegradable plastics

Biodegradable materials break down naturally by the action of microorganisms. New types of biodegradable plastics are being developed but these are still a very small proportion of the plastics in everyday use. Most are condensation polymers that are made from renewable plant materials such as corn and starch. Another approach 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.

One example of a biodegradable addition polymer is polyvinyl alcohol. It is made by replacing side groups in polyvinyl ethanoate with hydroxyl groups as shown in Figure 10.2.23. The hydroxyl side groups form hydrogen bonds with water molecules, making the polymer soluble in water. It can be used to make water-soluble hospital laundry bags, sealed sachets containing laundry detergent or pesticides, and bags for waste disposal.

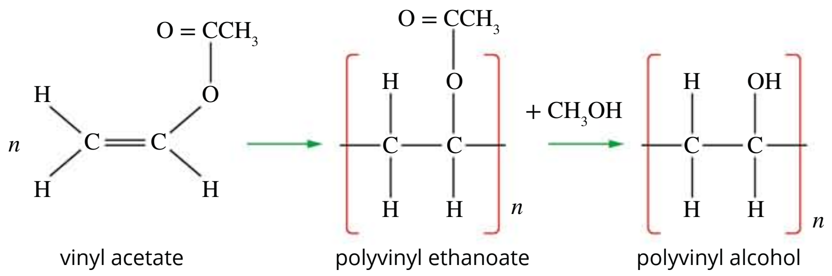


FIGURE 10.2.23 Polymerisation of vinyl ethanoate produces polyvinyl ethanoate, which is then reacted with an alcohol to produce polyvinyl alcohol.

Recycling plastics

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 10.2.24. 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.

The other method of plastic recycling involves depolymerisation, in which polymers are broken down into monomers. These monomers are then used in the production of new polymers. Figure 10.2.25 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 10.2.24 Reprocessing plastic by shredding and blow moulding new products.

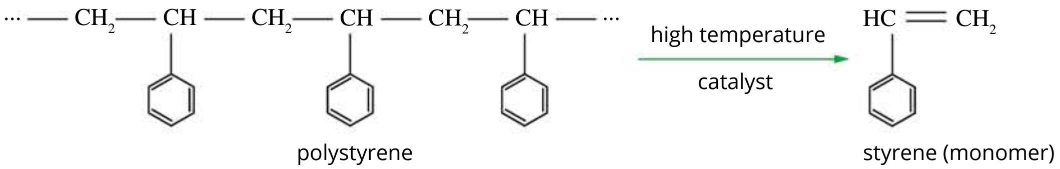


FIGURE 10.2.25 Depolymerisation of polystyrene at high temperature with a catalyst re-forms styrene monomers.

A numbering scale is used to identify plastics for recycling (Figure 10.2.26).

PETE	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 and other condensation polymers
bottles for soft drinks, water, shampoo, 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 10.2.26 International number code used to identify recyclable plastics.

10.2 Review

SUMMARY

- Materials composed of polymers offer an almost limitless variety of properties, enabling them to be used for many different purposes.
- The percentage crystallinity of a polymer is a measure of the relative amounts of crystalline (ordered) regions and amorphous (disordered) regions in the material.
- No polymer is entirely crystalline. Some are entirely amorphous; most consist of both structures.
- Polymers can be designed for a particular purpose by selecting suitable monomers, reaction conditions or additives.
- Factors that affect the physical properties of polymers include the:
  - polarity of side groups in the polymer
  - use of more than one monomer (copolymers)
  - polymer chain length
  - extent of branching of polymer chains, e.g. LDPE and HDPE
  - arrangement of side groups in the polymer chain
  - inclusion of additives such as plasticisers with the polymer.
- A copolymer is a polymer that is made from more than one monomer.
- Plasticisers are organic molecules that soften a plastic because they weaken intermolecular attractions between polymer chains.
- 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 ($CH_2=CH_2$)

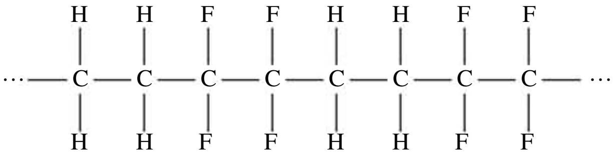
b Vinyl chloride ($CH_2=CHCl$)

c Styrene ($CH_2=CHC_6H_5$)

d Propene ($CH_2=CHCH_3$)

e Acrylonitrile ($CH_2=CHCN$)

2 Label the parts of this copolymer molecule and indicate the name of the corresponding monomers used to form the chain.



$$\begin{array}{ccccccccccccccccc} & H & & H & & F & & F & & H & & H & & F & & F & \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ \cdots - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - \cdots \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ & H & & H & & F & & F & & H & & H & & F & & F & \end{array}$$

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)

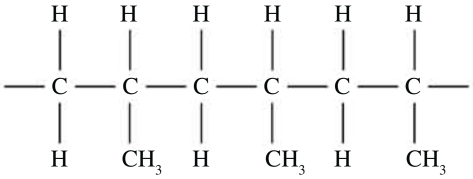
4 Identify whether the following features of a polymer chain will increase or decrease the crystallinity of the polymer material.

a Isotactic alignment of side groups

b Less branching

c Larger side groups

5 A typical section of a certain polymer molecule is shown below.



$$\begin{array}{ccccccccccccc} & H & & H & & H & & H & & H & & H & \\ & | & & | & & | & & | & & | & & | & \\ - & C & - & C & - & C & - & C & - & C & - & C & - \\ & | & & | & & | & & | & & | & & | & \\ & H & & CH_3 & & H & & CH_3 & & H & & CH_3 & \end{array}$$

a What word describes the arrangement of the side groups in this polymer?

b Draw the monomer from which this polymer is produced.

c Identify how many repeating monomer units are shown.

d Would you expect this polymer section to be part of a crystalline or amorphous region? Explain your answer.

6 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

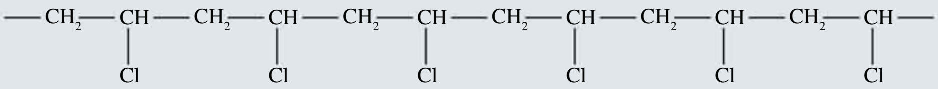
Chapter review

KEY TERMS

addition polymer
addition polymerisation
amorphous region
atactic
biodegradable
condensation polymer
conductive polymer
copolymer
cross-links
crystalline region
elastomer
high density polyethene
isotactic
low density polyethene
monomer
photoconductive
plastic
plasticiser
polymer
polymerisation
side group
syndiotactic
thermoplastic
thermosetting
unsaturated
vulcanisation
Ziegler–Natta catalyst

Types of polymers

1 A segment of a PVC polymer is shown here.



$$-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}-$$

- **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?

2 Define the following terms.

- **a** Monomer
- **b** Thermoplastic
- **c** Thermosetting
- **d** Cross-link
- **e** Plasticiser

3 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.

4 Which of the following molecules can act as monomers in addition polymerisation?

- **A** Propene
- **B** Propane
- **C** Chloroethene
- **D** CH_2=CHF

5 Ethene (C_2H_4) is the smallest alkene.

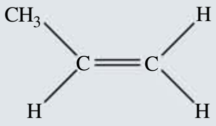
- **a** Why is it described as unsaturated?
- **b** Draw the structural formula of ethene.
- **c** Could ethane (C_2H_6) act as a monomer? Explain.

6 Use polyethene as an example to explain the following terms.

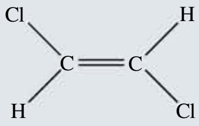
- **a** Addition polymerisation
- **b** Unsaturated and saturated
- **c** Empirical formula

7 Draw a section of the polymer made from each of these monomers in an addition polymerisation process.

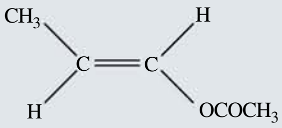
a



b



c



8 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.

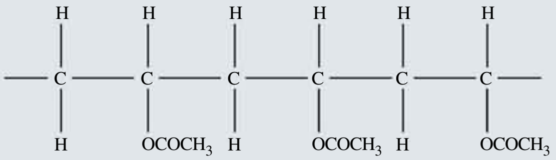
9 Use a diagram to explain how an elastomer is able to stretch and return to its original shape.

10 How does the strength of the inter-chain bonding differ between thermosetting and thermoplastic polymers?

11 Why do thermosetting polymers decompose rather than melt when heated strongly?

Designing polymers for a purpose

12 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.

13 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

14 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?

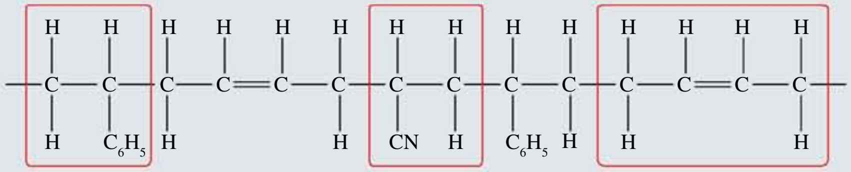
15 What properties are most likely to cause a polymer to contain crystalline regions?

16 **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.

17 How is ultra-high molecular weight polyethene different from HDPE?

18 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.



19 Explain how the following polymer production techniques will affect the properties of a polymer.

- **a** Production conditions that favour longer polymer molecules
- **b** Incorporation of side groups with benzene rings ($-C_6H_5$)

20 Is a plastic that can be recycled more likely to be thermoplastic or thermosetting?

Connecting the main ideas

21 Elastic bands, golf balls and saucepan handles are made from polymers with some cross-linking.

- **a** Which material has the greatest degree of cross-linking?
- **b** Describe the properties of the material you chose in part **a** to support your answer.

22 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?

UNIT 1 • Area of Study 2

REVIEW QUESTIONS

How can the versatility of non-metals be explained?

Multiple-choice questions

1 Element X is in group 14 of the periodic table. Element Y is in group 16. The most likely formula for a compound between X and Y is:

A X_4Y_{16}
B $X_{16}Y_4$
C XY_4
D XY_2

2 The formula for hydrogen cyanide is HCN. The number of electrons shared between the carbon and nitrogen atom is:

A 2
B 4
C 6
D 8

3 The empirical formula of a molecular compound is best defined as the:

A actual number and type of each element present
B simplest whole number mole ratio of each ion present
C simplest whole number mole ratio of each element present
D simplest whole number mass ratio of each element present

4 The total number of atoms in 3.5 mol of pentan-1-ol is:

A 63
B 3.5×10^{23}
C 2.1×10^{24}
D 3.8×10^{25}

5 Which one of the following alternatives lists only compounds that are likely to be found in crude oil?

A C_2H_4, C_3H_7OH, C_8H_{16}, C_8H_{18}
B C_2H_6, C_4H_{10}, C_8H_{18}, $C_{16}H_{34}$
C C_2H_4, C_2H_6, C_2H_5OH, CH_3COOH
D C_2H_4, C_2H_5COOH, C_6H_{12}, C_8H_{16}

6 One of the four hydrocarbons listed below is analysed.

It was found that 0.235 mol of the hydrocarbon has a mass of 16.0 g. The hydrocarbon is:

A CH_4
B C_3H_6
C C_5H_8
D C_6H_{14}

7 A hydrocarbon is found to contain 80.0% carbon. The molecular formula of this hydrocarbon could be:

A C_4H
B CH_3
C CH_4
D C_2H_6

8 The hydrocarbon with the formula C_3H_8 is:

A propane
B 1-propane
C 1-propene
D propene

9 What is the name of the first member of the alkyne family?

A Methyne
B Methene
C Ethyne
D Ethene

10 Which one of the following is not a member of the alkyne homologous series?

A C_2H_2
B C_3H_8
C C_6H_{10}
D $C_{10}H_{18}$

11 How many different alkenes are there with the molecular formula C_4H_8?

A 1
B 2
C 3
D 4

12 Which of the following gives the correct shape for each of the molecules listed?

	Linear	V-shaped	Tetrahedral
A	CO_2	H_2S	CH_4
B	H_2	CO_2	NH_3
C	HF	H_2O	NH_3
D	H_2O	NH_3	CH_4

13 Dispersion forces are the only intermolecular attraction between molecules of:

A HF
B OF_2
C NF_3
D CF_4

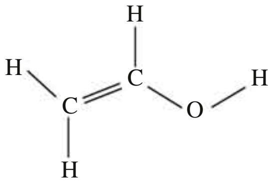
14 Which one of the following alternatives correctly describes the intermolecular forces in pure samples of F_2, HF and CH_3F?

	F_2	HF	CH_3F
A	Dispersion forces only	Dispersion forces and hydrogen bonds	Dispersion forces and dipole–dipole attraction
B	Dispersion forces and hydrogen bonds	Dispersion forces and hydrogen bonds	Dispersion forces and hydrogen bonds
C	Dispersion forces only	Dispersion forces and hydrogen bonds	Dispersion forces and hydrogen bonds
D	Dispersion forces	Dispersion forces and dipole–dipole attraction	Dispersion forces and dipole–dipole attraction

15 Which one of the following alternatives lists the compounds in order of increasing boiling points?

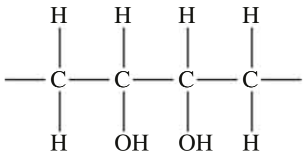
A Ethane, propane, ethanol, propan-1-ol
B Ethane, ethanol, propane, propan-1-ol
C Ethanol, propan-1-ol, ethane, propane
D Ethanol, ethane, propan-1-ol, propane

16 Polyvinyl alcohol is a polymer often used as a water soluble film in packaging. The monomer used to form polyvinyl alcohol is given below.

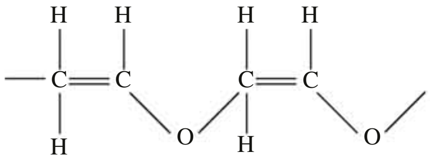


Which one of the following structures shows a possible segment of the polymer?

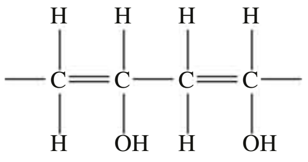
A



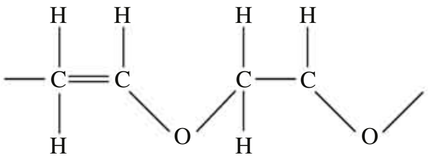
B



C



D



17 It would be possible to tell whether the particles in a compound were held together by ionic or covalent bonds by measuring the compound's:

A melting temperature
B hardness and brittleness
C electrical conductivity in the solid state
D electrical conductivity in the liquid (molten) state.

18 Polyethene is a polymer that has a wide range of uses. It can be produced as a high density product (HDPE) or a lower density form (LDPE) that is softer and more flexible.

Compared to LDPE, HDPE has:

A higher softening temperature due to a greater degree of branching of the polymer chain
B higher softening temperature due to a smaller degree of branching of the polymer chain
C lower softening temperature due to a greater degree of branching of the polymer chain
D lower softening temperature due to a smaller degree of branching of the polymer chain.

19 The percentage of crystalline regions in a polymer can be increased during manufacture. Which of the following statements about a polymeric material with an increased percentage of crystalline regions is correct?

I The polymer is stronger.
II The polymer is more transparent.
III The polymer has a higher softening temperature.

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

20 Graphenes and fullerenes are classified as carbon nanomaterials. Which of the following is equivalent to one nanometre?

I 10^{-6} mm
II 10^{-9} mm
III 10^{-12} mm
IV 10^{-9} m

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

Short-answer questions

21 Draw the structure of each of the following compounds and include any non-bonding pairs of electrons. Give the name of the shape of the molecule and predict whether the molecule is polar or non-polar.

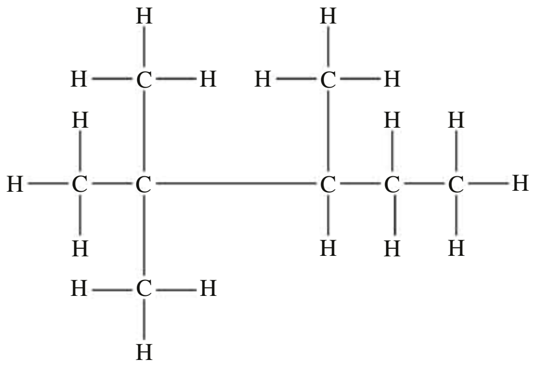
- **a** H_2S
- **b** PF_3
- **c** CCl_4
- **d** CS_2
- **e** SiH_4

22 Crude oil is an important resource to our society.

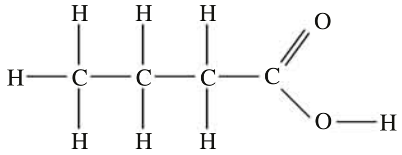
- **a** What is the origin of crude oil?
- **b** Crude oil is not a pure substance but a mixture.
  - **i** Briefly describe the composition of crude oil.
  - **ii** Give the molecular formula of two hydrocarbons present in crude oil.

23 Give the name of each of the following compounds.

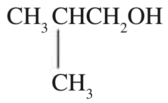
- **a** $CH_3C{=}CCH_3$
- **b** $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
- **c**



- **d**



- **e**



$$\underset{\displaystyle CH_3}{CH_3\overset{}{C}H}CH_2OH$$

24 Draw the structural formula of each of the following compounds.

- **a** Hex-1-ene
- **b** Propanoic acid
- **c** Ethylpropanoate
- **d** 2-Methylpropan-2-ol
- **e** Pent-2-yne

25 Give a condensed structural formula (a semistructural formula) for each of the following compounds.

- **a** Hexanoic acid
- **b** 4-ethyl-2,2-dimethylheptane
- **c** Butan-2-ol
- **d** Propyne
- **e** 2,4-Dimethylhex-1-ene

26 Provide concise explanations for each of the following observations.

- **a** The melting temperature of ice (solid H_2O) is 0°C but a temperature of over 1000°C is needed to decompose water molecules to hydrogen and oxygen gases.
- **b** Most substances are denser in their solid state than in their liquid state yet solid water (ice) floats on liquid water.
- **c** A molecule of ethyne (C_2H_2) is linear but a molecule of hydrogen peroxide (H_2O_2) is not.

27 Ammonia (NH_3) is a constituent of many cleaning products for bathrooms.

- **a** Draw an electron dot formula of an ammonia molecule, including non-bonding electron pairs.
- **b** Draw a structural formula for two ammonia molecules. Clearly show, and give the name of, the shape of these molecules. On your diagram, label the type of bonds that exist between the:
  - atoms within each ammonia molecule
  - two ammonia molecules.
- **c** Draw a structural formula for a molecule of:
  - **i** nitrogen gas
  - **ii** carbon dioxide gas.
- **d**
  - **i** Explain why the bonds between nitrogen molecules and those between molecules of carbon dioxide are of the same type even though the bonds inside these molecules differ in strength and polarity.
  - **ii** Explain why the bonds between ammonia molecules are different from those between nitrogen molecules or carbon dioxide molecules.

28 Consider the following molecules: oxygen (O_2) and hydrogen peroxide (H_2O_2).

- **a** Draw the structure of each molecule.
- **b** Which one has the stronger intramolecular bonds? Explain your choice.
- **c** **i** What sort of interactions exist between molecules of oxygen?
  - **ii** What sort of interactions exist between molecules of hydrogen peroxide? Are these stronger or weaker than those between oxygen molecules?
- **d** Unlike nitrogen atoms, oxygen atoms do not form triple bonds in molecules. Explain why, in terms of the electronic configurations of these two atoms.

29 Consider the following molecules: HCl, HF, H_2O, H_2S, CH_4, F_2, H_2, O_2.

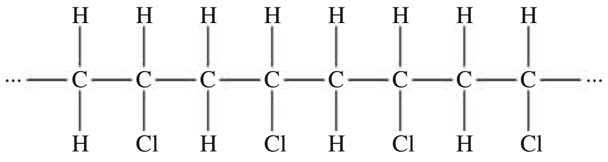
- **a** List the molecules that are polar molecules.
- **b** List the molecules that would have dipole–dipole bonding as their main intermolecular force.
- **c** List the molecules that have a linear shape.
- **d** List the molecules that are capable of hydrogen bonding.
- **e** List the molecules that contain a double bond.
- **f** Which substance in the list above would have the lowest boiling temperature? Give a reason for your answer.

30 Diamond and graphite are allotropes of carbon. Although they are similar in some respects, they are very different in their structure and uses.

- **a** Give a brief definition of the term 'allotrope'.
- **b** Describe the similarity in the bonding of these two materials.
- **c** Compare the structures of diamond and graphite.
- **d** Graphite is an excellent conductor of electricity while diamond is unable to conduct electricity. Explain this difference in terms of the structure of the lattices.
- **e** Graphite is used as a lead in pencils. With reference to the bonding in the lattice explain why graphite can be used this way.

31 Polymers are very large covalent molecular substances.

- **a** The following is a representation of a section of an addition polymer.



Draw the structure of the monomer from which this polymer was formed.

- **b** A small section of a thermosetting polymer is heated over a flame.
  - **i** Describe what observations you would expect to make.
  - **ii** Describe the structure of thermosetting polymers and use it to explain your answer to part **bi**.

32 Using a suitable example where possible, clearly explain the difference between the following pairs of terms.

- **a** A monomer and a polymer
- **b** A thermoplastic polymer and a thermosetting polymer
- **c** A branched polymer and a cross-linked polymer
- **d** Crystalline and non-crystalline regions of a polymer

33 Element X forms a compound with oxygen in which the ratio of the number of atoms of X to the number of atoms of oxygen is 2:3. X makes up 59.7 % of the mass of the compound.

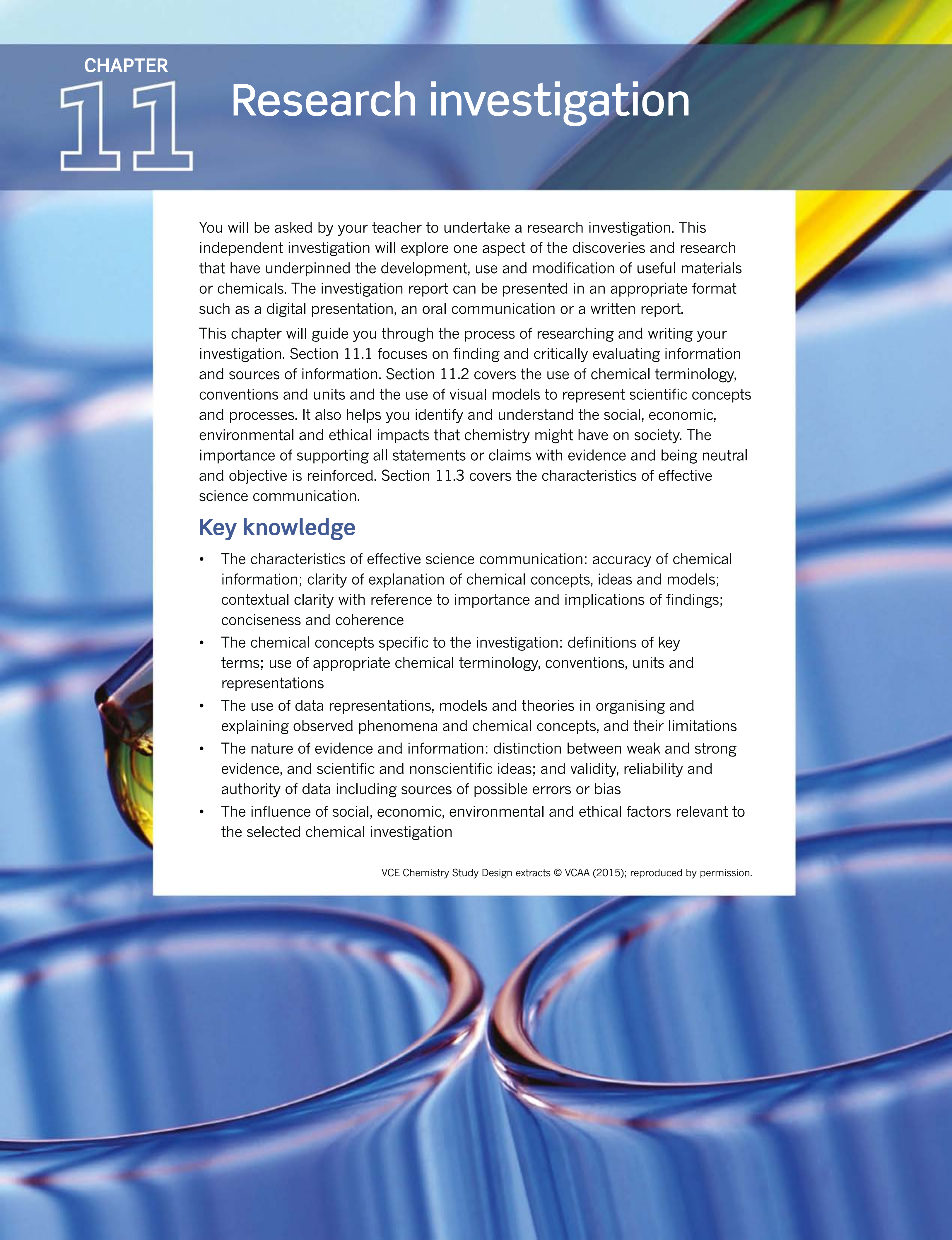
Calculate the molar mass of X and use it to identify this element.

34 A compound consists of carbon, hydrogen and oxygen only. It contains 54.54% carbon and 36.36% oxygen.

- **a** Determine the empirical formula of this compound.
- **b** 0.350 mol of this compound has a mass of 30.8 g. Calculate the relative molecular mass of the compound.
- **c** Determine the molecular formula of the compound.
- **d** There are several compounds with this molecular formula. Draw the structural formula and give the name of two compounds with this molecular formula. The two compounds chosen must belong to different families of carbon compounds.

35 A compound consists of carbon, chlorine and hydrogen. A sample of 4.738 g of the compound contains 0.476 g of carbon and 4.22 g of chlorine.

- **a** Determine the empirical formula of the compound.
- **b** Given that an amount of 0.326 mol of the compound has mass of 39.0 g, calculate the molar mass and then deduce the molecular formula of the compound.
- **c** Draw the structure of the compound.
- **d** This compound is a liquid at room temperature. What kind of interactions are present between molecules of this compound?
- **e** What mass of this compound contains 7.2×10^{23} atoms of chlorine?



CHAPTER 11

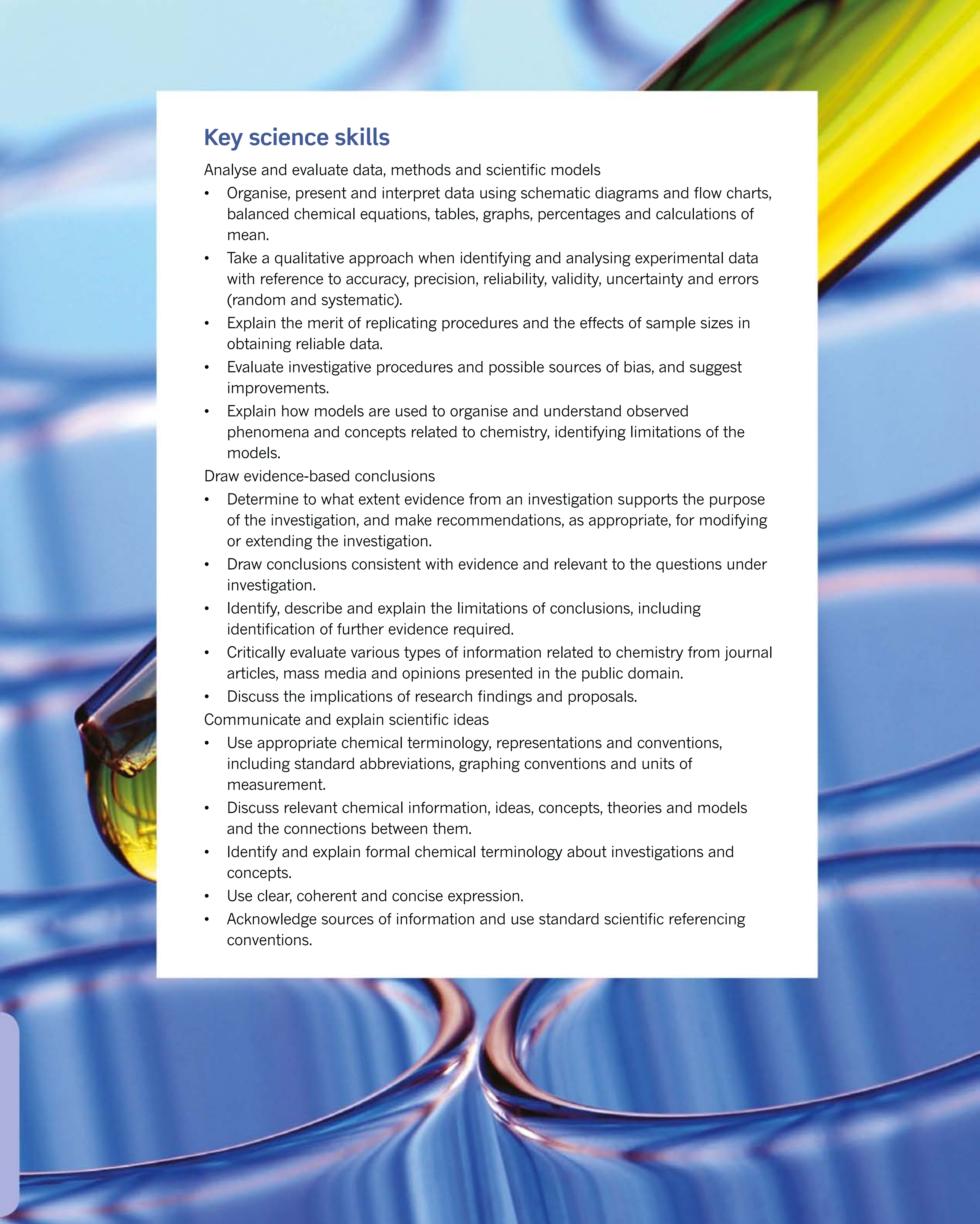
Research investigation

You will be asked by your teacher to undertake a research investigation. This independent investigation will explore one aspect of the discoveries and research that have underpinned the development, use and modification of useful materials or chemicals. The investigation report can be presented in an appropriate format such as a digital presentation, an oral communication or a written report.

This chapter will guide you through the process of researching and writing your investigation. Section 11.1 focuses on finding and critically evaluating information and sources of information. Section 11.2 covers the use of chemical terminology, conventions and units and the use of visual models to represent scientific concepts and processes. It also helps you identify and understand the social, economic, environmental and ethical impacts that chemistry might have on society. The importance of supporting all statements or claims with evidence and being neutral and objective is reinforced. Section 11.3 covers the characteristics of effective science communication.

Key knowledge

- The characteristics of effective science communication: accuracy of chemical information; clarity of explanation of chemical concepts, ideas and models; contextual clarity with reference to importance and implications of findings; conciseness and coherence
- The chemical concepts specific to the investigation: definitions of key terms; use of appropriate chemical terminology, conventions, units and representations
- The use of data representations, models and theories in organising and explaining observed phenomena and chemical concepts, and their limitations
- The nature of evidence and information: distinction between weak and strong evidence, and scientific and nonscientific ideas; and validity, reliability and authority of data including sources of possible errors or bias
- The influence of social, economic, environmental and ethical factors relevant to the selected chemical investigation



Key science skills

Analyse and evaluate data, methods and scientific models

- Organise, present and interpret data using schematic diagrams and flow charts, balanced chemical equations, tables, graphs, percentages and calculations of mean.
- Take a qualitative approach when identifying and analysing experimental data with reference to accuracy, precision, reliability, validity, uncertainty and errors (random and systematic).
- Explain the merit of replicating procedures and the effects of sample sizes in obtaining reliable data.
- Evaluate investigative procedures and possible sources of bias, and suggest improvements.
- Explain how models are used to organise and understand observed phenomena and concepts related to chemistry, identifying limitations of the models.

Draw evidence-based conclusions

- Determine to what extent evidence from an investigation supports the purpose of the investigation, and make recommendations, as appropriate, for modifying or extending the investigation.
- Draw conclusions consistent with evidence and relevant to the questions under investigation.
- Identify, describe and explain the limitations of conclusions, including identification of further evidence required.
- Critically evaluate various types of information related to chemistry from journal articles, mass media and opinions presented in the public domain.
- Discuss the implications of research findings and proposals.

Communicate and explain scientific ideas

- Use appropriate chemical terminology, representations and conventions, including standard abbreviations, graphing conventions and units of measurement.
- Discuss relevant chemical information, ideas, concepts, theories and models and the connections between them.
- Identify and explain formal chemical terminology about investigations and concepts.
- Use clear, coherent and concise expression.
- Acknowledge sources of information and use standard scientific referencing conventions.

11.1 Planning a research investigation

In this section, you will learn how to plan your research investigation. The main steps of the planning phase of a research investigation are:

- choosing a research question
- understanding the question
- developing an outline to guide your research.

This section will also focus on how to critically evaluate sources of information and distinguish between opinion and evidence, weak evidence and strong evidence, and scientific and non-scientific ideas.

FIGURE 11.1.1 An offshore oil rig. Crude oil is one of the topics you can choose for your research investigation.

CHOOSING A TOPIC

Your teacher may let you choose one of the following topics to investigate, or let you develop your own research question in one of the research fields shown in Table 11.1.1.

TABLE 11.1.1 Research investigation options

Option 1: The origin of the elements
Possible questions that you could explore: • How are atoms ‘seen’? • Are there more elements to be discovered? • What are electrons, protons and neutrons made of? • How do we know what elements are in the universe? • What is the evidence that living things are made of stardust? • Why are the ten most abundant elements in the universe not the same as the ten most abundant elements on Earth? • How does the abundance of elements on Earth compare with the abundance of elements in humans? • Would there be life if elements did not form compounds? • Why are the nuclei of some elements unstable?
Option 2: The development of the periodic table
Possible questions that you could explore: • Is alchemy chemistry? • How can lead be transformed into gold? • On what basis are alternative forms of the periodic table constructed? • Where would an element with an atomic number of 130 be placed in the modern periodic table, what properties would it have and how likely is it to be discovered? • Why is the periodic table still a ‘work in progress’? • Why is it difficult to place hydrogen in the modern periodic table? • Is it worthwhile finding any more new elements? • Why aren’t all the metals placed together in the periodic table? • What makes some elements magnetic? • Why do transition metals have multiple oxidation states? • Is it an advantage or a disadvantage for elements to be unreactive?

continued >

TABLE 11.1.1 continued

Option 3: The lanthanoids and actinoids

Possible questions that you could explore:

- Why are some lanthanoids and actinoids highly sought after?
- Can we live without lanthanoids and actinoids?
- Based on their usefulness for society, how would you compare the value of lanthanoids and actinoids with the value of other metal groups in the periodic table?
- Is it worth sending people to the Moon to mine for lanthanoids and actinoids?
- How are the lanthanoids and actinoids extracted from their ores?
- Do the lanthanoids and actinoids rust or corrode?
- Where are the lanthanoids and actinoids located in the periodic table and why have they been placed there?

Option 4: Using light to solve chemical puzzles

Possible questions that you could explore:

- What is a crystal, and why do crystals have regular faces?
- What makes synchrotron light useful?
- What can a synchrotron tell us about the differences between salt and sugar crystals?
- How does the composition of a crystal relate to the bonding within and the ratios of the elements present?
- Given that crystals are not alive or functioning, how is it that crystal structures are used to understand biological functions?
- What significant discoveries contributed to the development of X-ray crystallography as an analytical technique?
- How does cryoprotection preserve protein samples for analysis in a synchrotron?
- How has the use of a synchrotron enabled Nobel Prize winning research to occur?
- Why use synchrotron light to determine crystal structure when other sources of X-rays can be used?
- How does the IR beamline at the Australian Synchrotron enable the study of organic molecules and covalent bonding patterns?

Option 5: Glass

Possible questions that you could explore:

- What would life be like without glass? What might have to be used instead?
- How are the special properties achieved in particular forms of glass such as transition lenses, bulletproof glass, safety glass, bendable glass, heatproof glass, glass that can be switched on or off to become transparent or opaque, coloured glass and fibreglass?
- How are glass ornaments, glass jewellery and specialised laboratory glassware created?
- How does lightning make glass?
- Is glass safer to use than other forms of storage vessels?
- How useful is the type of glass that is produced as a by-product when iron is extracted from its ore in a blast furnace?

Option 6: Crude oil

Possible questions that you could explore:

- Do we need crude oil?
- Why does the composition of crude oil vary between different oil wells?
- How do different crude oil extraction methods compare in terms of their ease of extraction and environmental impacts?
- What might we do if crude oil supplies run out?
- How does the time taken to produce crude oil compare with the time taken to use it?
- What fuels and other chemicals are derived from crude oil? How is crude oil processed to obtain them?
- Why are tar balls found on beaches after an oil spill?
- What are some of the issues surrounding society's demand for and use of crude oil? What strategies are being used to address some of these issues?

Option 7: Surfactants

Possible questions that you could explore:

- How do surfactants help clean up oil spills?
- Why is it difficult to remove oil from bird feathers? Why can water birds drown if they still have detergent on their feathers?
- How are surfactants used in cooking, cosmetics and personal hygiene?
- How do hair shampoos differ from conditioners?
- How are soaps different from detergents?
- Why are different detergents made for cleaning different surfaces? How does their composition differ?
- How are surfactants designed for biodegradability?
- Does surfactant biodegradability affect performance?
- How can surfactants protect dams from drying out?
- What is the role of natural surfactants in the human body in breathing and digestion?

Option 8: Polymers and composite materials

Possible questions that you could explore:

- Are the biomaterials that replace body parts as effective as the original materials with reference to their properties and function?
- How can biomimicry help in developing new materials?
- How do new materials improve sporting performance?
- What are some of the new-generation composite materials that have been designed to meet the emerging demands posed by space programs, and medical and technological developments?
- Should cars be made from shape memory metals?
- What makes some materials ‘smart’?
- How do different types of radiation affect the structure and properties of polymer films?
- What applications for conductive polymers could be possible?
- What properties might a new ‘super material’ have, what might it be made from and what difference could it make to people’s lives?
- Why would it be an advantage for polymers not to be biodegradable?
- How are new polymer and composite materials tested for safety?

Option 9: Nanomaterials

Possible questions that you could explore:

- What useful materials have resulted from nanomaterial research and what could be produced in future?
- How are nanochemists able to ‘see’ nanoparticles and manipulate atoms to build particular nanomaterials?
- Why do nanomaterials have different properties from their related macromaterials?
- Are nanomaterials safe?
- What difference can nanomaterials make to society and the environment?
- What can nanobots do?
- How are nanomaterials used in medicine and research?

Option 10: The life cycle of a selected material or chemical

Possible questions that you could explore:

- What is the story behind the discovery of a selected material or chemical and why is it important?
- What is the relationship between the properties and structure and the nature and strength of the chemical bonding within a selected material or chemical?
- What are the main features of the life cycle of a selected material or chemical and how can these features be represented? (They may include the extraction and processing of the raw materials; the manufacturing processes used, its packaging, distribution and use; any recycling and reuse; and its disposal at the end of its useful life.)
- What health and safety and environmental issues are involved in the manufacture, use and disposal of a selected material or chemical and how are these managed?
- What happens to a selected material or chemical at the end of its life?

UNDERSTANDING THE QUESTION

Once you have selected a research question, you need to be able to identify key words within the question. Start by looking at chemical terminology and language and other key words.

It is important that you can interpret what a research question is asking you to do. To do this, you need to:

- 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 11.1.2 has examples of guiding words, research questions and command verbs.

TABLE 11.1.2 Examples of guiding words, research questions and command verbs

Guiding word	Example research questions	What are you being asked to do? What are the command verbs?
What	**What** difference can nanomaterials make to society and the environment? **What** are electrons, protons and neutrons made of?	Identify and describe specific examples, evidence, reasons and analogies from a variety of possibilities. *Identify* and *describe*.
Where	**Where** would an element with an atomic number of 130 be placed in the modern periodic table, what properties would it have and how likely is it to be discovered?	Identify and describe giving reasons for a place or location. *Identify* and *describe*.
How	**How** are atoms 'seen'? **How** can lead be transformed into gold? **How** do different crude oil extraction methods compare in terms of their ease of extraction and environmental impacts?	Identify and describe in detail a process or mechanism. Give examples using evidence and reasons. *Identify* and *describe*.
Why	**Why** are the ten most abundant elements in the universe not the same as the ten most abundant elements on Earth? **Why** do transition metals have multiple oxidation states? **Why** does the composition of crude oil vary between different oil wells?	Explain in detail the causes, reasons, mechanisms and evidence for. *Identify* and *describe*.
Would	**Would** there be life if elements did not form compounds?	Evaluate. Justify, giving reasons for and against (using evidence, analogies, comparisons). *Evaluate*, *assess*, *justify*.
Is/are	**Are** there more elements to be discovered? **Is** it an advantage or a disadvantage for elements to be unreactive? **Is** it worth sending people to the Moon to mine for lanthanoids and actinoids?	Evaluate. Justify, giving reasons and evidence. *Evaluate*, *assess*, *justify*.
On what basis	**On what basis** are alternative forms of the periodic table constructed?	Evaluate. Justify using reasons and evidence. Evaluate, assess, justify.
Can	**Can** we live without lanthanoids and actinoids?	Evaluate and assess. Is it possible? Give reasons, suggest possible alternatives. *Evaluate*, *assess*, *justify*, *create*.
Do/does	**Does** surfactant biodegradability affect performance? **Do** the lanthanoids and actinoids rust or corrode? **Do** we need crude oil?	Evaluate. Justify using reasons and evidence for and against. *Evaluate*, *assess*, *justify*.
Should	**Should** cars be made from shape memory metals?	Evaluate pros and cons, implications and limitations. Make a judgement. *Evaluate*, *assess*, *justify*, *create*.
Might	What **might** we do if crude oil supplies run out? What would life be like without glass? What **might** have to be used instead?	Evaluate. Justify, giving reasons for and against (using evidence, analogies, comparisons). *Evaluate*, *assess*, *justify*, *compare*, *contrast*, *create*.

Once you identify the guiding words, try to clarify what the question is asking you to do. Some examples are stated here.

- '**How** are atoms seen?' You need to identify and describe in detail the mechanisms or processes used for 'seeing' atoms.
- '**What** are electrons, protons and neutrons made of?' You need to identify and describe in detail the type of matter comprising electrons, protons and neutrons.
- '**Why** does the composition of crude oil vary between different oil wells?' You need to explain the process of crude oil synthesis and how this may have varied.

PREPARING A RESEARCH OUTLINE

It is important to develop an outline or skeleton of your investigation as this will help you identify the information you need. An outline helps you to be organised and focused, which is important when you are managing your time and resources.

Your teacher will specify the requirements for your research investigation. For example, you may need to write 1000 words answering the research question and provide five credible references.

Sample outline for 'How are atoms seen?'

Guiding word: **How?** This means you need to identify and describe in detail a process or mechanism. In this case, the process to be described is 'seeing atoms'.

1. Introductory paragraph introducing and defining key words and phrases: 'atoms' and 'seeing atoms' (Suggest 200 words)
   - What is an atom?
   - What does it mean to 'see' an atom?
   - Issues, complications, difficulties
2. Make a list of different features and characteristics required to 'see' atoms
   - Preview each characteristic and feature
3. Write a paragraph for each feature or characteristic (600 words is an appropriate total length)
   - Describe in detail and give an example, where possible, to illustrate the point.
4. Final paragraph (200 words)
   - Briefly summarise and answer the research question, include limitations and further research

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 include:

- newspaper articles and opinion pieces
- journal articles (from peer-reviewed journals)
- magazine articles
- government reports
- global databases, statistics and surveys
- laboratory work
- computer simulations and modelling
- interviews with relevant professionals (Skype™, email interviews).

Some reputable science journals and magazines are:

- *Cosmos*
- *Double Helix* (CSIRO)
- *ECOS*
- *Nature*
- *New Scientist*
- *Popular Science*
- *Scientific American*.

FIGURE 11.1.2 Use a variety of sources to ensure your information is correct and complete.

CRITICALLY EVALUATING INFORMATION

Not all sources are **credible**. It is essential to critically evaluate the content and its origin. Questions you should always ask when evaluating a source include:

- Who created this message? 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?
- How often is the information referred to by other researchers?
- 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

Sources of potential bias

Information can be obtained from a wide variety of sources, and you should be aware of the origin of the information to understand whether or not the source is likely to be expressing a particular **bias** or **agenda**.

Individuals or organisations with a **vested interest** (such as a financial interest) in the results of research may not present all of the information. When data or evidence is not presented objectively, it is said to be biased. For example, a food manufacturer may want to highlight the nutritional benefits of a product without giving equal prominence to less favourable aspects of an analysis.

Reputable scientists clearly state their affiliations and potential **conflict of interest** in articles submitted to peer-reviewed journals. Commonly, research projects are funded by government and non-government **grants**. Any funding associated with a research project should be clearly stated in connection with the author details in a peer-reviewed journal article. This provides **transparency** and enables the reader to judge whether the research may or may not be biased.

Scientific verses non-scientific ideas

Science is a way of explaining things. It is based on the systematic collection and analysis of data and evidence to answer questions.

Reputable scientists publish their research findings in peer-reviewed journals. Peer-reviewed journals are those that have qualified scientists in a particular field review any research before it is published in the journal to ensure that its methods are scientifically sound and the conclusions are supported by evidence.

In general, the peer-review system works well. However, occasionally, bad research is published after going through peer-review. In these cases, the scientific community writes to the journal stating their concerns and the articles are **retracted**. For example, an article published in the reputable medical journal *The Lancet* suggesting a link between autism and the measles, mumps and rubella vaccine was subsequently discredited and retracted.

Beware of publications or information that is presented as science but is not scientifically valid. Non-scientific ideas and writing can be identified by:

- a lack of data or evidence
- bias—only part of the data or evidence is considered (usually the data supporting the claim)
- poorly collected data or evidence; for example, basing data or evidence on a **sample group** that is too small or not representative of the whole
- invalid conclusions (that is, not supported by evidence)
- lack of objectivity—appealing to emotion rather than presenting facts and evidence impartially.

EVALUATING EVIDENCE

Strong evidence is credible, transparent, valid and reliable.

Validity

Validity refers to whether the evidence is in fact supporting the argument. Evidence should be relevant to the question and should support the conclusion. To learn more about validity in the context of an investigation, refer to Chapter 21.

Reliability

Reliability refers to the notion that the experiment or data collection can be repeated many times and will obtain consistent results. Reliability depends on:

- establishing a control to ensure that the results are due to changes in the independent variable
- replicating the experiment or data collection to account for errors.

Errors and limitations

Reputable sources will clearly state the limitations and errors of the reported research. There are two types of errors:

- **systematic errors**
- **random errors**.

Systematic errors

A systematic error is an error that is consistent and will occur again if the investigation is repeated in the same way. Systematic errors are usually a result of instruments that are not calibrated correctly or methods that are flawed. For example, if a weighing balance is not regularly calibrated, then it may consistently read higher or lower than the true value, producing a systematic error.

Random errors

Random errors occur by chance. For example, they may occur because the researcher does not have the skills or knowledge required to use a piece of equipment. Random errors can be reduced by repeating the experiment several times and calculating an average value.

AVOIDING PLAGIARISM

Plagiarism is using other people's work without acknowledging them as the author or creator. To avoid plagiarism, include a reference every time you report the work of others; for example, at the end of a sentence or following a diagram. If you use a direct quotation from a source, enclose it in quotation marks. This will ensure you give credit to the original author and it will enable the reader to find the original source.

References and bibliography

A **bibliography** is a list of resources referred to in your research. It includes details about each resource. In order to avoid plagiarising the work of others, it is very important that you acknowledge where you have found information. All sources must be listed at the end of the report in alphabetical order (by author last name or organisation name). The referencing needs to give the reader the opportunity of easily locating the source.

As you gather resources, you should also begin compiling your references in a separate document. This will prevent you from wasting time later trying to relocate your sources, and will be the basis of your bibliography.

APA (American Psychological Association) style is the most commonly used referencing style. Table 11.1.3 gives examples of how to write citations and references of different types of sources using APA academic referencing style.

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 bibliography.

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.

TABLE 11.1.3 APA academic referencing style

Resource type	Information required	Example
Print book	• Author's surname and initials • Date of publication • Title • Edition number • Publisher's name • Place of publication	Rickard G., Phillips G., Monckton S., Roberson P., Hamer J., Whalley K. (2005), *Science Dimensions 1*, Pearson Education, Melbourne
Digital book	• Author's surname and initials • Date of publication • Title • Edition number • Publisher's name • Date website was accessed • Website address	Commons C., Commons P., Hogendoorn B., Clarke W., Derry L., Huddart E., O'Shea P., Porter M., Quinton G., Ross B., Sanders P., Sanders R., Spence R. (2015), *Pearson Lightbook Chemistry Western Australia 11*, Pearson Education, accessed 29 June 2015, from http://staging.lightbook.pearsonplaces.com.au/CH11_WA/unit/CH11_WA-U01
Article	• Author's surname and initials • Date of publication • Title • Journal/magazine title • Volume • Page numbers	Chiappini, C., De Rosa, E., Martinez, J.O., Liu, X., Steele, J., Stevens, M.M., & Tasciotti, E. (2015). Biodegradable silicon nanoneedles delivering nucleic acids intracellularly induce localized in vivo neovascularization. *Nature Materials*, *14*(5), 532–539
Internet	• Author's surname and initials, or name of organisation or title • Year website was written or last revised • Date website was accessed • Website address	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

Keeping track of sources

Categorising the information and evidence you find while you are researching will make it easier to locate information later and to write your final investigation. Categories you might use while researching could include:

- research methods
- key findings
- evidence
- research relevance
- use
- **stakeholders** and impacts
- future concerns.

Record information from resources in a clear way so you can retrieve it and use it. An example of a useful method of doing this is in a table like Table 11.1.4.

TABLE 11.1.4 Recording information from different resources

Bibliographic information	
Summary of content	
Relevant findings and evidence	
Limitations, bias or flaws within the article	
Useful quotations	
Additional notes	

11.1 Review

SUMMARY

- It is important to understand exactly what a research question is asking you to do.
- Develop an outline to guide your research.
- Use a variety of reliable and credible sources to locate information and evidence.
- Critically evaluate evidence and information—for example, consider who wrote the content, for what purpose it was written, who it was written for and what biases or agendas may be involved.
- Science is a way of explaining things. It is based on the systematic and objective collection and analysis of data and evidence. Beware of writing that is presented as scientific writing, but which does not in fact have a scientific basis.
- Scientific writing uses unbiased, objective, accurate, formal language. Scientific writing should also be concise and qualified.
- Beware of non-scientific ideas, which are not based on facts and evidence.
- Ensure the evidence used in research is credible, transparent, valid and reliable.
- Record and acknowledge use of other people's work to avoid plagiarism and to add credibility to a report.
- Researching and collecting evidence in a methodical manner will assist in locating information later and in writing your final research investigation.

KEY QUESTIONS

1 Name the command verbs for the following.
  a Assess the implications and limitations of, make judgements about
  b Look for similarities and differences between
  c Look for differences between
  d Use valid reasons or evidence to support a conclusion

2 Identify what the following question is asking you to do: What is the chemistry underlying the Japanese nuclear accident in Fukushima in 2011?
  A Identify and describe how an earthquake caused the Japanese nuclear accident in Fukushima in 2011.
  B Identify and describe the chemistry of the Fukushima reactor site.
  C Identify and describe the history of the building and design of the Fukushima nuclear plant.
  D Identify and describe the chemistry of nuclear fuels and the effect of radioactivity release to the environment.

3 Decide whether each of the following is a primary or secondary resource.
  a This Year 11 chemistry textbook
  b An article published in the journal *Nature*
  c A scientific practical report outlining the aim, method, results, discussion and conclusion of a Year 11 student's experiment that they designed and conducted
  d An article published in *Cosmos* magazine

4 Identify two of the following examples where bias is most likely to be involved.
  A A company advertisement for a product stating a reputed benefit.
  B An independently appointed working party reporting to a government regarding the advantages and disadvantages of adopting a policy.
  C A research scientist who has obtained a grant from a pharmaceutical company.
  D A student doing research as part of her post-graduate degree.

5 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

6 What is the correct way to cite in text the following source 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 biodegradeability.
  B However, Selke et al. did not find any significant difference in biodegradeability[1].
  C However, Selke et al. did not find any significant difference in biodegradeability (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 biodegradeability (Evaluation of biodegredation-promoting additives for plastics. *Environmental Science & Technology*).

11.2 Communicating scientific ideas

This section describes the characteristics of effective science communication. It explains how chemical concepts and processes should be presented using the correct chemical terminology, conventions and units. Models and other visual representation of data are also described.

Finally, this section examines the social, economic, environmental and ethical implications that scientific research can have and presents techniques for identifying and analysing those relevant to your study.

EXPLAINING CHEMICAL CONCEPTS AND PROCESSES

To explain chemical concepts, it is important to first identify key words and main ideas and define them. In a paragraph, you need to present the key words followed by an explanation of what each is or does. Usually, only one concept is covered in a paragraph.

You should assume your reader has no knowledge of the topic. However, remember that there is a limit on the length of your investigation. Therefore, present concepts and definitions succinctly, while still ensuring that the audience can comprehend them. Consider your fellow students as your audience unless your teacher gives different instructions.

Presenting scientific ideas

An efficient way of presenting complex data and explaining scientific concepts is through photographs, graphs, tables and scientific models such as flow charts and diagrams. Ensure you include:

- a descriptive title
- labels, captions or descriptions
- numbering; for example, Figure 1, Figure 2 etc. or Table 1, Table 2 etc.
- a source if the work is not your own or is adapted from work that is not your own.

Models

Models are representations of concepts or processes aimed at assisting their understanding. Visual models are very useful because they allow complex information to be presented and understood more easily and quickly than text might allow. When presenting data or ideas as models, it is important to recognise and acknowledge the limitations of the models.

A type of visual model commonly used in science is diagrams. Diagrams are simplified drawings showing structures or processes. An example of a diagram representing a molecule is shown in Figure 11.2.1. A common limitation of diagrams is that they often do not show the exact relationship between their components; for example, sizes of structures or distances between components.

Diagrams may also oversimplify concepts. It is important to think about the original purpose of the diagram and the information you want to convey, and limit the use of your diagram to that purpose.

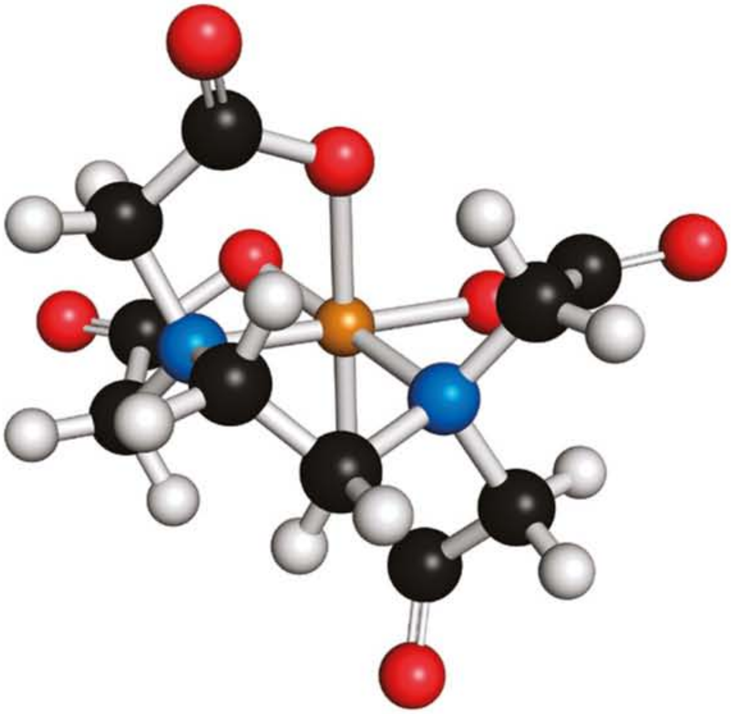


FIGURE 11.2.1 This diagram represents a molecule. A limitation of this diagram is that the distances between its components are not accurate.

Flow charts convey the steps in a process or method. The flow chart in Figure 11.2.2 shows how polymers used in the production of a consumer item can be decomposed. A limitation of flow charts is that the details of the process are omitted. Of course, simplification is often a benefit of visual models.

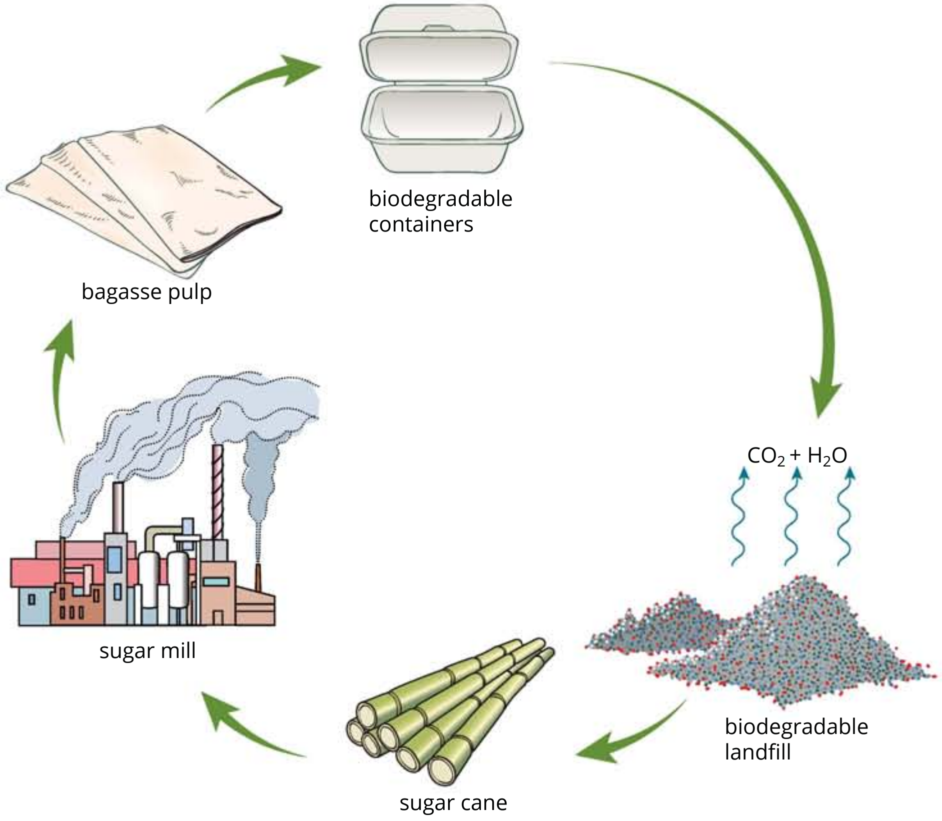


FIGURE 11.2.2 This flow chart shows how polymers used in the production of a consumer item can be decomposed. A limitation of this diagram is that it does not indicate the timeframe or details involved in this process.

Using tables and graphs

In general, tables provide more detailed data than graphs. However, it is easier to observe trends and patterns in graphs, making them a very useful tool for presenting evidence. Pie charts illustrate percentages well, while bar charts and line graphs illustrate relationships between variables well. A sample graph is presented in Figure 11.2.3. More information on tables and graphs can be found in Chapter 21.

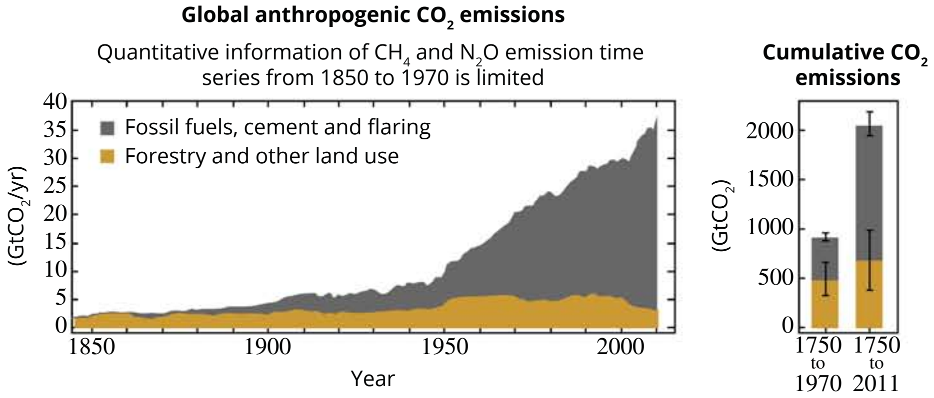


FIGURE 11.2.3 This graph presents the carbon dioxide emissions from fossil fuel combustion, cement and flaring (open-air burning of natural gas) and the carbon dioxide emissions from forestry and other land use.

General rules to follow when presenting a graph include the following.

- Use a descriptive title.
- Represent the **independent variable** on the *x*-axis and the **dependent variable** on the *y*-axis.
- Clearly label axes with both the variable and the unit in which it is measured.
- Make axes proportionate to the data.
- Keep the graph simple and uncluttered.

Difficult words on diagrams or graphs etc. should be explained, such as the headings in Figure 11.2.3. Alternatively, re-express them more simply in your own terms that are appropriate for your audience.

Chemical terminology, conventions and units

Using appropriate chemical terminology, conventions and units is also important. Table 11.2.1 has examples of the most common terms used in chemistry.

TABLE 11.2.1 The most common terms used in chemistry

Chemical term	Definition	Examples
Element	Substance whose atoms have the same atomic number. Atoms of different elements have different atomic numbers	Sodium, chlorine, tin
Compound	Substance consisting of two or more elements combined in fixed proportions. A chemical formula can be written for a pure compound	H_2O, NaCl
Substance	Element, compound	H_2, diamond, H_2O
Particle	An atom, ion, molecule, proton, neutron, electron	Ne, Na^+, H_2O, H^+, ^{12}C, e^-
Atom	Building block of matter. The smallest unit of an element	Na, He, C, Sn
Molecule	Two or more atoms covalently bonded together	H_2O, Water, C_4H_{10}, butane, $C_6H_{12}O_6$ glucose
Ion	A positively charged or negatively charged atom or group of atoms resulting from the loss or gain of one or more electrons.	Na^+, Cl^-, NO_3^-
Cation	Positively charged ion	Na^+, Mg^{2+}, Al^{3+}, NH_4^+
Anion	Negatively charged ion	Cl^-, O^{2-}, PO_4^{3-}
Network layer lattice	Covalently bonded layer lattice	Graphite
Network lattice	Covalently bonded lattice in which the bonds extend in three dimensions	Diamond, silicon dioxide

Table 11.2.2 describes some chemical naming conventions.

TABLE 11.2.2 Chemical naming conventions

Application	Convention	Examples
Naming elements	Do not capitalise the first letter, unless at the start of a sentence	Carbon, hydrogen
Element symbols	Elemental symbols First letter is capitalised, subsequent letter (if present) is lower case	N, Na, Ne, Ni
Naming transition metals that can form ions of different charges (oxidation states)	Write the name of the transition metal, followed by a Roman numeral in brackets	Cu^{+}, name is copper(I) ion Cu^{2+}, name is copper(II) ion
Naming ionic compounds	Name the cation before the anion	Sodium chloride Tin(IV) chloride
Writing ionic formulas	Write the cation before the anion	$NaCl$ $SnCl_4$
Use of brackets in chemical formulas	To indicate atoms that need to be considered together	$Al_2(CO_3)_3$
Use of brackets in condensed structural (semistructural) formulas	Use of brackets can indicate which groups of atoms are attached to a central atom (such as a carbon atom) Brackets can indicate which group of atoms is repeated, for example repeating CH_2 groups	$CH_3CH(CH_3)CH_3$ $CH_3(CH_2)_5CH_3$

Examples of uses and limitations of some commonly used chemical conventions and representations are presented in Table 11.2.3.

TABLE 11.2.3 Examples of uses and limitations of some commonly used chemical conventions and representations

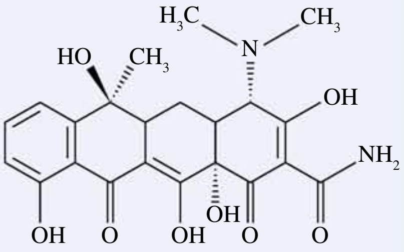
Representation	Use	Limitations	Example
Empirical formula	Determined by experiment, shows the simplest ratio of atoms of each element in a compound	Does not necessarily show the actual number of atoms in a molecule	C_2H_5, H_2O, $NaCl$
Molecular formula	Gives the actual number of atoms of each element in a molecule of a compound	Does not show the arrangement of atoms in a molecule	C_4H_{10}, H_2O
Structural formula	Shows the relative location of atoms within a molecule in two dimensions	Does not show the arrangement of atoms in three dimensions	Tetracycline structural formula 
Condensed structural (semistructural) formula	Enables a structural formula to be drawn	Does not show the arrangement of atoms in three dimensions	$CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$

Table 11.2.4 presents the main quantities and units used in chemistry.

TABLE 11.2.4 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
Relative isotopic mass	I_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} or M)

IDENTIFYING AND CONSIDERING RELEVANT SOCIAL, ECONOMIC, ENVIRONMENTAL AND ETHICAL FACTORS

The development, use or modification of materials or chemicals usually has an impact on society. To understand the impact on individuals and society, you should identify the following factors relevant to your topic as shown in Figure 11.2.5.

- **Social** factors are those related to individuals, communities and society.
- **Economic** factors are those related to costs and resources.
- **Environmental** factors are those related to the air, water, minerals, organisms etc.
- **Ethical** factors are those related to moral principles, and determining what is right and wrong.

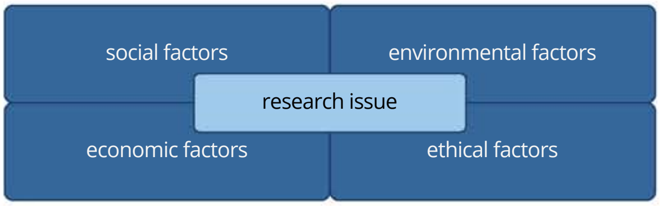


FIGURE 11.2.5 Think about any social, economic, environmental and ethical implications related to the topic you are researching.

It is important that you systematically consider different stakeholders, thus incorporating insights and perspectives related to social, economic, legal or ethical issues. Often there is overlap between each category.

Identify the stakeholders and consider how each may be affected by the issue.

Social issues might include:

- Who is directly involved?
- Who will benefit?
- Who might be negatively affected?

Economic issues might include:

- Who will pay for the research?
- Who will pay for the development, production or application?
- Will this cause loss of profit for another party?
- Will there be any costs involved for the government?

Environmental issues might include:

- How might this affect the environment?
- What short-term and long-term costs will this cause in terms of natural resources?

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 it fair?
- Who is it available to?
- Does it prevent anyone from gaining their basic needs?
- How can this impact on future ethical decisions or issues? For example, even if an application is ethical, could it clear the path to other applications that are unethical?

Example: What is the chemistry underlying the Japanese nuclear accident in Fukushima in 2011?

Social issues include:

- What is the impact on people?
- What is the impact on farming and agriculture?
- Will tax payers pay for health expenses?

Economic issues include:

- What are the costs of infrastructure?
- What are the costs of unemployment due to health and job losses?
- What are the costs of health expenses?

Environmental issues include:

- What is the impact of radioactive substances on water, air, plants, animals?
- What is the impact on scenery and biodiversity in the area affected?

Ethical issues include:

- What are the benefits versus costs of nuclear energy?
- Who has the right to decide on the form of energy used?
- Who could be affected by this form of energy?

11.2 Review

SUMMARY

- Ensure key words and concepts are defined in an investigation. Assume your reader has no knowledge of the topic.
- Present scientific ideas accurately and concisely. Visual models may assist in representing complex concepts or processes.
- When presenting data or ideas in model forms, it is important to recognise and acknowledge the limitations of your models.
- When researching issues, identify the social, economic, environmental and ethical factors associated with the issue.
- Support any scientific premise with evidence.

KEY QUESTIONS

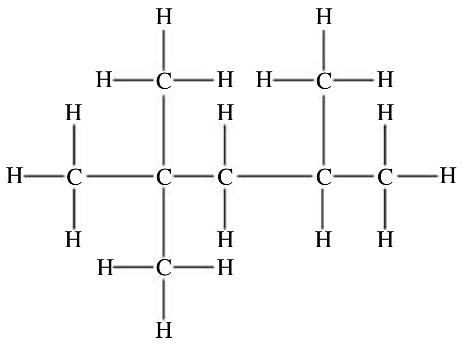
1 Choose the best option to replace the graph title 'Global anthropogenic CO_2 emissions' in Figure 11.2.3 on page 274.

A Anthropogenic effect on CO_2 emissions
B Global anthropometric CO_2 emissions
C Global CO_2 emissions resulting from human activities
D Global anthropogenic CO_2 emanations

2 List the advantages and limitations of each of the following models.

a Space-filling models
b Ball-and-stick models
c Structural formulas

3 An acceptable condensed structural formula for this compound (2,2,4-trimethylpentane) is:



A $CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$
B C_8H_{18}
C $CH_3CH_3CCH_3CH_2CH_3CHCH_3$
D C_4H_9

4 Classify the following factors related to manufacturing sulfuric acid as social, economic, environmental or ethical.

a Creation of jobs
b Protocol for safe disposal of sulfuric acid
c Production of useful materials
d Release of sulfur dioxide and sulfur trioxide can cause acid rain

5 Which of the following is the correct symbol for the unit gram?

A G
B g
C gram
D Gramme

11.3 Writing a scientific report

This section covers the main characteristics of effective science communication, including objectivity, clarity, conciseness and coherence. It also presents ideas on how to organise the information collected, determine its relevance to the investigation and decide where it fits in the presentation.

Finally, it emphasises that conclusions should be consistent with the evidence presented and the purpose of the investigation.

STRUCTURING A REPORT

Your report should have a clear, logical structure.

Introduction:

- The first paragraph should introduce your research topic and define key terms.

Body paragraphs:

- Each subsequent paragraph should cover one main idea.
- The first sentence of each paragraph should summarise the content of the paragraph.
- 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 title of the investigation.
- The conclusion should include limitations.
- It should 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. It is also important to explain connections between ideas, concepts, theories and models. Figure 11.3.1 lists the questions you need to consider when writing your investigation report.

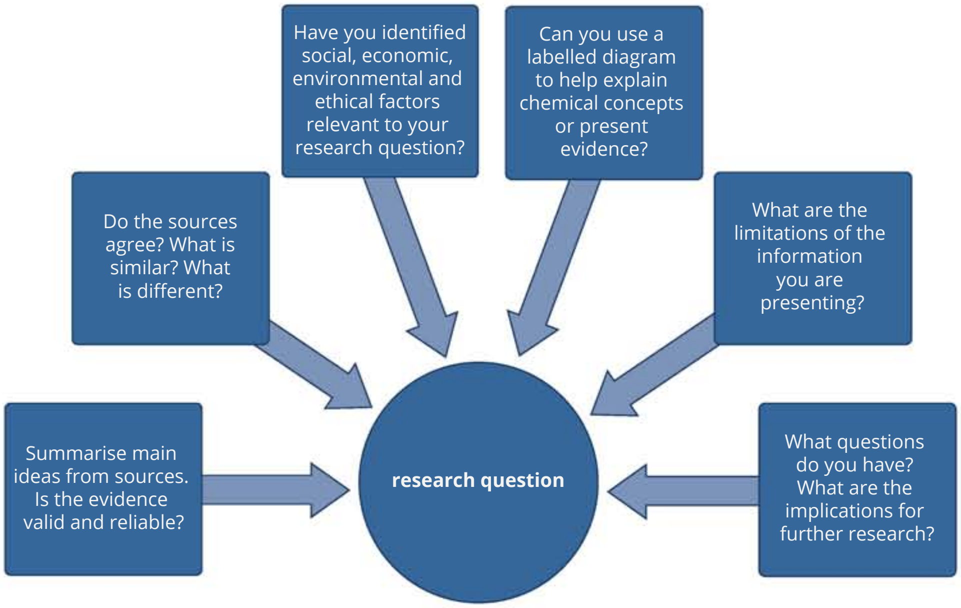


FIGURE 11.3.1 Discuss relevant information, ideas, concepts, implications and make sure your discussion is relevant to the question under investigation.

Once you have analysed your sources, annotate your outline, indicating where you will use evidence and what the source of that evidence is. Try to introduce only one idea per sentence and one theme per paragraph.

For example, for a report on 'Experimental research into biodegradability of plastics', the third paragraph might contain information from:

- Selke et al. (2015)—no significant effect
- Chiellini et al. (2007)—significant effect
- Different experimental procedures
- Chiellini received funding from the manufacturer.

A report should include analysis and synthesis of your sources. Therefore, the information from different sources needs to be explicitly connected and it should be clear where sources agree and disagree. In this example, the final sentences could be:

> Selke and colleagues reported that in testing of five additives added to commonly manufactured polymers, none resulted in significant biodegradation after three years (Selke et al., 2015). These findings are in contrast with those of Chiellini who reported significant biodegradability of polyethene polymers with the use of the same additives (Chiellini et al., 2007). The study by Chiellini tested degradation of polymers with additives in water, whereas Selke's study tested degradation in compost, soil and laboratory tests (Chiellini et al., 2007; Selke et al., 2015). Apart from the different experimental techniques used, Chiellini's study acknowledged funding from a manufacturer of the additives used in the testing. This raises the question of the reliability of this evidence as Chiellini and colleagues may have been biased, having received payment for the study.

WRITING FOR SCIENCE

Scientific reports are usually written in an objective or unbiased style. This is in contrast with English writing that most often uses the subjective techniques of **rhetoric** or **persuasion**. Read Table 11.3.1, which contrasts persuasive and scientific writing styles.

TABLE 11.3.1 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 pungent 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 on 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 11.3.2.

TABLE 11.3.2 Examples of first-person and third-person narrative

First person	Third person
I put 50 g marble chips in a conical flask and then added 10 mL of 2 M hydrochloric acid.	First, 50 g of marble chips was weighed into the conical flask and then 10 mL of 2 M 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 that are less verbose (contain too many words). Read Table 11.3.3, which shows some examples of more concise wording.

TABLE 11.3.3 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 may be …
A total of five experiments	Five experiments
End result	Result
In the event that	If
Shorter in length	Shorter

Visual support

Identify concepts that can be explained using visual models and information that can be presented in graphs or diagrams. This will not only reduce the word count of your work but will also make it more accessible for your audience.

EDITING YOUR REPORT

Editing your report is an important part of the process. After editing your report, save new drafts with a different file name and always back up your files in another location.

Pretend you are reading your report for the first time when editing. Once you have completed a draft, it is a good idea to put it aside and return to it with 'fresh eyes' a day later. This will help you find areas that need further work and give you the opportunity to improve them. Look for content that is:

- ambiguous or unclear
- repetitive
- awkwardly phrased
- too lengthy
- not relevant to your research question
- poorly structured
- lacking evidence
- lacking a reference (if it is another researcher's work).

Use a spellchecker tool to help you identify typographical errors, but first, check that your spellchecker is set to Australian English. Also be wary of words that are commonly misused, for example:

- where/were
- their/they're/there
- affect/effect
- which/that.

11.3 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. Scientific writing should also be concise and qualified.
- Visual support can assist in conveying scientific concepts and processes efficiently.
- Ensure you edit your final report.

KEY QUESTIONS

1 Which of the following statements is written in scientific style?

A The results were fantastic ...
B The data in Table 2 indicates ...
C The researchers felt ...
D The smell was awful ...

2 Which of the following statements is written in first-person narrative?

A The researchers reported ...
B Samples were analysed using ...
C The experiment was repeated three times ...
D I reported ...

3 A procedure was repeated 30 times. How should the following statement be rewritten?
Many repeats of the procedure were conducted.

4 Which one of the following would not support a strong conclusion to a report?

A The concluding paragraphs are relevant and provide supporting evidence.
B The concluding paragraphs are written in emotive language.
C The concluding paragraphs include reference to limitations of the research.
D The concluding paragraphs include suggestions for further avenues of research.

Chapter review

11

KEY TERMS

affiliation
agenda
bias
bibliography
conflict of interest
credible
dependent variable
economic
environmental
ethical
expertise
grant
independent variable
persuasion
phenomenon
plagiarism
primary source
random error
reliability
reputation
retracted
rhetoric
sample group
secondary source
social
stakeholders
systematic errors
transparency
validity
vested interest

Planning a research investigation

1 Identify what the following question is asking you to do: What chemical and physical properties of noble gases distinguish these elements from other elements?
   - **A** Describe the chemical and physical properties of noble gases.
   - **B** Identify and describe the key differences between different groups of elements.
   - **C** Identify and describe the key differences in observed properties of noble gases and other elements in the periodic table.
   - **D** Identify and describe the chemical and physical properties of lanthanoids and actinoids.

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 Which of the following consists only of secondary sources of information?
   - **A** An interactive periodic table, an article published in a science magazine, a science documentary, a practical report written by a Year 11 student
   - **B** An article published in a peer-reviewed science journal, an article published in a science magazine, a science documentary
   - **C** An interactive periodic table, an article published in a science magazine, a science documentary, this Year 11 textbook
   - **D** A science article published in a newspaper, an article published in a science magazine, a science documentary, a practical report written by a Year 11 student

Communicating scientific ideas

4 Identify the purpose of the diagram in Figure 11.4.1.
   - **A** To show how quickly the water cycle takes place
   - **B** To add colour to a report
   - **C** To show how the various stages of the water cycle are related to each other
   - **D** To describe the process involved when water evaporates

FIGURE 11.4.1

5 The correct naming convention for the compound $CuCl_2$ is:
   - **A** copper chloride
   - **B** copper(I) chloride
   - **C** copper(II) chloride
   - **D** chloride copper.

6 Which type of factor is not addressed in this excerpt?

> Three-dimensional printing technologies have the genuine potential to improve medical treatments for conditions ranging from bone cancer and arthritis to glaucoma and hearing loss.
>
> One major concern about the development of personalised medicine is the cost of treatments. Until recently it has been thought that advances in personalised medicine go hand-in-hand with increasing disparities in health between rich and poor. Should these treatments only be available to those who can pay the additional cost?

A Ethical
B Economical
C Environmental
D Social

Writing a scientific report

7 Match the following terms with their definitions: reliability of data, critical thinking, precision, validity of data, authority of data, accuracy.

a How close a measured value is to the actual value.
b Analysing and evaluating data and evidence.
c How many decimal places an experimental value can be reported.
d How well an experiment tests an hypothesis. If the data obtained is used to reach a logical conclusion.
e How repeatable an experiment is.
f How credible the data is.

8 **a** What is the purpose of this poster in Figure 11.4.2?
   A To give an objective, scientific comparison of butter versus margarine
   B To persuade the reader to consume butter
   C To persuade the reader to consume margarine
   D To convince the reader to avoid consuming butter and margarine

b Select the sentences that contain persuasive language.

Margarine or Butter.
What's in it for you?

The ingredients* margarine may contain are:

Fats and Oils:
Edible fats
Edible oils
Salt/Potassium chloride
Antioxidants:
Butylated hydroxyanisole
Tert-butylhydroquinone
Emulsifiers:
Phospholipids
Mono- and di-glycerides of fat forming fatty acids
Flavourings and flavour enhancers:
Disodium guanylate
Disodium inosinate
Thaumatin
Monosodium glutamate
Natural Colourings:
Xanthophylls
Annatto
β-apo-8'-carotenal
β-apo-8'-carotenoic acid methyl or Ethyl ester
Turmeric
Curcumin
Crocetin
Vitamins A and D
Skim milk powder

The ingredients* butter may contain are:

Milkfat
Salt/Potassium chloride
Vitamins

Butter and margarine have the same number of kilojoules† (calories). But, as you can see, that's where the similarity ends. Butter. It tastes better, naturally.

DAIRY GOOD.
Good food. Good taste.
AUSTRALIAN DAIRY CORPORATION.

*Source: Food Standards Code 1987. †Source: Metric Tables of Composition of Australian Foods. Commonwealth Department of Health 1977

ADC 20

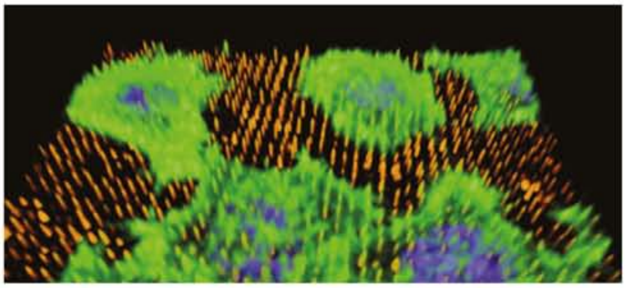
FIGURE 11.4.2

Connecting the main ideas

9 Read the following extract.

COSMOS Magazine

Invisible mending for the human body: Silicon sheets covered with nanoneedles may one day help heal burns and assist with organ transplants. Viviane Richter reports 20 April 2015



A person with severe burns could one day be wrapped in bandages lined with invisible needles say researchers at Imperial College in London. The team has developed sheets of silicon coated with nanoneedles that could boost the healing capacity of tissues by puncturing thousands of cells at once, delivering a shot of DNA into each one.

The silicon nanoneedles were made by Molly Stevens and her team, who published their results in *Nature Materials* in March. Preventing unsightly scars from burns is one of their possible applications. 'It's a very powerful way of accessing the inside of the cell' says Mark Prausnitz, chemical engineer at the Georgia Institute of Technology.

One reason for introducing new DNA into cells is to reprogram the way they respond to damage. But placing DNA inside cells is tricky. Viruses are nature's experts at slipping DNA into unsuspecting cells, and some researchers have used modified viruses as a DNA delivery service—but the viruses can mix in their own genes, which can be dangerous to the patient.

Alternatively, DNA can be injected using a syringe. But delivering DNA this way can only be done one cell at a time—hardly efficient for reprogramming whole tissues, such as burnt skin or torn muscle.

So Stevens and her team developed silicon sheets coated with nanoneedles, which can inject DNA into a whole layer of cells at once.

Thanks to the techniques developed by the computer industry, silicon can be shaped with nanoscale accuracy. The team bombarded silicon wafers with charged particles to partially etch away the silicon and leave a surface bristling with tiny needles. Through an electron microscope, Stevens' material looks like a bed of nails, each nail one-thousandth the width of a human hair and one-thousandth the length of a grain of rice.

Each nanoneedle contains tiny pores that can be filled with DNA—for example, DNA that codes for a signalling molecule called VEGF. Cells exude VEGF to encourage blood vessel growth around them. VEGF is released naturally during embryonic development, and also after injury.

Could the nanoneedles upload this DNA to cells? To find out, the team implanted DNA-loaded nanoneedle sheets onto muscle tissue in mice. After one week, there was a six-fold increase in the formation of new blood vessels in the muscle around the implant—and the researchers saw no signs of inflammation.

The successful test suggests the sheets of nanoneedles might be used to help organ transplants take hold. Transplanted organs often struggle integrating into the body as they take time to build blood vessels. Nanoneedle-assisted genetic programming could help. After delivering their DNA, the minute, porous silicon needles would be broken down by the body within four days and excreted as non-toxic orthosilicic acid.

'We are excited and focused on taking this material forward', says Stevens. The material is made by etching nanoneedles on to 8-centimetre silicon wafers. Her team is working on flexible bandage versions that could be more easily applied to the skin or inside the body during surgery, or after an accident such as a burn.

How soon could we see Stevens' nanoneedles in the clinic? Prausnitz is cautious. 'It's the new technology at the party—it looks really good and has promise. But limitations may be found over the course of further development'. He is, however, optimistic the porous nanoneedle material could find many uses—perhaps being loaded up with drugs or antibodies as well as DNA.

a Select the best bold response to complete each of the following statements.

  i This article focuses mainly on the **social/environmental/ethical/economic** implications of nanoneedles.

  ii Nanoneedles are created by **growing/bombarding/synthesising/injecting** charged particles.

b Select the sentence that contains an analogy to help communicate a scientific idea to a non-specialist audience.

c Is this article written in a scientific way? Give two reasons for your decision.

d What addition to this article would further improve its credibility?

  A Glossary

  B References

  C Summary

  D Introduction

UNIT 2

What makes water such a unique chemical?

AREA OF STUDY 1

How do substances interact with water?

Outcome 1: On completion of this unit the student should be able to relate the properties of water to its structure and bonding, and explain the importance of the properties and reactions of water in selected contexts.

AREA OF STUDY 2

How are substances in water measured and analysed?

Outcome 2: On completion of this unit the student should be able to measure amounts of dissolved substances in water and analyse water samples for salts, organic compounds and acids and bases.

AREA OF STUDY 3

Practical investigation

Outcome 3: On completion of this unit the student should be able to design and undertake a quantitative laboratory investigation related to water quality, and draw conclusions based on evidence from collected data.

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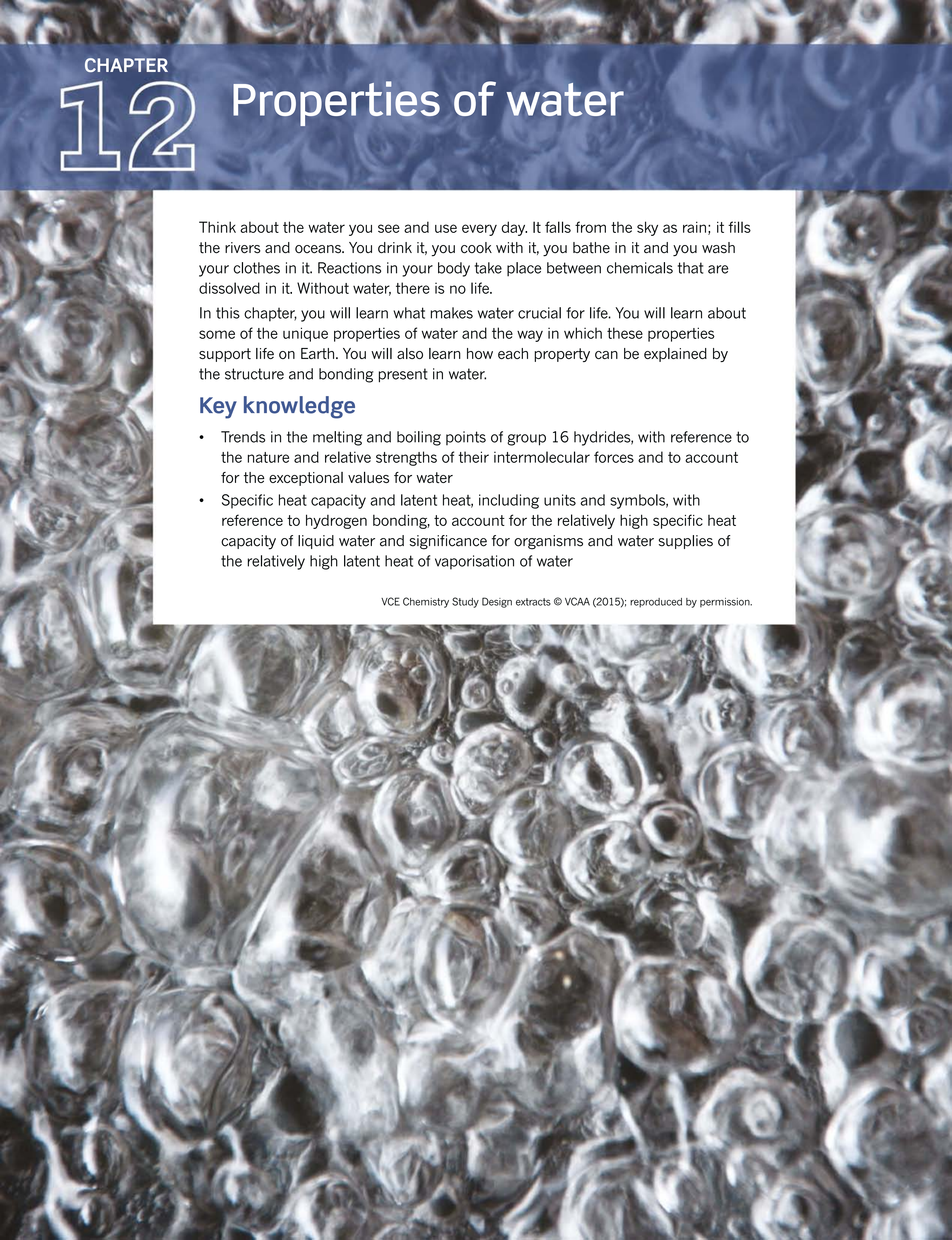

CHAPTER 12

Properties of water

Think about the water you see and use every day. It falls from the sky as rain; it fills the rivers and oceans. You drink it, you cook with it, you bathe in it and you wash your clothes in it. Reactions in your body take place between chemicals that are dissolved in it. Without water, there is no life.

In this chapter, you will learn what makes water crucial for life. You will learn about some of the unique properties of water and the way in which these properties support life on Earth. You will also learn how each property can be explained by the structure and bonding present in water.

Key knowledge

- Trends in the melting and boiling points of group 16 hydrides, with reference to the nature and relative strengths of their intermolecular forces and to account for the exceptional values for water
- Specific heat capacity and latent heat, including units and symbols, with reference to hydrogen bonding, to account for the relatively high specific heat capacity of liquid water and significance for organisms and water supplies of the relatively high latent heat of vaporisation of water

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12.1 Essential water

Water is a special chemical. It moderates our weather, shapes our lands and is essential for the existence of life. Water is the most abundant liquid on Earth, covering more than 70% of our planet. The total water supply is estimated to be more than 1.3 billion cubic kilometres.

This water on Earth constantly cycles, as shown in Figure 12.1.1. It is in continuous movement between land, ocean, rivers and creeks and the atmosphere. Warmth from the Sun causes the water in oceans, lakes and rivers to evaporate and become vapour in the air. As water vapour rises, the air temperature drops and the water vapour condenses to form droplets, which merge to form clouds. When the water droplets are large enough, water falls back to Earth as rain, ice or snow, depending on the air temperature.

Other processes also add water to the atmosphere. When fossil fuels undergo combustion, water is a product and is released into the air. Water also evaporates from the leaves, stems and flowers of plants.

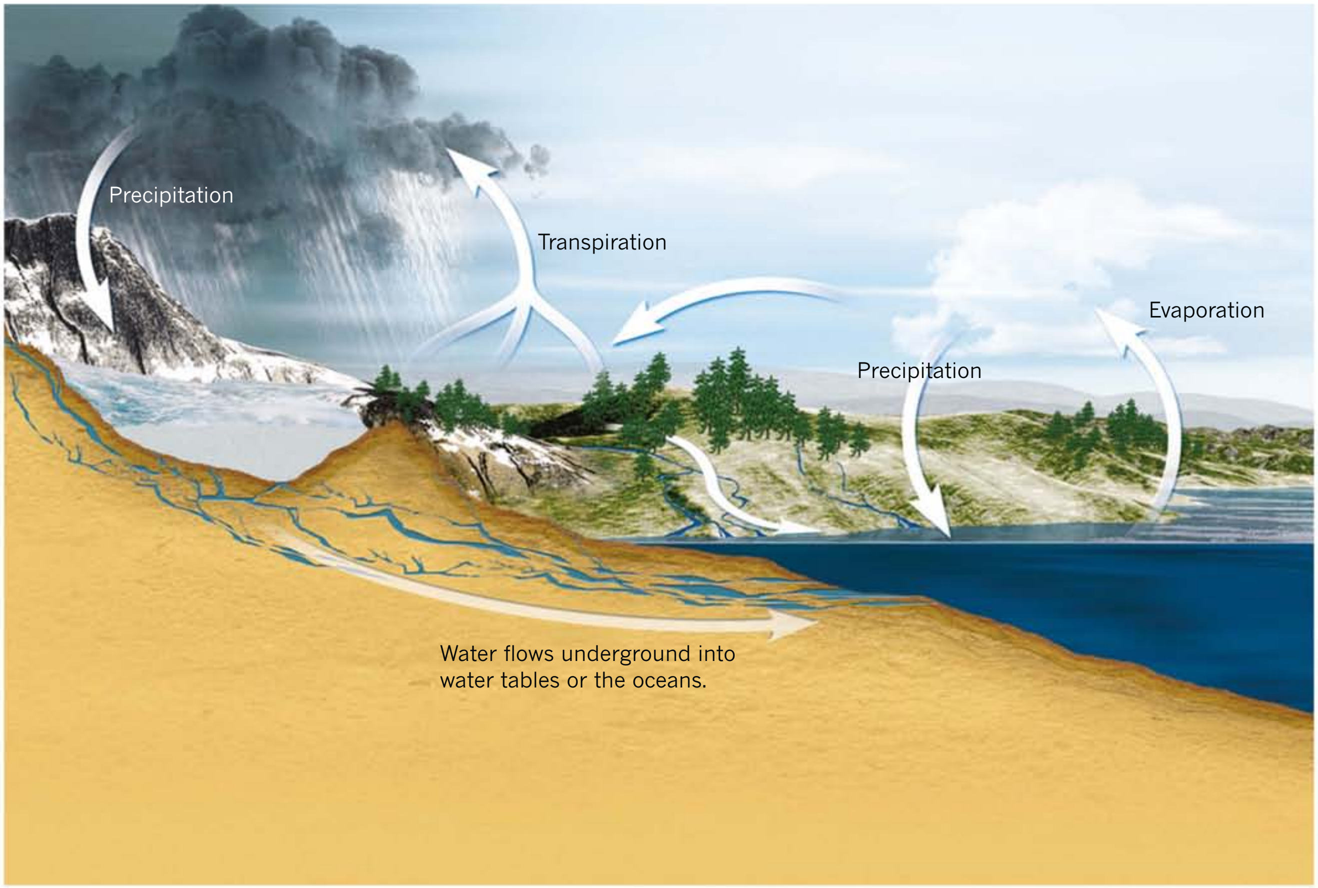

FIGURE 12.1.1 The water cycle. The arrows show some of the ways water on Earth is redistributed.

Water and life are so strongly linked that space scientists search the universe for water in their quest to discover possible life beyond our planet. It is the unique properties of water that allow it to support life.

These properties can be explained by looking at the structure of a water molecule and the **hydrogen bonding** that occurs between the water molecules.

WATER AND HYDROGEN BONDING

Structure of water

Water has the chemical formula H_2O, which means that each water molecule contains two hydrogen atoms and one oxygen atom. Hydrogen and oxygen are both non-metals so they bond with each other by sharing electrons. Each hydrogen atom shares one electron with the oxygen atom and the oxygen atom shares one electron with each hydrogen atom. The sharing of electrons means these **intramolecular bonds** are covalent.

Each oxygen atom also has two **lone pairs** (non-bonding pairs) of electrons that contribute to the molecule's shape. A water molecule is V-shaped (or bent) as shown in Figure 12.1.2. The lone pairs of electrons on the oxygen atom have greater repulsion than the electrons forming the single bonds between oxygen and hydrogen. This pushes the hydrogen atoms closer together, giving the overall bent shape (the shape of molecules was explained in detail in section 7.1 on page 156).

The covalent bonds in a water molecule are **polar**. The oxygen atom has a higher **electronegativity** than the hydrogen atoms. This means that the electrons in the O–H bonds are more strongly attracted to the oxygen atom. Uneven sharing of the electrons gives the oxygen atom a partial negative (δ–) charge and each hydrogen atom carries a partial positive charge (δ+).

Since the bonding electrons are distributed unevenly across the water molecule, the molecule can be described as a **dipole**. Figure 12.1.3 shows how the individual dipoles of the O–H bonds in water add together, resulting in an overall molecular dipole.

Polar bonds and polar molecules were explained in detail in section 7.2 on page 161.

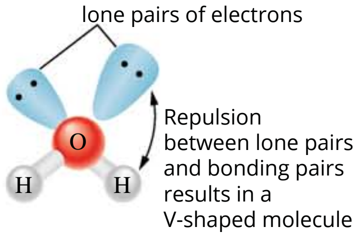

FIGURE 12.1.2 In this diagram of the valence structure of water, the two hydrogen atoms (white) form a V-shape with a central oxygen atom (red).

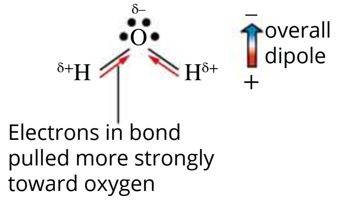

FIGURE 12.1.3 A water molecule has an overall dipole. The oxygen atom has a partial negative charge while the hydrogen atoms both have partial positive charges.

Water molecules are polar and have a permanent overall dipole.

Hydrogen bonding

The main type of **intermolecular force** between molecules in water is a hydrogen bond. The hydrogen bonds are formed by an **electrostatic attraction** between the partial positive charge on a hydrogen atom on one water molecule and a lone pair of electrons on the oxygen atom of a neighbouring water molecule.

Figure 12.1.4 shows the hydrogen bonding between molecules of water. Each water molecule is colour-coded to show its polarity. The two hydrogen atoms in each water molecule have a slight positive charge (white), while the central oxygen atom has a slight negative charge (red). The black dashed lines represent the hydrogen bonds that form between water molecules. (For more details on hydrogen bonding, see section 7.3 on page 168.)

Because there is a large electronegativity difference between oxygen and hydrogen atoms, the partial charges on a water molecule are relatively large. The electrostatic attraction between these opposite partial charges makes the hydrogen bonds between water molecules quite strong.

As Figure 12.1.5 shows, each water molecule can form hydrogen bonds with up to four other water molecules.

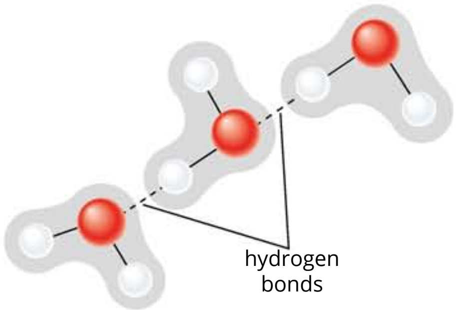

FIGURE 12.1.4 The hydrogen bonding between molecules of water.

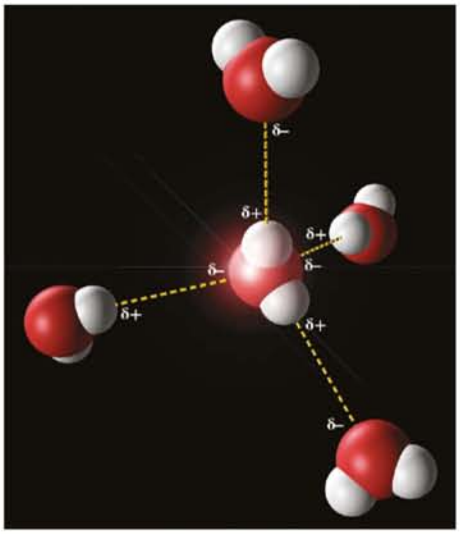

FIGURE 12.1.5 Each water molecule can form hydrogen bonds to four other water molecules.

WATER HAS RELATIVELY HIGH MELTING AND BOILING POINTS

Compared to other molecules of a similar size, water has high boiling and melting points. This can most easily been seen through the observed trends in these properties for the group 16 hydrides.

Trends in group 16 hydrides

The group 16 elements include oxygen (O), sulfur (S), selenium (Se), tellurium (Te) and polonium (Po). Each of these elements can bond with hydrogen to form compounds known as **hydrides**. Water is a group 16 hydride. Others are listed in Table 12.1.1.

TABLE 12.1.1 Names and formulas of the group 16 hydrides

Element	Name and formula of hydride	Formula
O	Water	H_2O
S	Hydrogen sulfide	H_2S
Se	Hydrogen selenide	H_2Se
Te	Hydrogen telluride	H_2Te
Po	Hydrogen polonide	H_2Po

The group 16 hydrides are all molecular compounds, so their melting and boiling points reflect the size of the forces between their molecules. The higher the melting and boiling points, the stronger the intermolecular forces must be because more energy is required to overcome the forces and allow the molecules to move apart from each other.

The melting and boiling points of the group 16 hydrides are shown in Table 12.1.2 and Figure 12.1.6.

TABLE 12.1.2 Melting and boiling points of the group 16 hydrides

Hydride	Melting point (°C)	Boiling point (°C)
H_2O	0	100
H_2S	–82	–60.7
H_2Se	–66	–41.5
H_2Te	–49	–2.2
H_2Po	–35	36.1

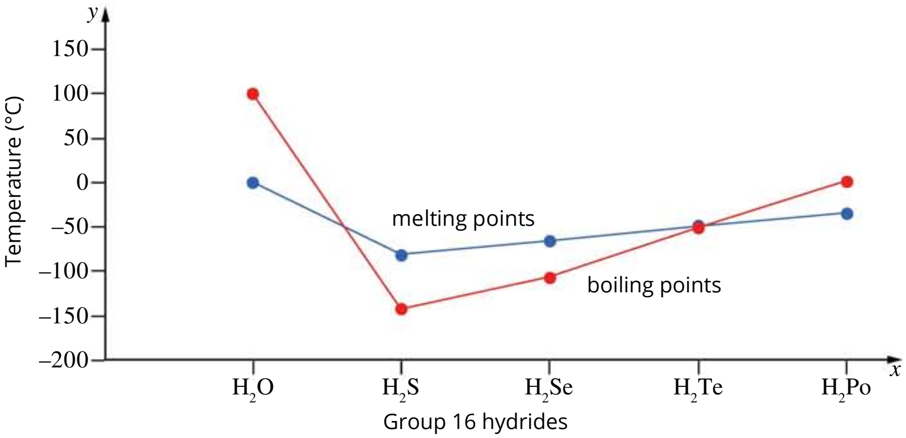

FIGURE 12.1.6 Graph showing the trend in melting and boiling points of water and other group 16 hydrides.

You can see from Figure 12.1.6 that, apart from water, there are clear trends in the melting and boiling points of the group 16 hydrides. The melting and boiling points both increase going down the group. This increase indicates that the intermolecular forces are also getting stronger down the group. The intermolecular forces responsible for this trend are dispersion forces. Dispersion forces increase in strength with increasing mass. H_2Po has a larger mass than H_2S and H_2Se; hence it has stronger dispersion forces and higher melting and boiling points.

ⓘ Despite being the smallest hydride, water has significantly higher melting and boiling points than other group 16 hydrides.

The melting and boiling points of water are exceptional

Water has a melting point of 0°C and a boiling point of 100°C. Both of these values are significantly higher than those of other group 16 hydrides. The values are also significantly higher than those of other molecular substances of a similar size, as can be seen in Figure 12.1.7.

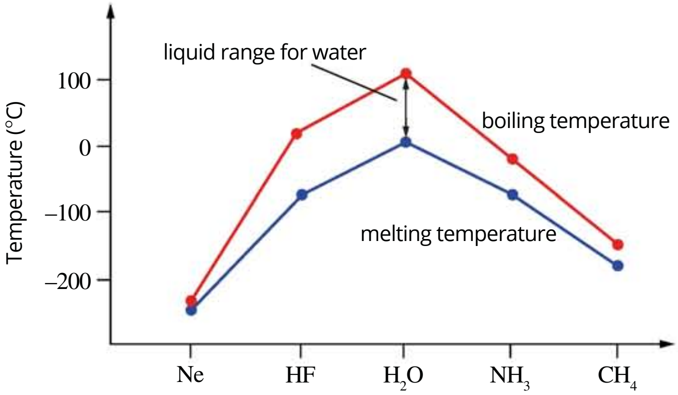

FIGURE 12.1.7 The melting and boiling points of water and other molecules of similar size.

It is the relatively strong hydrogen bonds between its molecules that give water its exceptional properties.

Each water molecule has the potential to form four hydrogen bonds with surrounding water molecules. There are two partially charged hydrogen atoms and two lone pairs of electrons on the oxygen atom in each molecule so all the hydrogen atoms and lone pairs in the molecule can be involved in hydrogen bonding.

A significant amount of energy is needed to disrupt all of the hydrogen bonds between water molecules, resulting in the higher melting points and boiling points observed for water.

Water expands on freezing

When a sample of water freezes, the resulting ice crystal lattice has a greater volume than when the sample of water was a liquid. Water has the unusual property of having a lower density in the solid phase than in the liquid phase.

This property of water is important to life on Earth. When water at the surface of rivers or lakes freezes, the low density of the ice means it remains on the surface. This surface layer of ice insulates the water below from the cold air temperatures, reducing the possibility that the entire river or lake will freeze, and allowing aquatic life to survive.

As liquid water is cooled, the water molecules move more slowly. Upon approaching the freezing temperature of water, the molecules arrange in a way where each water molecule forms four hydrogen bonds to four neighbouring water molecules, as shown in Figure 12.1.8.

This creates a very open arrangement of molecules, meaning that the water molecules in ice are more widely spaced than in liquid water. Therefore, ice is less dense than liquid water. When ice melts, the water molecules move more freely and move closer together.

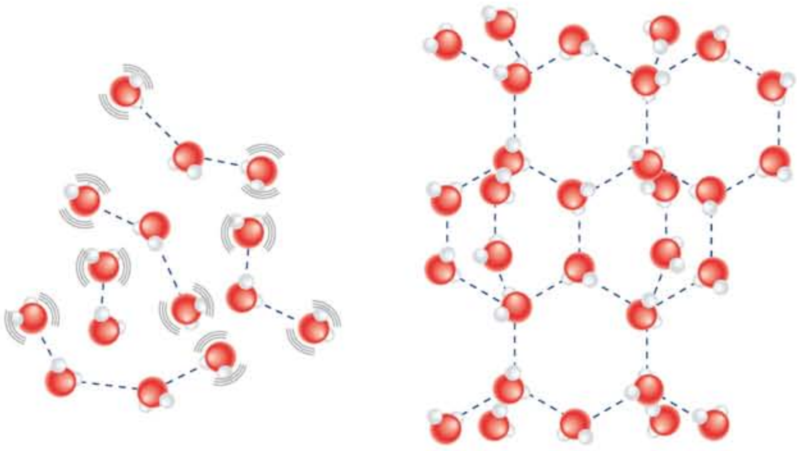

FIGURE 12.1.8 The arrangement of water molecules in liquid water (left) and ice (right).

CHEMFILE

The deep blue sea

When light passes through water, the vibration of O–H bonds in water molecules, combined with the hydrogen bonds between molecules, causes a small amount of light to be absorbed in the red part of the visible colour spectrum. This leaves the remaining complementary colour, which is blue, for you to see. You cannot see this colour in small volumes of water. However, when light travels through several metres of water or ice, you can see the blue colour.

FIGURE 12.1.9 Large volumes of water or ice appear blue.

12.1 Review

SUMMARY

- A water molecule is V-shaped and contains polar covalent bonds.
- Water molecules are polar because an overall dipole exists as a result of the unsymmetrical nature of the polar O–H bonds.
- As a result of the O–H bonds in water molecules, the forces that attract one water molecule to another are relatively strong hydrogen bonds.
- Each water molecule can form up to four hydrogen bonds with other water molecules.
- The strength of water's hydrogen bonds means relatively large amounts of energy are required to disrupt the bonds and separate the molecules from each other. This gives water relatively high melting and boiling points.
- Water has significantly higher melting and boiling points than the other group 16 hydrides.
- With the exception of water, the melting and boiling points of the group 16 hydrides increase going down the group. This is due to the increasing strength of dispersion forces.
- Ice is less dense than liquid water because of its unique geometric arrangement of water molecules as a result of hydrogen bonding.

KEY QUESTIONS

1 **a** List the physical properties that make water unique.

b Explain the significance of polarity and hydrogen bonding in relation to these properties of water.

2 The overall structure of a water molecule is important in explaining its unique properties. Draw a diagram of the valence structure of water, indicating any partial charges and dipoles.

3 Explain why a water molecule can form up to four hydrogen bonds with other water molecules.

4 With the exception of water, the group 16 hydrides exhibit a trend in boiling and melting points.

a Sort the group 16 hydrides (H_2O, H_2Po, H_2S, H_2Se, H_2Te) from lowest to highest boiling point.

b Why is it that water does not follow the trend of the other group 16 hydrides?

5 **a** Describe the forces that must be overcome in order for ice to melt.

b Sketch, or describe, a portion of a lattice of ice.

c Explain why ice is less dense than liquid water.

12.2 Heat capacity

Several of the ways that water supports life on Earth are based on how water interacts with heat energy. One particular property of water is that it requires a relatively large quantity of heat energy to raise its temperature by one degree.

In this section, you will learn about the concept of **heat capacity** and why relatively large quantities of heat energy are required to raise the temperature of water (Figure 12.2.1). When you walk on the beach on a hot summer's day, the dry sand can be burning hot on your feet while the shallow water at the edge of the sea is cool. Both surfaces are receiving and absorbing similar amounts of heat energy from the Sun, but the temperature of each is markedly different.

FIGURE 12.2.1 On a hot day, the sand at the beach can be hot to touch while the water is pleasantly cool.

HEAT CAPACITY

The heat capacity of a substance is a measure of the substance's capacity to absorb and store heat energy. It is a measure of how much energy the substance absorbs as its temperature increases. When the same quantity of heat energy is applied to two substances with different heat capacities, they will undergo different temperature changes.

This can be seen with water and ethanediol. Water has a higher specific heat capacity than ethanediol. When you heat equal amounts of the two liquids with the same amount of heat energy, the temperature of the two liquids will rise by different amounts. As shown in Figure 12.2.2, when 100 g of water and 100 g of ethanediol are heated with the same amount of energy, the beaker containing water will increase in temperature by a smaller amount than the ethanediol.

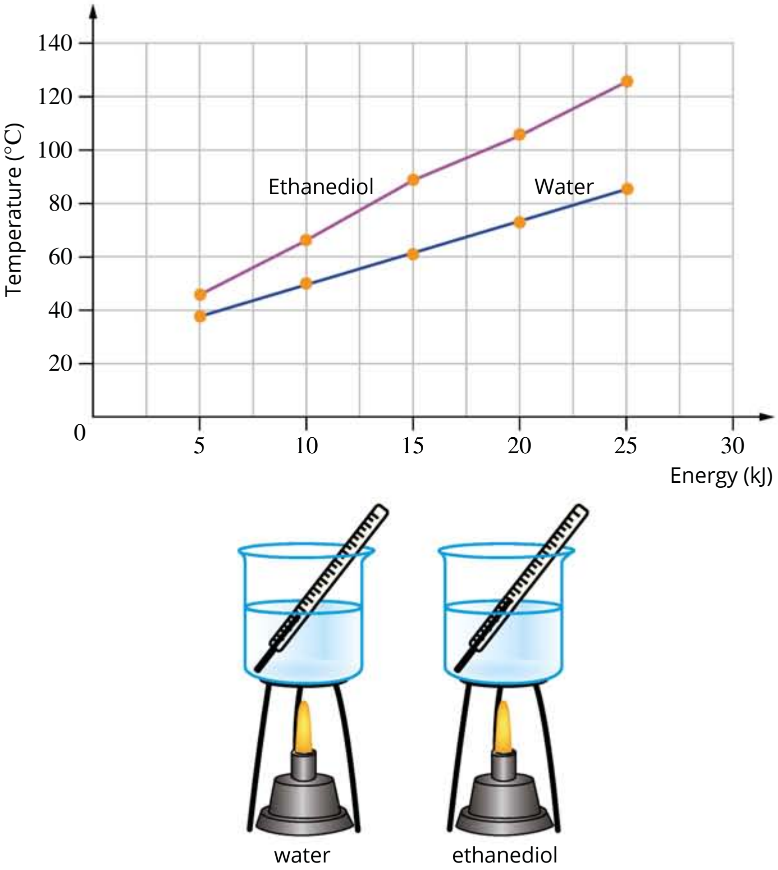

FIGURE 12.2.2 When 100 g of water and 100 g of ethanediol are heated with the same amount of energy, the temperature of the beaker containing water will increase less than the temperature of the ethanediol.

Specific heat capacity

The **specific heat capacity** of a substance measures the amount of energy (in joules) needed to increase the temperature of a certain amount (usually 1 gram) of that substance by 1°C.

Specific heat capacity is given the symbol *C* and is expressed in joules per grams per degrees Celsius, i.e. $\text{J g}^{-1}\,°\text{C}^{-1}$.

Specific heat capacity (*C*) is a measure of the energy required to raise 1 g of substance by 1°C. It is reported in units of $\text{J g}^{-1}\,°\text{C}^{-1}$.

TABLE 12.2.1 Specific heat capacities of common substances

Substance	Specific heat capacity ($\text{J g}^{-1}\,°\text{C}^{-1}$)
Water	4.18
Ethanediol	2.42
Ethanol	2.4
Sand	0.48
Copper	0.39
Lead	0.16

The specific heat capacities of some common substances are listed in Table 12.2.1. You can see that the value for water is relatively high. Water will absorb more energy than the other substances before its temperature changes.

Metals, covalent molecules and composite substances exhibit a variety of specific heat capacities, as seen in Figure 12.2.3. The top row illustrates metals, the middle row of substances shows some small molecular substances.

The specific heat capacity of a substance is a reflection of the types of bonds holding the molecules, ions or atoms together in the substance. The relatively high specific heat capacity of water is related to the number and strength of the hydrogen bonds between water molecules and the third row shows composite materials.

The specific heat capacity of a substance reflects the type of bonding in that substance. For covalent molecules, this will depend on the strength of the intermolecular forces between molecules.

FIGURE 12.2.3 Heat capacities of some selected substances.

Specific heat capacity of water

Water has a specific heat capacity of 4.18 J g^{-1} °C^{-1}. This means that 4.18 joules of heat energy are needed to increase the temperature of 1 gram of water by 1°C.

The specific heat capacity of water is relatively high. This is because of the presence of hydrogen bonds between water molecules. Hydrogen bonds are stronger than other intermolecular forces and they are able to absorb and store large amounts of heat energy before they break.

As water is a liquid, it is often convenient to measure a quantity of water as a volume, in mL or L, rather than as a mass measured in grams. 1 mL of water has a mass of 1 g, so it is easy to convert a given volume of water to mass:

- 1 mL of water weighs 1 g.
- 100 mL of water weighs 100 g.
- 250 mL of water weighs 250 g.

The density of liquid water is 1 g mL^{-1}, so volumes of water in millilitres (mL) are equal to the mass of water in grams (g).

Calculations using specific heat capacity

The specific heat capacity of a substance can be used to calculate the heat energy in joules required to increase the temperature of a given mass of substance by a particular amount. Heat energy is given the symbol *q*.

A useful equation can be written:

Heat energy = specific heat capacity × mass × temperature change

Using symbols, the equation can be written:

$q = C \times m \times \Delta T$

where *q* is the amount of heat energy (J), *C* is the specific heat capacity (J g^{-1} °C^{-1}), *m* is the mass (g) and ΔT is the temperature change (°C).

The energy required to increase a known mass of substance by a particular temperature is given by the formula $q = C \times m \times \Delta T$.

Worked example 12.2.1

CALCULATING THE AMOUNT OF ENERGY REQUIRED TO HEAT A SPECIFIED MASS OF A SUBSTANCE USING SPECIFIC HEAT CAPACITY

Calculate the heat energy, in kJ, needed to increase the temperature of 200 g of water by 15.0°C.

Thinking	Working
Find the specific heat capacity (*C*) of the substance from Table 12.2.1.	The specific heat capacity of water is 4.18 J g^{-1} °C^{-1}.
To calculate the quantity of heat energy in joules, use the formula: $q = C \times m \times \Delta T$	$q = 4.18 \times 200 \times 15.0$ $= 1.25 \times 10^4$ J
Express the quantity of energy in kJ. Remember that to convert from J to kJ, you multiply by 10^{-3}.	$q = 1.25 \times 10^4 \times 10^{-3}$ $= 12.5$ kJ

Worked example: Try yourself 12.2.1

CALCULATING THE AMOUNT OF ENERGY REQUIRED TO HEAT A SPECIFIED MASS OF A SUBSTANCE USING SPECIFIC HEAT CAPACITY

Calculate the heat energy, in kJ, needed to increase the temperature of 375 g of water by 45.0°C.

CHEMFILE

Biological importance of water's high heat capacity

The high heat capacity of water means water will absorb a relatively large amount of energy before it heats up. This makes water resistant to sudden temperature changes, and plants and animals that live in water survive without experiencing wide temperature fluctuations.

Many living organisms are mainly composed of water. Water's high heat capacity allows organisms to maintain consistent internal body temperatures, regardless of the external environment.

FIGURE 12.2.4 Fish and coral in the sea can survive due to the relatively consistent temperature of the sea water. Water's high heat capacity makes it resistant to temperature fluctuations.

12.2. Review

SUMMARY

- Heat capacity is a measure of a substance's capacity to absorb and store heat energy.
- The specific heat capacity of a substance measures the quantity of energy (in joules) needed to increase the temperature of a certain amount (usually 1 gram) of that substance by 1°C.
- The specific heat capacity of water is relatively high due to the ability of the hydrogen bonds between water molecules to absorb and store heat energy.
- The heat energy required to increase a given mass of substance by a particular temperature can be calculated using the equation:
  $q = C \times m \times \Delta T$
  where q is heat energy (J), C is the specific heat capacity (J g^{-1} °C^{-1}), m is mass of the substance (g) and ΔT is the temperature change (°C).
- The mass of a sample of liquid water in grams (g) is equal to its volume in millilitres (mL).

KEY QUESTIONS

1. Which one of the following statements best describes the specific heat capacity of a substance?
   A Specific heat capacity is a measure of the heat energy required to increase the temperature of a substance from its melting point to its boiling point.
   B A substance with high specific heat capacity is less resistant to temperature change than a substance with low heat capacity.
   C A substance with high specific heat capacity contains bonds that are unable to absorb a lot of energy.
   D Specific heat capacity is a measure of the heat energy that can be absorbed by the bonds in a substance.
2. Figure 12.2.3 shows the specific heat capacities of some substances. Order the substances from the one that absorbs the least amount of energy to the one that absorbs the most for the same increase in temperature.
3. Calculate the heat energy, in J, needed to increase the temperature of 5.0 g of sand by 12°C. The specific heat capacity of sand is 0.48 J g^{-1} °C^{-1}.
4. Calculate the heat energy, in kJ, needed to increase the temperature of 1.5 kg of water by 15°C.
5. **a** How much energy, in kJ, will be required to heat 600 mL of water in a kettle from 21°C to 100°C?
   b Given that the specific heat capacity of lead is 0.16 J g^{-1} °C^{-1}, how much energy would it take to raise the same mass of lead by the same number of degrees as the water described in part **a**?
6. A 250 mL beaker of water at a temperature of 22°C is heated with the addition of 10 kJ of energy. Calculate the temperature reached by the beaker of water.
7. A 500 g sample of an unknown substance was heated with the addition of 9.75 kJ of energy. The temperature is noted to rise from 25°C to 75°C. Calculate the specific heat capacity and use Table 12.2.1 to identify the unknown substance.

12.3 Latent heat

When you perspire (sweat), your body uses a very effective method to cool down (Figure 12.3.1). The water released onto your skin as sweat does not readily evaporate. Rather, it sits on the surface of your skin absorbing relatively large amounts of heat energy from the body before it evaporates as a gas.

In combination with its high specific heat capacity, it is the **latent heat** of water that makes it such an effective coolant. In this section you will learn about latent heat and its significance to living organisms and water supplies.

FIGURE 12.3.1 One of the signs of an increasing body temperature on a hot day or during exercise is when you start to perspire. Your body cools itself by releasing water onto the surface of your skin.

LATENT HEAT

When a solid is heated at constant pressure, the temperature of the solid increases until it reaches its melting point. The temperature then remains constant as the solid melts, even though further energy is being absorbed.

Similarly, when a liquid reaches its boiling point, its temperature remains constant until all of the liquid has evaporated. Think about a pot of boiling water. The temperature remains at 100°C until all of the water in the pot has evaporated.

Figure 12.3.2 shows how in both cases, at the melting point and boiling point of the substance, the temperature remains constant until the phase change is complete. Heat is still flowing into the substance but the temperature does not change. Once a solid has completely melted, or a liquid has completely evaporated, if heating continues, then the temperature of the substance starts to increase again.

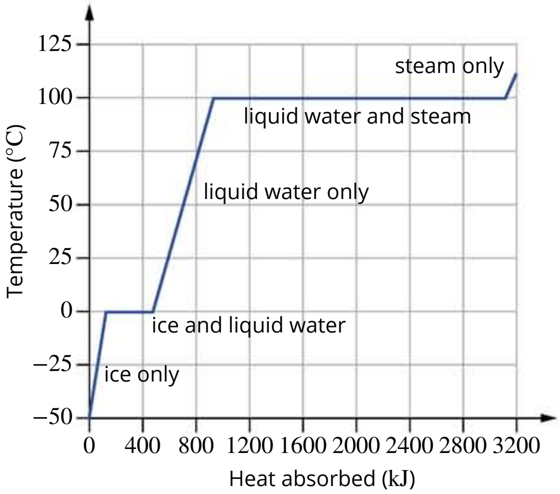

FIGURE 12.3.2 Latent heat is the energy absorbed by a substance in order to change state at its melting or boiling temperature. For a pure substance, such as water in this case, the horizontal regions of the heating curve show where latent heat is being absorbed and the temperature is not changing.

Even though the temperature does not change while the phase change is taking place, the substance is still absorbing energy. This energy is referred to as latent heat and is defined as the energy absorbed by a fixed amount of substance as it changes state from a solid to a liquid or a liquid to a gas at its melting point or boiling point respectively.

Latent heat is the energy required to change a fixed amount of substance, usually 1 mole, from either a solid to a liquid or a liquid to a gas. Over the period of time that latent heat is being absorbed, the temperature of a substance will not change.

Values of latent heat

Latent heat values are a measure of the quantity of heat energy required to melt or boil a given amount of a solid or liquid. Latent heat values are given the symbol L and have the unit kilojoules per mole, kJ mol^{-1}.

The **latent heat of fusion** of a substance is the heat needed to change 1 mole of the substance from a solid to a liquid at its melting point.

The **latent heat of vaporisation** of a substance is the heat needed to change 1 mole of the substance from a liquid to a gas at its boiling point.

Latent heat of water

The latent heat of fusion of water is 6.0 kJ mol^{-1}. This means that 6.0 kJ of energy is needed to change 1 mole of water from a solid to a liquid at 0°C. This energy is needed to disrupt the ice lattice by breaking some of the hydrogen bonds between water molecules.

The latent heat of vaporisation of water is 44.0 kJ mol^{-1}. This means that 44.0 kJ is needed to change the state of 1 mole of water from a liquid to a gas at 100°C. This relatively large quantity of energy is required to completely break the hydrogen bonds between the water molecules so they can separate and form a gas.

The latent heat values of water and some other substances are listed in Table 12.3.1. Much like specific heat capacity, latent heat depends on the strength of the intermolecular forces between molecules of the substance.

TABLE 12.3.1 Latent heat values for some common molecular substances

Substance	Latent heat of fusion (kJ mol^{-1})	Latent heat of vaporisation (kJ mol^{-1})
Water	6.0	44.0
Hydrogen	0.06	0.45
Oxygen	0.22	3.4

As you can see, the latent heat values of water are relatively high. This is due to the strength and number of water's hydrogen bonds relative to its molecular size.

Significance of water's latent heat of vaporisation

Cooling system for living organisms

The high latent heat of vaporisation of water means it takes a relatively large amount of energy to vaporise sweat on your body's surface. As sweat evaporates, it extracts a large quantity of heat from your body, which cools you down very effectively.

If the latent heat of vaporisation of water were low, only a little heat would vaporise the water and you would have to sweat more to extract heat to cool down the body. A higher loss of body fluid would be required to maintain a safe temperature and you would be at greater risk of dehydration (Figure 12.3.3).

FIGURE 12.3.3 A sweating cyclist would be at much greater risk of dehydration if water did not have such a high latent heat of vaporisation.

FIGURE 12.3.4 The Maroondah Reservoir in Melbourne. The water level would be depleted by evaporation more quickly if water had a lower latent heat of vaporisation.

Longevity of water supplies

Much of Australia's freshwater supplies are stored in open reservoirs such as the Maroondah Reservoir in Melbourne, shown in Figure 12.3.4. Although evaporation losses from storage facilities can potentially be large, they would be far greater if water had a lower latent heat of vaporisation.

CHEMISTRY IN ACTION

Removing excess heat

Many items of technology that you use every day generate excess heat. If the heat is not removed, the heat energy can build up and result in equipment failure. A good example of this is a car's engine. The combustion of fuel is a highly exothermic reaction, giving off a large amount of heat to the environment. If the engine overheats, this can cause permanent damage. Excess heat is removed from the engine by water. Water is cycled through the engine by a series of pipes and then returns to the radiator where the heat energy is transferred from the water to the metal of the radiator and then to the air passing through the grill (Figure 12.3.5).

This can occur because of the high specific heat capacity of water. Thus, water is able to absorb a large amount of heat energy from the engine of the car.

The same principle has been applied to water-based coolant systems for high-level computers that generate significant amounts of heat from their CPUs (central processing units) and 3D-graphics cards. Figure 12.3.6 shows a computer CPU with connectors for liquid cooling tubes. Traditional methods of cooling such as fans are often insufficient to keep the temperature within the operating conditions required. The greater heat capacity of water allows the systems to be cooled more efficiently, preventing fluctuations in temperature that can damage the components.

Water's ability to absorb large amounts of heat energy is used across a variety of industries including, electronics, battery technologies and even on a massive scale in the cooling towers of electrical power plants.

FIGURE 12.3.5 Car radiators make use of the high specific heat capacity of water to discharge excess heat from the engine and maintain performance.

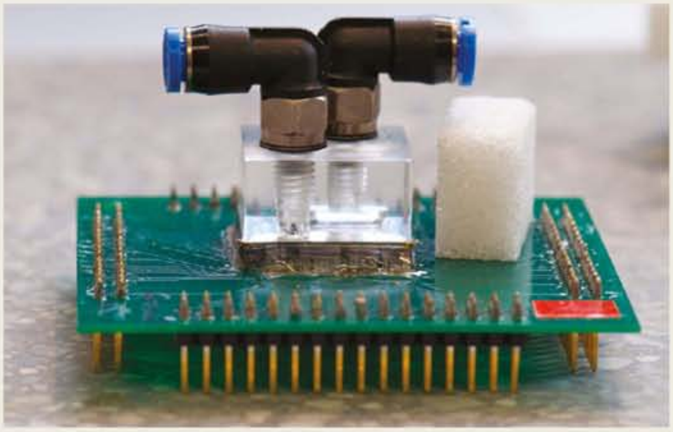

FIGURE 12.3.6 Liquid cooling of CPUs allows for greater efficiency and performance in computing technology. The use of liquid coolants such as water allows for more even temperatures to be maintained around the sensitive components of high-level computers.

Calculations involving latent heat

The amount of heat required to change the state of a given amount of a substance can be calculated if the value of the latent heat for the substance is known.

The amount of heat energy required for a change in state is equal to:

Amount of substance, in mol × latent heat value

This can be written as:

$q = n \times L$

where q is the heat energy (kJ), n is the amount (mol) of the substance changing state and L is the latent heat value of fusion or vaporisation (kJ mol^{-1}).

The heat energy required for a state change is given by the formula $q = n \times L$. Always check if the change is from liquid to gas or solid to liquid and substitute the appropriate latent heat value.

Worked example 12.3.1

CALCULATING THE HEAT ENERGY REQUIRED TO EVAPORATE A GIVEN MASS OF WATER AT ITS BOILING TEMPERATURE

Calculate the heat energy, in kJ, required to evaporate 200 g of water at 100°C.

Thinking	Working
Determine the amount, in mol, of the substance using the formula: $n = \frac{m}{M}$	$n = \frac{200}{18.0}$ $= 11.1$ mol
Find the relevant latent heat value of the substance.	Water is being evaporated, so the latent heat of vaporisation of water is required. $L = 44.0$ kJ mol^{-1}
Calculate the heat energy, in kJ, using the formula: $q = n \times L$	$q = 11.1 \times 44.0$ $= 488$ kJ

Worked example: Try yourself 12.3.1

CALCULATING THE HEAT ENERGY REQUIRED TO EVAPORATE A GIVEN MASS OF WATER AT ITS BOILING TEMPERATURE

Calculate the heat energy, in kJ, required to evaporate 75.0 g of water at 100°C.

12.3 Review

SUMMARY

- Latent heat is the energy absorbed by a fixed amount of substance as it changes state from a solid to a liquid or a liquid to a gas.
- The latent heat of vaporisation of a substance is the heat energy needed to change 1 mole of the substance from a liquid to a gas at its boiling point.
- The latent heat of vaporisation of water is a relatively high 44.0 kJ mol^{-1}. This has significance for organisms and water supplies.
- The latent heat of fusion of a substance is the heat energy needed to change 1 mole of the substance from a solid to a liquid at its melting point.
- The latent heat of fusion of water is a relatively high 6.0 kJ mol^{-1}.
- The heat energy required to change the state of a substance can be determined using the equation $q = n \times L$.

KEY QUESTIONS

1 A heating curve for a substance is produced by plotting the temperature change against the energy input. When this is done from the melting point to the boiling point of a substance, two flat regions are observed. Explain what the flat regions of the graph represent.

2 What type of bonding is responsible for water's relatively high latent heat values?

3 Explain why water's latent heat of vaporisation is much higher than its latent heat of fusion.

4 Calculate the heat energy, in kJ, required to evaporate 2.50 mol of water at 100°C.

5 A student places a beaker containing 100 mL of water over a lit Bunsen burner but gets distracted and does not notice that the beaker boils dry. Calculate the amount of heat energy, in kJ, that was absorbed by the water in the beaker as it evaporated at 100°C.

6 Calculate the heat energy, in kJ, required to melt 300 g of ice at 0°C.

Chapter review

KEY TERMS

dipole
electronegativity
electrostatic attraction
heat capacity
hydride
hydrogen bond
intermolecular force
intramolecular bond
latent heat
latent heat of fusion
latent heat of vaporisation
lone pair
polar
specific heat capacity

Essential water

1 Copy and complete the following sentences about water and its properties.

Water is a ____________ molecule. Within a single molecule, hydrogen and oxygen atoms are held together by strong ________ _________. Between different molecules, the most significant forces are __________ __________.

It is the relatively ________ strength of the intermolecular forces that gives water its unique properties of relatively:

- ________ boiling point, ________°C
- ________ latent heat values, ______ kJ mol^{-1} and ______ kJ mol^{-1}
- ____________ specific heat capacity, ________ J g^{-1} °C^{-1}.

2 Figure 12.4.1 shows the arrangement of water molecules in ice. Identify the parts of the diagram labelled **a**–**d**.

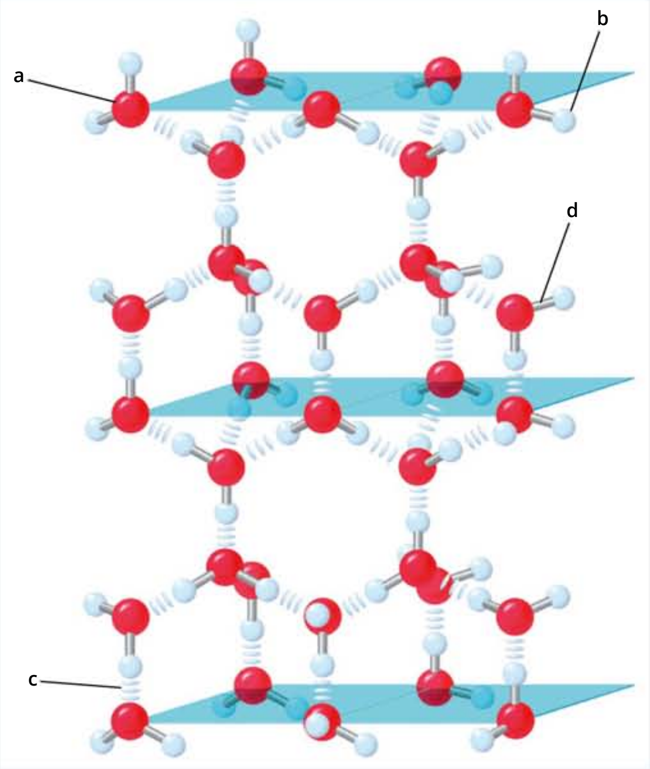

FIGURE 12.4.1

3 Water boils at 100°C. However, a much higher temperature (1000°C) is needed to decompose water molecules into hydrogen gas and oxygen gas.

a Using water as an example, explain the meaning of the terms ‘intermolecular’ and ‘intramolecular’ forces.

b Which of the two types of forces described in part **a** is stronger? Justify your answer by using the information at the beginning of the question.

4 Hydrogen sulfide and water are both group 16 hydrides. Explain why water exhibits a much higher boiling point than hydrogen sulfide.

5 In your own words, discuss the significance of polarity and hydrogen bonding in relation to the high boiling point of water.

6 An evaporative air conditioner is used to cool the air inside some buildings. The cooler lowers the air temperature by using heat from the air to evaporate water. Select the property that is most important when water is used in an evaporative air conditioner.

Heat capacity

7 When heat energy is applied to a substance, the temperature increase of the substance depends on which of the following?

A The mass of the substance

B The types of bonds present in the substance

C The amount of heat energy transferred to the substance

D All of the above

8 A student boils water to make a cup of coffee. Calculate the energy required, in kJ, to raise 250 mL of water from 18°C to 100°C. Express your answer to three significant figures.

9 Calculate the quantity of energy, in kJ, required to raise the temperature of 1.500 L of water from 23°C to 90°C.

10 Calculate the heat energy, in kJ, needed to increase the temperature of 1.0 kg of ethanol by 4.0°C. The specific heat capacity of ethanol is 2.4 J g^{-1} °C^{-1}.

11 A copper pan of mass 750 g at a temperature of 25°C is placed on a stovetop and heated with the addition of 12.5 kJ of heat energy. Given that the heat capacity of copper is 0.39 J g^{-1} °C^{-1}, calculate the final temperature of the pan.

12 A rock weighing 15 g is placed next to a campfire and absorbs 50 J of energy, increasing in temperature by 8.0°C. Calculate the specific heat capacity of the rock.

Latent heat

13 Match the following terms with their definitions: latent heat of fusion, specific heat capacity, latent heat of vaporisation, boiling point.

- **a** The temperature at which a liquid boils to form a gas
- **b** The heat energy required to melt a solid to a liquid at its melting point
- **c** The amount of heat energy required to increase 1 g of a substance by 1°C.
- **d** The heat energy required to evaporate a liquid to a gas at its boiling point

14 Select the correct statement about the effect of latent heat on the temperature of a substance.

- **A** Absorption of latent heat by a substance will cause only a small increase in the temperature of the substance.
- **B** Absorption of latent heat by a substance will have no effect on the temperature of the substance.
- **C** Absorption of latent heat by a substance will cause a significant increase in the temperature of the substance.
- **D** Absorption of latent heat by a substance will cause a small decrease in the temperature of the substance.

15 A student was asked to record the temperature changes as a sample of ice was heated. The ice was placed in a beaker and heated with a Bunsen burner for 20 minutes. The graph in Figure 12.4.2 shows the temperature, in degrees Celsius, recorded at 1 minute intervals.

FIGURE 12.4.2

- **a** Explain what is happening, at a molecular level, between 2.0 and 4.0 minutes on the graph.
- **b** Even though heating is continued for 20 minutes, no further temperature rise is observed after 16 minutes. What happens to the added heat between 16 and 20 minutes?

16 Calculate the heat energy required to evaporate 250 g of water at its boiling temperature.

17 Calculate the mass of water that could be evaporated at 100°C if 1000 kJ of heat were absorbed by the water.

18 Calculate the difference, to the nearest kJ, in the amount of heat energy required to melt 500 g of ice at 0°C and to evaporate 500 g of water at 100°C.

19 In your own words, explain the significance of water's high latent heat of vaporisation to living organisms.

Connecting the main ideas

20 200 g of water is placed in one beaker and 200 g of ethanol in another. Both are initially at the same temperature. The specific heat capacity of ethanol is 2.4 J g^{-1} $°C^{-1}$ and that of water is 4.18 J g^{-1} $°C^{-1}$. Each beaker is heated by the addition of 5 kJ of heat energy. The molecular structures of water and ethanol are shown in Figure 12.4.3.

- **a** How would you expect the temperature of the ethanol to compare to that of the water after heating?
- **b** Explain your answer to part **a**, making reference to the specific heat capacities and the strength of the bonding that would exist between molecules.

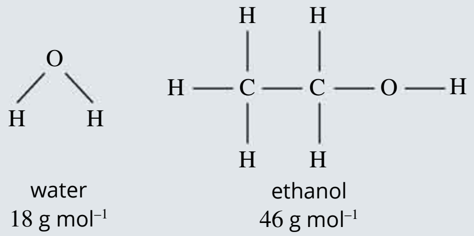

FIGURE 12.4.3

21 A 25 g piece of an unknown metal alloy at 150°C is dropped into an insulated container with 200 g of ice. Calculate the specific heat capacity of the metal, given that 9.0 g of ice melted.

CHAPTER 13

Water, the universal solvent

Think back to the last time you dissolved a solid in a liquid. One moment the solid has volume, shape and colour; the next it is added to water and, with a little bit of stirring, it quickly seems to disappear.

Many different substances dissolve in water, from molecular compounds such as sugar to ionic compounds such as sodium chloride. Water is often described as the universal solvent because of the wide range of substances it can dissolve.

In this chapter, you will learn about the ways that different types of substances dissolve in water, as well as how to predict whether a compound is likely to be soluble.

Key knowledge

- The comparison of solution processes in water for molecular substances and ionic compounds
- Precipitation reactions represented by balanced full and ionic equations, including states
- The importance of the solvent properties of water in selected biological, domestic or industrial contexts

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13.1 Water as a solvent

FIGURE 13.1.1 When solid potassium permanganate is added to water, it dissolves. The particles disperse into the solution and move around freely.

Water is an excellent solvent. This is one of its most important properties. Almost all biological processes and many industrial processes occur in water. These systems are known as **aqueous** environments.

When substances are dissolved in water, the particles are free to move throughout the **solution**. When two aqueous reactants are combined in a reaction vessel, the dissolved reactant particles mix freely. This increases the chances of the reactants coming into contact. Because of the increased movement of the reactant particles, interactions between reactants are generally much more effective than if the same reactants were mixed as solids.

In Figure 13.1.1, you can see how the deep purple colour of potassium permanganate spreads through the water as the solid dissolves. Eventually the liquid will appear completely purple as the particles continue to mix and move.

This section looks at the importance of the solvent properties of water to living organisms and modern industry, as well as the process of dissolving. Sections 13.2 and 13.3 will explore in more detail the type of bonds that form when molecular and ionic substances dissolve in water.

FORCES BETWEEN SOLUTE AND SOLVENT PARTICLES

Aqueous solutions

An aqueous solution is formed when a solid, liquid or gas is dissolved in water. The substance being dissolved is called the **solute** and the liquid in which the substance is dissolved is the **solvent**.

The solute of an aqueous solution can change but the solvent will always be water. You can have an aqueous solution of salt (saline) or an aqueous solution of sugar. Table 13.1.1 lists some common aqueous solutions.

TABLE 13.1.1 Some everyday aqueous solutions

Solution	Solute/s	Solvent
Saline solution (for use with contact lenses)	Sodium chloride	Water
Soft drink	Carbon dioxide, sugar, flavour, colour	Water
Coffee	Coffee, sugar	Water

All solutions have the following characteristics.

- The solute and the solvent cannot be distinguished from each other. This means the solution is **homogeneous**.
- The dissolved particles are too small to see.
- The amount of dissolved solute can vary from one solution to another.

In a homogeneous solution, the solute and solvent particles cannot be distinguished from each other. Every part of the solution is the same as any other part.

EXTENSION

Suspensions and colloids

When a substance is mixed with water, it does not always dissolve to form a solution. It could also form a **suspension** or a **colloid**.

A suspension is a **heterogeneous** mixture (a mixture with visible distinguishable parts) that forms when a solute does not dissolve significantly in a solvent. Some particles will settle out over time and in many cases you can separate them from the solvent by using filter paper. Chalk in water and red blood cells in plasma are suspensions. Figures 13.1.2 and 13.1.3 show blood before and after it is separated into its component parts.

FIGURE 13.1.2 On first glance, blood looks like a homogeneous mixture.

FIGURE 13.1.3 Centrifuging blood separates it into clear layers, demonstrating that blood is actually a heterogeneous suspension. Here you can see the plasma on top and the red blood cells on the bottom.

A colloid is a mixture of particles that consists of smaller clusters of ions or molecules. These are evenly dispersed throughout the solvent and do not settle on standing. For example, milk is a colloid of a fat and an aqueous solution (Figure 13.1.4). Milk solids and fat are finely dispersed throughout the more aqueous components of the milk. Other common colloids include mayonnaise, paint and ink.

FIGURE 13.1.4 Milk is a colloid. Small particles are dispersed throughout the liquid.

Process of dissolving

The process of a substance dissolving in another substance is called **dissolution**. When the two substances are liquids, you can say they are **miscible**.

During dissolution the following processes occur.

- The particles of the solute are separated from one another.
- The particles of the solvent are separated from one another.
- The solute and solvent particles are attracted to each other.

For a solution to form, the solute particles must interact with the solvent molecules. The solute particles are surrounded by solvent molecules and carried throughout the solution.

Forces involved in dissolving

For a substance to dissolve, there must be a change in the way particles in the solute and solvent interact. This means you need to look at the forces of attraction that occur between the particles.

It is useful to think of three different forces of attraction when considering if and how a substance will dissolve in water. These are the forces:

- holding the particles of the substance (solute) together before it is added to the solvent
- holding the solvent molecules together. In water, these forces are **hydrogen bonds**
- that can form between the solute particles and solvent molecules if the substance dissolves.

For a substance to dissolve, the attractive forces that form between the solute and solvent particles must be sufficient to overcome the forces between the particles in the solute and the forces between the solvent molecules.

For a substance to be soluble, the solute–solvent interactions must be stronger than the solute–solute and solvent–solvent interactions.

Figure 13.1.5 shows that as a solute dissolves, the solute particles separate and become evenly distributed in the solvent. If the attraction between the solute and solvent particles is not strong enough, then the substance will not readily dissolve.

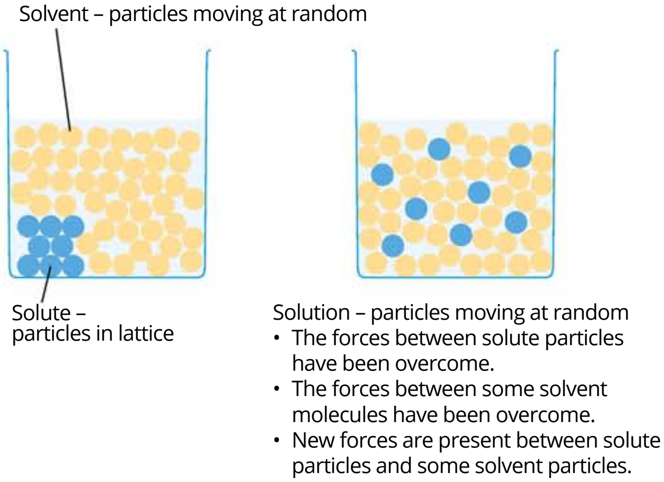


FIGURE 13.1.5 The rearrangement of particles when a solute dissolves in a solvent. The solute particles separate and become evenly distributed in the solvent.

You can use a 'like dissolves like' rule to predict whether a substance is likely to dissolve in another substance. The general statement that a solvent will only dissolve 'like' solutes tells you that:

- **polar** solvents will generally dissolve substances consisting of polar molecules or charged ions, but will not dissolve solutes made up of **non-polar** molecules
- non-polar solvents can dissolve substances consisting of non-polar molecules, but will not dissolve ones with polar molecules or ions.

Oil and other non-polar molecular substances do not dissolve well in water because the only intermolecular forces in these substances are dispersion forces, whereas the strong intermolecular forces of hydrogen bonding exist between the water molecules. These hydrogen bonds between water molecules are much stronger than the dispersion forces that could occur between molecules of oil and water. As a result, the attraction between the water molecules cannot be overcome and the water molecules do not separate to form a solution with the oil molecules.

CHEMFILE

Water cannot cool a mouthful of chilli

The chemical that gives a chilli its heat is capsaicin. Capsaicin (Figure 13.1.6) is a non-polar molecule that cannot dissolve in water. When you drink water after eating chilli, it will not rinse the capsaicin away, so the burning sensation remains.

Common advice given to cool your mouth after eating chillies is to drink milk. As milk is largely aqueous, the capsaicin does not dissolve in the milk, but a protein in milk breaks the bonds between capsaicin and pain receptors in the mouth.

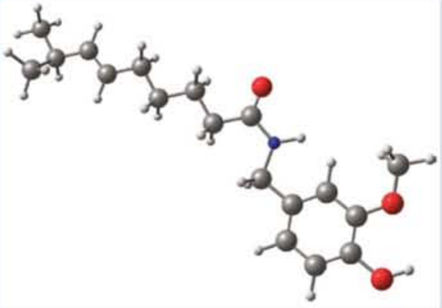


FIGURE 13.1.6 The structure of capsaicin contains mostly non-polar groups. The molecule will not interact with polar water molecules and so it is not soluble.

You can observe the 'like dissolves like' rule with the miscibility of different liquids. Figure 13.1.7 shows a solution of ethanol and water. The polar nature of the ethanol molecule means it readily dissolves in water, which is also polar. When mixed, a homogeneous solution is formed with no separation between solute and solvent.

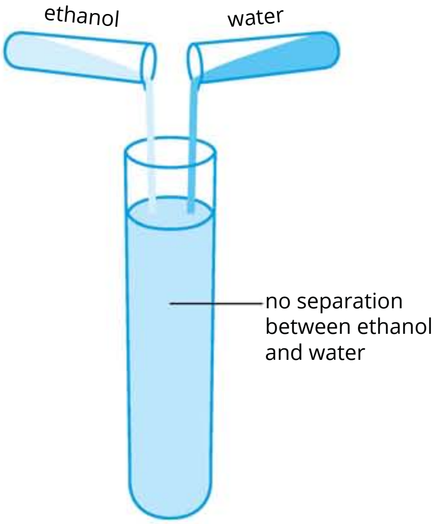


FIGURE 13.1.7 The polar compound ethanol is completely miscible in water. A homogeneous solution is formed on mixing.

In contrast, hexane is immiscible in water. Hexane is composed of non-polar molecules that will not interact with the polar water molecules. Figure 13.1.8 shows that when hexane and water are mixed, two layers form and the less dense hexane sits on top of the water.

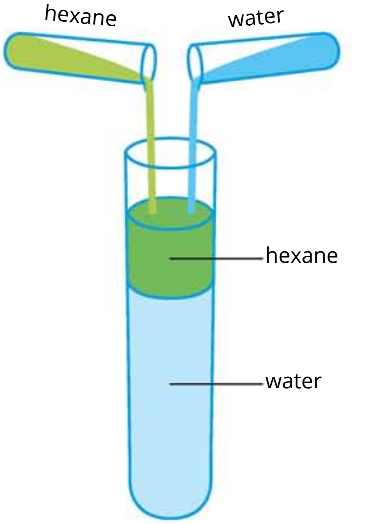


FIGURE 13.1.8 Hexane is a non-polar molecular compound that is not miscible in water. Two layers are formed with the non-polar liquid sitting on top of the water layer.

Like hexane, olive oil is also composed of non-polar molecules. When olive oil and hexane are mixed with each other, the 'like dissolves like' rule applies and the two non-polar liquids readily mix with each other to form a homogeneous solution (Figure 13.1.9).

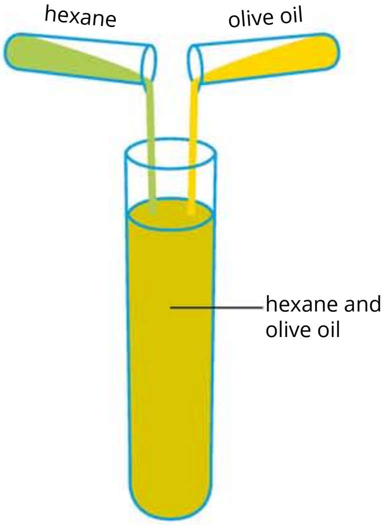


FIGURE 13.1.9 Hexane and olive oil are both non-polar molecular compounds and so are completely miscible.

ℹ Use the 'like dissolves like' principle to predict if something will dissolve in a solvent.

IMPORTANCE OF THE SOLVENT PROPERTIES OF WATER

Water's unique properties make it essential to life, particularly its ability to dissolve an enormous range of different solutes. The importance of water's solvent properties is evident in biological, domestic and industrial contexts.

Biological contexts

Biological contexts are those that involve living things. The human body is 66% water by weight. For biological organisms, water provides a system to transport nutrients and soluble wastes. It also transports essential reagents for chemical reactions to cells and tissues.

The circulatory system of the body (Figure 13.1.10) forms a transportation network. Essential nutrients, ions and molecules dissolved in water are carried to your organs, brain and tissues. The flow of blood through the circulatory system also carries away waste products.

Most plants are approximately 90% water. Nutrients in the soil dissolve in water and are absorbed into the root systems of plants. Once absorbed by the plant, the nutrients are transported around as dissolved solutes.

Cyclists like those in Figure 13.1.11 require a continual supply of energy to their muscles. The reactions in your body providing you with energy, or making your muscles contract, are occurring in aqueous solution. Chemical reactions occur when reactants make contact with each other. Solutions provide good environments for reactions because reactants can move freely, collide and react with each other.

People who are unwell are often unable to eat or drink. Essential nutrients can be administered to patients as a solution. Figure 13.1.12 shows an intravenous drip being used to provide saline solution directly into the bloodstream. The same method can also be used to administer solutions containing dissolved medications.

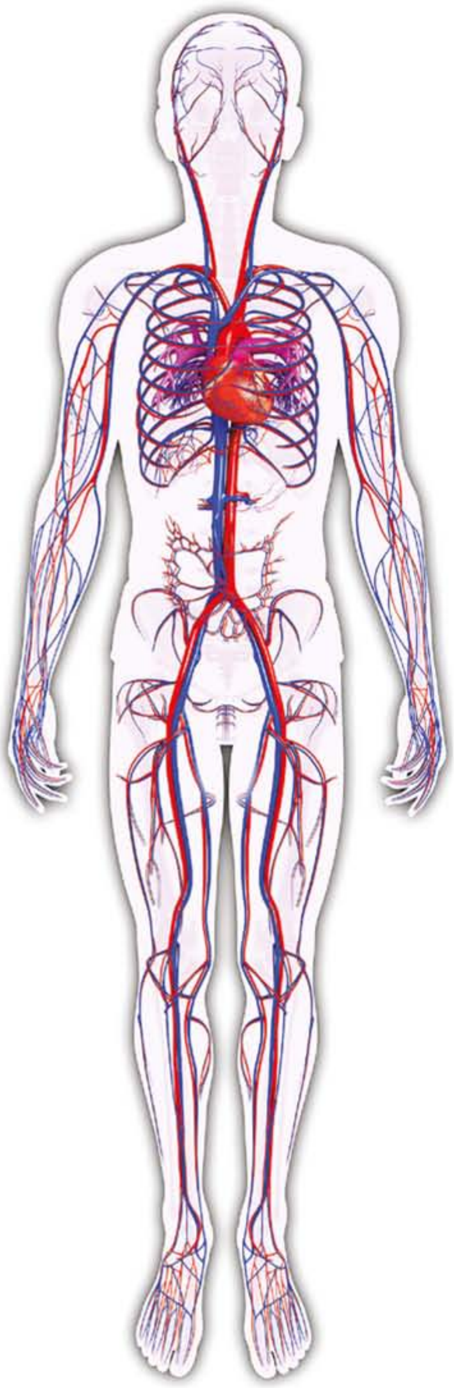


FIGURE 13.1.10 The circulatory system of the body transports many ions and molecules dissolved in water. The solute particles include nutrients and waste products from the body's metabolic processes.

FIGURE 13.1.11 The chemical reactions that provide energy and muscle contractions for these cyclists take place in solution.

FIGURE 13.1.12 Saline solution contains dissolved sodium chloride, in concentrations similar to that in blood. It can be added to the body directly through veins to increase the blood volume and treat dehydration and other conditions.

Domestic contexts

Every day you are likely to make use of the solvent properties of water in your home. Figure 13.1.13 highlights just a few of the ways aqueous solutions are used domestically.

FIGURE 13.1.13 (a) Saline solution, a solution of sodium chloride, is used for cleaning and storing contact lenses. (b) Soft drink is a solution of sugar, colour, flavour and carbon dioxide in water. (c) Many people argue that cooking perfect pasta requires salt to be dissolved in the boiling water. (d) Water-based paints account for 80% of the paints sold in the residential market.

Industrial contexts

Industrial contexts are those that involve the processing of raw materials and manufacture of products in factories. The development of water-soluble fertilisers and water-soluble medications such as aspirin are just a few of the ways that industry uses the solvent properties of water, as shown in Figures 13.1.14 and 13.1.15.

Water is widely used as a solvent in industry (Figure 13.1.16) because it dissolves many different substances and is non-toxic and readily available.

FIGURE 13.1.14 Water-soluble fertilisers are spread over fields to enhance crop growth.

FIGURE 13.1.15 Soluble aspirin. The pharmaceutical industry has developed many water-soluble medicines that are more rapidly absorbed by a patient.

FIGURE 13.1.16 Water is widely used as a solvent in industry to make substances such as foods, medicines, fertilisers, paints, pesticides, adhesives and paper.

13.1 Review

SUMMARY

- A solution is a homogeneous mixture in which molecules or ions are evenly dispersed throughout a solvent.
- Solutions in which water is the solvent are called aqueous solutions.
- A solution forms when the bonds between the solute and solvent particles are sufficiently strong to compete with attractive forces between the solute particles and between the solvent particles.
- 'Like dissolves like' is a rule that predicts that polar solutes will dissolve in polar solvents and non-polar solutes will dissolve in non-polar solvents.
- Water's solvent properties make it essential to life. It provides transport of nutrients in living organisms and provides an aqueous environment for chemical reactions.
- Water is used extensively as a solvent in domestic and industrial applications.

KEY QUESTIONS

1 Identify each of the following components of a glass of wine as solute, solvent or solution.
  - **a** Water
  - **b** Wine
  - **c** Ethanol
  - **d** Sugar

2 What is the one thing that all aqueous solutions have in common?

3 Classify the following substances as likely to be soluble or insoluble in water.
  - **a** Ammonia (NH_3)
  - **b** Oxygen gas (O_2)
  - **c** Hydrogen chloride (HCl)
  - **d** Methanol (CH_3OH)
  - **e** Methane (CH_4)
  - **f** Hydrogen fluoride (HF)
  - **g** Carbon dioxide (CO_2)

4 Sodium chloride is very soluble in water. Explain what can be concluded about the forces present between the solute and solvent particles.

5 Match each of the following terms with the correct definition: dissolution, solution, solvent, solute, soluble, insoluble.
  - **a** Capable of dissolving
  - **b** Incapable of dissolving
  - **c** The minor component of a solution
  - **d** The process by which a substance is dissolved in a solvent
  - **e** A liquid mixture in which a solute is dispersed throughout a solvent
  - **f** The major component of a solution

6 Which one of the following molecules is likely to dissolve best in hexane, a non-polar solvent: CH_4, NH_3, HF, H_2S? Explain your reasoning.

7 Sugar is soluble in water. Explain the three steps involved when sugar molecules dissolve to form an aqueous sugar solution.

13.2 Water as a solvent of molecular substances

Most molecular substances are insoluble (or only very sparingly soluble) in water. However, some smaller molecules, such as ammonia (NH_3), hydrogen chloride (HCl) and sugar ($C_{12}H_{22}O_{11}$), dissolve well in water. Solutions in which a molecular substance is at least one of the solutes include brick cleaner, various liquid fertilisers and drinks such as wine and cordial (Figure 13.2.1).

There are two main ways in which molecular compounds dissolve well in water. In this section, you will explore both of these ways in detail.

FIGURE 13.2.1 Lemon cordial is a solution that contains several dissolved molecular substances.

MOLECULAR COMPOUNDS THAT FORM HYDROGEN BONDS WITH WATER

One way a molecular compound might dissolve in water is if its molecules form hydrogen bonds with water molecules. An example of such a molecule is ethanol.

Ethanol (C_2H_5OH) is a liquid at room temperature. Its molecules contain the polar –OH group, with lone pairs of electrons on the oxygen atom. The presence of the hydrogen atoms bonded to the electronegative oxygen atom allow an ethanol molecule to form hydrogen bonds.

Molecular compounds that can form hydrogen bonds are often soluble in water.

Figure 13.2.2 shows how hydrogen bonds form between molecules in pure ethanol.

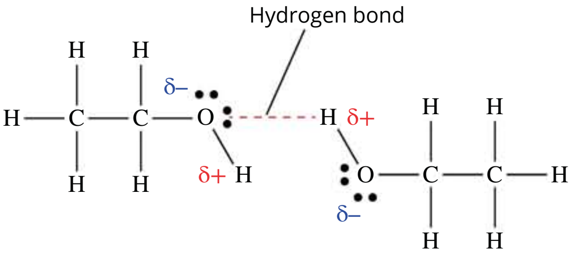


FIGURE 13.2.2 Hydrogen bonding in pure ethanol. The intermolecular hydrogen bond is formed between the lone pair electrons on the oxygen atom of one ethanol molecule and the electron-deficient hydrogen atom of an adjacent ethanol molecule.

When ethanol is added to water, it dissolves. The two solutions are miscible. Figure 13.2.3 shows how hydrogen bonds form between the ethanol and surrounding water molecules.

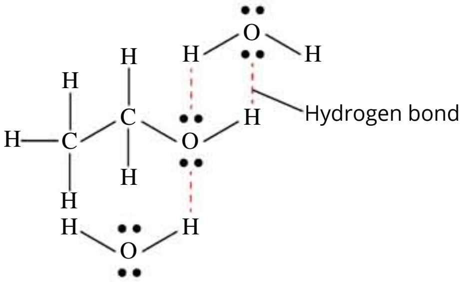


FIGURE 13.2.3 Hydrogen bonding between ethanol and water.

Because the strength of the intermolecular forces between the solute and the solvent are similar, the two substances can readily interact with each other. Therefore, water and ethanol molecules mix freely with each other, held together in solution by hydrogen bonds.

In summary, when ethanol dissolves in water, hydrogen bonds between:

- water molecules break
- ethanol molecules break
- ethanol molecules and water molecules form.

An equation for the dissolution of ethanol can be written to represent this process:

$$C_2H_5OH(l) \xrightarrow{H_2O(l)} C_2H_5OH(aq)$$

Note that the formula of water sits above the arrow. This is because there is no direct reaction between the water and the ethanol. The two substances simply mix together. No chemical change occurs; only the state symbol for ethanol is altered from (l) to (aq), indicating it is now dissolved in water.

When a polar molecular substance dissolves in water by forming hydrogen bonds, the equation for dissolution places water above the arrow.

Other polar compounds that form hydrogen bonds with water

Sugars including glucose, fructose and sucrose can all dissolve in water by forming hydrogen bonds. The structure of each of these sugars is shown in Figure 13.2.4. As with ethanol, their molecules also contain the polar –OH group.

Glucose

Fructose

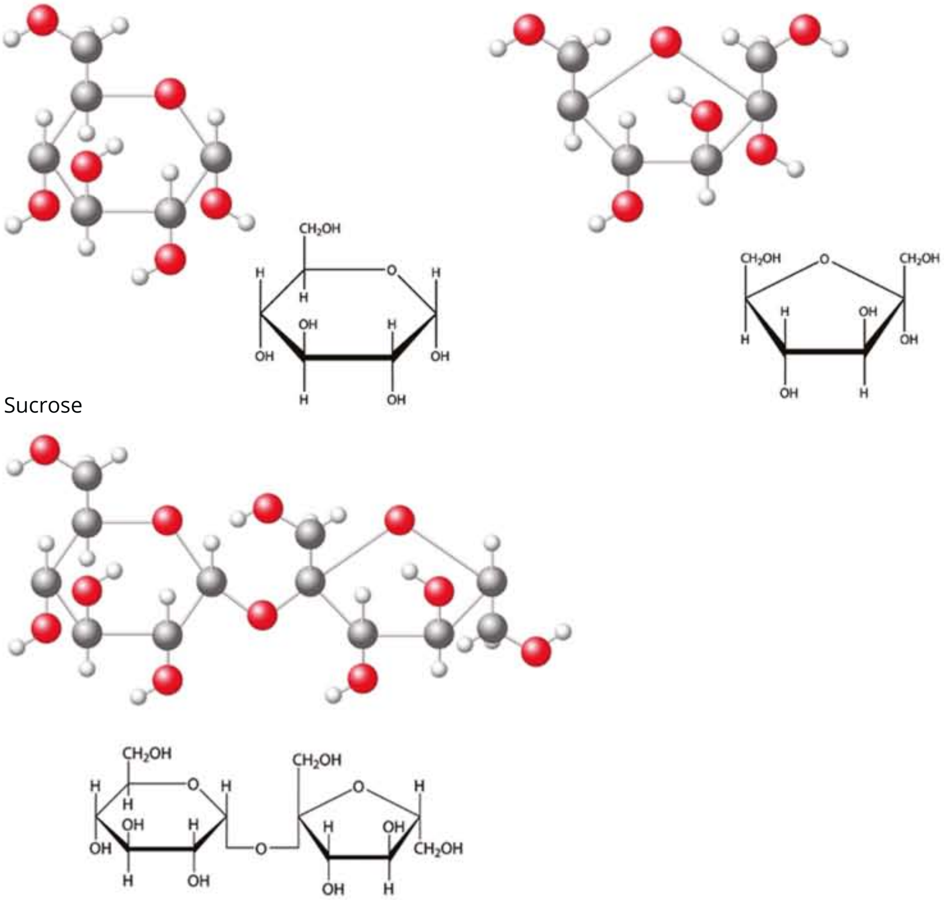


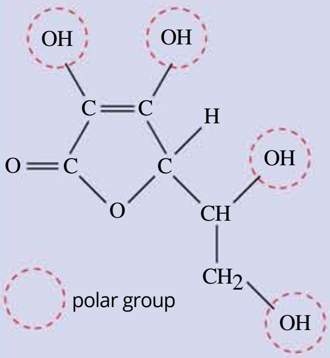
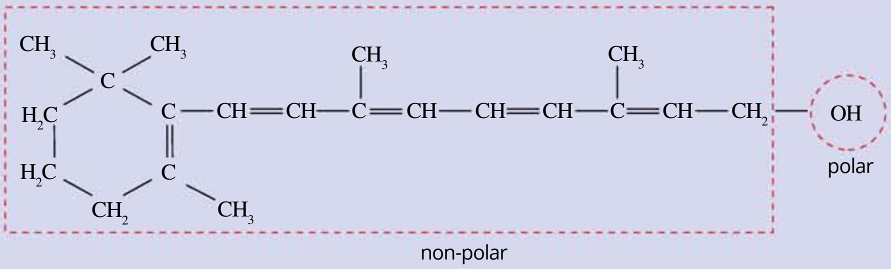
FIGURE 13.2.4 These are the molecular structures of common sugars: glucose (the sugar found in our blood), fructose (fruit sugar) and sucrose (table sugar—the sugar used to sweeten tea and coffee). Each of these sugars can dissolve in water because of the presence of polar –OH groups.

The more polar the molecules of a molecular compound are, the more likely the compound is to dissolve in water. Some molecules have a polar section and a non-polar section. In general, the larger the non-polar section of the molecule, the less soluble it is in water. You encountered this concept in sections 9.3 and 9.4 when looking at the **solubility** of alcohols and carboxylic acids.

Non-polar molecular substances do not have charged ends so there is no significant attraction to water molecules. The only force of attraction that exists between non-polar substances and water are weak dispersion forces, which are not strong enough to overcome the relatively strong hydrogen bonding between water molecules.

Table 13.2.1 compares the structures and properties of vitamin C and vitamin A. Both molecules contain the polar –OH group, but only vitamin C is soluble in water. The higher proportion of polar –OH groups on the vitamin C molecule allows it to form sufficient hydrogen bonds with water to overcome the strong attraction between water molecules, therefore dissolving to form a solution.

TABLE 13.2.1 Comparison of the solubility and structures of vitamin C and vitamin A

	Vitamin C	Vitamin A
Structure	 Vitamin C: • contains four polar –OH groups • molecule quite polar.	 Vitamin A: • contains one polar –OH group • molecule largely non-polar.
Solubility	Highly soluble in water, insoluble in fats	Soluble in fats, insoluble in water
Biological significance	The high solubility of vitamin C means it is excreted in urine so it must form a regular part of the diet.	Vitamin A is not excreted in urine but is stored in body fat. The body can tolerate a diet low in vitamin A for a limited period.

MOLECULAR COMPOUNDS THAT IONISE

Some compounds have molecules with one or more covalent bonds that are so polar they break when the compound is placed in water. Hydrogen chloride is such a compound. Hydrogen chloride (HCl) is a gas at room temperature. Chlorine is much more electronegative than hydrogen so the H–Cl covalent bond is highly polar; the molecule forms a **dipole**.

When hydrogen chloride is added to water, the hydrogen atom in HCl forms such a strong attraction to the oxygen atom in a water molecule that the H–Cl covalent bond breaks. The two electrons that made up the H–Cl covalent bond remain with the more electronegative Cl atom and the newly formed hydrogen ion (H^+) joins the water molecule.

Figure 13.2.5 shows that when the hydrogen ion (H^+) bonds to the water molecule, it forms a new ion known as the **hydronium ion** (H_3O^+).

Since the Cl atom has gained an electron, it has a negative charge, forming a chloride ion (Cl^-).

Highly polar molecular compounds will form ions when dissolved in water.

The HCl is said to have become **ionised**; that is, it has undergone a process that has produced ions (Figure 13.2.5).

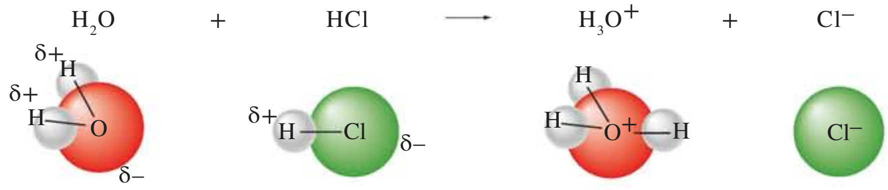


FIGURE 13.2.5 The dipole–dipole attraction between the molecules of water and hydrogen chloride leads to the breaking of the polar covalent bond between the hydrogen and chlorine atoms. New ions, hydronium and chloride, are formed in a process called ionisation.

Figure 13.2.6 shows how the two ions produced in the reaction of HCl with water (Cl^- and H_3O^+) become **hydrated**. The charged ions are surrounded by other polar water molecules. They are held in solution by **ion–dipole attractions**. (Ion–dipole attractions will be discussed in section 13.3.)

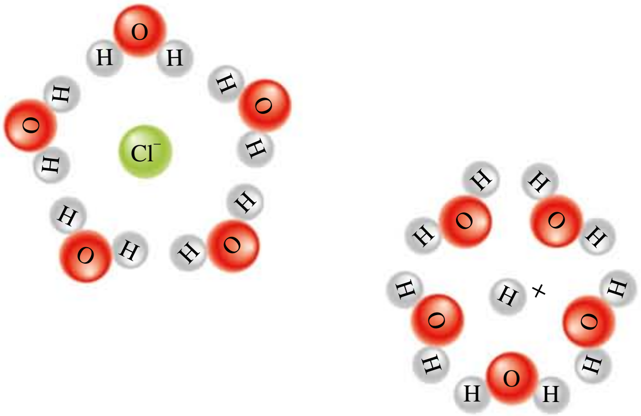


FIGURE 13.2.6 When HCl molecules ionise in water, the newly formed ions are surrounded by adjacent water molecules. The charges of the ions interact strongly with the polar water molecules. For simplicity, the hydronium ion (H_3O^+) is represented by the hydrogen ion (H^+).

In summary, when hydrogen chloride dissolves in water:

- polar covalent bonds within hydrogen chloride molecules break, producing hydrogen ions (H^+) and chloride ions (Cl^-)
- a covalent bond forms between each H^+ and an H_2O molecule, forming H_3O^+ ions
- ion–dipole attractions form between the H_3O^+ and Cl^- ions and polar water molecules.

An equation can be written to represent this process:

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

You should note two important points about this equation.

- Water is a reactant because there has been a rearrangement of atoms to form new substances.
- The aqueous state of the H_3O^+ and Cl^- ions tells you that they are hydrated in solution.

Other polar molecular compounds that ionise

Other compounds that dissolve in water by ionising include the common acids nitric acid (HNO_3), sulfuric acid (H_2SO_4) and ethanoic acid (CH_3COOH).

Ammonia (NH_3) is another polar molecule that can dissolve in water. Ammonia can dissolve by either forming hydrogen bonds with water or by reacting to form the ammonium ion (NH_4^+). The process by which ammonia forms the ammonium ion will be looked at in detail in Chapter 15.

CHEMFILE

Dissolved molecules in a fish tank

Many people keep fish at home in a small tank. Unfortunately, many pet fish do not live for quite as long as their owners hoped.

One of the biggest killers of aquarium fish is ammonia poisoning. Fish produce ammonia as a waste product. Ammonia is a polar molecule that readily dissolves in water, and is toxic to fish. Bacteria colonies living in a fish tank break down the ammonia produced by fish to other non-toxic products. In a healthy tank (Figure 13.2.7), a balance exists between ammonia production by fish and breakdown by bacteria.

FIGURE 13.2.7 Fish in this tank produce the molecular compound ammonia (NH_3) as a waste product. Bacteria living in the tank break down the toxic ammonia to harmless products.

13.2 Review

SUMMARY

- Water is a good solvent for some polar molecular compounds.
- Some polar molecular compounds dissolve by forming hydrogen bonds with water.
- Some covalent molecular compounds are so polar that they dissolve in water by ionising to form hydrated ions.
- Table 13.2.2 summarises the two ways that molecular compounds dissolve in water.

TABLE 13.2.2 Summary of the two ways in which polar molecular compounds can dissolve in water

Type of solute	Example of solute	Bond broken in the solute	Bonds formed with water	Equation
Polar covalent molecule that can hydrogen bond	Ethanol, C_2H_5OH	Hydrogen bonds between ethanol molecules	Hydrogen bonds between ethanol and water molecules	$C_2H_5OH(l) \xrightarrow{H_2O(l)} C_2H_5OH(aq)$
Polar molecules that ionise	Hydrogen chloride, HCl	Covalent bond between hydrogen and chlorine atoms in the HCl molecule	Covalent bond between H^+ from HCl and oxygen atom in water molecule, forming H_3O^+ ions. H_3O^+ and Cl^- ions form ion–dipole bonds with water molecules.	$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

KEY QUESTIONS

1 Which of the following substances are likely to dissolve in water by forming hydrogen bonds with water molecules.

A Ammonium sulfate ($(NH_4)_2SO_4$)
B Methanol (CH_3OH)
C Diamond (C)
D Hydrogen chloride (HCl)
E Ethylene glycol ($HOCH_2CH_2OH$)
F Sodium hydroxide (NaOH)
G Hydrogen gas (H_2)

2 Methanol (CH_3OH) and glucose ($C_6H_{12}O_6$) form hydrogen bonds with water. They will dissolve in water without ionising. Write chemical equations to represent the dissolving process for each of these compounds.

3 With reference to the bonds that are broken and new bonds that are formed, describe how ethanol dissolves in water.

4 Hydrogen iodide (HI) will ionise when it dissolves in water. The ionisation reaction is similar to that of HCl. Write a chemical equation to represent the dissolving process for this compound.

5 Hydrogen chloride dissolves in water by ionisation. Using the terms provided, complete the following sentences to describe the process of how ionisation occurs. Some terms may be used more than once.

ion–dipole bonds / hydrogen bonds / covalent bonds / hydronium / ionises / H^+

___________ within hydrogen chloride molecules are broken.

___________ between water molecules are broken. The HCl ________ and produces Cl^- and H^+ ions. _________ form between ___ ions and water to produce __________ ions. ________ form between the Cl^- and H_3O^+ ions and polar water molecules.

13.3 Water as a solvent of ionic compounds

Sports drinks are advertised to athletes as a way to replace the electrolytes lost in sweat during exercise (Figure 13.3.1). The electrolytes are dissolved ionic substances such as sodium chloride and potassium phosphate.

Many ionic substances are soluble in water. However, not all ionic substances dissolve readily in water. In this section, you will look at how ionic substances dissolve and learn how to predict whether an ionic compound will be soluble in water.

FIGURE 13.3.1 Sports drinks are used by athletes to replace water and dissolved ionic solutes.

DISSOLUTION OF AN IONIC LATTICE IN WATER

Many ionic compounds dissolve readily in water. Sodium chloride is a typical ionic compound that exists as a solid at room temperature. In Figure 13.3.2, you can see the arrangement of sodium cations (Na^+) and chloride anions (Cl^-) in a three-dimensional ionic lattice. The ions are held together by strong electrostatic forces between the positive and negative charges of the ions.

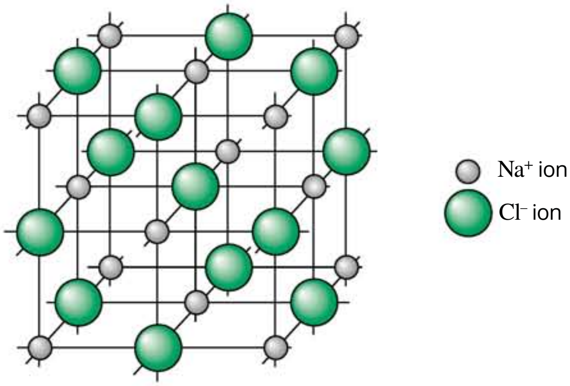


FIGURE 13.3.2 A representation of the crystal lattice of the ionic compound sodium chloride.

When an ionic compound such as sodium chloride is added to water, the positive ends of the water molecules are attracted to the negatively charged chloride ions and the negative ends of the water molecules are attracted to the positively charged sodium ions (Figure 13.3.3). The attraction between an ion and a polar molecule such as water is described as an ion–dipole attraction.

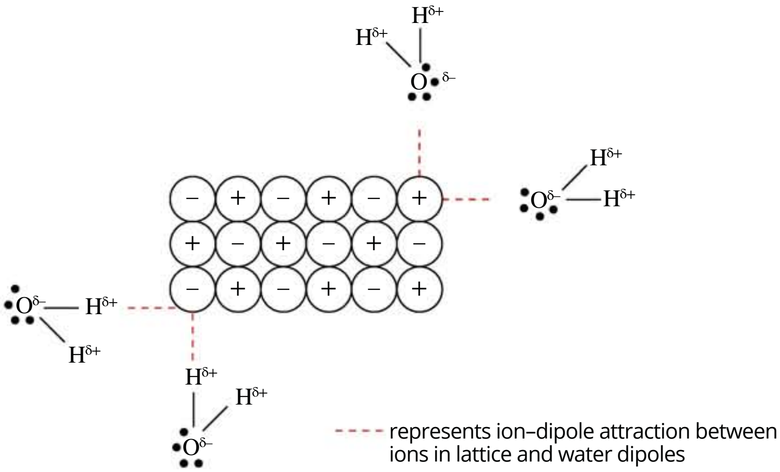


FIGURE 13.3.3 Electrostatic attraction occurs between the negative ions in a NaCl lattice and the hydrogen atoms in polar water molecules. Electrostatic attraction also occurs between the positive ions in the lattice and the oxygen atoms in water molecules.

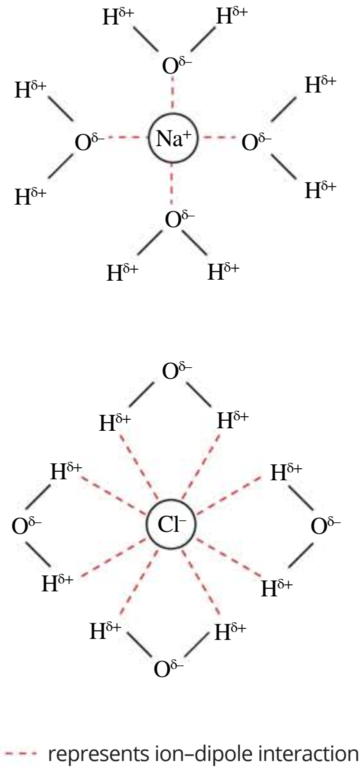


FIGURE 13.3.4 Ion–dipole attraction between the ions and adjacent water molecules to form hydrated sodium and chloride ions.

Water molecules are in a continuous state of random motion. If the ion–dipole attractions between the ions and the water molecules are strong enough, the water molecules can pull the sodium and chloride ions on the outer part of the crystal out of the lattice and into the surrounding solution.

Sodium ions and chloride ions pulled out of the lattice become surrounded by water molecules. These ions are said to be **hydrated**. Water molecules are arranged around the ions as shown in Figure 13.3.4. Note the different arrangements of the water molecules around the positive and negative ions. The hydrogen atoms in the water molecule are more positive so they are orientated towards the negative chloride ion. The positive sodium ion is surrounded by the more negative oxygen atom of the water molecules.

The process of separating positive and negative ions from a solid ionic compound to form hydrated ions when an ionic compound dissolves in water is called **dissociation**.

Although the ionic bonds within the lattice are strong, the ions can be pulled away from the lattice by the interactions of many water molecules.

In summary, when sodium chloride dissolves in water:

- ionic bonds within the sodium chloride lattice are broken
- hydrogen bonds between water molecules are broken
- ion–dipole attractions form between ions and polar water molecules.

An equation can be written to represent the dissociation process:

$$NaCl(s) \xrightarrow{H_2O(l)} Na^+(aq) + Cl^-(aq)$$

Note that the formula of water sits above the arrow. This is because there is no direct reaction between the water and the sodium chloride. No chemical change occurs; only the state symbol for sodium chloride is altered from (s) to (aq), indicating it is now dissolved in water. (You may omit the H_2O from this equation if you wish.)

It is important to note that dissociation of ionic compounds is simply freeing ions from the lattice so that they can move freely throughout the solution. This is different from ionisation of molecular compounds where new ions are formed by the reaction of the molecule with water.

Ionic substances dissolve by dissociation. Ion–dipole bonds are formed between the ions and water molecules.

INSOLUBLE IONIC COMPOUNDS

Not all ionic compounds are soluble in water. For example, limestone ($CaCO_3$) is almost completely insoluble in water. Limestone caves such as those seen in Figure 13.3.5 are formed over a long period of time as $CaCO_3$ is dissolved and redeposited. The ionic compound $Ca_3(PO_4)_2.Ca(OH)_2$, which gives strength to bones and teeth, is also (fortunately) insoluble in water.

FIGURE 13.3.5 Limestone caves are formed by limestone (calcium carbonate) dissolving over very long periods of time. This photograph is of a limestone cave at Loch Ard Gorge, Victoria.

Insoluble ionic compounds do not dissolve in water because the energy required to separate the ions from the lattice is greater than the energy released when the ions are hydrated.

Although substances are usually described as 'soluble' or 'insoluble', this is a generalisation. Substances that are described as 'insoluble' tend to dissolve very slightly. Those that are described as 'soluble' dissolve to varying extents.

Substances are rarely ever completely 'soluble' or 'insoluble'. The solubility of substances can be considered as a scale.

The SNAPE rule

A handy way to remember many of the soluble salts is with the initials SNAPE. Salts that contain one or more of the following ions are soluble:

- **S**odium (Na^+)
- **N**itrate (NO_3^-)
- **A**mmonium (NH_4^+)
- **P**otassium (K^+)
- **E**thanoate (CH_3COO^-)

Solubility tables

A **solubility table** can be used to determine whether common ionic compounds are soluble in water. Anions and cations are listed with indications of their solubility in different compounds. Table 13.3.1 is a sample solubility table listing ionic compounds that are soluble in water. Note that for some ions there are exceptions. Insoluble compounds are given in Table 13.3.2.

TABLE 13.3.1 Relative solubilities of soluble ionic compounds

Soluble in water (>0.1 mol dissolves per L at 25°C)	Exceptions: insoluble (<0.1 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	$PbCl_2$, $PbBr_2$
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

TABLE 13.3.2 Relative solubilities of 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.

CHEMFILE

The Dead Sea

The Dead Sea, a salt lake in the Middle East, is one of the saltiest bodies of water on Earth. The concentration of dissolved ionic compounds, including salt, in the water makes the Dead Sea roughly 8.6 times saltier than the ocean. This prevents fish and aquatic plants from living in it. There is so much dissolved salt in the water that people can easily float in the Dead Sea due to natural buoyancy; the density of the salt water is greater than the density of the human body (Figure 13.3.6).

FIGURE 13.3.6 The Dead Sea contains so many dissolved ions it is easy to float.

Using a solubility table to predict solubility

The solubility tables provided as Tables 13.3.1 and 13.3.2 can be used to predict whether a particular ionic substance will be soluble, slightly soluble or insoluble in water.

Worked Example 13.3.1 shows you a systematic way of using a solubility table to determine whether an ionic compound will be soluble or insoluble in water.

Worked example 13.3.1

DETERMINING IF IONIC COMPOUNDS ARE SOLUBLE OR INSOLUBLE IN WATER

Is barium sulfide (BaS) soluble or insoluble in water? You will need to refer to the solubility tables to complete this question.

Thinking	Working
Identify the ions that are present in the ionic compound.	Barium (Ba^{2+}) and sulfide (S^{2-})
Check the solubility tables to see if compounds containing the cation are usually soluble or insoluble in water.	Barium ions do not appear in the table. This is no help, so look for the other ion.
Check the solubility tables to see if compounds containing the anion are usually soluble or insoluble in water.	Compounds containing sulfide ions are usually insoluble in water. So, barium sulfide will be insoluble in water.

Worked example: Try yourself 13.3.1

DETERMINING IF IONIC COMPOUNDS ARE SOLUBLE OR INSOLUBLE IN WATER

Is ammonium phosphate ($(NH_4)_3PO_4$) soluble or insoluble in water? You will need to refer to the solubility tables to complete this question.

13.3 Review

SUMMARY

- Soluble ionic compounds dissociate in water to form hydrated ions.
- In a hydrated ion, water molecules are attracted to the central ion by ion–dipole attractions.
- Table 13.3.3 summarises the way soluble ionic compounds dissolve in water.
- The SNAPE rule can be used to predict the solubility of an ionic compound.
- A solubility table can also be used to determine whether a particular ionic compound is likely to be soluble or insoluble in water.

TABLE 13.3.3 Summary of the way in which soluble ionic compounds dissolve in water

Type of solute	Example	Bond broken in the solute	Bonds formed with water	Equation
Soluble ionic compounds	Sodium chloride (NaCl)	Ionic bonds between Na^+ and Cl^- ions	Ion–dipole attractions between dissociated ions and polar water molecules	$NaCl(s) \xrightarrow{H_2O(l)} Na^+(aq) + Cl^-(aq)$

KEY QUESTIONS

1 Sodium nitrate ($NaNO_3$) and calcium hydroxide ($Ca(OH)_2$) will both dissociate when they dissolve in water. Write chemical equations to represent the dissolving process for each of these compounds.

2 Redraw the representations of Na^+ and Cl^- ions below, then show the correct orientation of water molecules around hydrated sodium and chloride ions. Use a V-shape to represent the shape of water molecules.

3 Which of the following substances would you expect to be soluble in water? Refer to Tables 13.3.1 and 13.3.2 to complete this question.

A Sodium carbonate
B Lead(II) nitrate
C Magnesium carbonate
D Ammonium sulfate
E Iron(II) sulfate
F Magnesium phosphate
G Zinc carbonate
H Sodium sulfide
I Silver chloride
J Barium sulfate

4 Which of the following compounds would you expect to be insoluble in water? Refer to Tables 13.3.1 and 13.3.2 to complete this question.

A Silver carbonate
B Zinc nitrate
C Copper(II) carbonate
D Silver chloride
E Lead(II) bromide
F Magnesium hydroxide
G Barium nitrate
H Aluminium sulfide

5 Write the formulas for the ions produced when these compounds dissolve in water.

a Sodium carbonate
b Calcium nitrate
c Potassium bromide
d Iron(III) sulfate
e Copper(II) chloride

6 Suggest reasons for each of the following.

a Concentrated deposits of nitrate compounds are only found in desert regions.
b The sea is a rich source of sodium, chloride and sulfate ions.

13.4 Precipitation reactions

PRECIPITATION REACTIONS

A **precipitation reaction** occurs if ions in solution combine to form a new compound that is insoluble in water. The insoluble compound formed in such a reaction is called a **precipitate**.

Precipitation reactions occur naturally in undersea hydrothermal vents. The vents release superheated solutions containing sulfides, which then combine with metal ions to form precipitates of mineral sulfides, creating the chimney-like structures seen in Figure 13.4.1. The areas around these chimneys are biologically rich, often hosting complex communities fuelled by the chemicals dissolved in the vent fluids.

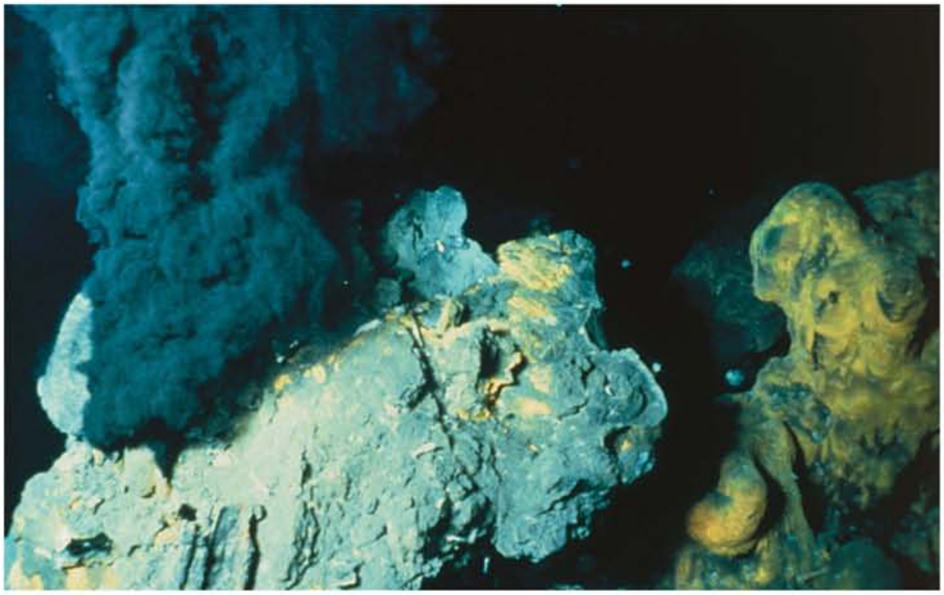


FIGURE 13.4.1 Undersea hydrothermal vents release superheated water containing sulfides, which form precipitates with metal ions.

FIGURE 13.4.2 Mixing aqueous solutions of sodium chloride and silver nitrate produces a solid, called a precipitate.

Precipitation reactions are used to remove minerals from drinking water, to remove heavy metals from wastewater and in the purification plants of reservoirs.

In this section you will look at what takes place during precipitation reactions.

Deducing the identity of a precipitate

When a colourless solution of silver nitrate is mixed with a colourless solution of sodium chloride, a white solid is formed, as shown in Figure 13.4.2. The white solid is the precipitate, but what is its composition? What is the solid compound that forms?

To understand what happens in the reaction between silver nitrate and sodium chloride, you need to identify the ions present in the reactant solutions and how they interact with each other.

- In the silver nitrate solution, there are silver ions (Ag^+) and nitrate ions (NO_3^-).
- In the sodium chloride solution, there are sodium ions (Na^+) and chloride ions (Cl^-).
- When one solution is added to the other, the mixture formed will contain all of the ions.

In both of these solutions, all the ions are moving around independently. As the ions move in the solution, they will collide with one another. If positive and negative ions collide, they may join together to form a new, insoluble precipitate.

Two new combinations of positive and negative ions are possible:

- sodium and nitrate ions (to form sodium nitrate)
- silver and chloride ions (to form silver chloride).

Tables 13.3.1 and 13.3.2 on page 323 indicate that sodium nitrate is soluble in water, but that silver chloride is insoluble. Therefore, the precipitate must be silver chloride.

The process for the precipitation reaction between sodium chloride and silver nitrate is shown in Figure 13.4.3. When the hydrated Ag^+ and Cl^- ions come into contact, the attraction between the ions is greater than that of the ions for the water molecules. An ionic lattice of AgCl is formed.

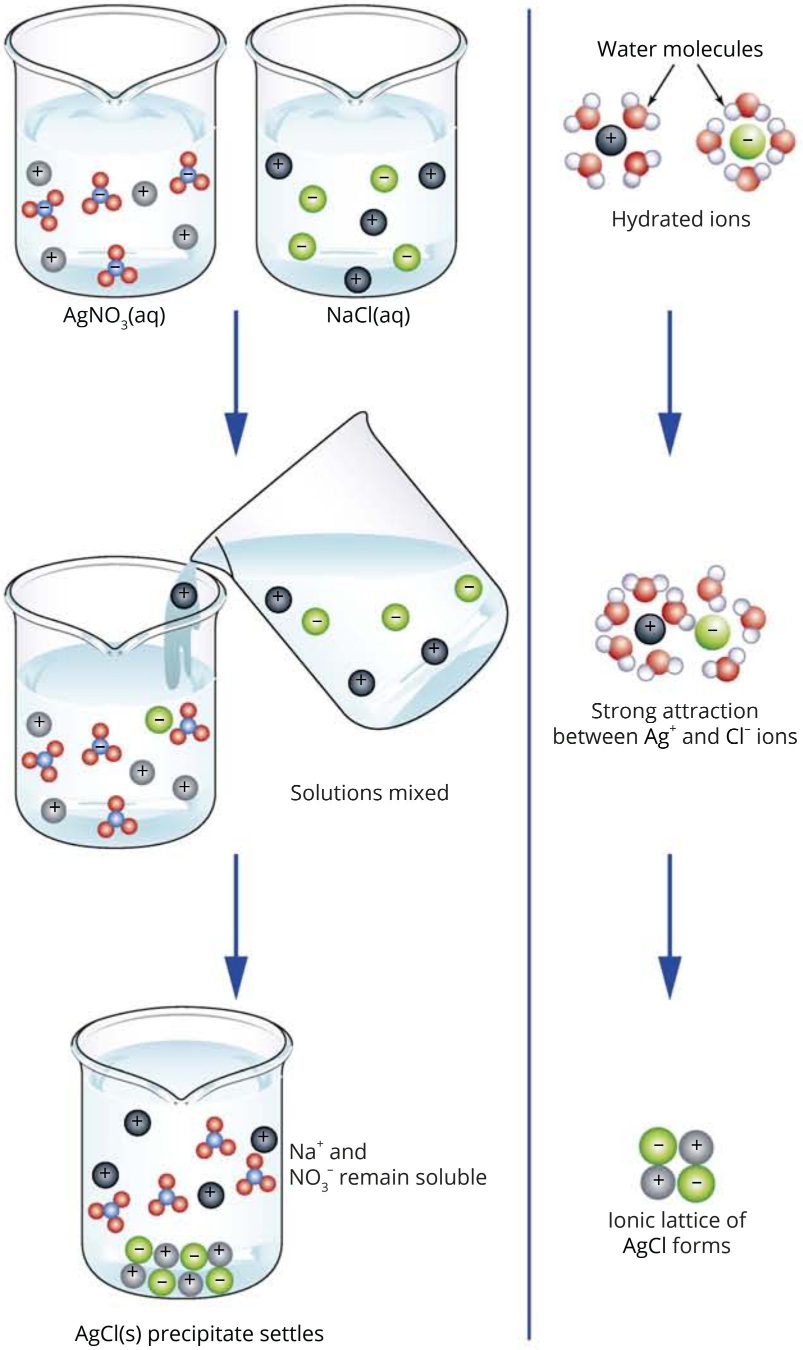


FIGURE 13.4.3 Pictorial representation of mixing aqueous solutions of sodium chloride and silver nitrate to produce a precipitate of silver chloride.

There is a simple way that allows you to work out which compound will form the precipitate in a reaction between two ionic solutions.

- Write down the formula for the positive ion of one of the compounds, followed by its negative ion. Repeat the process for the second compound. For example, Ag^+, NO_3^-, Na^+, Cl^-.
- Then draw two lines. The first line joins the positive ion of the first solution to the negative ion of the second. The second line joins the negative ion of the first solution to the positive ion of the second (Figure 13.4.4).

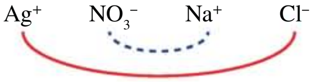


FIGURE 13.4.4 Working out which compound is the precipitate in a reaction.

- Finally, use solubility tables to work out which of the two combinations of ions will result in an insoluble compound. This will be the precipitate. The other ions will remain in solution.

It is important for chemists to be able to predict whether a precipitate will form in a reaction and what this precipitate will be. Worked Example 13.4.1 takes you through the process of predicting the products of a precipitation reaction.

Worked example 13.4.1

PREDICTING THE PRODUCTS OF A PRECIPITATION REACTION

What precipitate, if any, will be produced when solutions of potassium hydroxide and lead(II) nitrate are added together? You will need to refer to the solubility tables (Tables 13.3.1 and 13.3.2) to complete this question.

Thinking	Working
Identify which ions are produced by each of the ionic compounds in the mixture.	$K^+(aq)$, $OH^-(aq)$, $Pb^{2+}(aq)$ and $NO_3^-(aq)$
Identify which two new combinations of positive and negative ions are possible in the mixture of the solutions.	$K^+(aq)$ and $NO_3^-(aq)$ $Pb^{2+}(aq)$ and $OH^-(aq)$
Use the solubility tables to check which, if any, of these combinations will produce an insoluble compound.	Compounds containing potassium ions are usually soluble, so potassium nitrate will not form a precipitate. Compounds containing hydroxide ions are usually insoluble, so lead(II) hydroxide will form a precipitate.

Worked example: Try yourself 13.4.1

PREDICTING THE PRODUCTS OF A PRECIPITATION REACTION

What precipitate, if any, will be produced when solutions of sodium sulfide (Na_2S) and copper(II) nitrate ($Cu(NO_3)_2$) are added together? You will need to refer to the solubility tables (Tables 13.3.1 and 13.3.2) to complete this question.

CHEMFILE

Limescale accumulation

Have you ever wondered where that flaky white build-up on the element of your kettle comes from?

When you boil water in the kettle, ions present in the water can precipitate out, leaving a white coating called limescale on the element (Figure 13.4.5).

FIGURE 13.4.5 The accumulation of limescale on domestic kettles is the result of precipitation of calcium carbonate as water is repeatedly boiled.

The amount of build-up depends on the type of water treatment in your area. Areas that have hard water (i.e. high levels of dissolved ions) have a bigger problem with limescale.

Limescale mostly consists of calcium carbonate ($CaCO_3$) that precipitates out as a crystalline solid when the water is boiled. High levels of limescale can build up in pipes and eventually restrict or even block the flow of water (Figure 13.4.6).

FIGURE 13.4.6 Accumulation of limescale in pipes is a result of precipitation of $CaCO_3$.

Limescale can be a big problem in the home. A coating as thin as 1.5 mm over a heating element can reduce its efficiency by as much as 12%.

Many modern houses use ion filters or water conditioners to remove dissolved ions from the water and reduce the accumulation of limescale.

Writing equations for precipitation reactions

Now that you can identify the precipitate that forms in a reaction, the next step is to show the complete reaction by writing a chemical equation.

The reaction between silver nitrate and sodium chloride solutions can be summarised in words as:

silver nitrate solution + sodium chloride solution → silver chloride solid + sodium nitrate solution

An alternative representation is an equation that uses formulas. This type of equation is called a **full equation**. The complete formulas of all the reagents and products are shown in the reaction. The state symbols for each of the species in the chemical reaction must be shown:

$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$

Although 'sodium nitrate' or '$NaNO_3(aq)$' is written as a product in these equations, the sodium ions and nitrate ions are not combined with each other. You will remember from section 13.3 that soluble ionic compounds form dissociated ions in solution and are free to move.

These ions are present at the start of the reaction and they are still there, as separate ions, at the end of the reaction. Because the ions have not been involved in forming a precipitate, they are said to be **spectator ions**.

Spectator ions do not undergo a chemical change in the reaction. In a precipitation reaction, they will always start as aqueous (aq) ions and will remain as aqueous ions after the reaction is complete.

Worked Example 13.4.2 looks at the process of writing full equations for precipitation reactions and identifying spectator ions.

Worked example 13.4.2

WRITING EQUATIONS FOR PRECIPITATION REACTIONS

Write a balanced equation for the reaction between iron(III) nitrate and sodium sulfide, in which the precipitate is iron(III) sulfide. Identify the spectator ions in this reaction.

Thinking	Working
Write an incomplete, unbalanced equation showing the reactants and the precipitate product. Include symbols of state.	$Fe(NO_3)_3(aq) + Na_2S(aq) \rightarrow Fe_2S_3(s)$
Add to the equation above the formula of the other compound formed in the reaction.	$Fe(NO_3)_3(aq) + Na_2S(aq) \rightarrow Fe_2S_3(s) + NaNO_3(aq)$
Balance the equation.	$2Fe(NO_3)_3(aq) + 3Na_2S(aq) \rightarrow Fe_2S_3(s) + 6NaNO_3(aq)$
Write the formulas of the ions that do not form a precipitate in the reaction. These are the spectator ions.	$Na^+(aq)$ and $NO_3^-(aq)$ are spectator ions.

Worked example: Try yourself 13.4.2

WRITING EQUATIONS FOR PRECIPITATION REACTIONS

Write a balanced equation for the reaction between copper(II) sulfate and sodium hydroxide, in which the precipitate is copper(II) hydroxide. Identify the spectator ions in this reaction.

Writing ionic equations for precipitation reactions

The essential feature of the reaction between silver nitrate and sodium chloride is the combination of silver ions and chloride ions to form a precipitate. This reaction can be summarised in an **ionic equation**:

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

Note that spectator ions are not included in an ionic equation. Only the species that change are included.

A simple way to write an ionic equation for a precipitation reaction is shown in the following example of the reactions between solutions of aluminium nitrate and sodium sulfide. The full equation for the precipitation reaction is:

$$2Al(NO_3)_3(aq) + 3Na_2S(aq) \rightarrow Al_2S_3(s) + 6NaNO_3(aq)$$

To write an ionic equation:

- Write down the formula of the precipitate on the right-hand side of the page. Include a symbol of state. Place an arrow to the left of it.

$$\rightarrow Al_2S_3(s)$$

- To the left of this formula, add the formulas of the ions that form the precipitate, in the ratio shown by the formula of the precipitate. Include state symbols.

$$2Al^{3+}(aq) + 3S^{2-}(aq) \rightarrow Al_2S_3(s)$$

- Check that the equation is balanced.

CHEMISTRY IN ACTION

The chemistry of colour

If you have ever walked through an art supplies store, you will have noticed displays selling paints with names that sound as though they belong in a chemistry laboratory. Names such as lead yellow, titanium white and cobalt blue are just a few of the colours still in use today (Figure 13.4.7).

FIGURE 13.4.7 Paint colours are often named after the pigments that were once used to make them. Many of these pigments were the product of precipitation reactions.

The names are not just for show. The colours that they represent have their basis in chemistry. All paints consist of a pigment (the colour) and a binder that holds the pigments in a suspension. Historically, paints were purchased as powdered pigments like those in Figure 13.4.8.

FIGURE 13.4.8 An array of different coloured pigments. Historically, pigments for paints were collected from minerals and other sources. However, in the 19th century a better knowledge of chemistry was used to manufacture pigments more reliably and in a larger variety of colours.

Artists would mix these pigments with their own binders, such as linseed oil, to produce the required paints. Ancient civilisations such as the Egyptians would grind minerals like lapis lazuli and ochre from the earth to make pigments. Early alchemists were able to manufacture synthetic pigments using precipitation reactions, collecting the coloured precipitates through filtration.

Prussian blue was a very popular colour through the 19th century and is made from a precipitate of iron(III) hexacyanoferrate(II). It has been used extensively in ceramics and painting, including the famous Japanese block print from the 1830s 'The Great Wave off Kanagawa' (Figure 13.4.9).

Pigments based on ionic precipitates provided a much wider array of colours to artists. This paved the way for the more flamboyant use of colour seen in the work of the French impressionists. Cadmium sulfide was used to make red pigments and cadmium red is still used widely today. Viridian, a deep green pigment, is manufactured from chromium(III) oxide dihydrate.

So the next time you visit an art gallery, take a moment to think about the complex chemistry that went into bringing those colours to life.

FIGURE 13.4.9 'The Great Wave off Kanagawa' (c. 1830–1833). This woodblock print is by the Japanese artist Hokusai (1760–1849). The deep blue tones were painted with a paint known as Prussian blue made from iron(III) hexacyanoferrate(II).

13.4 Review

SUMMARY

- A precipitation reaction occurs when two solutions of compounds are mixed and a solid product is formed. The solid product is called a precipitate.
- Solubility tables can be used to predict which compound, if any, will precipitate in a reaction.
- Ions that are not directly involved in the formation of the precipitate are called spectator ions.
- Full and ionic equations can be written for precipitation reactions.
- Ionic equations do not include spectator ions.

KEY QUESTIONS

1 Use the solubility tables to identify the precipitate formed, if any, when the following solutions are mixed.
  - a Silver nitrate and potassium carbonate
  - b Potassium hydroxide and lead(II) nitrate
  - c Magnesium chloride and sodium sulfide
  - d Sodium chloride and iron(II) sulfate

2 a Name the precipitate formed when aqueous solutions of the following compounds are mixed.
    - i K_2S and $MgCl_2$
    - ii $CuCl_2$ and $AgNO_3$
    - iii KOH and $AlCl_3$
    - iv $MgSO_4$ and NaOH
  - b Write a fully balanced chemical equation for each reaction.

3 For each of the following precipitation reactions, write:
    - i a full chemical equation
    - ii an ionic equation.
  - a $AgNO_3(aq) + NaCl(aq) \rightarrow$
  - b $CuSO_4(aq) + Na_2CO_3(aq) \rightarrow$
  - c $(NH_4)_2SO_4(aq) + BaCl_2(aq) \rightarrow$
  - d $K_2S(aq) + Pb(NO_3)_2(aq) \rightarrow$
  - e $CaCl_2(aq) + Na_3PO_4(aq) \rightarrow$
  - f $NaOH(aq) + Pb(NO_3)_2(aq) \rightarrow$

4 For each of the reactions in Question 3, identify the spectator ions.

Chapter review

13

KEY TERMS

aqueous
colloid
dipole
dissociation
dissolution
full equation
heterogeneous
homogeneous
hydrated
hydrogen bond
hydronium ion
ion–dipole attractions
ionic equation
ionise
miscible
non-polar
polar
precipitate
precipitation reaction
solubility
solubility table
solute
solution
solvent
spectator ion
suspension

Water as a solvent

1 Many of the solvent properties of water depend on its structure and bonding. List all the bonds present in a sample of water from weakest to strongest. Remember to include all intramolecular and intermolecular bonding.

2 Explain why water is such a good solvent for polar and ionic substances.

3 Nitrogen gas (N_2) and ethene (C_2H_6) are both insoluble in water, whereas ethanol (C_2H_5OH) is soluble. Refer to the bonding in each of the molecules to explain these differences.

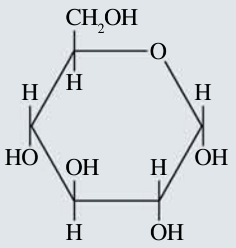
4 Explain, with reference to its structure and bonding, why octane does not dissolve in water.

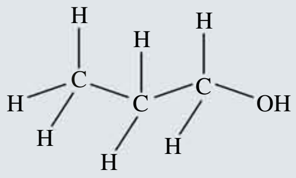
5 Briefly describe two examples of the importance of water as a solvent in:

- **a** a biological context
- **b** a domestic context
- **c** an industrial context.

Water as a solvent of molecular substances

6 Classify the following substances according to the way they dissolve in water: $C_6H_{12}O_6$, HI, I_2, C_2H_4, C_3H_7OH, HNO_3, CH_4.
The structures of $C_6H_{12}O_6$ and C_3H_7OH are shown to assist you.





7 A student conducts an experiment to investigate the solubility of CH_4 and CH_3OH molecules in three different solvents, X, Y and Z. The student finds that the CH_3OH molecules dissolve well in solvent Y but do not dissolve in solvent X. The student also finds that CH_4 partially dissolves in solvent Z and completely dissolves in solvent X. List each of the solvents in order from most polar to least polar. Explain your reasoning.

8 DDT is a hazardous agricultural insecticide, which has been banned in many countries. It is only slightly soluble in water but is very soluble in fats and oils, so accumulates in the fat deposits of animals. What can you deduce about the polarity of the DDT molecule from its solubility characteristics?

Water as a solvent of ionic compounds

9 **a** What is the name given to the process that ionic solids undergo when dissolving in water?

- **b** What ions will be produced when the following compounds are added to water?
  - **i** $Cu(NO_3)_2$
  - **ii** $ZnSO_4$
  - **iii** $(NH_4)_3PO_4$

10 What ions would be produced when the following compounds are added to water?

- **a** Potassium carbonate
- **b** Lead(II) nitrate
- **c** Sodium hydroxide
- **d** Sodium sulfate
- **e** Magnesium chloride
- **f** Zinc nitrate
- **g** Potassium sulfide
- **h** Iron(III) nitrate

11 Write equations to show the dissociation of the following compounds when they are added to water.

- **a** Magnesium sulfate
- **b** Sodium sulfide
- **c** Potassium hydroxide
- **d** Copper(II) ethanoate
- **e** Lithium sulfate

12 What particles are present in the solution that forms when HCl gas is bubbled through water?

13 Briefly explain why the arrangement of water molecules around dissolved magnesium ions is different from that around dissolved chloride ions.

14 Write the formulas of three carbonate compounds that are:

- **a** soluble in water
- **b** insoluble in water.

15 Write the formulas of three sulfate compounds that are:

- **a** soluble in water
- **b** insoluble in water.

16 Briefly describe what happens to the forces between solute and solvent substances when an ionic substance such as potassium bromide dissolves in water.

Precipitation reactions

17 Consider the reaction represented by the following equation:

$NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

Indicate whether the following statements about the reaction and equation are true or false.

- **a** The equation represents a precipitation reaction.
- **b** Ionic compounds that contain sodium or nitrate ions are always soluble.
- **c** The precipitate in this reaction is $AgNO_3$.
- **d** The equation is an example of an ionic equation.
- **e** Silver chloride is insoluble in water.
- **f** The sodium and chlorine ions can be described as spectator ions.

18 Copy and complete the following table. Identify which reaction mixtures will produce precipitates and write their formulas.

	NaOH	KBr	NaI	$MgSO_4$	$BaCl_2$
$Pb(NO_3)_2$					
KI					
$CaCl_2$					
Na_2CO_3					
Na_2S					

19 Consider the following ions: SO_4^{2-}, PO_4^{3-}, Br^-, S^{2-}. Which of these ions would combine with $Fe^{2+}(aq)$ to give a precipitate?

20 What precipitate will be formed (if any) when the following solutions are mixed?

- **a** Barium nitrate and sodium sulfate
- **b** Sodium chloride and copper(II) sulfate
- **c** Magnesium sulfate and lead(II) nitrate
- **d** Potassium chloride and barium nitrate

21 Write full balanced chemical equations and ionic equations for each of the following precipitation reactions.

- **a** $NH_4Cl(aq) + AgNO_3(aq) \rightarrow$
- **b** $FeCl(aq) + Na_2S(aq) \rightarrow$
- **c** $Fe(NO_3)_3(aq) + KOH(aq) \rightarrow$
- **d** $CuSO_4(aq) + NaOH(aq) \rightarrow$
- **e** $Ba(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow$

22 Write a full chemical equation and ionic equation for the reaction that takes place when solutions of the following compounds are mixed. In each case, name the spectator ions. Refer to the solubility tables on page 323 to help identify the precipitate for each reaction.

- **a** Copper(II) sulfate and sodium carbonate
- **b** Silver nitrate and potassium chloride
- **c** Sodium sulfide and lead(II) nitrate
- **d** Iron(III) chloride and sodium hydroxide
- **e** Iron(III) sulfate and potassium hydroxide

Connecting the main ideas

23 Match the type of compound with the way it is likely to behave in water.

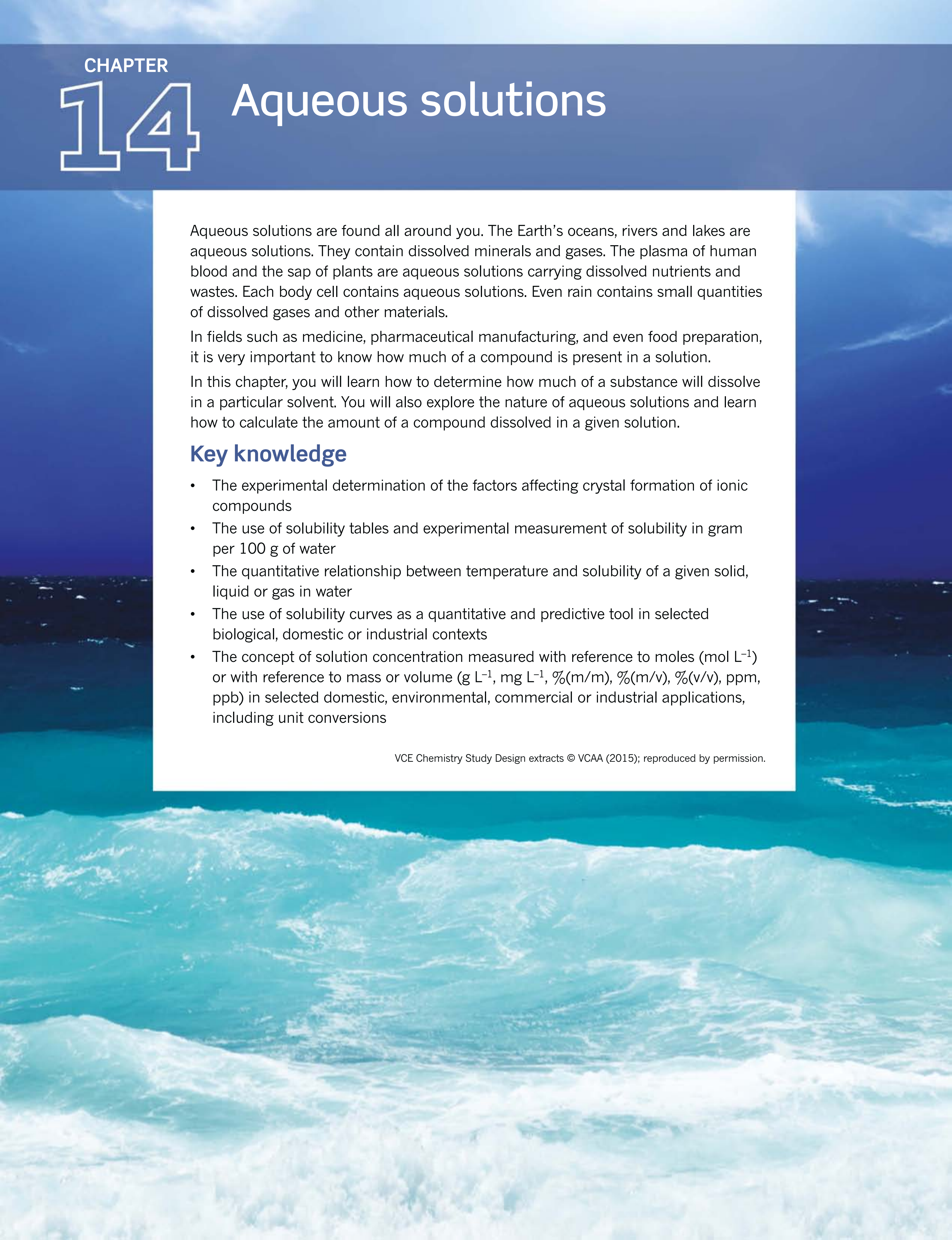
- **i** Ionic compound
- **ii** Compound composed of polar molecules with –OH groups
- **iii** Compound composed of small polar molecules in which a hydrogen atom is covalently bonded to an atom of a group 17 element
- **iv** Non-polar molecular compound
- **v** Compound composed of covalent molecules with a large non-polar end and one –OH group.

- **a** Does not dissolve in water because a large proportion of the molecule is non-polar
- **b** Dissolves in water by ionising, then forming ion–dipole bonds with water
- **c** Does not dissolve in water
- **d** Dissolves in water by forming hydrogen bonds with water molecules
- **e** Dissolves in water by dissociating, then forming ion–dipole bonds with water

24 Give concise explanations for the following observations.

- **a** Ammonia (NH_3) and methane (CH_4) are both covalent molecular substances. Ammonia is highly soluble in water, but methane is not.
- **b** Glucose ($C_6H_{12}O_6$) and common salt (NaCl) are very different compounds. Glucose is a covalent molecular substance, whereas common salt is ionic, yet both of these substances are highly soluble in water.

25 Glucose ($C_6H_{12}O_6$) and common salt (NaCl) both form clear colourless solutions when dissolved in water. Suggest a test you could perform in the laboratory to tell the two solutions apart.



CHAPTER

14 Aqueous solutions

Aqueous solutions are found all around you. The Earth's oceans, rivers and lakes are aqueous solutions. They contain dissolved minerals and gases. The plasma of human blood and the sap of plants are aqueous solutions carrying dissolved nutrients and wastes. Each body cell contains aqueous solutions. Even rain contains small quantities of dissolved gases and other materials.

In fields such as medicine, pharmaceutical manufacturing, and even food preparation, it is very important to know how much of a compound is present in a solution.

In this chapter, you will learn how to determine how much of a substance will dissolve in a particular solvent. You will also explore the nature of aqueous solutions and learn how to calculate the amount of a compound dissolved in a given solution.

Key knowledge

- The experimental determination of the factors affecting crystal formation of ionic compounds
- The use of solubility tables and experimental measurement of solubility in gram per 100 g of water
- The quantitative relationship between temperature and solubility of a given solid, liquid or gas in water
- The use of solubility curves as a quantitative and predictive tool in selected biological, domestic or industrial contexts
- The concept of solution concentration measured with reference to moles (mol L^{-1}) or with reference to mass or volume (g L^{-1}, mg L^{-1}, %(m/m), %(m/v), %(v/v), ppm, ppb) in selected domestic, environmental, commercial or industrial applications, including unit conversions

14.1 Solubility

The solubility of a substance is a measure of how much of the substance will dissolve in a given amount of a **solvent**. For example, glucose is very soluble in water and is used by your body as a readily available energy source. Most rocks are made of minerals that are insoluble in water, but **limestone** (which contains calcium carbonate) is slightly soluble and so caves form in areas of limestone rock over long periods.

In this section, you will learn how to measure the solubility of some compounds in water and how to predict whether a compound will be soluble or not.

DEFINITION OF SOLUBILITY

In chemistry, the term **solubility** has a specific meaning. It refers to the maximum amount of a **solute** (substance that is dissolved) that can be dissolved in a given quantity of a solvent (the common quantity often used is 100 g) at a certain temperature. Table 14.1.1 gives the solubility of some common substances in 100 g of water at 18°C.

TABLE 14.1.1 Solubility of solutes at 18°C

Solute	Solubility (g per 100 g of water)
Sugar (sucrose)	200
Salt (sodium chloride)	35
Limestone (calcium carbonate)	0.0013

Different kinds of solutions

There are three terms that can be used to describe the different solutions that result from dissolving solutes in solvents. They are:

- saturated
- unsaturated
- supersaturated.

A **saturated solution** is one in which no more solute can be dissolved at a particular temperature.

An **unsaturated solution** contains less solute than is needed to make the solution saturated. Unsaturated solutions can dissolve more solute.

A **supersaturated solution** is an unstable solution that contains more dissolved solute than a saturated solution. If this type of solution is disturbed, some of the solute will separate from the solvent as a solid.

Figure 14.1.1 shows a supersaturated solution of sodium ethanoate. Supersaturated sodium ethanoate is prepared by cooling a saturated solution very carefully so that solid crystals do not form. Adding a small **seed crystal** to the supersaturated solution causes the solute to **crystallise** (form solid crystals) so that a saturated solution remains.

FIGURE 14.1.1 Crystals of sodium ethanoate form after a seed crystal is added to a supersaturated solution of the compound.

SOLUBILITY CURVES

The solubility of many substances changes significantly as the temperature changes. For example, you can dissolve more chocolate powder in hot milk than in cold milk. For most solids, increasing the temperature increases the solubility in a liquid. This is because at higher temperatures, both the solute and solvent have more energy to overcome the forces of attraction that hold the particles together in the solid.

The relationship between solubility and temperature can be represented by a **solubility curve** as shown in Figure 14.1.2.

Solubility curves show the solubility of a substance as a function of temperature. For the solubility curves featured in Figure 14.1.2, note that:

- each point on a curve represents the maximum amount of the solute that can be dissolved in 100 g of water at a particular temperature. Therefore, each point on the curve represents a saturated solution
- any point below a curve represents an unsaturated solution
- any point above a curve represents a supersaturated solution
- for most solids, as temperature increases, the solubility increases.

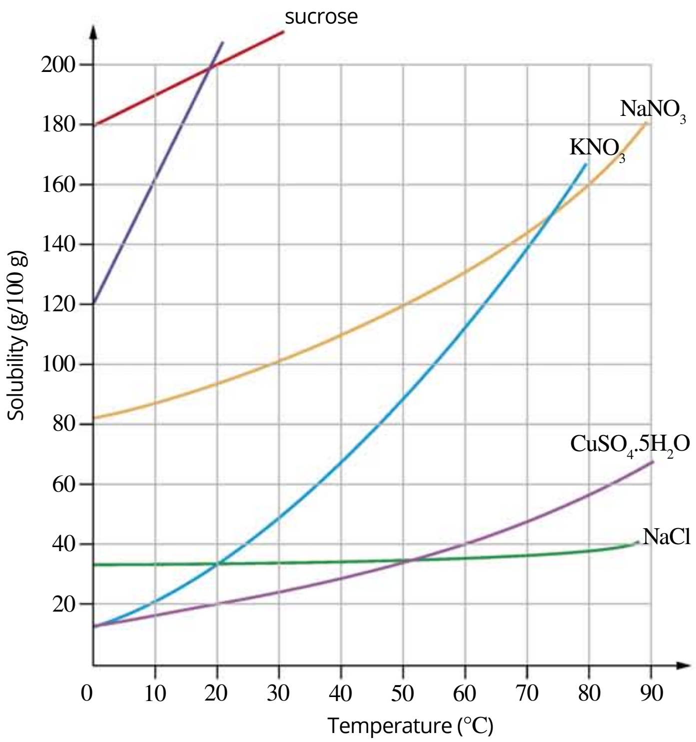
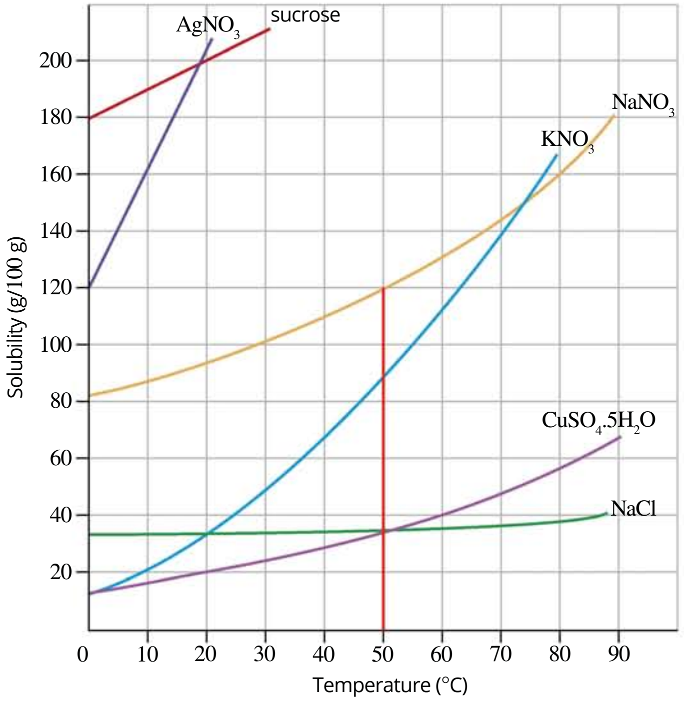
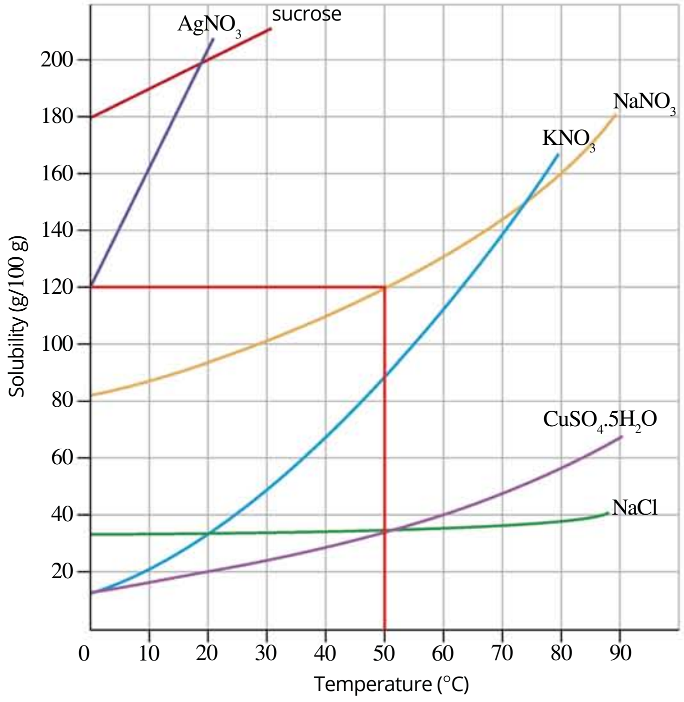


FIGURE 14.1.2 Solubility curves for some common chemicals.

Worked example 14.1.1

SOLUBILITY CURVE CALCULATIONS

Use Figure 14.1.2 on page 337 to find how many grams of sodium nitrate ($NaNO_3$) will dissolve in 100 g of water at 50°C.

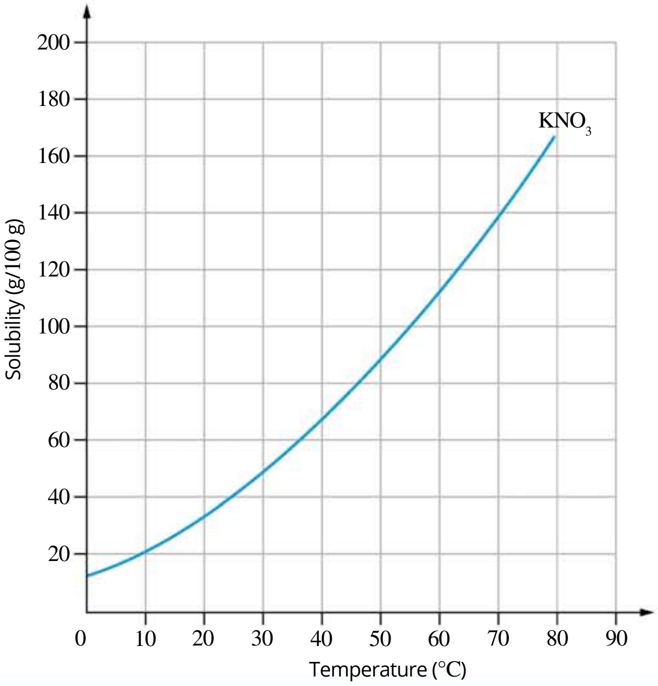
<table>
<tr><th>Thinking</th><th>Working</th></tr>
<tr><td>Points on a solubility curve show the maximum amount of the solute that will dissolve in 100 g water at a given temperature.
Draw a vertical line from the required temperature on the horizontal axis to intersect with the appropriate solubility curve.</td><td>Draw a vertical line from 50°C on the horizontal axis to intersect with the solubility curve for $NaNO_3$.

</td></tr>
<tr><td>Draw a horizontal line from the intersection point of the vertical line drawn in the previous step. The point where this horizontal line intersects with the vertical axis will give the mass of dissolved substance.</td><td>
</td></tr>
</table>

Read the solubility from the graph.	The horizontal line intersects with the vertical axis at 120 g. Therefore, the mass of $NaNO_3$ that will dissolve in 100 g of water at 50°C is 120 g.

Worked example: Try yourself 14.1.1

SOLUBILITY CURVE CALCULATIONS

Use the solubility curve below to find how many grams of potassium nitrate (KNO_3) will dissolve in 100 g of water at 70°C.



More calculations using solubility curves

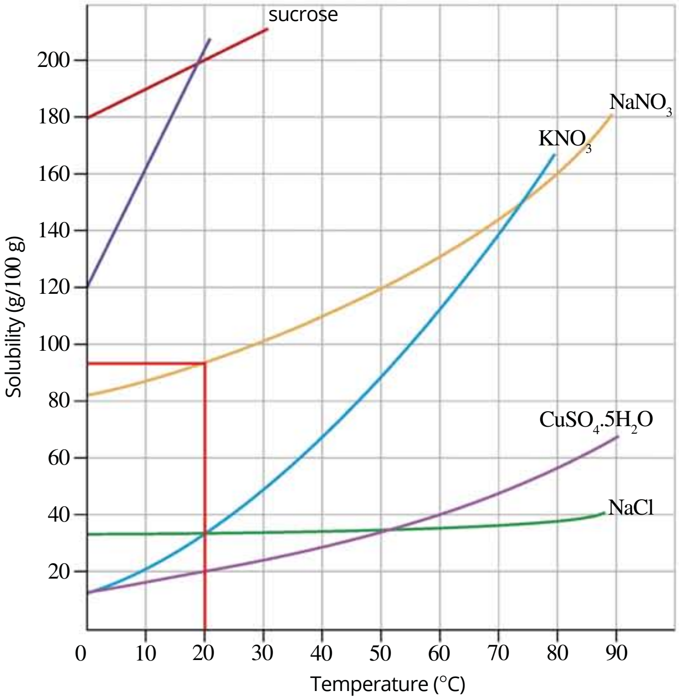
Solubility curves allow you to directly calculate the mass of a compound that will dissolve in 100 g water at different temperatures. It is also possible to use the curves to calculate solubilities of compounds in quantities of water other than 100 g. Worked Example 14.1.2 shows you how.

Worked example 14.1.2

SOLUBILITY CURVES

An 80 g sample of sodium nitrate ($NaNO_3$) is added to 200 mL of H_2O at 20°C.

Use Figure 14.1.2 on page 337 to calculate how much more $NaNO_3$ must be added to make the solution saturated with $NaNO_3$ at 20°C.

Thinking	**Working**
Use the solubility curve to find the mass of solute in a saturated solution of 100 g of H_2O at the required temperature.	Draw a line from 20°C on the horizontal axis to the solubility curve for $NaNO_3$ and find the corresponding value on the vertical axis. The value is 92 g. 
Use the amount of solute that will dissolve in 100 g of H_2O to find the mass of solute to make a saturated solution in the mass of H_2O for this question.	The density of water is 1.0 g mL^{-1}, so 200 mL of water will weigh 200 g. So twice the mass of solute can dissolve in 200 g of water as in 100 g. $m(NaNO_3) = 2 \times 92$ $= 184$ g
To find out how much extra solute you need to add, find the difference between the mass of solute needed to make a saturated solution and how much has already been added.	80 g of $NaNO_3$ has already been added to 200 g H_2O. So the extra mass of $NaNO_3$ needed: $= 184 - 80$ $= 104$ g

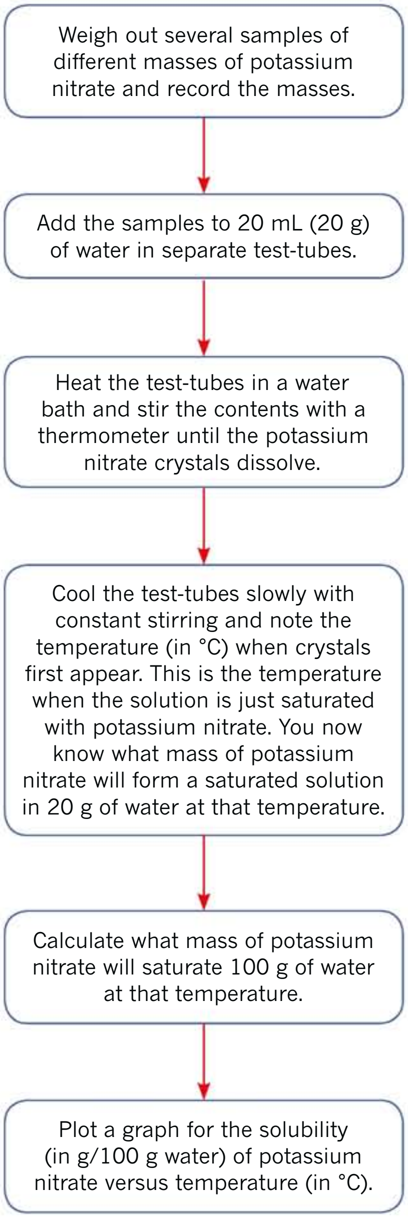
Worked example: Try yourself 14.1.2

SOLUBILITY CURVES

A 120 g sample of sodium nitrate ($NaNO_3$) is added to 300 mL of H_2O at 40°C. Use Figure 14.1.2 on page 337 to calculate how much more $NaNO_3$ must be added to make the solution saturated with $NaNO_3$ at 40°C.

Making your own solubility curve

Solubility curves can be developed relatively easily in a school laboratory. For example, a solubility curve for potassium nitrate in water can be derived in a group activity by carrying out the following steps.



Weigh out several samples of different masses of potassium nitrate and record the masses.

Add the samples to 20 mL (20 g) of water in separate test-tubes.

Heat the test-tubes in a water bath and stir the contents with a thermometer until the potassium nitrate crystals dissolve.

Cool the test-tubes slowly with constant stirring and note the temperature (in °C) when crystals first appear. This is the temperature when the solution is just saturated with potassium nitrate. You now know what mass of potassium nitrate will form a saturated solution in 20 g of water at that temperature.

Calculate what mass of potassium nitrate will saturate 100 g of water at that temperature.

Plot a graph for the solubility (in g/100 g water) of potassium nitrate versus temperature (in °C).

14.1 Review

SUMMARY

- Solubility is a measure of how much solute will dissolve in a given amount of solvent at a specified temperature.
- Solubility curves show how the solubility of a compound changes with temperature.
- Solubility curves can be used to calculate the amount of a substance that will dissolve in a given amount of solvent at a specified temperature.
- The solubility of most solids in water increases as the temperature increases.

KEY QUESTIONS

1 Determine whether the following solutions are unsaturated, saturated or supersaturated. Use Table 14.1.1 on page 336 to help you.

  a A solution containing 35 g of sodium chloride dissolved in 100 g of water at 18°C

  b A solution containing 0.00045 g of calcium carbonate dissolved in 100 g of water at 18°C

  c A solution containing 110 g of sugar dissolved in 50 g of water at 18°C

2 35 g of sodium chloride will dissolve in 100 g of water at 18°C to form a saturated solution. A number of different solutions were made by dissolving the following masses of sodium chloride in 50 g of water at 18°C. Which solution would be supersaturated?

  A 9 g

  B 3.5 g

  C 20 g

  D 17.5 g

3 Look at Figure 14.1.3 and determine which coloured points correspond to saturated, unsaturated or supersaturated solutions of potassium nitrate.

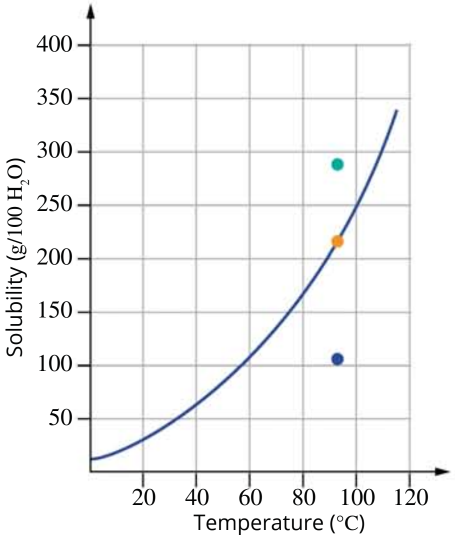


FIGURE 14.1.3 Solubility curve for potassium nitrate.

Use Figure 14.1.2 on page 337 to answer Questions 4–6.

4 Find the mass of solute that could dissolve in the following situations:

  a $CuSO_4.5H_2O$ in 100 g of water at 60°C

  b $AgNO_3$ in 100 g of water at 10°C

  c KNO_3 in 50 g of water at 24°C

5 What mass of the following compounds will dissolve in 200 g of water at 30°C to form a saturated solution?

  a $CuSO_4.5H_2O$

  b $NaNO_3$

  c NaCl

6 Indicate whether the following solutions would be saturated, unsaturated or supersaturated.

  a 200 g of sodium nitrate ($NaNO_3$) dissolved in150 g water at 50°C

  b 400 g of sucrose dissolved in 200 g water at 70°C

  c 8 g of copper(II) sulfate ($CuSO_4.5H_2O$) dissolved in 20 g water at 80°C

14.2 Crystallisation

You have probably seen rocky outcrops near the sea where salt crystals have formed from seawater in shallow pools, like those in Figure 14.2.1. The seawater may have been left there after a storm or high tide. As the water evaporates in the sun and wind, the concentration of the salt in the water increases until the solution becomes **saturated**. Further evaporation results in the salt coming out of solution and forming solid deposits. This process is called **crystallisation**.

FIGURE 14.2.1 White crystals of salt are left behind at the edge of a rock pool where seawater has evaporated.

In this section, you will look more closely at what occurs during the process of crystallisation.

PROCESS OF CRYSTALLISATION

Methods of crystallisation

Crystallisation from solutions occurs when an unsaturated solution becomes saturated and crystals form. There are two main ways in which this can happen.

Cooling a solution may reduce the solubility of a dissolved solute to the point where not all of the substance present is soluble. An example of this occurs when copper(II) sulfate crystals form after a hot solution of the compound is cooled. At lower temperatures, less of the compound can dissolve in the water and a point will be reached when the solution becomes saturated. Further cooling will result in crystals being formed.

Alternatively, crystallisation can occur as a result of the evaporation of solvent from a solution. For example, salt forms as water evaporates from seawater. This process produced the crystals of salt seen in Figure 14.2.1.

Variables affecting crystal growth

Several factors affect the formation of crystals from solutions. Some of these factors can affect the size of crystals formed.

Rate of cooling of a solution or molten compound

The rate of temperature change during cooling can affect the size of the crystals that are formed.

- Slow cooling generally produces large crystals.
- Rapid cooling produces smaller crystals.

This is true whether crystals are formed from a solution or as a molten compound cools below its melting point.

CHEMFILE

Salt

In Australia, salt is made from seawater in salt pans (Figure 14.2.2). The concentration of sodium chloride in seawater is approximately 35 g L^{-1}. Seawater is released into shallow ponds and the water evaporates due to heat from the Sun. As the volume of water decreases, the concentration of salt increases. Eventually, the solution becomes saturated and the salt begins to crystallise out. Australia's hot climate makes it very suitable for producing salt by evaporation, and it is a major exporter of salt.

FIGURE 14.2.2 Salt is produced by the evaporation of water from seawater.

FIGURE 14.2.3 Large crystals of copper(II) sulfate formed by slowly cooling a saturated solution of the compound.

You can investigate this phenomenon in a laboratory. For example, a saturated solution of copper(II) sulfate can be cooled at different rates. Some of the solution could be cooled quickly by placing it in a refrigerator. Another sample could be cooled slowly by allowing it to sit in an insulated dish. The slower cooling results in larger crystals, as shown in the Figure 14.2.3.

Igneous rocks illustrate the effects of cooling rates on crystal size. The molten magma from the Earth's interior that forms these rocks can cool down quickly on the Earth's surface during volcanic activity, or very slowly underground. Figure 14.2.4 shows a section of granite, a rock that forms when magma cools below the Earth's surface. As it cools below the surface, the rate of temperature change is slow so granite contains large crystals.

On the other hand, basalt is a rock that forms when magma flows out from a vent in the Earth and over surrounding land. This results in rapid cooling of the magma and formation of small crystals. The basalt plains around Melbourne and much of southwestern Victoria were formed in this way (Figure 14.2.5). The bluestone paving and kerb stones used for many streets and lanes in the city and older suburbs of Melbourne were cut from these basalt deposits.

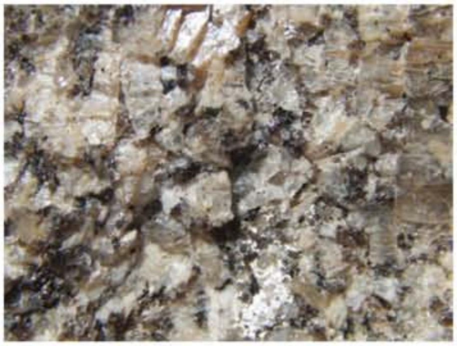


FIGURE 14.2.4 Large crystals (or grains) in granite.

FIGURE 14.2.5 The rock columns at the Organ Pipes National Park near Melbourne are basalt extrusions.

Rate of evaporation of solvent

If crystals are formed by evaporation, then the rate of evaporation of the solvent will affect the size of the crystals. Generally, a faster rate of evaporation results in smaller crystals. This can be investigated in the laboratory by placing solutions of a chemical in different situations where the rate of evaporation of the solvent varies, for example in a cupboard and on a windowsill.

Nucleation

Crystallisation occurs more rapidly if a 'nucleus' is present in the solution on which the new crystals can form. A nucleus can be provided by adding a single seed crystal of the compound itself. Even a small solid impurity in the solution, such as a speck of dust or a scratch on the container wall can act as a nucleus. You saw an example of this in Figure 14.1.1.

Nature of the compound

Different compounds produce different-shaped crystals. Figure 14.2.6 shows two different-shaped crystals. Sodium chloride crystals are cubic in shape; the crystals of alum (potassium aluminium sulfate, $KAl(SO_4)_2$) are octahedral.

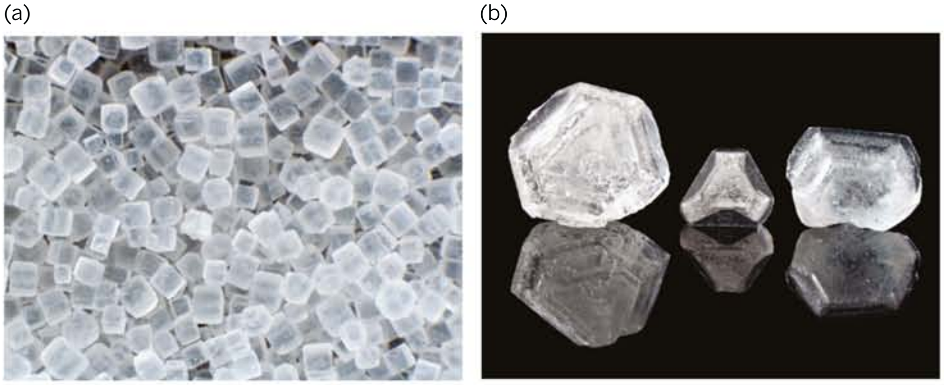


FIGURE 14.2.6 (a) Cubic crystals of table salt (sodium chloride) and (b) octahedral crystals of alum, $KAl(SO_4)_2$.

Calculations involving crystallisation

You can predict how much of a compound will crystallise out of a solution as temperature decreases using a solubility curve. Worked Example 14.2.1 shows how this can be done.

Worked example 14.2.1

CRYSTALLISATION

50 g of potassium nitrate (KNO_3) is dissolved in 100 g water at 40°C. What mass of KNO_3 crystals will form if the temperature is reduced to 20°C? You will need to refer to Figure 14.1.2 on page 337 to complete this question.

Thinking	**Working**
Identify the mass of solute dissolved in the original solution.	Mass of KNO_3 in solution = 50 g
Find the maximum mass of solute that will remain dissolved in 100 g water at the final temperature.	The solubility curve of shows that the maximum mass that will dissolve at 20°C is 32 g.
Calculate the mass of solute crystals that will form in the solution at the final temperature.	Mass of crystals formed = original mass – remaining mass = 50 – 32 = 18 g

Worked example: Try yourself 14.2.1

CRYSTALLISATION

200 g of sucrose is dissolved in 100 g water at 20°C. What mass of sucrose crystals will form if the temperature is reduced to 10°C?

Uses of solubility curves in the workplace

Sometimes it is important to know how much of a solute will precipitate out of a solution as it cools to a particular temperature, or if all the solute will stay dissolved. Two examples, one from industry and one from biological research, illustrate how solubility curves can be used to help in situations like this.

Example 1: Crystallising sugar from sugar cane syrup

In Australia, table sugar (sucrose) is prepared in large quantities from sugar cane. During processing, the cane is crushed to release juice. Impurities are removed and water is evaporated from the juice until the solution becomes saturated and the sugar begins to crystallise out. Chemists use solubility curves like the one in Figure 14.2.7 to predict the amount of sucrose that will crystallise at different temperatures and solubilities.

In this solubility curve, the area marked 'supersaturation curve' indicates the conditions under which crystals will form spontaneously. In the 'metastable region', seed crystals must be added to induce crystallisation. In areas below the saturation curve, the solution is unsaturated and crystals will not form.

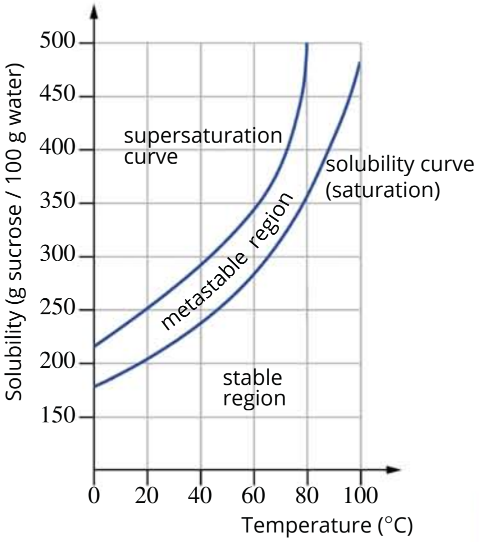


FIGURE 14.2.7 A solubility curve for sucrose used to predict the amount of sugar that will crystallise out under different conditions.

Example 2: Research on therapeutic proteins

Therapeutic proteins are compounds that are manufactured in the laboratory for use as pharmaceuticals. Synthetic insulin is an example of a therapeutic protein. Therapeutic proteins need to remain dissolved when injected into the body.

Most biological reactions and many industrial processes take place in solution. Laboratory workers in medical, pharmaceutical and industrial fields need to know the temperature ranges at which compounds remain dissolved. If the temperature of the solutions they are using does not stay within a certain range, then reactants may crystallise out and interfere with the desired reactions.

Solubility curves allow researchers to make accurate predictions about the solubility at different temperatures of the compounds under investigation. They can then ensure that work will not be disrupted by unexpected and unwanted crystallisation.

SOLUBILITY OF LIQUIDS AND GASES IN WATER

It is generally true that as temperature increases, the solubility of solids in solution increases. However, the solubility of liquids in other liquids does not show clear trends in solubility as the temperature changes.

Gases generally become less soluble as the temperature increases. The graph in Figure 14.2.8 shows the solubility of different gases in water at varying temperatures.

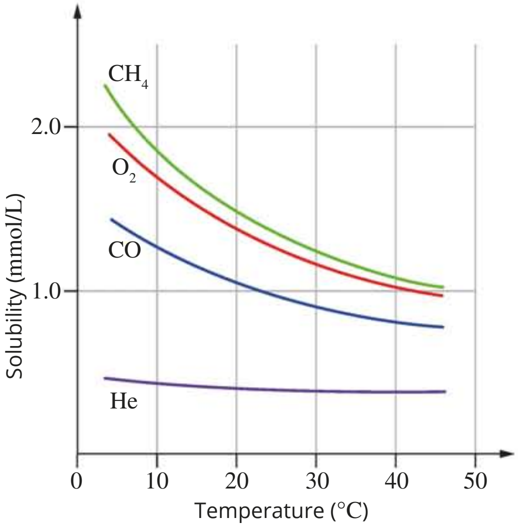


FIGURE 14.2.8 Solubility curves for some gases.

Table 14.2.1 shows the solubility of some common gases in water at different temperatures. For each gas, it can be seen that as temperature increases, less gas is able to dissolve in water.

TABLE 14.2.1 Solubility of some gases in water at different temperatures

Gas	Solubility (g of gas per kg of water) at 0°C	Solubility (g of gas per kg of water) at 20°C	Solubility (g of gas per kg of water) at 60°C
Oxygen	0.069	0.043	0.023
Carbon dioxide	3.4	1.7	0.58
Nitrogen	0.029	0.019	0.011
Methane	0.040	0.023	0.011
Ammonia	897	529	168

FIGURE 14.2.9 Bubbles of air appear as water is heated. This is because solubility of gases decreases at higher temperatures.

In Figure 14.2.9, you can see the bubbles that appear when water is first heated are not steam (water vapour) but air bubbles. Some of the air that was dissolved in the water comes out of solution as the temperature increases and the gas becomes less soluble.

You may have noticed that soft drinks will go 'flat' more quickly if they are left standing in the sun on a hot day than if they are in a cold refrigerator (Figure 14.2.10 on page 347). The dissolved carbon dioxide in the drink comes out of solution as the drink heats up.

The effect of temperature on the solubility of a gas can have environmental implications. If the temperature of the water in rivers, lakes and oceans increases even slightly, it will contain less dissolved oxygen. This can have serious consequences for oxygen-breathing aquatic organisms, such as the Australian Murray River cod in Figure 14.2.11 on page 347.

FIGURE 14.2.10 Soft drinks left standing in the sun go 'flat' quickly.

FIGURE 14.2.11 Fish, such as this native Australian Murray River cod, are susceptible to lowered levels of oxygen in natural waters.

Therefore, hot water from power stations and other industries must be cooled before it can be discharged into waterways. Even a small increase in water temperature can cause the oxygen concentration in the water to drop below levels that are necessary for aquatic life to survive.

14.2 Review

SUMMARY

- Crystallisation occurs when a solution is cooled to the point where it becomes saturated with solute and the solute begins to form solid crystals.
- As the temperature of a solution increases, the solubility of solids generally increases and the solubility of gases decreases. Liquids show no overall trend in solubility with temperature.
- Crystallisation can occur from a solution when:
  – the temperature of the solution decreases
  – solvent evaporates.
- Factors that can affect crystallisation, including crystal size, are:
  – rate of cooling of solution
  – rate of evaporation of solvent
  – nucleation
  – nature of the compound.
- Solubility curves can be used to predict the amount of a compound that will precipitate from solution at a particular temperature.
- Solubility curves can be used as predictive tools in different fields of industry and research.

KEY QUESTIONS

Refer to Table 14.2.1 on page 346 to answer Questions 1 and 2.

1 0.033 g of oxygen was dissolved in 1 kg water at 20°C. If the temperature of the solution was increased to 60°C, what mass of oxygen would leave the solution?

A 0.033 g
B 0.056 g
C 0.036 g
D 0.010 g

2 A saturated solution of carbon dioxide in water was made by bubbling the gas through 500 g water at 40°C. What is the approximate mass of carbon dioxide that dissolved?

A 0.57 g
B 1.14g
C 1.7 g
D 3.4 g

Refer to Figure 14.1.2 on page 337 to answer Questions 3–5.

3 140 g of potassium nitrate (KNO_3) is dissolved in 100 g of water at 70°C. The temperature of the solution is then cooled to 55°C.
What mass of KNO_3 will crystallise out of solution?

A 33 g
B 40 g
C 100 g
D 140 g

4 Calculate the mass of crystals that will form when a solution containing 60 g of $CuSO_4.5H_2O$ in 100 g of water at 90°C is cooled to 60°C.

5 55 g of sodium nitrate was dissolved in 50 g of water at 80°C. What mass of sodium nitrate will remain dissolved if the solution was cooled to 50°C?

6 Explain why granite crystals are a different size from basalt crystals.

14.3 Concentration of solutions

The concentration of a solution describes the relative amount of solute and solvent present in the solution. A solution in which the ratio of solute to solvent is high is said to be concentrated. Cordial that has not had any water added to it is an example of a **concentrated solution**. A solution in which the ratio of solute to solvent is low is said to be a **dilute solution**. A quarter of a teaspoon of sugar dissolved in a litre of water will produce a dilute solution that tastes slightly sweet.

'Concentrated' and 'dilute' are general terms. However, sometimes you need to know the actual concentration of a solution—the exact ratio of solute to solvent. The use of exact solution concentrations is important in the prescription of medicines, chemical manufacturing and chemical analysis.

UNITS OF CONCENTRATION

Chemists use different measures of concentration depending on the situation. The most common measures describe the amount of solute in a given amount of solution.

Some examples of units of concentration are:

- mass of solute per litre of solution (grams per litre, g L^{-1})
- moles of solute per litre of solution (moles per litre, mol L^{-1}). (You will look more closely at this unit of concentration in section 14.4.)
- parts per million (ppm)
- percentage by mass.

Units of concentration measured in this way have two parts.

- The first part gives information about how much solute there is.
- The second part gives information about how much solution there is.

For example, if a solution contains sodium chloride (NaCl) with a concentration of 17 g L^{-1}, then (first part) 17 g of NaCl is dissolved in every (second part) 1 L of the solution.

You will now look at how to perform calculations of concentration using different units.

Concentration in grams per litre (g L^{-1})

The concentration of a solution in grams per litre (g L^{-1}) indicates the mass, in grams, of solute dissolved in 1 litre of the solution. For example, if the concentration of sodium chloride in seawater is 20 g L^{-1}, this means that in 1 L of seawater there is 20 g of sodium chloride. A formula used to calculate the concentration in g L^{-1} is:

$$\text{concentration (g L}^{-1}\text{)} = \frac{\text{mass of solute (in g)}}{\text{volume of solution (in L)}}$$

Worked example 14.3.1

CALCULATING CONCENTRATION IN g L^{-1} (GRAMS PER LITRE)

What is the concentration, in g L^{-1}, of a solution containing 8.00 g of sodium chloride in 500 mL of solution?

Thinking	Working
Change the volume of solution so it is expressed in litres.	500 mL $= \frac{500}{1000}$ $= 0.500$ L
Calculate the concentration in g L^{-1}.	$c = \frac{\text{mass of solute (in g)}}{\text{volume of solution (in L)}}$ $= \frac{8.00}{0.500}$ $= 16.0$ g L^{-1}

Worked example: Try yourself 14.3.1

CALCULATING CONCENTRATION IN g L^{-1} (GRAMS PER LITRE)

What is the concentration, in g L^{-1}, of a solution containing 5.00 g of glucose in 250 mL of solution?

Concentration in parts per million (ppm)

When very small quantities of solute are dissolved to form a solution, the concentration is often measured in **parts per million (ppm)**. For example, the concentration of mercury in fish that is suitable for consumption is usually expressed in parts per million. The maximum concentration allowed for sale in Australia is 1 ppm (Figure 14.3.1).

In simple terms, the concentration in parts per million can be thought of as the mass in grams of solute dissolved in 1 000 000 g of solution. This can also be expressed as the mass in milligrams of solute dissolved in 1 kg of solution, because there are 1 million milligrams in a kilogram.

For example, a solution of sodium chloride that has a concentration of 154 ppm contains 154 mg of sodium chloride dissolved in 1 kg of solution. A formula used to calculate the concentration of a solution in ppm is:

$$\text{concentration (ppm)} = \frac{\text{mass of solute (in mg)}}{\text{mass of solution (in kg)}}$$

FIGURE 14.3.1 Fish sold in Australia must have no more than 1 ppm of mercury (Australia New Zealand Food Standards Code).

Worked example 14.3.2

CALCULATING CONCENTRATION IN PARTS PER MILLION (PPM)

A saturated solution of calcium carbonate was found to contain 0.0198 g of calcium carbonate dissolved in 2000 g of solution. Calculate the concentration, in ppm, of calcium carbonate in the saturated solution.

Thinking	Working
Calculate the mass of solute in mg. Remember: mass (in mg) = mass (in g) × 1000	Mass of solute (calcium carbonate) in mg: = 0.0198 × 1000 = 19.8 mg
Calculate the mass of solution in kg. Remember: $\text{mass (in kg)} = \frac{\text{mass (in g)}}{1000}$	$\text{Mass of solution in kg} = \frac{2000}{1000}$ = 2.000 kg
Calculate the concentration of the solution in mg kg^{-1}. This is the same as concentration in ppm.	Concentration of calcium carbonate in ppm $= \frac{\text{mass of solute (in mg)}}{\text{mass of solution (in kg)}}$ $= \frac{19.8}{2.000}$ = 9.90 mg kg^{-1} = 9.90 ppm

Worked example: Try yourself 14.3.2

CALCULATING CONCENTRATION IN PARTS PER MILLION (PPM)

A sample of tap water was found to contain 0.0537 g of NaCl per 250.0 g of solution. Calculate the concentration of NaCl in parts per million (ppm).

Concentration in milligrams per litre (mg L^{-1})

If, for example, the concentration of cadmium in a sample of waste water was 5 mg L^{-1}, this means that in 1 litre of the waste water there will be 5 mg of cadmium. Concentrations in mg L^{-1} may be calculated using the formula:

$$\text{concentration (mg L}^{-1}) = \frac{\text{mass of solute (in mg)}}{\text{volume of solution (in L)}}$$

Concentrations in mg L^{-1} in and ppm are equivalent

You saw earlier that a concentration of solution measured in units of ppm has the same value as concentration measured in mg kg^{-1}. Since 1 litre of solution has a mass of almost exactly 1 kilogram, then a concentration measured in mg L^{-1} will also have the same value in units of ppm, i.e.

$$1 \text{ ppm} = 1 \text{ mg kg}^{-1} = 1 \text{ mg L}^{-1}$$

For example, the concentration, in mg L^{-1} and ppm, of 2.0 litres of a sugar solution containing 0.050 g of sugar can be calculated as follows:

$$0.050 \text{ g of sugar} = 50 \text{ mg}$$

$$\text{concentration (mg L}^{-1}) = \frac{50}{2.0}$$

$$= 25 \text{ mg L}^{-1} = 25 \text{ ppm}$$

Concentration in parts per billion (ppb)

For concentrations that are very small, the unit of **parts per billion (ppb)** can be used. If the concentration of a solution of a pesticide is 5 ppb, this means that in 1 billion grams of the solution, there will be 5 g of pesticide. Concentrations in units of ppb have the same value as concentrations in units of μg (microgram) per kg. A formula for calculating concentration in ppb is:

$$\text{concentration (ppb)} = \frac{\text{mass of solute (in μg)}}{\text{mass of solution (in kg)}}$$

Other units of concentration

You might have noticed symbols such as w/w, w/v or v/v on the labels of some foods, drinks and pharmaceuticals. These symbols represent other concentration units based on masses and volumes of solutes and solutions. These are useful in practical situations because people are familiar with these quantities (Figure 14.3.2).

FIGURE 14.3.2 Consumer products from hardware stores and supermarkets show a wide range of concentration units on their labels.

Percentage by mass (m/m)

Percentage by mass describes the mass of solute, measured in grams, present in 100 g of the solution.

Normal saline solution for washing contact lenses has a concentration of 0.9%(w/w). This can also be written as 0.9%(m/m). The abbreviation w/w indicates that the percentage is based on the weights or, more correctly, masses of both solute and solution. A concentration of 0.9% indicates that there is 0.9 g of sodium chloride dissolved in 100 g of solution.

Percentage by volume (v/v)

The abbreviation v/v indicates that the percentage is based on volumes of both solute and solution. The same units must be used to record both volumes. Percentage by volume is a more convenient unit to use than w/w when the solute is a liquid.

Just like percentage by mass, percentage by volume is frequently expressed as volume per 100 mL of solution. For example, the wine label in Figure 14.3.3 shows 14.0% alc./vol. This means the wine contains 14.0% alcohol (ethanol) by volume (14.0%(v/v)). There will be 14.0 mL of alcohol in 100 mL of the wine.

For example, a 200 mL glass of champagne contains 28 mL of alcohol. The concentration as %(v/v) of alcohol in this solution can be calculated as follows:

$$\text{concentration (\% v/v)} = \frac{\text{volume of solute (in mL)}}{\text{volume of solution (in mL)}} \times 100\%$$

$$= \frac{28}{200} \times 100\%$$

$$= 14\%(\text{v/v})$$

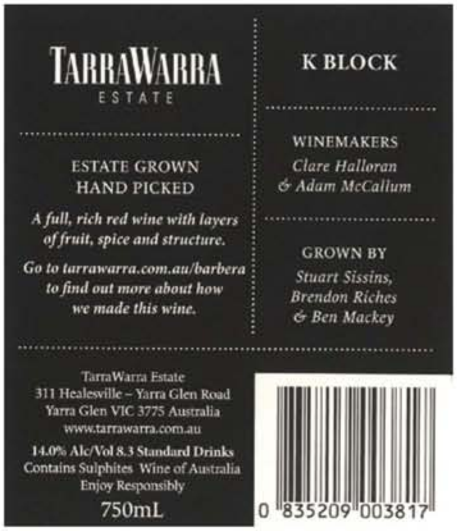


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FIGURE 14.3.3 The label from a bottle of Yarra Valley wine that shows the alcohol concentration in units of %(v/v).

Percentage mass/volume (m/v)

Percentage mass/volume describes the mass of solute, measured in grams, present in 100 mL of the solution.

For example, if a solution of plant food contains a particular potassium compound at a concentration of 3%(m/v), this indicates that there is 3 g of potassium in 100 mL of solution.

CHEMFILE

Saline drip

A 'saline drip' is sometimes used during medical procedures to replenish body fluids in patients (Figure 14.3.4). The solution used contains sodium chloride, commonly with a concentration of 0.9%(m/v). That means that 100 mL of the solution contains 0.9 g of sodium chloride.

FIGURE 14.3.4 A saline drip is a solution of sodium chloride.

14.3 Review

SUMMARY

- The concentration of a solution is defined as the quantity of solute dissolved in a quantity of solution.
- Concentration units have two parts. The first part provides information about the quantity of solute. The second part provides information about the quantity of solution.
- The concentrations of solutions can be expressed in different units including g L^{-1}, mg L^{-1}, %(m/m), %(m/v), %(v/v), ppm and ppb.

KEY QUESTIONS

1 What is the concentration, in g L^{-1}, of a 60 mL solution that contains 5.0 g of sugar?

A 300

B 0.83

C 12

D 83

2 Calculate the concentration of the following solutions in ppm.

a 25 mg of $CaCl_2$ dissolved in 5.0 kg of solution

b 1.25 g of lead nitrate dissolved in 2000 g of solution

c 4.0×10^{-3} g of $MgSO_4$ dissolved in 150 g of solution

3 The nutrition panel on a flavoured milk drink states that it contains 35.0 g of sugar and 7.5 g of fat in every 250 mL serving. What are the concentrations of sugar and fat expressed as %(m/v)?

4 Ciguatoxin is a dangerous toxin that is found in some fish in Australia's tropical waters. The amount of this chemical that can kill a 70 kg human is approximately 15 mg. What is the lethal concentration of the toxin in a human body in parts per billion (ppb)?

14.4 Molar concentration

In the previous section you saw that units of concentration such as g L^{-1}, %(m/m) and %(v/v) are commonly used on the labels of consumer products found in supermarkets, pharmacies and hardware stores. Another unit of concentration that is commonly used by chemists is mol L^{-1}.

In this section, you will learn how to carry out calculations using this unit of concentration.

CONCENTRATION IN MOLES PER LITRE

FIGURE 14.4.1 These containers contain solutions with concentrations shown in units of mol L^{-1}.

Concentrations expressed in moles per litre (mol L^{-1}) allow chemists to compare the amount, in moles, of atoms, molecules or ions present in a given volume of solution.

For example, a 0.1 mol L^{-1} solution of hydrochloric acid would contain 0.1 moles of HCl in 1 L of the solution. (A bottle of HCl of this concentration is shown in Figure 14.4.1.)

The concentration, in mol L^{-1}, of a solution can be calculated as follows:

$$\text{concentration (mol L}^{-1}\text{)} = \frac{\text{amount of solute (in mol)}}{\text{volume of solution (in L)}}$$

$$c = \frac{n}{V}$$

where c is the concentration (mol L^{-1}), n is the amount (mol) and V is the volume (L).

The concentration of a solution in moles per litre is often referred to as the **molarity**, or molar concentration of the solution, and is given the unit M.

A solution containing 1 mole of solute dissolved in 1 litre of solution can therefore be described in several different ways. You can say that the solution:

- has a concentration of 1 mole per litre
- has a concentration of 1 mol L^{-1}
- is 1 molar
- is 1 M
- has a molarity of 1 M.

The symbol M was used earlier to represent molar mass. Take care not to confuse the two different uses, one is a quantity symbol, the other a unit symbol.

Worked example 14.4.1

CALCULATING MOLAR CONCENTRATIONS (MOLARITY)

Calculate the molar concentration of a solution that contains 0.105 mol of potassium nitrate dissolved in 200 mL of solution.

Thinking	Working
Convert the given volume to litres.	$V(KNO_3) = \frac{200}{1000}$ $= 0.200$ L
Calculate the molar concentration using the formula: $c = \frac{n}{V}$	$c(KNO_3) = \frac{n}{V}$ $= \frac{0.105}{0.200}$ $= 0.525$ mol L^{-1} or 0.525 M

Worked example: Try yourself 14.4.1

CALCULATING MOLAR CONCENTRATIONS (MOLARITY)

Calculate the molar concentration of a solution that contains 0.24 mol of glucose dissolved in 500 mL of solution.

Calculating molarity given the mass of solute

Sometimes you will know the mass of a solute and volume of solution and want to calculate the molarity. Two main calculations are involved.

1 Calculate the number of moles of solute from its mass.

2 Calculate the concentration using the number of moles and the volume (in litres).

Worked example 14.4.2

CALCULATING MOLARITY GIVEN THE MASS OF SOLUTE

Calculate the concentration, in mol L^{-1}, of a solution that contains 16.8 mg of silver nitrate ($AgNO_3$) dissolved in 150 mL of solution.

Thinking	**Working**
Convert the volume to litres.	$V(AgNO_3) = \frac{150}{1000}$ $= 0.150$ L
Convert the mass to grams.	$m(AgNO_3) = \frac{16.8}{1000}$ $= 0.0168$ g
Calculate the molar mass of the solute. To do this, add up the atomic masses of all the atoms in the compound.	$M(AgNO_3) = 107.9 + 14.0 + (3 \times 16.0)$ $= 169.9$ g mol^{-1}
Calculate the number of mol of solute using the formula: $n = \frac{m}{M}$	$n(AgNO_3) = \frac{m}{M}$ $= \frac{0.0168}{169.9}$ $= 9.89 \times 10^{-5}$ mol
Calculate the molar concentration using the formula: $c = \frac{n}{V}$	$c(AgNO_3) = \frac{n}{V}$ $= \frac{9.89 \times 10^{-5}}{0.150}$ $= 6.59 \times 10^{-4}$ mol L^{-1} or 6.59×10^{-4} M

Worked example: Try yourself 14.4.2

CALCULATING MOLARITY GIVEN THE MASS OF SOLUTE

Calculate the concentration, in mol L^{-1}, of a solution that contains 4000 mg of ethanoic acid (CH_3COOH) dissolved in 100 mL of solution.

Calculating the number of moles of solute in a solution

The formula used to calculate the molarity of a solution is $c = \frac{n}{V}$. If you rearrange the formula, you can use it to calculate the number of moles of solute in a solution of given concentration and volume:

$$n = c \times V$$

where n is the amount (mol), c is the concentration (mol L^{-1}) and V is the volume (L).

Worked example 14.4.3

CALCULATING THE NUMBER OF MOLES OF SOLUTE IN A SOLUTION

Calculate the amount, in moles, of ammonia (NH_3) in 25.0 mL of a 0.3277 M ammonia solution.

Thinking	**Working**
Convert the given volume to litres.	$V(NH_3) = \frac{25.0}{1000}$ $= 0.0250$ L
Calculate the amount of compound, in moles, using the formula: $n = c \times V$	$n(NH_3) = c \times V$ $= 0.3277 \times 0.0250$ $= 8.19 \times 10^{-3}$ mol

Worked example: Try yourself 14.4.3

CALCULATING THE NUMBER OF MOLES OF SOLUTE IN A SOLUTION

Calculate the amount, in moles, of potassium permanganate ($KMnO_4$), in 100 mL of a 0.0250 M solution of the compound.

14.4 Review

SUMMARY

- Molarity is defined as the number of moles of solute per litre of solution.
- Molarity is calculated using the formula $c = \frac{n}{V}$, where c is the concentration in mol L^{-1}, n is the amount in moles and V is the volume in litres.
- The formula $n = c \times V$ can be used to calculate the number of moles of solute in a given volume of solution.

KEY QUESTIONS

1 Hydrogen peroxide solutions for hair bleaching are sold as 120 mL solutions containing 5.00 g of H_2O_2 dissolved in water. What is the molar concentration of hydrogen peroxide in this bleaching product?

A 0.81 %(m/v)
B 1.23 M
C 41.7 g L^{-1}
D 1.23×10^{-3} mol L^{-1}

2 Calculate the molar concentration of the following solutions.

a A 25.0 mL solution that contains 2.0×10^{-3} mol of NaCl
b A 4.1 L solution that contains 1.23 mol of CH_3COOH
c A 9.3×10^3 L solution that contains 1.8×10^3 mol of KCl

3 Calculate the molar concentration of the following solutions.

a An 8.0 L solution that contains 2.0 mol of NaCl
b A 500 mL solution that contains 0.25 mol of $MgCl_2$
c A 200 mL solution that contains 0.0876 mol of sucrose

4 Calculate the molar concentration of a 250 mL solution that contains 5.09 g of $AgNO_3$.

5 Calculate the molar concentration of a 1.55 L solution that contains 1.223 g of $CaCl_2$.

6 Calculate the amount, in mol, of solute in each of the following solutions.

a 0.10 L of 0.22 M KOH solution
b 10 mL of 0.64 M NaI solution
c 15.6 mL of 0.0150 M $CuSO_4$ solution
d 1.5×10^{-1} mL of 5.2M HCl solution

14.5 Dilution

FIGURE 14.5.1 Pesticide solutions used in aerial spraying are prepared by diluting a concentrated solution of the pesticide compound.

Many commercially available domestic and industrial products come in the form of concentrated solutions. Examples are pesticides (Figure 14.5.1), fertilisers, detergents, fruit juices, acids and other chemicals. A major reason for using concentrates is to save on transportation costs. Diluted solutions contain a lot of water and that extra mass has to be transported, which increases costs. It is also more convenient to buy concentrated products and dilute with water at home or in the workplace.

Everyday examples of dilution are:

- adding water to cordial
- a laboratory technician making a 1 M solution of hydrochloric acid from a bottle of concentrated hydrochloric acid
- a home gardener diluting fertiliser concentrate to spray on the lawn
- a farmer diluting weedkiller concentrate to spray on a wheat crop
- an assistant in a commercial kitchen diluting concentrated detergent solution before using it to wash dishes.

In this section, you will learn how to calculate the concentrations of solutions before and after they have been diluted.

CALCULATING CONCENTRATIONS WHEN SOLUTIONS ARE DILUTED

The process of adding more solvent to a solution is known as **dilution**. When a solution is diluted, its concentration is decreased.

For example, if 50 mL of water is added to 50 mL of 0.10 mol L^{-1} sugar solution, the amount of sugar remains unchanged but the volume of the solution in which it is dissolved doubles. As Figure 14.5.2 shows, this means the sugar molecules are spread further apart during the dilution process, and so the concentration of the sugar solution is decreased (it will become 0.050 mol L^{-1} in this instance).

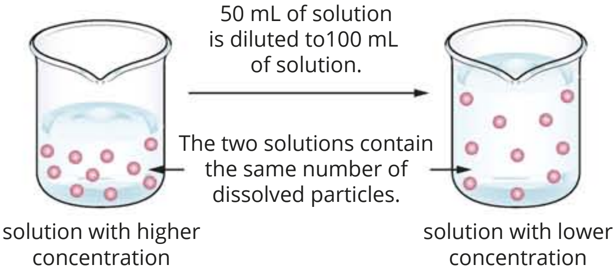

FIGURE 14.5.2 Dilution does not change the number of solute particles but the concentration of the solute decreases.

It is important to recognise that diluting a solution (by adding more solvent) does not change the amount of solute present.

Suppose you had V_1 litres of a solution and the concentration was c_1 mol L^{-1}. The amount of solute, in mole, is given by:

$$n_1 = c_1 \times V_1$$

Suppose water was added to make a new volume, V_2, and change the concentration to c_2. The amount of solute, n_2, in this diluted solution is given by:

$$n_2 = c_2 \times V_2$$

Since the number of moles of solute has not changed, $n_1 = n_2$; therefore:

$$c_1V_1 = c_2V_2$$

This formula is useful when solving problems involving diluted solutions. (Note that this formula can also be used with different concentration and volume units, as long as they are the same on both sides.)

Worked example 14.5.1

QUESTIONS INVOLVING DILUTION

Calculate the concentration of the solution formed when 10.0 mL of water is added to 5.00 mL of 1.2 M HCl.

Thinking	Working
Write down the value of c_1 and V_1. Note: c_1 and V_1 refer to the original solution, before water was added.	$c_1 = 1.2$ M $V_1 = 5.00$ mL
Write down the value of V_2. Note: V_2 is the total volume of the original solution plus the added water.	$V_2 = 10.0 + 5.00$ $= 15.0$ mL
Transpose the equation $c_1V_1 = c_2V_2$ to allow calculation of the concentration, c_2, of the new solution.	$c_1V_1 = c_2V_2$ $c_2 = \frac{c_1V_1}{V_2}$
Calculate the concentration of the diluted solution.	$c_2 = \frac{1.2 \times 5.00}{15.0}$ $= 0.40$ M

Worked example: Try yourself 14.5.1

QUESTIONS INVOLVING DILUTION

Calculate the concentration of the solution formed when 95.0 mL of water is added to 5.00 mL of 0.500 M HCl.

CHANGING THE UNITS OF CONCENTRATION

At times it is useful to change, or 'convert', concentration values from one unit to another unit. One way to do this is in a series of simple steps. Worked Example 14.5.2 shows how this can be done.

Worked example 14.5.2

CONCENTRATION UNIT CONVERSIONS

What is the concentration, in ppm, of a 0.00200 M solution of NaCl? Remember that concentration in ppm is the same as mg L^{-1}.

Thinking	Working
Calculate the number of moles of solute in 1.00 L of the solution.	$n(\text{NaCl}) = c \times V$ $= 0.00200 \times 1.00$ $= 0.00200$ mol
Calculate the mass, in grams, of solute in 1.00 L of the solution.	$M(\text{NaCl}) = 35.5 + 23.0$ $= 58.5$ g mol^{-1} $m(\text{NaCl}) = n \times M$ $= 0.00200 \times 58.5$ $= 0.117$ g
Calculate the mass, in mg, of solute in 1.00 L of the solution.	$m(\text{NaCl}) = 0.117 \times 1000$ $= 117$ mg
Express the concentration of the solute in ppm.	$c(\text{NaCl}) = 117$ ppm

Worked example: Try yourself 14.5.2

CONCENTRATION UNIT CONVERSIONS

What is the concentration, in ppm, of a 0.0100 M solution of NaOH? Remember that concentration in ppm is the same as mg L^{-1}.

14.5 Review

SUMMARY

- Numerical problems involving dilution can be solved using the formula:

  $$c_1V_1 = c_2V_2$$

  where *c* is concentration and *V* is volume.

  When using this formula, c_1 and c_2 must be in the same units of concentration and V_1 and V_2 must be in the same units of volume.
- One type of concentration unit can be converted to another unit in simple steps. For example, units of %(m/m) can be converted to units of mol L^{-1}.

KEY QUESTIONS

1 Calculate the final concentration of each of the following diluted solutions.
- **a** 10.0 mL of water is added to 5.0 mL of 1.2 M HCl.
- **b** 1.0 L of water is added to 3.0 L of 0.10 M HCl.
- **c** 5.0 mL of 0.50 M HCl is added to 95.0 mL of water.

2 What volume of 10 M hydrochloric acid would be required to prepare 250 mL of a 0.30 M HCl solution?
- **A** 7.5 L
- **B** 133 L
- **C** 0.133 L
- **D** 0.0075 L

3 The concentration of a solution of ammonia (NH_3) is 1.5%(m/v). What is the molar concentration of a solution produced by diluting 25.0 mL of this solution with 250 mL of water?

4 The concentration of a solution of NaOH is 17.0%(m/v). What is the concentration of this solution in mol L^{-1}?

Chapter review

KEY TERMS

concentrated solution
crystallisation
crystallise
dilute solution
dilution
limestone
molarity
parts per billion (ppb)
parts per million (ppm)
saturated
saturated solution
seed crystal
solubility
solubility curve
solute
solvent
supersaturated solution
unsaturated solution

Refer to Figure 14.1.2 on page 337 for Questions 1–4.

Solubility

1 What mass of the following compounds will dissolve in 50 g of water at 30°C to form a saturated solution?

- **a** $NaNO_3$
- **b** $CuSO_4.5H_2O$
- **c** KNO_3

2 What is the maximum mass of solute that will dissolve in the following situations?

- **a** Sucrose in 500 g of water at 20°C
- **b** $CuSO_4.5H_2O$ in 40 g of water at 60°C

3 What is the minimum temperature required to dissolve 40 g of $AgNO_3$ in 25 g of water?

Crystallisation

4 160 g of KNO_3 was dissolved in 200 g water at 60°C. What mass of crystals would form if the temperature were decreased to 30°C?

5 What effect does increasing the temperature have on the concentration of gases available to aquatic animals and plants?

6 A gas forms a saturated solution when 0.50 mmol dissolves in 500 mL water at 23°C. Use Figure 14.2.8 on page 346 to decide what the gas is most likely to be.

7 If 2.0 kg water absorbed 1200 g of ammonia at 10°C, what mass of the gas would leave the solution if the temperature of the solution was increased to 20°C? (Refer to Table 14.2.1 on page 346.)

Concentration of solutions

8
- **a** What is the concentration, in ppm, of lead in a 6.0 kg solution that contains 12 mg of lead?
- **b** What is the concentration as percentage by mass?

9 What is the concentration, in %(m/m), of a 300 g solution of KNO_3 that contains 15 g of solute?

10 In each 5.0 mL dose of a cold and flu medicine, there is 2.00 mg of the active ingredient. What is the concentration of this chemical, in mg L^{-1} and %(m/v)?

Molar concentration

11 160 mL of a solution contains 0.380 mol of NaBr. What is the molar concentration of the solution?

12 What is the molar concentration of a 2.0 L solution containing 30 g of NaOH?

13 Calculate the molar concentration of a sodium sulfate solution that has a concentration of 4.26%(m/v).

14 How many moles of solute are present in the following solutions?

- **a** 12 mL of 0.22 M NaI
- **b** 150 mL of 0.0250 M $KMnO_4$
- **c** 7.2 L of 3.15×10^{-3} M KBr

15 What is the mass, in grams, of solute present in the following solutions?

- **a** 100 mL of 1.20 M NH_3
- **b** 20 mL of 0.50 M $AgNO_3$

Dilution

16 Water is added to 50.0 mL of 5.00 M HCl until the total volume is 250 mL. What is the concentration of HCl in the diluted solution?

17 How much water must be added to 25 mL of a 4.0 M solution of potassium carbonate solution to dilute it to a concentration of 1.6 M?

18 1.50 mL of a 0.0500 M solution of calcium chloride ($CaCl_2$) was diluted with water to a volume of 10.0 L. What was the concentration of Cl^- ions in the diluted solution in ppm?

Connecting the main ideas

19 Copy and complete the diagram in Figure 14.6.1 by inserting into the white boxes the processes required to convert between the quantities in the yellow boxes. The answer to the top left box is given to you.

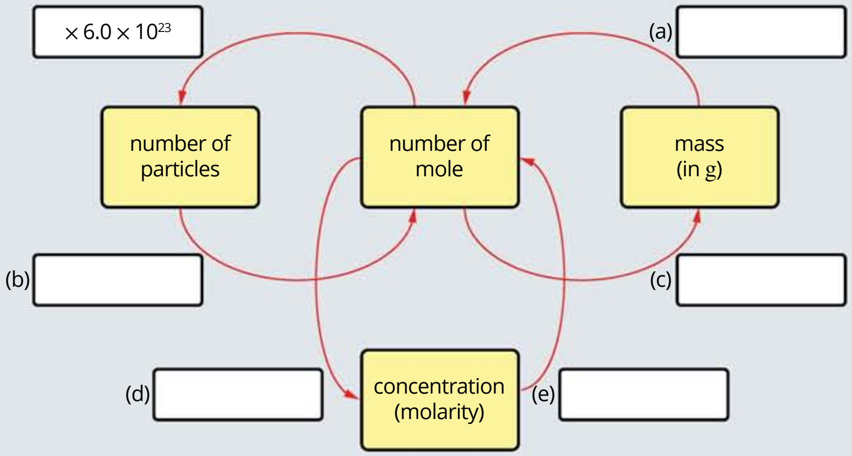

FIGURE 14.6.1 Converting quantities and calculating concentration.

20 The following questions refer to the solubility curve of potassium nitrate (KNO_3) shown in Figure 14.6.2.

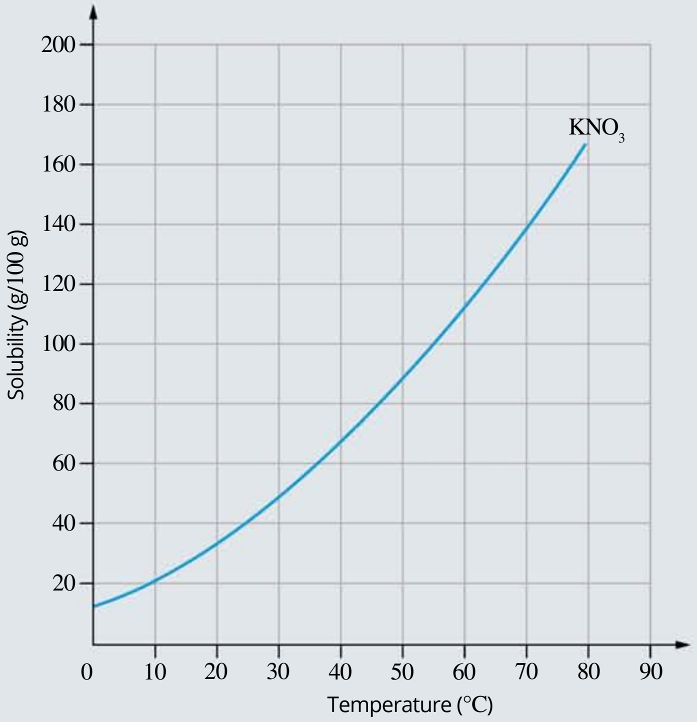

FIGURE 14.6.2 Solubility curve for potassium nitrate.

a What mass of potassium nitrate will dissolve in 500 g of water at 70°C?

b If 25 g of KNO_3 was added to 50 g of water at 70°C, how much must be added to make a saturated solution?

c If 100 g of KNO_3 is added to 50 g of water at 40°C, what mass will remain undissolved?

d What is the molar concentration of the potassium nitrate solution prepared in part **c**? (Assume that 1 g of water gives 1 mL of solution.)

Refer to Figure 14.1.2 on page 337 for Questions 21 and 22.

21 A saturated solution of sodium nitrate was prepared by dissolving the maximum amount of solute in water at 50°C.

a What mass will dissolve in 150 g of water?

b The solution was cooled to 30°C and some the solute crystallised. What mass of crystals would be formed?

c These crystals were isolated and dissolved in 250 mL of water. What is the molar concentration of this solution?

d What is the concentration, in g L^{-1}, of a solution prepared by adding 50 mL of the sodium nitrate solution prepared in part **c** to 700 mL of water?

22 What is the molar concentration of a saturated $CuSO_4.5H_2O$ solution at 20°C? (Assume that 1 g of water gives 1 mL of solution.)

CHAPTER 15

Acid–base reactions in water

Acids and bases have an important and diverse role. They are found in homes and are used extensively in industry and agriculture. Acids and bases are also the reactants and products of many chemical reactions that take place in environmental and biological systems.

In this chapter, you will study a theory that explains the characteristic reactions of acids and bases. You will learn to represent the common reactions of acids and bases using ionic equations and investigate the distinction between strong and weak acids, and concentrated and dilute acids. Finally, you will apply your understanding of acid–base chemistry to a contemporary environmental issue—increasing ocean acidity.

Key knowledge

- The Brønsted–Lowry theory of acids and bases including polyprotic acids and amphiprotic species, and writing balanced ionic equations for their reactions with water including states
- The ionic product of water, the pH scale and the use of pH in the measurement and calculations of strengths of acids and bases and dilutions of solutions
- The reactions of acids with metals, carbonates and hydroxides, including balanced full and ionic equations, with states indicated
- The causes and effects of a selected issue related to acid–base chemistry
- The distinction between strong and weak acids and bases, and between concentrated and dilute acids and bases, including common examples

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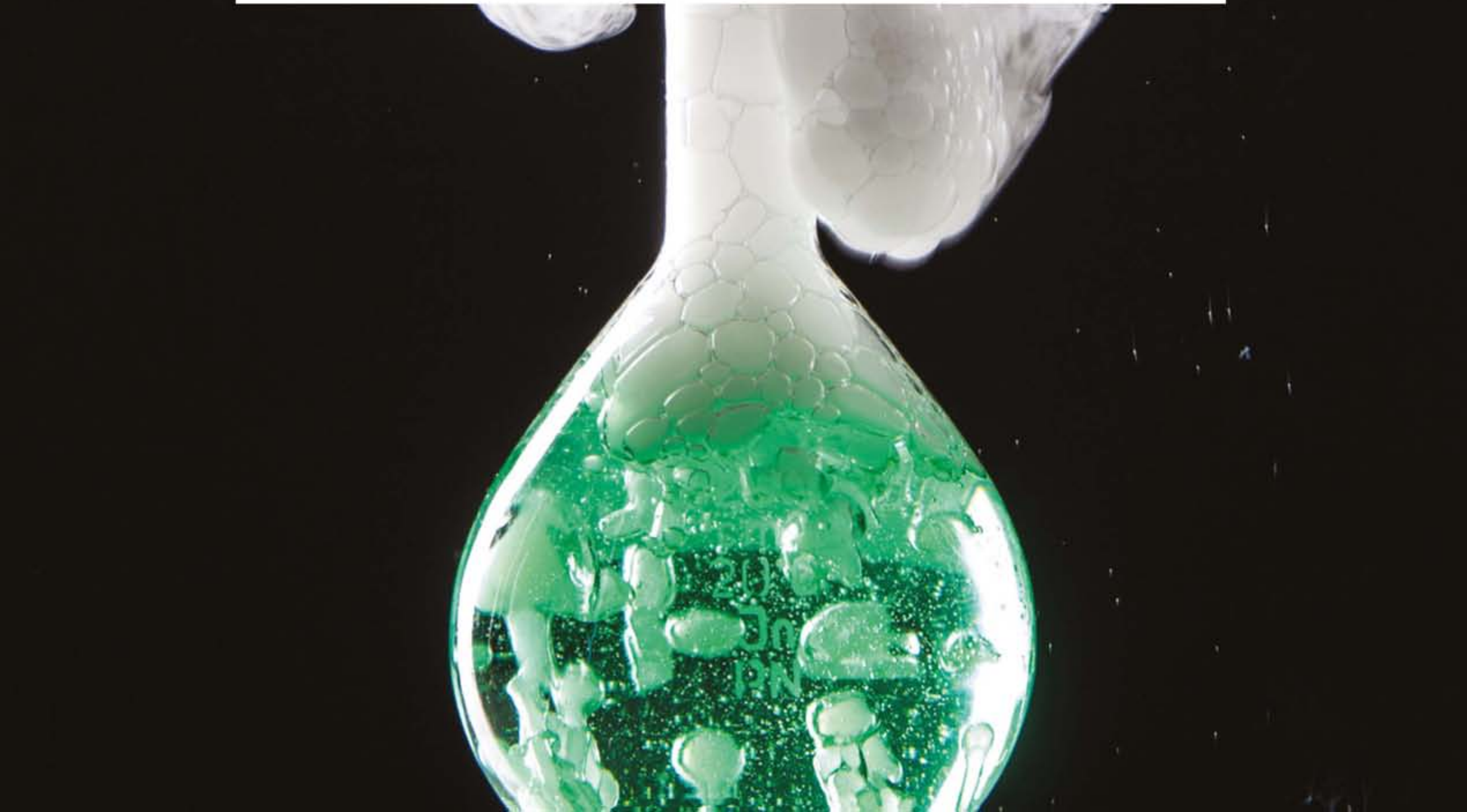


15.1 Introducing acids and bases

Acids and **bases** make up some of the household products in your kitchen and laundry (Figure 15.1.1). In this section, you will be introduced to a theory that explains the chemical properties of acids and bases, helping you to explain their usefulness within the home and industry. You will also look at how the **acidity** of a solution can be measured, therefore defining the solution as a strong or weak acid.

FIGURE 15.1.1 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 have an important role in our bodies. Table 15.1.1 gives the names, chemical formulas and uses of some common acids.

TABLE 15.1.1 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 acid (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 amongst 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 15.1.2).

FIGURE 15.1.2 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 or oils to produce water-soluble soaps. A soluble base is referred to as an **alkali**.

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.

Table 15.1.2 gives the names, chemical formulas and uses of some common bases.

TABLE 15.1.2 Common bases and their uses

Name	Formula	Uses
Sodium hydroxide (caustic soda)	$NaOH$	Used in drain and oven cleaners, and 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, to overcome indigestion
Sodium carbonate	Na_2CO_3	Used in the manufacture of washing powder and glass

CHEMFILE

Handle strong bases with care

Bases feel slippery to the touch because they react with fats in our 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 15.1.3 shows the safety instructions on a can of oven cleaner.

FIGURE 15.1.3 Oven cleaner removes fatty deposits by turning them into soap. Note the safety instructions.

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 15.1.3.

TABLE 15.1.3 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.

For example, in the 17th century, British scientist Robert Boyle described the properties of acids in terms of taste, their action as solvents, and how they changed the colour of certain vegetable extracts (similar to red cabbage juice seen in Figure 15.1.4). He also noticed that alkalis (soluble bases) could reverse the effect that acids had on these extracts.

FIGURE 15.1.4 Natural acid–base indicators are found in plants such as red cabbage. Red cabbage extract turns a different colour in (from left to right) strong acid, weak acid, neutral solution, weak base and strong base.

It wasn't until the late 18th century that 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.

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

- Acids are substances that produce hydrogen ions (H^+) in water.
- Bases **dissociate** (break up) 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.

THE 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 very soluble in water. The molecules **ionise** in water according to the following reaction:

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

In an aqueous solution of hydrogen chloride, nearly all the hydrogen chloride is present as ions—virtually no molecules of hydrogen chloride remain. This solution is known as hydrochloric acid.

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, the HCl has acted as an acid. The water molecule has accepted a proton from the HCl molecule, so the water has acted as a base. This is outlined in Figure 15.1.5.

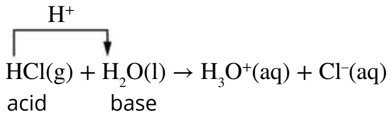


FIGURE 15.1.5 The reaction between hydrochloric acid and water is an example of an acid–base reaction, which involves a transfer of protons from an acid to a base.

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

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

or

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

However, writing the hydronium ion as $H^+(aq)$ in an equation makes it harder to see that a proton transfer has occurred. The hydronium ion is therefore usually written as $H_3O^+(aq)$ in this chapter.

The structural formulas of the hydronium ion and the water molecule are shown in Figure 15.1.6.

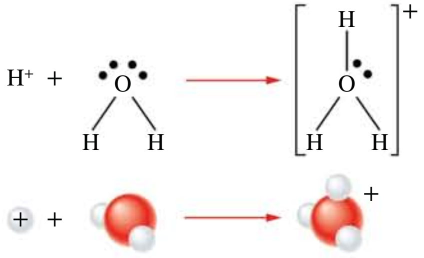


FIGURE 15.1.6 Formation of the hydronium ion.

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.

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 is two species that differ by a proton, i.e. H^+. For the reaction between HCl and H_2O, the conjugate pairs are HCl/Cl^- and H_3O^+/H_2O.

The relationship between acid–base conjugate pairs is represented in Figure 15.1.7.

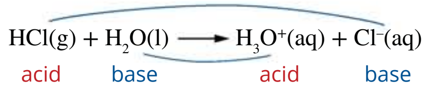


FIGURE 15.1.7 Conjugate acid–base pairs are formed when an acid donates a proton to a base.

In the reaction between NH_3 and H_2O (shown in Figure 15.1.8), 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.

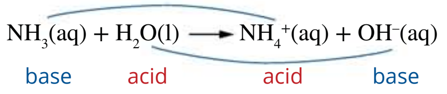


FIGURE 15.1.8 The reaction between ammonia and water, showing the conjugate acid–base pairs.

Figure 15.1.9 shows the formulas of some common acids and bases and their conjugates.

Acids ... donate a proton to form:	$- H^+$	
HCl		Cl^-
H_2SO_4		HSO_4^-
HNO_3		NO_3^-
H_3O^+		H_2O
CH_3COOH		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:	$+ H^+$	
OH^-		H_2O
NH_3		NH_4^+
CO_3^{2-}		HCO_3^-
PO_4^{3-}		HPO_4^{2-}
CH_3COO^-		CH_3COOH
O^{2-}		OH^-

FIGURE 15.1.9 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 reaction below, water donates a proton to NH_3 and acts as an acid.

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

These reactions are represented in Figure 15.1.10.

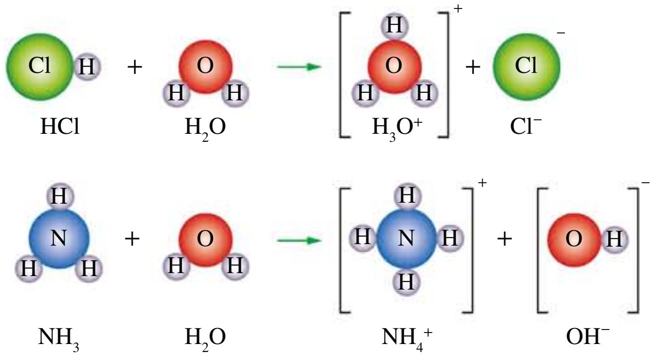


FIGURE 15.1.10 The amphiprotic nature of water is demonstrated by its reactions with HCl and NH_3.

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 15.1.11.

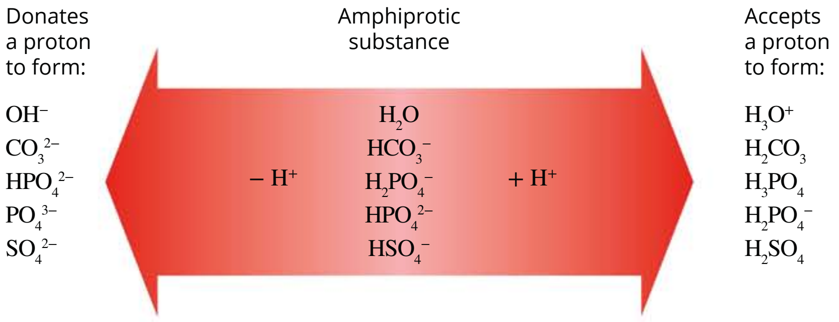


FIGURE 15.1.11 Substances that are amphiprotic.

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^-) reacts according to the equations:

$$\underset{\text{base}}{HCO_3^-(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

$$\underset{\text{acid}}{HCO_3^-(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

Since HCO_3^- can act as both an acid and a base, it is amphiprotic.

Although both reactions are possible for all amphiprotic substances in water, generally one of these reactions dominates. The dominant reaction can be identified by measuring the pH (a measure of the amount of hydronium ion in solution) of the solution. (You will look more closely at pH in section 15.3.)

MONOPROTIC ACIDS

Monoprotic acids can donate only one proton. These acids include hydrochloric acid (HCl), hydrofluoric acid (HF), nitric acid (HNO_3) and ethanoic acid (CH_3COOH).

While ethanoic acid contains four hydrogen atoms, each molecule can donate only one proton to produce an ethanoate ion (CH_3COO^-) and is therefore a monoprotic acid. Only the hydrogen that is part of the highly polar O–H bond is donated. This hydrogen atom is called the **acidic proton** (Figure 15.1.12).

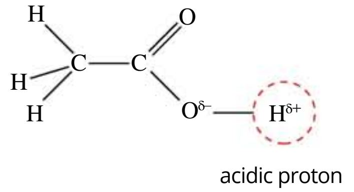


FIGURE 15.1.12 The structure of ethanoic acid. Each molecule can donate only one proton to a water molecule when ethanoic acid reacts with water.

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, such as sulfuric acid (H_2SO_4) and carbonic acid (H_2CO_3) can donate two protons.

A diprotic acid ionises in two stages, for example sulfuric acid.

Stage 1:

$$H_2SO_4(l) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq)$$

Sulfuric acid is described as a **strong acid** in water because it readily donates a proton and so this stage occurs almost to completion. Virtually no H_2SO_4 molecules are found in an aqueous solution.

Stage 2:

The HSO_4^- ion formed can also act as an acid. In a 1.0 M solution, only a small proportion of those ions reacts further to produce H_3O^+ ions and SO_4^{2-} ions.

$$H_2SO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$$

HSO_4^- is described as a **weak acid** because it is only partially ionised. A double (reversible) arrow indicates that an incomplete reaction occurs. (You will learn more about strong and weak acids later in this chapter.) Therefore, a solution of sulfuric acid contains hydrogen ions, hydrogen sulfate ions and sulfate ions.

Triprotic acids

Triprotic acids can donate three protons. These include phosphoric acid (H_3PO_4) and boric acid (H_3BO_3). A triprotic acid, such as phosphoric acid, 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 M 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.

15.1 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?

$H_2SO_4(l) + HNO_3(l) \rightarrow HSO_4^-(l) + H_2NO_3^+(l)$

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 What is the conjugate acid of the following bases?

a NH_3 **c** HPO_4^{2-} **e** O^{2-}

b CH_3COO^- **d** CO_3^{2-}

5 Show 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 acting as an acid and a base with water.

a HCO_3^- **c** HSO_4^-

b HPO_4^{2-} **d** H_2O

15.2 Strength of acids and bases

The acid solutions in the two beakers shown in Figure 15.2.1 are of equal concentration, yet the acid in the beaker on the left reacts more vigorously with zinc than the acid on the right. The acid on the left is described as a stronger acid than the one in the beaker on the right.

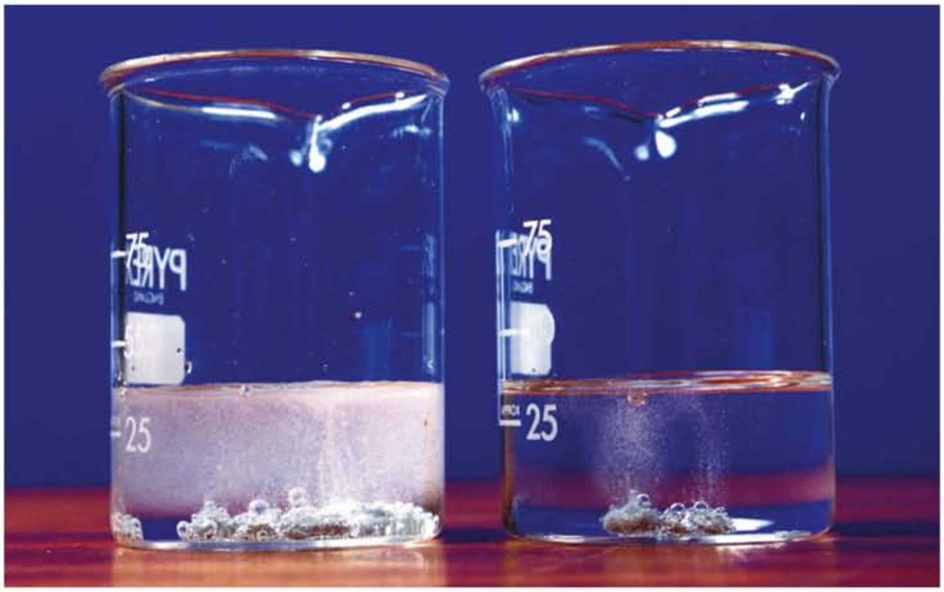


FIGURE 15.2.1 Zinc reacts more vigorously with a strong acid (left) than with a weak acid (right). The acid solutions are of equal concentration and volume.

In section 15.1, you learned 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 pH (a measure of the amount of hydronium ion in solution). (pH will be looked at more closely in section 15.3.)

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.

Since aqueous solutions of acids and bases are most commonly used, it is convenient to use an acid's tendency to donate a proton to water, or a base's tendency to accept a proton from water, as a measure of its strength.

Table 15.2.1 gives the names and chemical formulas of some strong and weak acids and bases.

TABLE 15.2.1 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 15.2.2a). 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 → 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 ions. In a 1.0 M solution of ethanoic acid (CH_3COOH), only a small proportion of ethanoic acid molecules are ionised at any one time (Figure 15.2.2b). A 1.0 M 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 M solution of ethanoic acid, the concentrations of $CH_3COO^-(aq)$ and H_3O^+ are only about 0.004 M.

The partial ionisation of a weak acid is shown in an equation using reversible (double) arrows:

$$\underset{\text{acid}}{CH_3COOH(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons CH_3COO^- + H_3O^+(aq)$$

Therefore, ethanoic acid is described as a weak acid in water (Figure 15.2.2).

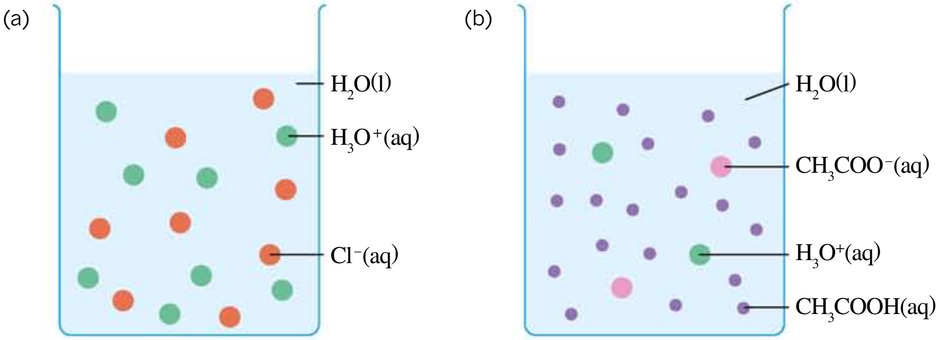


FIGURE 15.2.2 (a) In a 1.0 M solution of a hydrochloric acid the acid molecules are completely ionised in water. (b) However, in a 1.0 M solution of ethanoic acid only a small proportion of the ethanoic acid molecules are ionised.

CHEMFILE

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 M 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 M ethanoic acid, the light only glows faintly. This is further evidence that hydrochloric acid is a stronger acid than ethanoic acid. The brighter light indicates the greater number of ions present in a solution of hydrochloric acid than in ethanoic acid.

Strong bases

The ionic compound sodium oxide (Na_2O) 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^-.

Weak bases

Ammonia is a covalent molecular compound that ionises in water by accepting a proton. This ionisation can be represented by the equation:

$$\underset{\text{base}}{NH_3(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Ammonia behaves as a base because it gains a proton. Water has donated a proton and so it behaves as an acid.

Only a small proportion of ammonia molecules are ionised at any instant, so a 1.0 M 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.

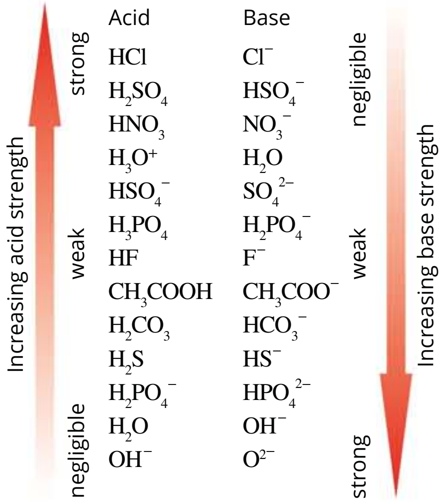
Relative strength of conjugate acid–base pairs

You will recall from section 15.1 that conjugate acids and bases differ by one proton (H^+). In the reaction represented by the equation:

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

HF is the conjugate acid of F^- and OH^- is the conjugate base of H_2O. HF and F^- are a conjugate acid–base pair. H_2O and OH^- are another conjugate acid–base pair in this reaction.

The stronger an acid is, the weaker is its conjugate base. Similarly, the stronger a base is, the weaker is its conjugate acid. The relative strength of some conjugate acid–base pairs is shown in Figure 15.2.4.



Acid	Base
HCl	Cl^-
H_2SO_4	HSO_4^-
HNO_3	NO_3^-
H_3O^+	H_2O
HSO_4^-	SO_4^{2-}
H_3PO_4	$H_2PO_4^-$
HF	F^-
CH_3COOH	CH_3COO^-
H_2CO_3	HCO_3^-
H_2S	HS^-
$H_2PO_4^-$	HPO_4^{2-}
H_2O	OH^-
OH^-	O^{2-}

FIGURE 15.2.4 The relative strength of some conjugate acid–base pairs.

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.

CHEMFILE

Super acids

Fluorosulfuric acid (HSO_3F) is one of the strongest acids known. It has a similar geometry to that of the sulfuric acid molecule (Figure 15.2.3). 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.

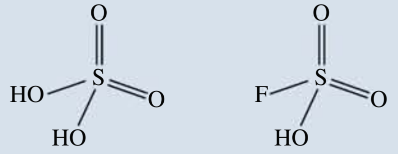


FIGURE 15.2.3 Structure of sulfuric acid (left) and fluorosulfuric acid (right) molecules.

Fluorosulfuric acid is classified as a **super acid**. Super acids are defined as 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 1 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.

However, in both cases, the hydrogen chloride is completely ionised—it is a strong acid. Similarly a solution of ethanoic acid may be concentrated or dilute. However, as it is partially ionised, it is a weak acid (Figure 15.2.5).

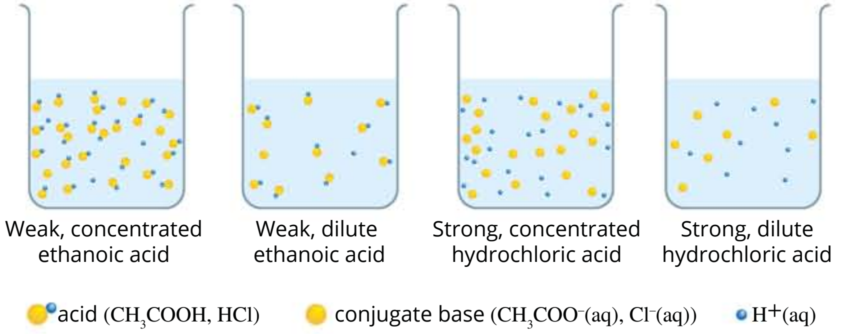


FIGURE 15.2.5 The concentration of ions in an acid solution depends on both the concentration and strength of the acid.

Terms such as 'weak' or 'strong' acids, or solutions classified as 'dilute' or 'concentrated' are qualitative (or descriptive) terms. Solutions can be given accurate, quantitative descriptions by stating concentrations in mol L^{-1} or g L^{-1}.

15.2 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.

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. 1.0 M solutions of which acid would you expect to be a better conductor of electricity? Explain why.

15.3 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 learned 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 as represented by the equation:

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

The production of the H_3O^+ ion and OH^- ion within this reaction can be seen in Figure 15.3.1.

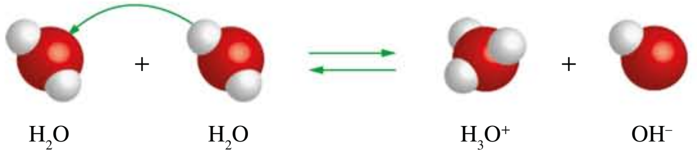


FIGURE 15.3.1 The ionisation of water molecules.

Pure water undergoes this **self-ionisation** to a very small extent. In this reaction, water behaves as both a very weak acid and as 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} M. 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:

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\ M^2 \text{ at } 25°C$$

Square brackets [ ] are often used to represent molar concentration.

Acidic and basic solutions

In solutions of acidic substances, H_3O^+ ions are formed by 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} M at 25°C. Since the product $[H_3O^+][OH^-]$ remains constant, the concentration of OH^- ions in an **acidic solution** at this temperature must be less than 10^{-7} M.

The opposite is true for **basic solutions**. The concentration of OH^- ions in a basic solution is greater than 10^{-7} M and that of H_3O^+ ions is less than 10^{-7} M.

In summary, at 25°C:

- pure water and **neutral solutions**: $[H_3O^+] = [OH^-] = 10^{-7}$ M
- acidic solutions: $[H_3O^+] > 10^{-7}$ M and $[OH^-] < 10^{-7}$ M
- basic solutions: $[H_3O^+] < 10^{-7}$ M and $[OH^-] > 10^{-7}$ M

The higher the concentration of H_3O^+ ions in a solution, the more acidic the solution is.

Calculating the concentration of H_3O^+ in aqueous solutions

The expression for K_w can be used to determine the concentrations of hydronium and hydroxide ions in solution, knowing that the value of K_w in solutions at 25°C is 1.00×10^{-14} M^2 .

Worked example 15.3.1

CALCULATING THE CONCENTRATION OF HYDRONIUM AND HYDROXIDE IONS IN AN AQUEOUS SOLUTION

For a 0.10 M HCl solution at 25°C, calculate the concentration of:

- H_3O^+ ions
- OH^- ions.

Thinking	Working
Find the concentration of the 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 M HCl will produce a solution with a concentration of H_3O^+ ions of 0.10 M: i.e. $[H_3O^+] = 0.10$ M
Use the expression for the ionisation constant of water to calculate the concentration of OH^- ions.	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ M^2 $[OH^-] = \frac{1.00 \times 10^{-14}}{[H_3O^+]}$ Since $[H_3O^+] = 0.10$ M $[OH^-] = \frac{1.00 \times 10^{-14}}{0.10}$ $= 1.0 \times 10^{-13}$ M

Worked example 15.3.1: Try yourself

CALCULATING THE CONCENTRATION OF HYDRONIUM AND HYDROXIDE IONS IN AN AQUEOUS SOLUTION

For a 5.6×10^{-6} M HNO_3 solution at 25°C, calculate the concentration of:

- H_3O^+
- 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 we describe hydrogen ion concentration. The use of pH greatly simplifies the measurement and calculation of acidity. Since the scale is based upon the negative logarithm of the hydrogen ion concentration, the pH of a solution *decreases* as the concentration of hydrogen ions *increases*.

pH of acidic and basic solutions

Figure 15.3.2 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 15.3.1.

FIGURE 15.3.2 A pH meter is used to measure the acidity of a solution.

TABLE 15.3.1 pH values of some common substances at 25°C

Solution	pH	$[H_3O^+]$ (M)	$[OH^-]$ (M)	$[H_3O^+] \times [OH^-]$
1.0 M HCl	0.0	1	10^{-14}	10^{-14}
Lemon juice	3.0	10^{-3}	10^{-11}	10^{-14}
Vinegar	4.0	10^{-4}	10^{-10}	10^{-14}
Tomatoes	5.0	10^{-5}	10^{-9}	10^{-14}
Rain water	6.0	10^{-6}	10^{-8}	10^{-14}
Pure water	7.0	10^{-7}	10^{-7}	10^{-14}
Seawater	8.0	10^{-8}	10^{-6}	10^{-14}
Soap	9.0	10^{-9}	10^{-5}	10^{-14}
Oven cleaner	13.0	10^{-13}	10^{-1}	10^{-14}
1.0 M NaOH	14.0	10^{-14}	10^{-0}	10^{-14}

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.

The reactions of acids and bases are important in a large variety of everyday applications. The high acidity of gastric juices is essential for protein digestion in the stomach. There is a complex system of pH control in your blood because even small deviations from the normal pH range of 7.35–7.45 for any length of time can lead to serious illness and death.

Indicators

One of the characteristic properties of acids and bases is their ability to change the colour of certain plant extracts. Litmus is a purple dye obtained from lichen. In the presence of acids, litmus turns red. The colouring of rose petals, blackberries and red cabbage is also altered by acids and bases. Such plant extracts are called indicators. (Common indicators and their pH ranges can be seen in Figure 15.3.3.)

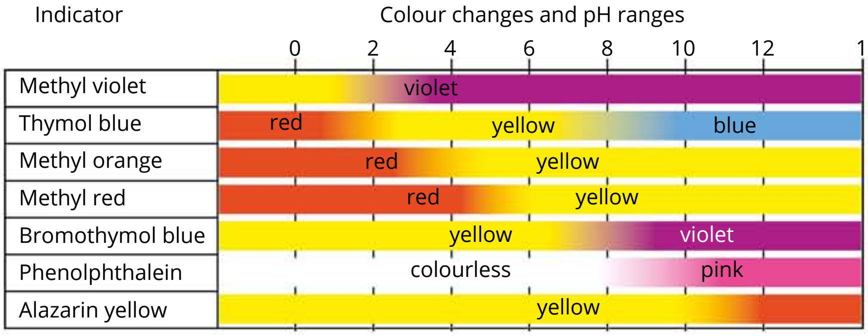


FIGURE 15.3.3 Common indicators and their pH ranges.

Indicators are themselves acids or bases. They change from one colour in acid to another in basic solution. Common indicators include methyl orange, phenolphthalein and litmus. The indicators that undergo a single colour change are also used for many analyses.

Universal indicator

Universal indicator (Figure 15.3.4) 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 15.3.4 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.

Calculations involving pH

pH can be calculated using the formula pH = $-\log_{10}[H_3O^+]$. Your scientific calculator has a logarithm function that will simplify pH calculations.

Worked example 15.3.2

CALCULATING THE pH OF AN AQUEOUS SOLUTION FROM $[H_3O^+]$

What is the pH of a solution in which the concentration of $[H_3O^+]$ is 0.14 M? Express your answer to two decimal places.

Thinking	**Working**
Write down the concentration of $[H_3O^+]$ ions in the solution.	$[H_3O^+] = 0.14$ M
Substitute the value of $[H_3O^+]$ into: $\text{pH} = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine the answer.	$\text{pH} = -\log_{10}[H_3O^+]$ $= -\log_{10}(0.14)$ (use your calculator) $= 0.85$

Worked example 15.3.2: Try yourself

CALCULATING THE pH OF AN AQUEOUS SOLUTION FROM $[H_3O^+]$

What is the pH of a solution in which the concentration of $[H_3O^+]$ is 6×10^{-9} M? Express your answer to two significant figures.

Worked example 15.3.3

CALCULATING pH IN A SOLUTION OF A BASE

What is the pH of a 0.005 M 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 the concentration of $[OH^-]$ ions.	$[OH^-] = 2 \times [Ba(OH)_2]$ $= 2 \times 0.005$ M $= 0.01$ M
Determine the $[H_3O^+]$ in the diluted solution by substituting the $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\ M^2$	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\ M^2$ $[H_3O^+] = \frac{K_w}{[OH^-]}$ $= \frac{1.00 \times 10^{-14}}{0.01}$ $= 1 \times 10^{-12}$ M
Substitute the value of $[H_3O^+]$ into: $\text{pH} = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine the answer.	$\text{pH} = -\log_{10}[H_3O^+]$ $= -\log_{10}(1 \times 10^{-12})$ (use your calculator) $= 12.0$

Worked example 15.3.3: Try yourself

CALCULATING pH IN A SOLUTION OF A BASE

What is the pH of a 0.01 M solution of $Ba(OH)_2$ at 25°C?

Worked example 15.3.4

CALCULATING pH IN A SOLUTION WHERE THE 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 $c = \frac{0.025}{0.100}$ $= 0.25$ M
Determine the $[H_3O^+]$ in the diluted solution by substituting the $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\ M^2$	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\ M^2$ $[H_3O^+] = \frac{K_w}{[OH^-]}$ $= \frac{1.00 \times 10^{-14}}{0.25}$ $= 4.0 \times 10^{-14}$ M
Substitute the value of $[H_3O^+]$ into: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine the answer.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(4.0 \times 10^{-14})$ (use your calculator) $= 13.40$

Worked example 15.3.4: Try yourself

CALCULATING pH IN A SOLUTION WHERE THE 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 15.3.5

CALCULATING $[H_3O^+]$ IN A SOLUTION OF A GIVEN pH

Calculate the $[H_3O^+]$ in a solution of pH 5.0 at 25°C.

Thinking	**Working**
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.	$[H_3O^+] = 10^{-pH}$ $= 10^{-5.0}$ $= 1 \times 10^{-5}$ M (or 0.00001 M)

Worked example 15.3.5: Try yourself

CALCULATING $[H_3O^+]$ IN A SOLUTION OF A GIVEN pH

Calculate the $[H_3O^+]$ in a solution of pH 10.4 at 25°C.

EXTENSION

Effect of temperature on pH

Earlier, we defined the ionisation constant of water as:

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\ M^2 \text{ at } 25°C$$

You can use this relationship to calculate either $[H_3O^+]$ or $[OH^-]$ at 25°C in different solutions. But what happens if the temperature is not 25°C?

From experimental data we know that the value of K_w increases as the temperature increases as shown in Table 15.3.2.

The pH of pure water is only 7.00 at 25°C. At other temperatures, even though the pH of pure water is not equal to 7.00, it can still be described as neutral because the concentrations of H_3O^+ and OH^- ions are equal.

TABLE 15.3.2 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

15.3 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:
  $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ M^2 at 25°C
- The concentration of $[H_3O^+]$ is measured using the pH scale:
  $$pH = -\log_{10}[H_3O^+]$$
- At 25°C the pH of a neutral solution is 7. The pH of an acidic solution is less than 7 and the pH of a basic solution is greater than 7.

KEY QUESTIONS

1 Calculate $[OH^-]$ at 25°C in an aqueous solution with $[H_3O^+] = 0.001$ M.
2 What is $[OH^-]$ in a solution at 25°C with $[H_3O^+] = 5.70 \times 10^{-19}$ M?
3 Calculate $[H_3O^+]$ at 25°C in an aqueous solution in which $[OH^-] = 1.0 \times 10^{-5}$ M.
4 What is the pH of a solution in which $[H_3O^+] = 0.01$ M?
5 Calculate the pH of a 0.001 M 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 mL solution that contains 0.365 g of dissolved HCl.

15.4 Dilution of acids and bases

Although acids are frequently purchased as concentrated solutions, you will often need to use them in a more diluted form. 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

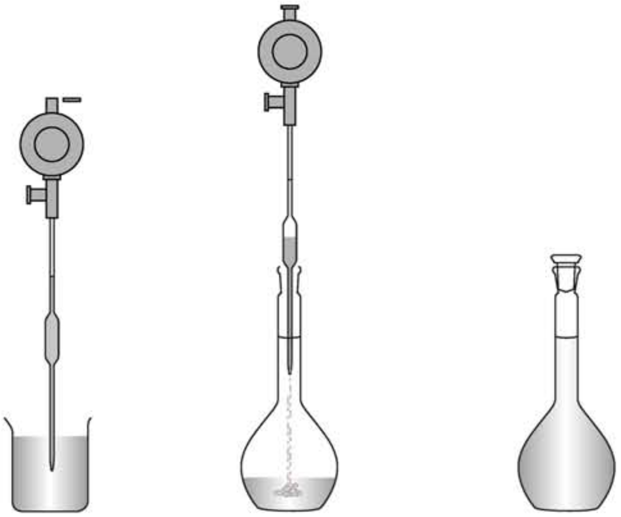
The **concentration** of acids and bases is usually expressed in units of mol L^{-1} or M. This is also referred to as molar concentration or **molarity**.

You will recall from Chapter 14 that 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 15.4.1. This is known as a **dilution**.



Measure out 10.0 mL of 10.0 mol L^{-1} HCl with a pipette.

Transfer to a 100.0 mL volumetric flask partly filled with water.

Fill the flask with distilled water to the calibration mark and shake thoroughly.

FIGURE 15.4.1 Preparing a 1.00 M HCl solution by diluting a 10.0 M 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; the volume of the solution increases and the concentration decreases. The change in concentration or volume can be calculated using the formula:

$$c_1V_1 = c_2V_2$$

where c_1 and V_1 are the initial concentration and volume, and c_2 and V_2 are the concentration and volume after dilution.

You can calculate the concentration of a dilute acid if you know the:

- volume of the concentrated solution
- concentration (molarity) of the concentrated solution
- total volume of water added.

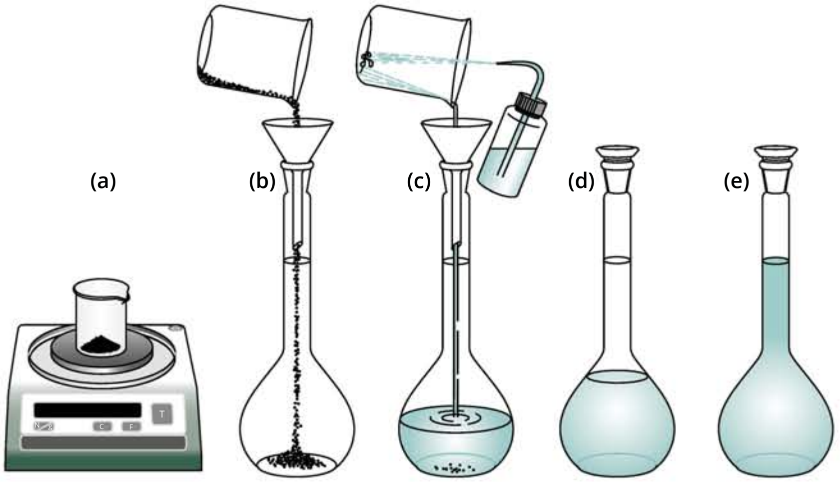
The molar concentration of some concentrated acids are shown in Table 15.4.1.

TABLE 15.4.1 Molar concentrations of some concentrated acids

Concentrated acid (% by mass)	Formula	Molarity (M)
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**, or
- dissolving a weighed amount of the base in a measured volume of water, as shown in Figure 15.4.2.



(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.

FIGURE 15.4.2 Preparing a solution by dissolving a weighed amount of base in a measured volume of water.

Worked example 15.4.1

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 M 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 M 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.	10.0 mL was added to 5.0 mL, the final volume is 15.0 mL. (In practice, small volume changes can occur when solutions are mixed; we will assume no volume changes occur.) $c_1 = 1.2$ M $V_1 = 5.0$ mL $V_2 = 15.0$ 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.	$c_2 = \frac{c_1 \times V_1}{V_2}$ $= 1.2 \times \frac{5.0}{15.0}$ $= 0.40$ M

Worked example 15.4.1: 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 M HNO_3.

Worked example 15.4.2

CALCULATING THE VOLUME OF WATER TO BE ADDED IN A DILUTION

How much water must be added to 30.0 mL of 2.50 M HCl to dilute the solution to 1.00 M?

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 M 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.	$c_1 = 2.50$ M $V_1 = 30.0$ mL $c_2 = 1.00$ M 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.	$V_2 = \frac{c_1 \times V_1}{c_2}$ $= \frac{2.50 \times 30.0}{1.00}$ $= 75.0$ 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 15.4.2: 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 M NaOH to dilute the solution to 2.00 M?

EFFECT OF DILUTION ON pH OF STRONG ACIDS AND BASES

Consider a 0.1 M solution of hydrochloric acid. HCl is a strong acid, so the concentration of H_3O^+ ions in this solution is 0.1 M. Since $\text{pH} = -\log_{10}[H_3O^+]$, the pH of this solution is 1.0 (see section 15.3 if you need to review this formula).

If this 1.0 mL solution is diluted by a factor of 10 to 10.0 mL by the addition of 9.0 mL of water, the concentration of H_3O^+ ions decreases to 0.01 M 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, note that 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.

We 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 15.4.3

CALCULATING THE pH OF A DILUTED ACID

5.0 mL of 0.010 M 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.	$c_1 = 0.010$ M $V_1 = 5.0$ mL $V_2 = 100.0$ mL $c_2 = ?$
Calculate c_2, which is the concentration of H_3O^+ after dilution, by transposing the formula: $c_1V_1 = c_2V_2$	$c_2 = \frac{c_1 \times V_1}{V_2}$ $= \frac{0.010 \times 5.0}{100.0}$ $= 0.00050$ M
Calculate pH using: $\text{pH} = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine pH.	$\text{pH} = -\log_{10}[H_3O^+]$ $= -\log_{10}(0.00050)$ $= 3.30$

Worked example 15.4.3: Try yourself

CALCULATING THE pH OF A DILUTED ACID

10.0 mL of 0.1 M HCl is diluted to 30.0 mL. Calculate the pH of the diluted solution.

Calculation of the pH of a base after dilution

The following steps and flow chart shown in Figure 15.4.3 show the sequence used to calculate the pH of a base after it has been diluted. Remember that pH is a measure of the hydronium ion concentration.

1 Calculate $[OH^-]$ in the diluted solution.

2 Calculate $[H_3O^+]$ using the expression for the ionic product of water:

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \text{ M}^2$$

3 Calculate the pH of the solution using $pH = -\log_{10}[H_3O^+]$ (Figure 15.4.3).

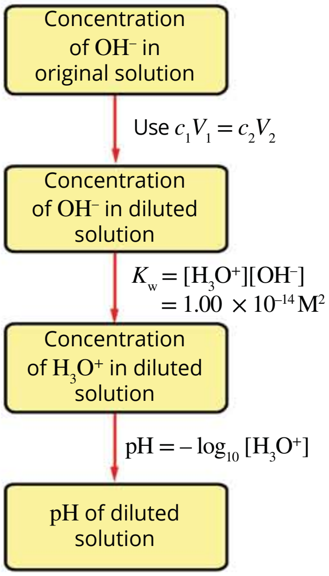


FIGURE 15.4.3 Calculating the pH of a diluted solution of a base.

Worked example 15.4.4

CALCULATING THE pH OF A DILUTED BASE

10.0 mL of 0.1 M 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 = 0.1 M V_1 = 10.0 mL V_2 = 100.0 mL c_2 = ?
Calculate c_2, which is $[OH^-]$ after dilution, by transposing the formula: $c_1V_1 = c_2V_2$	$c_2 = \frac{c_1 \times V_1}{V_2}$ $= \frac{0.1 \times 10.0}{100.0}$ $= 0.01$ M
Determine $[H_3O^+]$ in the diluted solution by substituting $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ M^2	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ M^2 $[H_3O^+] = \frac{K_w}{[OH^-]}$ $= \frac{1.00 \times 10^{-14}}{0.01}$ $= 1 \times 10^{-12}$ M
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 15.4.4: Try yourself

CALCULATING THE pH OF A DILUTED BASE

15.0 mL of 0.02 M KOH is diluted to 60.0 mL. Calculate the pH of the diluted solution.

15.4 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 M HCl. What is the concentration of the diluted acid?

2 How much water must be added to 10 mL of a 2.0 M sulfuric acid solution to dilute it to 0.50 M?

3 What volume of water must be added to dilute a 20.0 mL volume of 0.600 M HCl to 0.100 M?

4 Describe the effect on the pH of a 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 M 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 M $HNO_3(aq)$

b 0.03 M HCl(aq)

c 0.01 M NaOH(aq)

d $10^{-4.5}$ M HCl(aq)

e 0.005 M $Ba(OH)_2(aq)$

15.5 Reactions of acids and bases

Acids were originally grouped together because of their similar chemical behaviour. Chemists use indicators, such as litmus, to identify acidic solutions. Acids and bases react readily with many other chemicals, and some of the early definitions of acids and bases were derived from these reactions.

In this section, you will learn to use the patterns in the reactions of acids and bases to predict the products that are formed.

GENERAL REACTION TYPES INVOLVING ACIDS AND BASES

Acids and bases react in many ways. However, it is possible to group some reactions together according to the similarity of the reactants involved and products formed. While the identification of products should be based on experimental data, these groups, or reaction types, can be useful. The reaction types you will be studying are the reaction of acids with:

- metal hydroxides
- metal carbonates and hydrogen carbonates
- reactive metals.

ACIDS AND METAL HYDROXIDES

Soluble metal hydroxides, such as NaOH, dissociate in water to form metal **cations** and hydroxide ions, $OH^-(aq)$. The products of a reaction of an acid with a metal hydroxide are an ionic compound, called a **salt**, and water.

The general rule for the reaction between acids and metal hydroxides can be expressed as:

acid + metal hydroxide → salt + water

For example, solutions of sulfuric acid and sodium hydroxide react to form sodium sulfate and water. This can be represented by the full (or overall) equation:

$$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

The salt formed in the reaction between sulfuric acid and sodium hydroxide is sodium sulfate. If water was evaporated from the reaction mixture, solid sodium sulfate would be left behind.

Salts

Salts consist of the positive ion or cation from the base and the negative ion or **anion** from the acid. In Chapter 4, you saw that the names of anions that contain oxygen often end in '-ate'; for example, sulfate, phosphate. The names of anions that do not contain oxygen end in '-ide'; for example, chloride, bromide.

Table 15.5.1 lists the names of salts formed from some **neutralisation reactions** of acids with metal hydroxides. Note that the name of the positive ion is listed first and the name of the negative ion from the acid is listed second.

TABLE 15.5.1 Salts formed from some common neutralisation reactions

Reactants (acid + metal hydroxide)	Name of salt formed	Formulas of ions present in the salt solution
Hydrochloric acid + potassium hydroxide	Potassium chloride	$K^+(aq) + Cl^-(aq)$
Hydrochloric acid + magnesium hydroxide	Magnesium chloride	$Mg^{2+}(aq) + Cl^-(aq)$
Nitric acid + sodium hydroxide	Sodium nitrate	$Na^+(aq) + NO_3^-(aq)$
Sulfuric acid + zinc hydroxide	Zinc sulfate	$Zn^{2+}(aq) + SO_4^{2-}(aq)$
Phosphoric acid + potassium hydroxide	Potassium phosphate	$K^+(aq) + PO_4^{3-}(aq)$
Ethanoic acid + calcium hydroxide	Calcium ethanoate	$Ca^{2+}(aq) + CH_3COO^-(aq)$

IONIC EQUATIONS

The hydroxide ions from metal hydroxides, such as sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$) and magnesium hydroxide ($Mg(OH)_2$), react readily with the hydrogen ion ($H^+(aq)$) from acids.

The reaction between an acid and a metal hydroxide can be represented by an **ionic equation** as well as by an overall equation. You were introduced to ionic equations when studying precipitation reactions in Chapter 13, page 330.

When writing ionic equations remember that:

- ionic equations are balanced with respect to both the number of atoms of each element and charge
- **spectator ions** are ions that are dissolved in the solution and are present as ions before and after the reaction, but are not involved in the reaction. These are omitted from the ionic equation
- if a reactant or product is a solid, liquid or a gas, it cannot be written as ions and it must be present in the ionic equation.

You also need to remember when writing ionic equations for neutralisation reactions:

- strong acids ionise in solution and are written as ions; for example, HCl in solution is written as $H_3O^+(aq) + Cl^-(aq)$. For the sake of simplicity, the hydronium ion ($H_3O^+(aq)$) can be written as a hydrogen ion ($H^+(aq)$)
- metal hydroxides and salts are ionic and, if soluble, dissociate in solution and are written as ions; for example, KOH dissolving in water is written as $KOH(s) \rightarrow K^+(aq) + OH^-(aq)$
- water is a covalent molecular substance that does not ionise to any significant extent. It is written as $H_2O(l)$.

Figure 15.5.1 is a diagrammatic representation of the ions in solutions of HCl and NaOH when mixed in a neutralisation reaction.

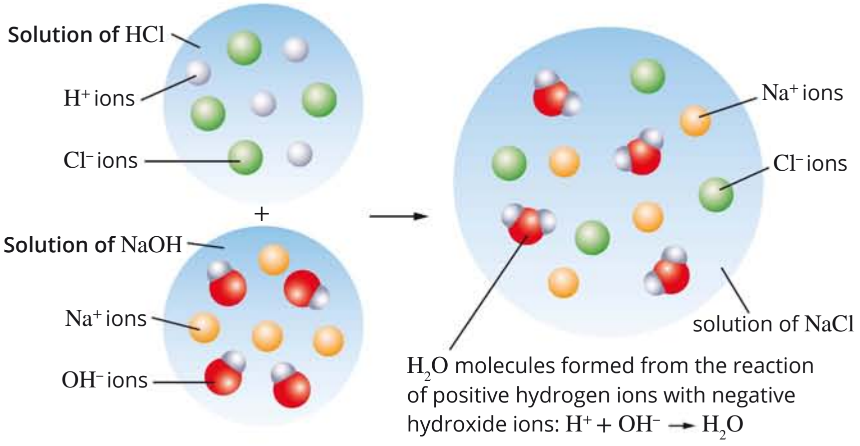


FIGURE 15.5.1 A representation of the reaction between $H^+(aq)$ and $OH^-(aq)$ ions that occurs when solutions of HCl and NaOH are mixed.

Worked example 15.5.1 indicates the steps to follow when writing ionic equations for the reactions of acids.

Worked example 15.5.1

WRITING AN IONIC EQUATION FOR AN ACID–BASE REACTION

Write an ionic equation for the reaction that occurs when hydrochloric acid is added to sodium hydroxide solution. A representation of this reaction is shown in Figure 15.5.1.

Thinking	Working
What is the general reaction? Identify the products formed.	acid + metal hydroxide → salt + water A solution of sodium chloride and water is formed.
Identify the reactants and products. Indicate the state of each, i.e. (aq), (s), (l) or (g).	Reactants: HCl(aq) is ionised in solution, forming $H^+(aq)$ and $Cl^-(aq)$. NaOH(aq) is dissociated in solution, forming $Na^+(aq)$ and $OH^-(aq)$. Products: Sodium chloride is dissociated and exists as $Na^+(aq)$ and $Cl^-(aq)$. Water is a molecular compound and its formula is $H_2O(l)$.
Write the equation showing all reactants and products, in ionised form where possible. (There is no need to balance the equation yet.)	$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$
Identify the spectator ions: the ions that have an (aq) state both as a reactant and as a product.	$Na^+(aq)$ and $Cl^-(aq)$
Rewrite the equation without the spectator ions. Balance the equation with respect to number of atoms of each element and charge.	$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ Note that if hydronium ions are represented as $H_3O^+(aq)$, rather than as $H^+(aq)$, this reaction would be written as: $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$

Worked example 15.5.1: Try yourself

WRITING AN IONIC EQUATION FOR AN ACID–BASE REACTION

Write an ionic equation for the reaction that occurs when sulfuric acid is added to potassium hydroxide solution.

NEUTRALISATION REACTIONS

If a solution of a metal hydroxide is added to a solution of an acid, the hydroxide ions will react with the hydronium ions. The acid and base are said to have been **neutralised** at the point when all the hydroxide ions have reacted with all the hydronium ions, forming water (H_2O).

CHEMISTRY IN ACTION

Benefits of neutralisation

A neutralisation reaction allows for the adjustment of the acidity of a solution. If excess acid is harmful, it can be neutralised by adding a base. Conversely, an environment that is too alkaline can be neutralised by adding an acid. Common examples of this include:

- Methanoic acid (otherwise known as formic acid) is released from the sting of ants, bees and nettles (Figure 15.5.2). If affected skin is rinsed with limewater or a dilute solution of ammonia, the acid becomes neutralised and is no longer painful to the person affected.

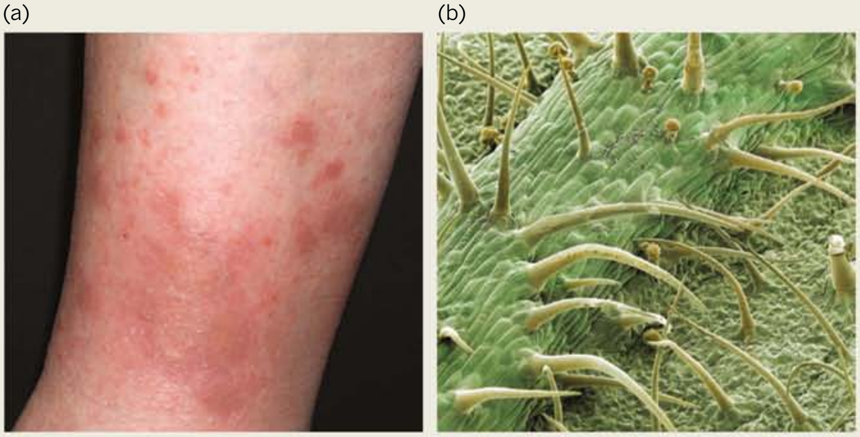


FIGURE 15.5.2 (a) Irritation on the leg of a person bitten by ants. (b) Scanning electron microscope image of a nettle (*Urtica* sp.) surface showing stinging, hair-like structures (colourised).

- The venom from wasps is alkaline. A common treatment for wasp bites is to rinse the site of the bite with vinegar (ethanoic acid, CH_3COOH) as this neutralises the base within the venom.
- Excess acid in the stomach is the cause of indigestion. This condition is treated with substances that neutralise acids. Antacid tablets are bases that neutralise the excess acid in the stomach.
- The bacteria occurring on tooth enamel feed on the sugars present in food. The products of their metabolism are acids that attack the enamel, which leads to tooth decay. This is why toothpastes (Figure 15.5.3) are weak bases.

FIGURE 15.5.3 A selection of toothpastes. These products are advertised as providing protection against tooth cavities, gum disease and tooth decay.

ACIDS AND METAL CARBONATES

The weathering of buildings and statues (Figure 15.5.4) is due in part to the reaction between acid rain and the carbonate minerals in the stone.

Acids reacting with metal carbonates and metal hydrogen carbonates produce carbon dioxide gas, together with a salt and water. Metal carbonates include sodium carbonate (Na_2CO_3), magnesium carbonate ($MgCO_3$) and calcium carbonate ($CaCO_3$).

The general reaction for metal carbonates with acids can be summarised as:

acid + metal carbonate → salt + water + carbon dioxide

For example, a solution of hydrochloric acid reacting with sodium carbonate solution produces a solution of sodium chloride, water and carbon dioxide gas. The reaction is represented by the equation:

$$2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

The reaction between hydrochloric acid and sodium carbonate is represented in Figure 15.5.5.

FIGURE 15.5.4 This statue has been heavily eroded by acid rain, which reacts with carbonate salts in limestone. Acid rain is formed when gases, such as sulfur dioxide and nitrogen oxides, dissolve in water to form acidic solutions.

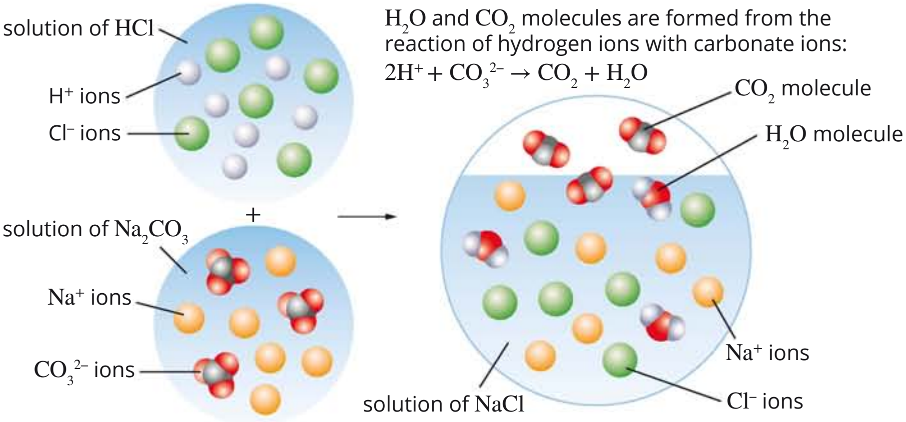


FIGURE 15.5.5 The reaction between solutions of sodium carbonate and hydrochloric acid.

Metal hydrogen carbonates (also known as bicarbonates) include sodium hydrogen carbonate ($NaHCO_3$), potassium hydrogen carbonate ($KHCO_3$) and calcium hydrogen carbonate ($Ca(HCO_3)_2$). Acids added to metal hydrogen carbonates also produce carbon dioxide together with a salt and water. The general reaction is:

acid + metal hydrogen carbonate → salt + water + carbon dioxide

For example, when solutions of hydrochloric acid and sodium hydrogen carbonate are mixed, the following reaction occurs:

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

The reactions between acids and metal carbonates, and reactions between acids and metal hydrogen carbonates, can also be represented as ionic equations by following steps similar to the steps for writing reactions between acids and bases.

CHEMFILE

Bicarbonate of soda

Self-raising flour contains tartaric acid and some sodium hydrogen carbonate (bicarbonate of soda) (Figure 15.5.6). It is used in baking cakes because on heating in the oven, the acid and hydrogen carbonate react. Carbon dioxide is released, which causes the cake mixture to rise.

FIGURE 15.5.6 Bicarbonate of soda leads to the production of carbon dioxide causing these muffins to rise.

Worked example 15.5.2

WRITING IONIC EQUATIONS FOR REACTIONS BETWEEN ACIDS AND METAL CARBONATES

What products are formed when a dilute solution of nitric acid is added to solid magnesium carbonate? Write an ionic equation for this reaction.

Thinking	Working
What is the general reaction? Identify the products.	acid + metal carbonate → salt + water + carbon dioxide Products of this reaction are magnesium nitrate in solution, water and carbon dioxide gas.
Identify the reactants and products. Indicate the state of each, i.e. (aq), (s), (l) or (g).	Reactants: Nitric acid is ionised in solution, forming $H^+(aq)$ and $NO_3^-(aq)$ ions. Magnesium carbonate is an ionic solid, $MgCO_3(s)$. Products: Magnesium nitrate is dissociated into $Mg^{2+}(aq)$ and $NO_3^-(aq)$ ions. Water has the formula $H_2O(l)$. Carbon dioxide has the formula $CO_2(g)$.
Write the equation showing all reactants and products. (There is no need to balance the equation yet.)	$H^+(aq) + NO_3^-(aq) + MgCO_3(s) \rightarrow Mg^{2+}(aq) + NO_3^-(aq) + H_2O(l) + CO_2(g)$
Identify the spectator ions.	$NO_3^-(aq)$
Rewrite the equation without the spectator ions. Balance the equation with respect to number of atoms of each element and charge.	The equation with spectator ions omitted is: $H^+(aq) + MgCO_3(s) \rightarrow Mg^{2+}(aq) + H_2O(l) + CO_2(g)$ The balanced equation is: $2H^+(aq) + MgCO_3(s) \rightarrow Mg^{2+}(aq) + H_2O^+(l) + CO_2(g)$ Note that if hydronium ions are represented as $H_3O^+(aq)$, rather than as $H^+(aq)$, this reaction would be written as: $2H_3O^+(aq) + MgCO_3(s) \rightarrow Mg^{2+}(aq) + 3H_2O(l) + CO_2(g)$

Worked example 15.5.2: Try yourself

WRITING IONIC EQUATIONS FOR REACTIONS BETWEEN ACIDS AND METAL CARBONATES

What products are formed when a solution of hydrochloric acid is added to a solution of sodium hydrogen carbonate? Write an ionic equation for this reaction.

TESTING FOR CARBONATE SALTS

Acids can be used to detect the presence of carbonate salts. Carbon dioxide is produced when an acid is added to a carbonate.

The **limewater test** is a simple laboratory test used to confirm the presence of carbon dioxide gas. Limewater is a saturated solution of calcium hydroxide ($Ca(OH)_2$). When carbon dioxide is bubbled through this solution, it will turn 'milky' or 'cloudy' in appearance (Figure 15.5.7) due to the precipitation of calcium carbonate:

$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

FIGURE 15.5.7 Limewater test. Carbon dioxide is bubbled through limewater, turning the limewater cloudy.

ACIDS AND REACTIVE METALS

When dilute acids are added to main group metals and some transition metals, bubbles of hydrogen gas are released and a salt is formed. In general, the equation for the reaction is:

acid + reactive metal → salt + hydrogen

Reactive metals include calcium, magnesium, iron and zinc, but *not* copper, silver or gold. For example, the reaction between dilute hydrochloric acid and zinc metal can be seen in Figure 15.5.8 and represented by the equation:

$$2HCl(aq) + Zn(s) \rightarrow ZnCl_2(aq) + H_2(g)$$

This reaction can also be represented by an ionic equation. In an aqueous solution, the hydrochloric acid is ionised and the salt, zinc chloride (a soluble ionic compound), is dissociated. The ionic equation can be determined as shown in the Worked example 15.5.3.

FIGURE 15.5.8 Hydrogen gas is produced from the reaction of zinc with dilute hydrochloric acid.

Worked example 15.5.3

WRITING IONIC EQUATIONS FOR REACTIONS BETWEEN ACIDS AND REACTIVE METALS

Write an ionic equation for the reaction that occurs when dilute hydrochloric acid is added to a sample of zinc metal.

Thinking	Working
What is the general reaction? Identify the products formed.	acid + reactive metal → salt + hydrogen Hydrogen gas and zinc chloride solution are produced.
Identify the reactants and products. Indicate the state of each, i.e. (aq), (s), (l) or (g).	Reactants: zinc is a solid, Zn(s). Hydrochloric acid is ionised, forming $H^+(aq)$ and $Cl^-(aq)$ ions. Products: hydrogen gas, $H_2(g)$. Zinc chloride is dissociated into $Zn^{2+}(aq)$ and $Cl^-(aq)$ ions.
Write the equation showing all reactants and products. (There is no need to balance the equation yet.)	$H^+(aq) + Cl^-(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + Cl^-(aq) + H_2(g)$
Identify the spectator ions.	$Cl^-(aq)$
Rewrite the equation without the spectator ions. Balance the equation with respect to number of atoms of each element and charge.	$2H^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + H_2(g)$

Worked example 15.5.3: Try yourself

WRITING IONIC EQUATIONS FOR REACTIONS BETWEEN ACIDS AND REACTIVE METALS

Write an ionic equation for the reaction that occurs when aluminium is added to a dilute solution of hydrochloric acid.

15.5 Review

SUMMARY

- Generalisations can be made about the likely products of reactions involving acids and bases:

  acid + metal hydroxide → salt + water

  acid + metal carbonate → salt + water + carbon dioxide

  acid + metal hydrogen carbonate → salt + water + carbon dioxide

  acid + reactive metal → salt + hydrogen
- Each of these reactions can be represented by full and ionic equations.
- An ionic equation only shows those ions, atoms or molecules that take part in the reaction.
- Spectator ions (ions that do not take part in the reaction) are not included in ionic equations.
- Ionic equations are balanced with respect to both the number of atoms of each element and charge.

KEY QUESTIONS

1 Write full and ionic chemical equations for the reactions between:
  a magnesium and sulfuric acid
  b calcium and hydrochloric acid
  c zinc and ethanoic acid
  d aluminium and nitric acid.

2 Name the salt produced in each of the reactions in Question 1.

3 For each of the following reactions write:
    i a full chemical equation to represent the reaction (remember to include states)
    ii an ionic equation.
  a Solid zinc oxide and sulfuric acid
  b Solid calcium and nitric acid
  c Solid copper(II) hydroxide and nitric acid
  d Solid magnesium hydrogen carbonate and hydrochloric acid
  e Solid tin(II) carbonate and sulfuric acid

4 Predict the products of the following reactions and write full and ionic chemical equations for each.
  a A solution of sulfuric acid is added to a solution of potassium hydroxide.
  b Nitric acid solution is mixed with sodium hydroxide solution.
  c Hydrochloric acid solution is poured on to some solid magnesium hydroxide.
  d Blue copper(II) carbonate powder is added to dilute sulfuric acid.
  e Dilute hydrofluoric acid is mixed with a solution of potassium hydrogen carbonate.
  f Dilute nitric acid is added to a spoon coated with solid zinc.
  g Hydrochloric acid solution is added to some marble chips (calcium carbonate).
  h Solid bicarbonate of soda (sodium hydrogen carbonate) is mixed with vinegar (a dilute solution of ethanoic acid).

15.6 Ocean acidity

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. As well as contributing to an increase in global warming, the increase in atmospheric carbon dioxide is also responsible for an increase in **ocean acidity**.

In this section, you will apply your understanding of acid–base chemistry to study the effects of increasing ocean acidity. This is a significant environmental, social and economic issue. You will investigate the chemistry behind ocean acidity and the impact of increasing levels of atmospheric carbon dioxide. You will also consider the effects of increased ocean acidity on the natural and human environment.

CARBON DIOXIDE IN NATURE

Carbon dioxide is essential to life on Earth. Through the carbon cycle shown in Figure 15.6.1, carbon is exchanged within the biosphere (the global sum of all ecosystems on Earth).

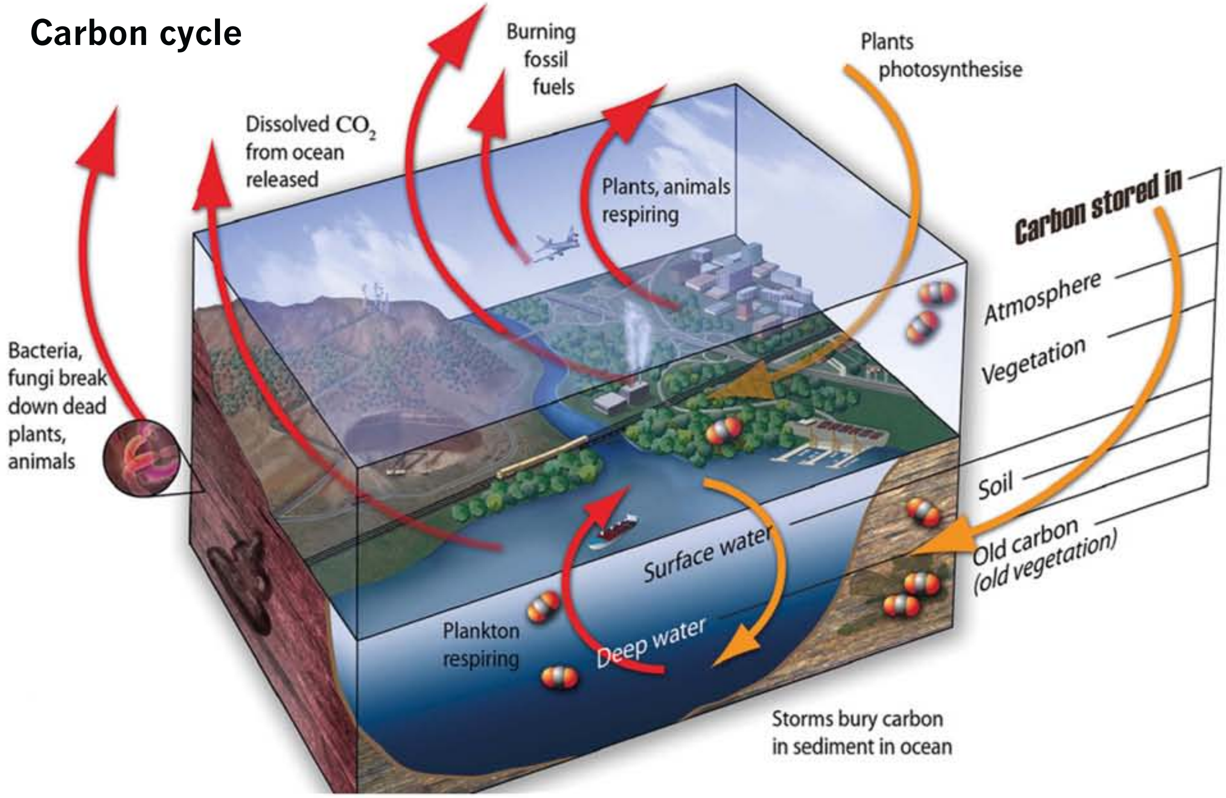


FIGURE 15.6.1 Carbon cycles between land, the atmosphere and the oceans.

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

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

Photosynthesis can only occur in the presence of sunlight and the pigment chlorophyll found in the green parts of the plant.

Carbon dioxide in the atmosphere

Studies have shown that the levels of atmospheric CO_2 have varied naturally over the last several thousand years. Scientists have used ratios of carbon isotopes to distinguish between natural and human-caused contributions. Human contributions to CO_2 levels since the Industrial Revolution (a period of time during the 18th and 19th centuries) have exceeded the natural fluctuations as can be seen in Figure 15.6.2.

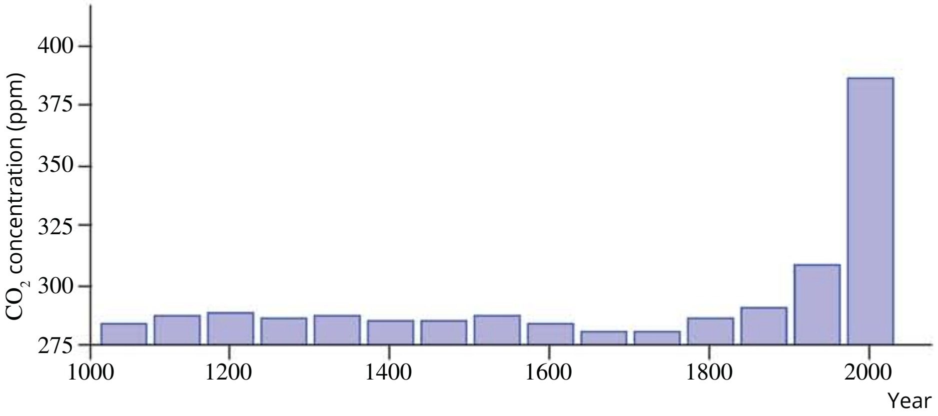


FIGURE 15.6.2 Concentrations of atmospheric carbon dioxide for the last 1000 years.

It is thought that the changes in atmospheric carbon dioxide levels are influencing surface land temperatures and causing global warming. Consequently, global weather patterns have altered and chemical processes in the oceans are also changing.

Carbon dioxide in the oceans

Carbon dioxide is slightly soluble in water. 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:

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

Most of the carbon dissolved in seawater is present as $CO_2(aq)$, but some reacts further to form carbonic acid:

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

Carbonic acid is a diprotic acid, ionising in two steps to form hydrogen carbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}):

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

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

This process can be seen in Figure 15.6.3.

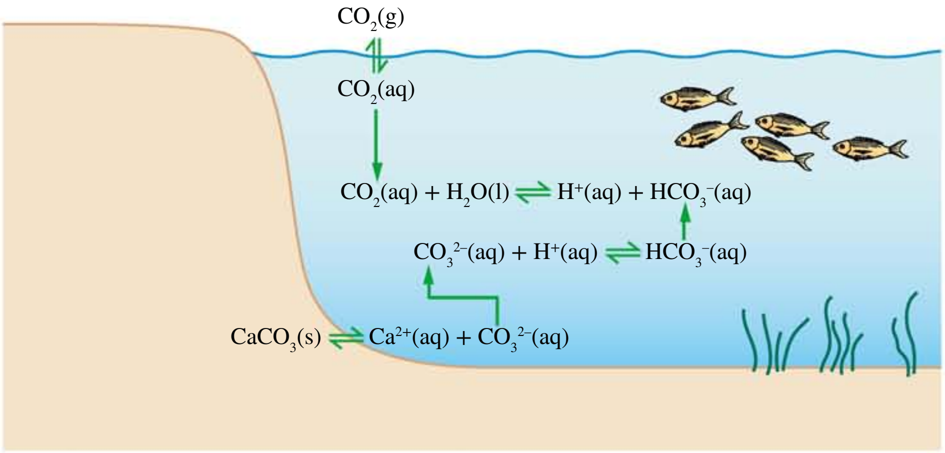


FIGURE 15.6.3 There is an interrelated set of reactions involving carbon in the ocean.

As levels of carbon dioxide in the atmosphere increase, more carbon dioxide dissolves in the ocean. This increases the concentration of carbonic acid, which in turn increases the concentration of $H_3O^+(aq)$ ions. The overall result is an increase in ocean acidity.

With increasing levels of carbon dioxide, the pH of the Earth's oceans is decreasing. The pattern of changes in pH and dissolved carbon dioxide expected over time can be seen in Figure 15.6.4. This, and increasing surface temperatures, affects the complex chemical systems in the oceans. These systems involve huge amounts of soluble metal salts such as calcium and sodium salts, carbonate ions, organic matter and gases.

CHEMFILE

Other gases in seawater

Other gases dissolved in seawater are oxygen (O_2), nitrogen (N_2), methane (CH_4) and small amounts of ammonia (NH_3) and hydrogen sulfide (H_2S). These gases can also contribute to changes in the pH of the water.

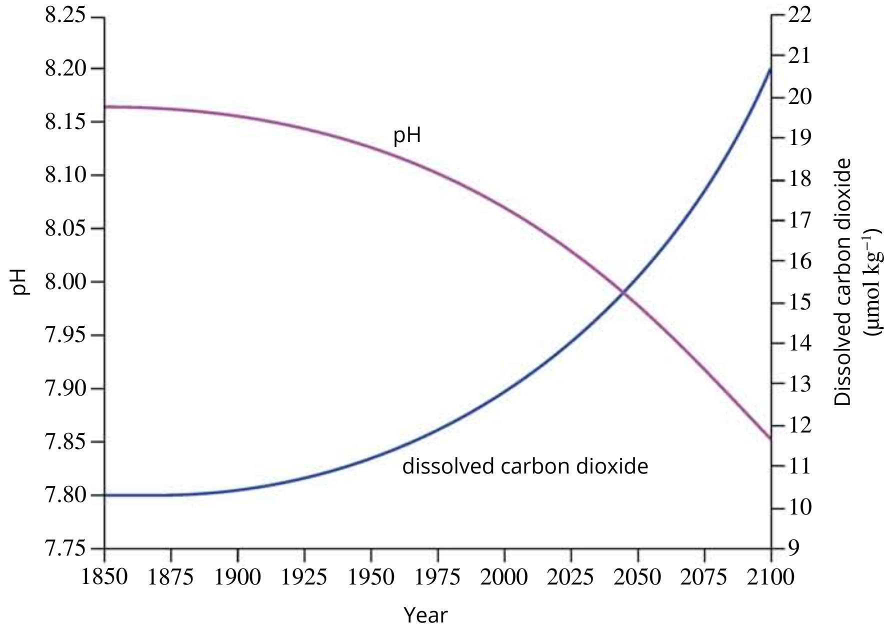


FIGURE 15.6.4 Historical (from 1850) and projected (to 2100) pH and dissolved CO_2 levels in the ocean.

Scientists have concluded that between one-third and one-half of the carbon dioxide emissions from human activity are absorbed by the oceans. Although this reduces the **greenhouse effect**, which is mainly due to carbon dioxide in the atmosphere, the pH of the oceans has decreased by 0.11 units since the Industrial Revolution. This represents a 30% increase in hydronium ion concentration in seawater.

ENVIRONMENTAL IMPACTS OF OCEAN ACIDITY

Ocean acidity is a global issue affecting all of the oceans. Increasing acidity has a detrimental effect on cold ocean organisms, such as plankton and krill (Figure 15.6.5), that are at the bottom of the food chain.

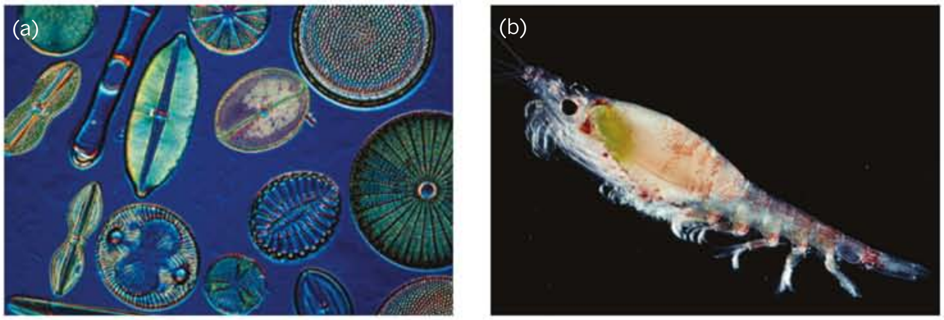


FIGURE 15.6.5 (a) Diatoms are single-celled algae that are an important component of plankton that forms the base of marine and freshwater food chains. (b) Krill feed on plankton and can be found in swarms kilometres wide. They are a major food source for many marine organisms, from small fish, such as sardines, to huge mammals, such as whales.

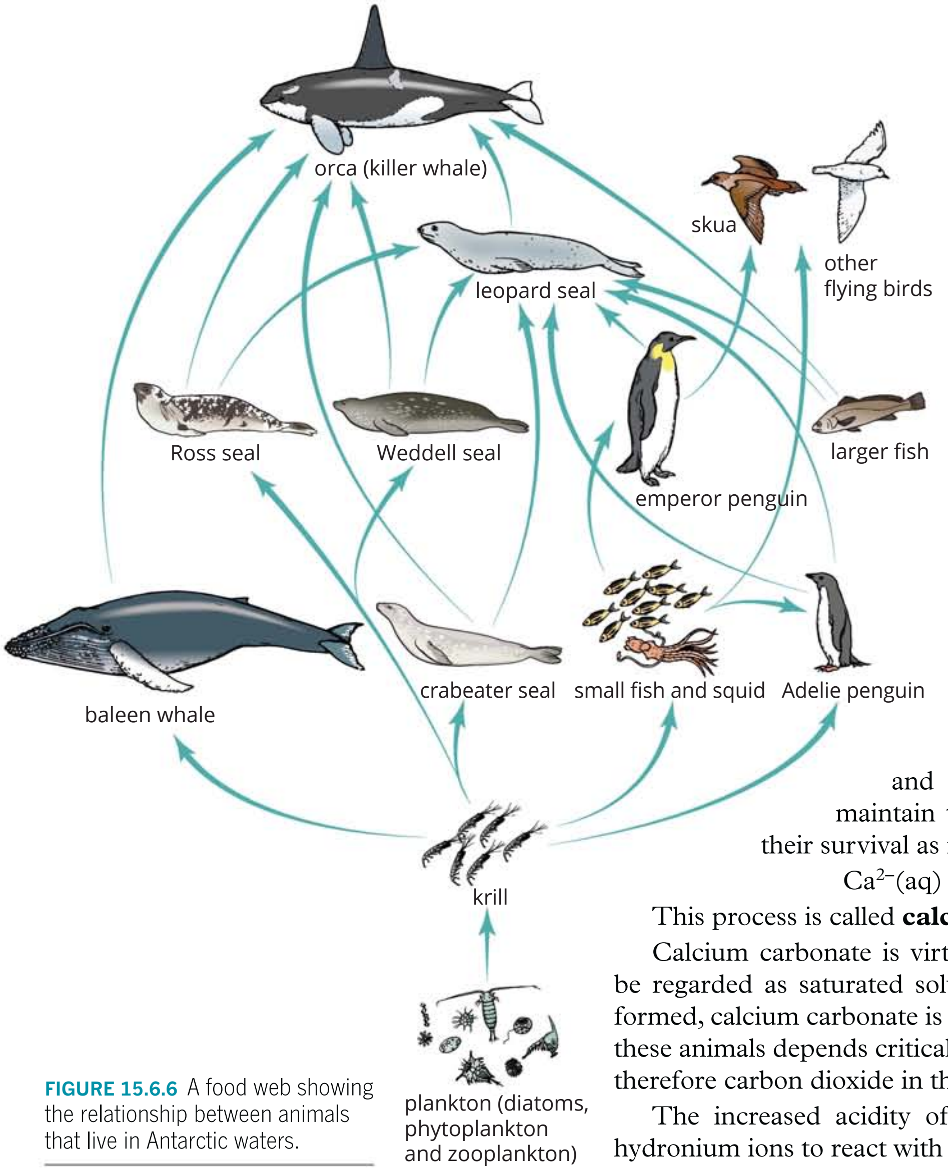


FIGURE 15.6.6 A food web showing the relationship between animals that live in Antarctic waters.

Plankton, such as diatoms, are a food source for krill, which, in turn, are consumed by animals higher up in the food chain. An example of a food chain involving these organisms can be seen in Figure 15.6.6.

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 will have a disastrous effect on the ecosystem of the ocean.

Calcification

Many aquatic organisms, including some corals and algae, as well as snails, shellfish, seastars, crabs and lobsters, have a protective covering made of calcium carbonate ($CaCO_3$).

These organisms absorb calcium ions and carbonate ions from seawater to build and maintain the calcium carbonate structure essential for their survival as represented in the following reaction:

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

This process is called **calcification**.

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 animals depends critically on the concentration of carbonate ions and therefore carbon dioxide in the oceans.

The increased acidity of the oceans causes some of the additional hydronium ions to react with carbonate ions in the following reaction:

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

This reaction has the effect of reducing the concentration of free CO_3^{2-} ions in seawater, making it more difficult for marine creatures to build or maintain their protective structures.

This process is called **decalcification**. It is estimated that the pH of the ocean will fall from 8.14 to 7.90 over the next 50 years, decreasing the rate and amount of calcification and putting coral reefs and other marine organisms at risk. Figure 15.6.7 shows the effect of decalicification on sea snails. The specimen on the left has a healthy glass-like shell with smooth edges. The shell of the specimen 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.

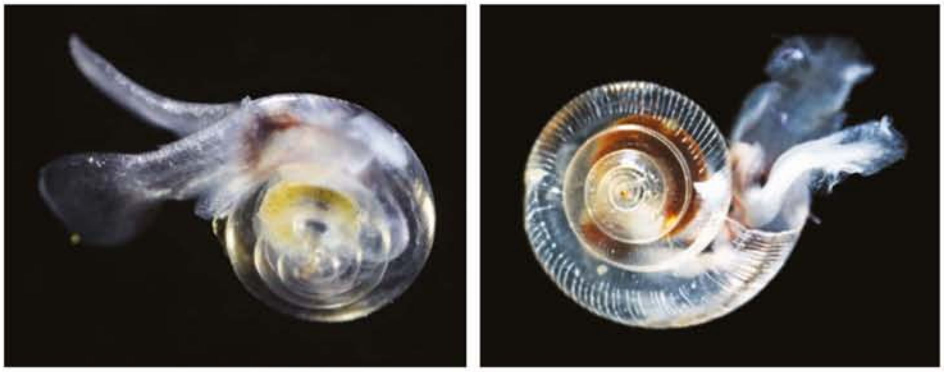


FIGURE 15.6.7 These tiny free-swimming sea snails are an important food source for other marine animals. The shell of the snail on the right is being dissolved by increasing ocean acidity.

IMPACT OF OCEAN ACIDITY ON HUMANS

Increased ocean acidity is predicted to have social and economic impacts, particularly for people in coastal communities. Some potential impacts are as follows.

- 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.
- Coastal protection: Coral reefs provide protection from storm and erosion. The destruction of coral reefs could threaten coastal communities.
- Tourism: The colour and diversity of coral reefs make them a popular tourist attraction. Their destruction will affect economies of communities that rely on tourism.

15.6 Review

SUMMARY

- An increasing concentration of atmospheric carbon dioxide is responsible for increasing ocean acidity.
- Carbonic acid is a weak diprotic acid that reacts with water to produce hydronium ions, hydrogen carbonate ions and carbonate ions.
- Some marine organisms use calcium ions and carbonate ions to protect themselves with layers of calcium carbonate.
- Absorption of increased amounts of carbon dioxide has increased the concentration of hydronium ions in seawater and lowered its pH.
- Hydronium ions can react with carbonate ions, reducing the concentration of free carbonate ions.
- Reduced carbonate ion concentration impairs the ability of some marine organisms to build and maintain calcium carbonate structures.
- Increased ocean acidity has environmental, economic and social impacts.

KEY QUESTIONS

1 Which one of the following lists best describes the species, apart from H_2O, that exist in an aqueous solution of carbon dioxide?

A $CO_2(aq)$ and $H_2CO_3(aq)$

B $CO_2(aq)$, $H_2CO_3(aq)$ and $H^+(aq)$

C $CO_2(aq)$, $H_2CO_3(aq)$, $H^+(aq)$ and $HCO_3^-(aq)$

D $CO_2(aq)$, $H_2CO_3(aq)$, $H^+(aq)$, $HCO_3^-(aq)$ and $CO_3^{2-}(aq)$

2 Write an equation for each of the ionisation steps of carbonic acid.

3 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?

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

Chapter review

15

KEY TERMS

acid
acid–base reaction
acidic proton
acidic solution
acidity
alkali
amphiprotic
anion
base
basic solution
Brønsted–Lowry theory
calcification
cation
concentrated solution
concentration
conjugate acid
conjugate acid–base pair
conjugate base
decalcification
dilution
diprotic acid
dissociate
greenhouse effect
hydronium ion
hydroxide ion
indicator
ionic equation
ionic product of water
ionisation
ionisation constant of water
ionise
limewater test
molarity
monoprotic acid
neutral solution
neutralisation reaction
neutralise
ocean acidity
pH scale
photosynthesis
polyprotic acid
salt
self-ionisation
solute
solution
spectator ions
strong acid
strong base
super acid
triprotic acid
weak acid
weak base

Introducing acids and bases

1 Identify the reactant that acts as an acid in each of the following reactions.

- **a** $NH_4^+(aq) + H_2O(l) \rightarrow NH_3(aq) + H_3O^+(aq)$
- **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** $CO_3^{2-}(aq) + CH_3COOH(aq) \rightarrow HCO_3^-(aq) + CH_3COO^-(aq)$

2 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.

3 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.

4 Using suitable examples, distinguish between:

- **a** a diprotic and an amphiprotic substance
- **b** a strong acid and a concentrated acid.

5 Draw a structural formula of the monoprotic ethanoic acid molecule. Identify which proton is donated in an acid–base reaction.

6 Identify which 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

7 Write an equation to show that perchloric acid ($HClO_4$) acts as a strong acid in water.

8 Write an equation to show that hypochlorous acid ($HClO_3$) acts as a weak acid in water.

9 Write an equation to show that ammonia (NH_3) acts as a weak base in water.

10 Write a balanced ionic equation showing the $H_2PO_4^-$ ion acting as a weak base in water.

Acidity of solutions

11 Calculate [OH^-] at 25°C in aqueous solutions with [H_3O^+] equal to:

a 0.001 M
b 10^{-5} M
c 5.7×10^{-9} M
d 3.4×10^{-12} M
e 6.5×10^{-2} M
f 2.23×10^{-13} M

12 What is the concentration of these ions in solutions, at 25°C, with the following pH values?

i hydronium ions
ii hydroxide ions

a 1
b 3
c 7
d 11.7

13 Human blood has a pH of 7.4. Is blood acidic, basic or neutral?

14 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?

15 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

16 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

17 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 ion, in mol, would be present in 500 mL of this solution?

18 Calculate the pH of each of the following mixtures at 25°C.

a 10 mL of 0.025 M HCl is diluted to 50 mL of solution.
b 20 mL of 0.0050 M KOH is diluted to 500 mL of solution.
c 10 mL of 0.15 M HCl is diluted to 1.5 L of solution.

19 The molarity of concentrated sulfuric acid is 18.0 M. What volume of concentrated sulfuric acid is required to prepare 1.00 L solution of 2.00 M H_2SO_4?

20 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?

21 40.0 mL of 0.10 M HNO_3 is diluted to 500.0 mL. Will the pH increase or decrease?

Reactions of acids and bases

22 Complete, and balance, the following chemical equations:

a $HNO_3(aq) + KOH(aq) \rightarrow$
b $H_2SO_4(aq) + K_2CO_3(aq) \rightarrow$
c $H_3PO_4(aq) + Ca(HCO_3)_2(s) \rightarrow$
d $HF(aq) + Zn(OH)_2(s) \rightarrow$

23 Which one of the following correctly identifies all the products formed when magnesium hydroxide reacts with hydrochloric acid?

A Water
B Chloride ions
C Magnesium ions
D Magnesium chloride precipitate
E Water, magnesium ions and chloride ions

24 Write a balanced ionic equation for the reaction between an acid HA and a soluble metal carbonate MCO_3.

25 Dilute hydrochloric acid is added to a white solid in a test-tube. A colourless gas is produced. The gas turns limewater cloudy. What is a possible identity of the white solid?

26 Hydrogen is produced when dilute sulfuric acid reacts with aluminium metal.

a Write a balanced full equation for this reaction.
b Write a balanced ionic equation for this reaction.

Ocean acidity

27 Write an ionic equation for the calcification reaction that is used by some marine organisms to build a hard, protective outer layer.

28 What is the name of the process in which plants take up carbon dioxide from the atmosphere?

29 Write the two steps in which carbonic acid ionises to form hydrogen carbonate ions and carbonate ions.

30 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?

Connecting the main ideas

31 A laboratory assistant forgot to label 0.1 M 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 Table 15.7.1. Identify each solution and briefly explain your reasoning.

TABLE 15.7.1 Unknown solutions and their pH and conductivity

Solution	Electrical conductivity	pH
A	Poor	11
B	Zero	7
C	Good	13
D	Good	1
E	Poor	3

32 **a** Write concise definitions for:

- **i** Brønsted–Lowry acid
- **ii** strong base
- **iii** molarity
- **iv** conjugate acid.

b Explain, with the aid of equations, why HCO_3^- is classified as amphiprotic.

33 Construct a concept map that demonstrates your understanding of the links between the following terms: acid, base, proton, hydrogen ion, hydronium ion, conjugate.

CHAPTER 16

Redox reactions in water

Some of the most colourful and energy-releasing reactions are classified as redox reactions. This group of reactions also includes some that are vitally important to our existence.

In this chapter, you will learn how redox reactions can be defined in terms of the loss and gain of electrons. You will understand how to write balanced half-equations that describe the transfer of electrons and then combine these half-equations to create an overall equation for the reaction.

Finally, you will become familiar with redox reactions such as metal displacement reactions and corrosion and you will be able to predict when these reactions will occur.

Key knowledge

- Oxidising and reducing agents, conjugate redox pairs and redox reactions including writing of balanced half and overall redox equations with states indicated
- The reactivity series of metals and metal displacement reactions including balanced redox equations with states indicated
- The causes and effects of a selected issue related to redox chemistry

16.1 Introducing redox reactions

FIGURE 16.1.1 Potassium burning in chlorine gas—a spectacular example of a redox reaction.

Your everyday life depends on a large number of chemical reactions. Many of these are **redox reactions** (*red*-uction; *ox*-idation). From the respiration reactions that enable your cells to produce energy, and the combustion reactions that warm your home, to the reactions in the batteries that keep your mobile phone working, redox reactions are occurring within you and around you all the time. The spectacular reaction between potassium and chlorine gas shown in Figure 16.1.1 is also an 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.

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 16.1.2. (You learned about this process in detail in Chapter 3, page 66.)

FIGURE 16.1.2 Molten iron from a blast furnace being poured into a bucket.

The extraction of iron from iron ore in a blast furnace can be represented by the equation:

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

In this reaction, the iron(III) oxide has lost oxygen and the carbon monoxide has gained oxygen. The iron(III) oxide is described as having been **reduced** and the carbon monoxide is described as having been **oxidised**.

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 a combination with oxygen.

The term 'reduction' was used long before this to describe the process of extracting metals from their ores. The word 'reduction' comes from the Latin *reduco*, meaning to restore. The process of metal extraction was seen as restoring the metal from its compounds, such as iron from iron oxide or copper from copper(II) oxide. The reduction of copper(II) oxide to form copper powder occurs when copper(II) oxide is heated in the presence of hydrogen or methane gas, as shown in Figure 16.1.3. Some fine particles of copper escape with the gas, causing the green flame.

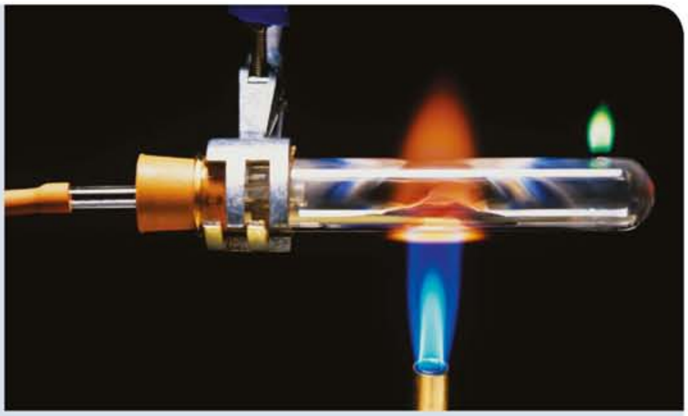


FIGURE 16.1.3 The reduction of copper(II) oxide to form copper powder occurs when it is heated in the presence of hydrogen or methane gas.

Transfer of electrons

If you have heated a piece of magnesium ribbon in an experiment as shown in Figure 16.1.4, you will remember that 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 (Mg^{2+}) ion. The half-equation for this part of the overall reaction is written as shown. The electronic configurations are also shown:

$$\underset{2,8,2}{Mg(s)} \rightarrow \underset{2,8}{Mg^{2+}(s)} + 2e^-$$

Notice that when electrons are lost, they appear as products in the half-equation.

At the same time, each oxygen atom in the oxygen molecule (O_2) gains two electrons (i.e. four electrons per oxygen molecule):

$$\underset{2,6}{O_2(g)} + 4e^- \rightarrow \underset{2,8}{2O^{2-}(s)}$$

Notice that when electrons are gained, they appear as reactants in the half-equation. The electrons that are gained by the oxygen have 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 widely used definition of oxidation and reduction.

Oxidation is defined as the loss of electrons.
Reduction is defined as the gain of electrons.

The definitions of oxidation and reduction can be recalled using the mnemonic or memory aid, OIL RIG, as shown in Figure 16.1.5.

Note that there is no overall loss of electrons, but a transfer of electrons from one atom to another. If an atom loses electrons, there must be another atom that gains electrons. Therefore, oxidation and reduction always occur simultaneously.

Other examples of redox reactions

Many redox reactions do not involve a reaction with oxygen. The reaction between potassium and chlorine shown in Figure 16.1.1 is an example:

$$2K(s) + Cl_2(g) \rightarrow 2KCl(s)$$

Oxidation half-equation: $K(s) \rightarrow K^+(s) + e^-$

Reduction half-equation: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$

Another example is the reaction between copper and sulfur:

$$Cu(s) + S(l) \rightarrow CuS(s)$$

Oxidation half-equation: $Cu(s) \rightarrow Cu^{2+}(s) + 2e^-$

Reduction half-equation: $S(l) + 2e^- \rightarrow S^{2-}(s)$

FIGURE 16.1.4 Magnesium ribbon burns brightly when heated in air to form a white powder, magnesium oxide.

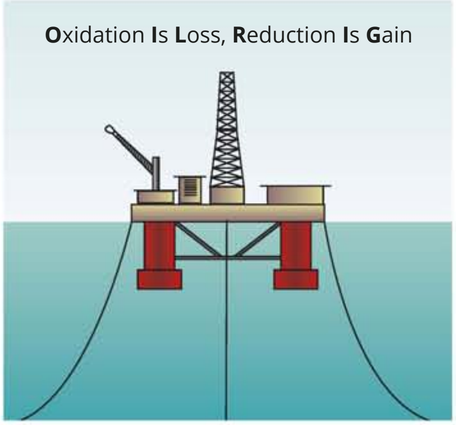


FIGURE 16.1.5 The mnemonic OIL RIG is a useful way to remember that Oxidation Is the Loss of electrons and Reduction Is the Gain of electrons.

Worked example 16.1.1

IDENTIFYING OXIDATION AND REDUCTION

Write the oxidation and reduction half-equations for the reaction with the overall equation:

$$2Li(s) + Br_2(l) \rightarrow 2LiBr(s)$$

Thinking	Working
Identify the ions in the product.	LiBr is made up of Li^+ and Br^- ions.
Write the half-equation for the oxidation of the reactant that forms positive ions and balance the equation with electrons.	$Li(s) \rightarrow Li^+(s) + e^-$
Write the half-equation for the reduction of the reactant that forms negative ions and balance the equation with electrons.	$Br_2(l) + 2e^- \rightarrow 2Br^-(s)$

Worked example: Try yourself 16.1.1

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

Just as an employment agent enables a client to become employed, an **oxidising agent** or **oxidant** enables or causes another chemical to be oxidised. Similarly, a **reducing agent**, or **reductant**, enables or causes another chemical to be reduced. Redox reactions always involve an oxidising agent and a reducing agent that react together.

In the reaction between magnesium and oxygen shown in Figure 16.1.6, 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.

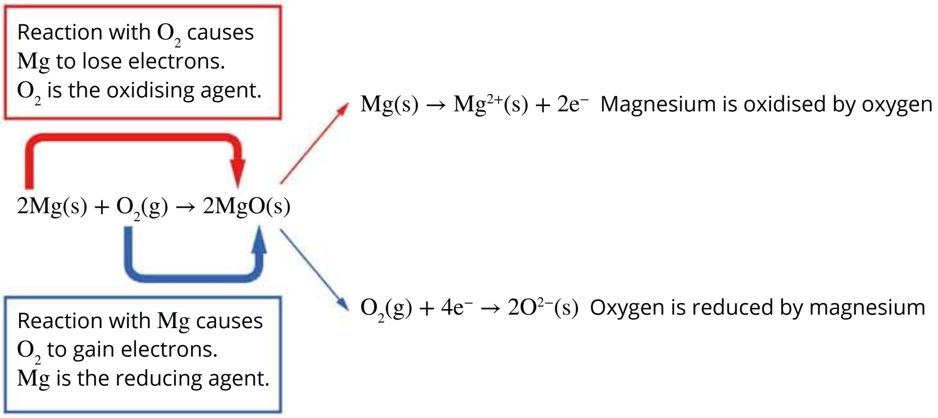


FIGURE 16.1.6 In the reaction between magnesium and oxygen, magnesium is the reducing agent and oxygen is the oxidising agent.

Since metals tend to lose electrons, they act as reducing agents.

Figure 16.1.7 summarises the list of redox terms introduced in this section.

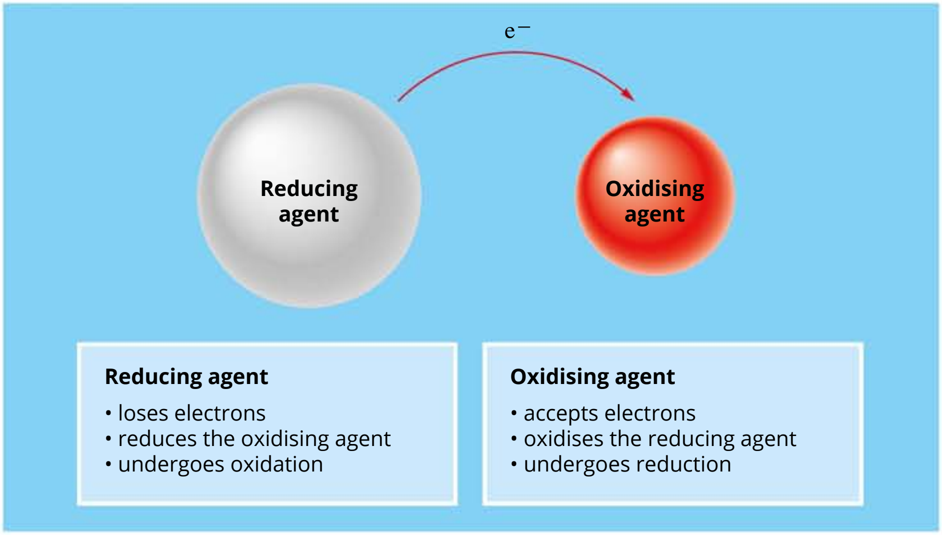


FIGURE 16.1.7 Summary of redox reaction terms.

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.

WRITING REDOX EQUATIONS

Writing simple half-equations

Half-equations enable you to see the detail of what is happening in a redox reaction. Like other chemical equations, half-equations must be balanced so there is the same number of atoms of each element on each side of the arrow. Similarly, charge must also be balanced. Half- and full equations should indicate the states of all the species in the reaction as well.

Worked example 16.1.2

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 16.1.2

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.

Writing an overall redox equation

When writing equations for redox reactions, the two half-equations are normally written first and then added together to obtain an overall equation.

An overall equation does not show any electrons transferred; all the electrons lost in the oxidation reaction are gained in the reduction reaction. One, or perhaps both, of the half-equations may need to be multiplied by a factor to ensure that the electrons balance and can be cancelled out in the overall equation.

Consider the reaction of sodium and chlorine gas. In this reaction, each Na atom is oxidised and loses one electron. Each Cl_2 molecule is reduced and gains two electrons:

$$Na(s) \rightarrow Na^+(s) + e^-$$
$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$$

Two Na atoms must therefore be oxidised to provide the electrons required by each chlorine molecule that is reduced. To write an overall equation for this reaction, the half-equation involving the oxidation of Na is multiplied by a factor of two before combining it with the half-equation for reduction of Cl_2:

$$2Na(s) \rightarrow 2Na^+(s) + 2e^-$$

You can now write the two half-equations and add them to find the overall equation:

$$2Na(s) \rightarrow 2Na^+ + 2e^-$$
$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$$

When the electrons have been cancelled, the overall equation is:

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

When writing an overall redox equation from two half-equations, you need to balance the number of electrons.

Worked example 16.1.3

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 16.1.3

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 16.1.8. 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 decrease 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, causing the silver ions to be reduced to metallic silver:

$$Ag^+ + e^- \rightarrow Ag$$

The silver metal formed causes light to be reflected, the lenses to darken, and the intensity of light reaching the eyes of a person wearing the glasses to be reduced. To prevent the silver metal and chlorine atoms forming silver chloride again immediately, copper(I) chloride is also added to the glass in tiny amounts. It 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 16.1.8 The lenses of these photochromic glasses darken in sunlight as a result of redox reactions involving silver chloride.

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. The reactant and the product that it forms are known as a **conjugate redox pair**.

Consider the half-equation in which zinc is oxidised:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

The zinc metal is a reducing agent because it would cause another reactant to gain electrons. In the half-equation $Zn^{2+}(aq)$ is formed. This is the conjugate oxidising agent. Zn(s) and $Zn^{2+}(aq)$ are a conjugate redox pair.

As another example, consider the half-equation in which $Cu^{2+}(aq)$ is reduced:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

The copper(II) ion is the oxidising agent, because it would cause another reactant to lose electrons. In the half-equation Cu(s) is formed. This is the conjugate reducing agent. Cu(s) and $Cu^{2+}(aq)$ are a conjugate redox pair. The conjugate redox pair is usually written as oxidant/reductant.

There are two conjugate redox pairs in a redox reaction, as shown in the two examples in Table 16.1.1.

An oxidising agent and its corresponding reducing agent are known as a conjugate redox pair.

TABLE 16.1.1 Identifying conjugate redox pairs in a redox reaction

	Example 1	Example 2
Overall equation	$Fe(s) + Sn^{2+}(aq) \rightarrow Fe^{2+}(aq) + Sn(s)$	$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$
Oxidation half-equation	$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Reduction half-equation	$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	$Ag^+(aq) + e^- \rightarrow Ag(s)$
Conjugate redox pairs	$Fe^{2+}(aq)/Fe(s)$ $Sn^{2+}(aq)/Sn(s)$	$Cu^{2+}(aq)/Cu(s)$ $Ag^+(aq)/Ag(s)$

16.1 Review

SUMMARY

- Redox (*red*-uction; *ox*-idation) 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. $Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$.
- The reducing agent (reductant) donates electrons to another substance, causing that substance to be reduced. The reductant is itself oxidised.
- Metals can act as reducing agents.
- 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 determine the overall redox equation. It may be necessary to multiply one or both half-equations by a factor to balance the electrons.
- In a redox reaction, a conjugate redox pair is made up of a reducing agent and the oxidising agent that is formed, or an oxidising agent and the reducing agent that is formed. The conjugate redox pair is usually written as oxidant/reductant.

KEY QUESTIONS

1 Identify each of the following half-equations as involving either oxidation or reduction.

- **a** $Na(s) \rightarrow Na^+(aq) + e^-$
- **b** $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$
- **c** $S(s) + 2e^- \rightarrow S^{2-}(aq)$
- **d** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

2 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** $O_2(g) \rightarrow O^{2-}(aq)$

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.
- **g** Identify the two conjugate redox pairs in this reaction.

4 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.

5 Some ions, such as the Cu^+ ion, can be either oxidised or reduced.

- **a** Write the formula for the product of the oxidation of the Cu^+ ion.
- **b** Write the formula for the product of the reduction of the Cu^+ ion.

6 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 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 ____________.

EXTENSION

Half-equations for complex redox reactions

Most laboratories have strong oxidising agents that can be used when a substance needs to be oxidised. For safety reasons, these are often stored together and well away from flammable materials, since they could cause a fire. This class of strong oxidising agents includes potassium permanganate, potassium dichromate and potassium chromate. To write the more complex redox half-equations for these oxidising agents, a specific method, involving the use of $H^+(aq)$ and $H_2O(l)$ has to be followed.

For example, consider the following redox reaction:

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$$

You can describe this reaction in words as follows: the permanganate ions oxidise iron(II) ions to iron(III) ions. The permanganate ions are reduced to manganese(II) ions.

In this extension, you will learn how to write the overall equation for a redox reaction such as this.

If you begin with the oxidation of iron(II) ions to iron(III) ions, then you have a simple half-equation:

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

The conversion of MnO_4^- to Mn^{2+} involves reduction. The following steps are used to balance this half-equation.

Worked example 16.1.4

WRITING HALF-EQUATIONS FOR COMPLEX REDOX REACTIONS

The conversion of MnO_4^- to Mn^{2+} involves reduction. Write the balanced half-equation and then combine the half-equations into a balanced redox equation.

Thinking	Working
Balance all atoms in the half-equation except oxygen and hydrogen.	$MnO_4^- \rightarrow Mn^{2+}$
Balance the oxygen atoms by adding water. (Oxygen atoms react to form water in acidic solution.)	$MnO_4^- \rightarrow Mn^{2+} + 4H_2O$
Balance the hydrogen atoms by adding H^+ ions (which are present in the acidic solution).	$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$
Balance the charges on both sides of the equation by adding electrons to the more positive side. Add states.	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
Add the oxidation half-equation to the reduction half-equation to obtain the overall equation, making sure that the number of electrons used in reduction equals the number of electrons released during oxidation.	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ $5 \times [Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-]$ $MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

Worked example: Try yourself 16.1.4

WRITING HALF-EQUATIONS FOR COMPLEX REDOX REACTIONS

Potassium dichromate ($K_2Cr_2O_7$) reacts with potassium iodide (KI) in acidified solution. The dichromate ion ($Cr_2O_7^{2-}$) is reduced to Cr^{3+}, and the iodide ion (I^-) is oxidised to I_2 .

Write:

a the half-equation for the oxidation of the I^- to I_2

b the half-equation for the reduction of $Cr_2O_7^{2-}$ to Cr^{3+}

c an overall ionic equation for the reaction.

(The potassium ions are spectator ions and do not appear in the overall equation.)

Extension questions

1 Write half-equations to represent the:

- **a** reduction of $SO_4^{2-}(aq)$ to $SO_2(g)$
- **b** oxidation of $H_2O_2(aq)$ to $O_2(g)$
- **c** oxidation of $H_2S(g)$ to $S(s)$
- **d** reduction of $MnO_4^-(aq)$ to $MnO_2(s)$
- **e** reduction of $Ta_2O_5(s)$ to $Ta(s)$
- **f** oxidation of $SO_3^{2-}(aq)$ to $SO_4^{2-}(aq)$
- **g** reduction of $IO_3^-(aq)$ to $I^-(aq)$.

2 Balance the following redox equations by separating them into two half-equations, balancing each equation, and then combining the pair into a balanced complete redox equation.

- **a** $H_2O_2(aq) + PbS(s) \rightarrow PbSO_4(s) + H_2O(l)$
- **b** $I_2(aq) + H_2S(g) \rightarrow I^-(aq) + S(s) + H^+(aq)$
- **c** $SO_3^{2-}(aq) + MnO_4^-(aq) + H^+(aq) \rightarrow SO_4^{2-}(aq) + Mn^{2+}(aq) + H_2O(l)$
- **d** $NO(g) + Cr_2O_7^{2-}(aq) + H^+(aq) \rightarrow NO_3^-(aq) + Cr^{3+}(aq) + H_2O(l)$

16.2 The reactivity series of metals

When metals undergo corrosion, some react quickly and vigorously with oxygen and water, and even more vigorously with acids. The reaction between other metals with oxygen is quite slow. Copper pipes oxidise slowly in the air, producing a brown-black copper oxide coating, while the reaction of magnesium ribbon in acid is more vigorous. These are all examples of redox reactions.

This section will examine the reactivity of different metals and describe how to write equations for reactions between metals and solutions of metal ions.

REACTIVITY OF METALS

Sodium, magnesium and iron are metals that are relatively easily oxidised. Sodium is oxidised so readily that it has to be stored under paraffin oil to prevent it from reacting with oxygen in the atmosphere. The oxidation of iron, which can eventually result in the formation of rust, can be an expensive problem.

Other metals do not corrode as readily. For example, platinum and gold are sufficiently inert to be found as pure elements in nature.

Figure 16.2.1 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.

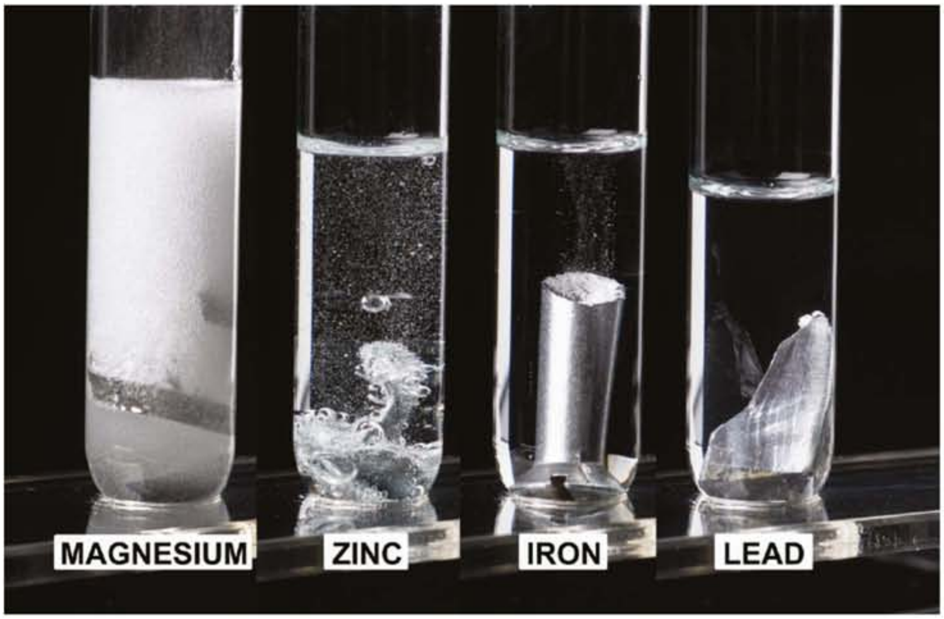


FIGURE 16.2.1 Some metals react with dilute acid to form a salt and hydrogen gas. The reaction between magnesium and dilute acid is extremely vigorous. The reaction between zinc and dilute acid is less vigorous. The reaction between iron and dilute acid is very slow. There is no reaction between lead and dilute acid. Based on this information, the order of metal reactivity from most reactive to least reactive is magnesium, zinc, iron and lead.

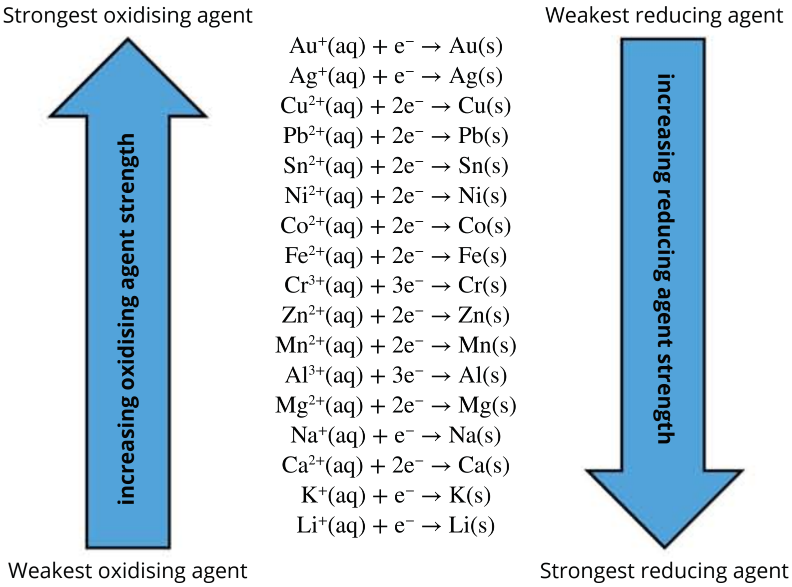
The metals can be ranked in a list according to their reactivity, or ability to act as reducing agents. Figure 16.2.2 shows such a ranking, which is also known as a **reactivity series**. The series shows the reduction half-equations for the metal cations as each cation gains electrons to form the corresponding 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. Remember that the most reactive metals are those that are oxidised most easily.

Metals, with their small number of valence electrons, generally act as reducing agents. A relatively small amount of energy is required to remove these valence electrons. In general, the lower the amount of energy required to remove the valence electrons, the more readily a metal will act as a reducing agent.

As you go down the reactivity series of metals in Figure 16.2.2, 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 therefore stronger reducing agents
- metal cations, which are on the left-hand side, become increasingly harder to reduce and 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.



$Au^+(aq) + e^- \rightarrow Au(s)$
$Ag^+(aq) + e^- \rightarrow Ag(s)$
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$
$Na^+(aq) + e^- \rightarrow Na(s)$
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$
$K^+(aq) + e^- \rightarrow K(s)$
$Li^+(aq) + e^- \rightarrow Li(s)$

FIGURE 16.2.2 Reactivity series of metals.

CHEMISTRY IN ACTION

The ages of discovery

Since the dawn of civilisation, our progress has been dependent 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 that produced the hard alloy, bronze, which 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, required higher temperatures to extract them from their ores and efficient production methods were invented much later. Wood was inadequate as a fuel to attain high enough temperatures, and the manufacture of charcoal led to the cheap manufacture of iron and weapons that 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 the invention of electricity in the late 1800s was needed to extract them 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. Consequently, these metals tend to be expensive to produce. Aluminium is produced using the electrolytic cells shown in Figure 16.2.3.

FIGURE 16.2.3 A row of electrolytic cells used for the modern production of aluminium.

What of our Modern Age? Historians may one day label ours as the Silicon, Aluminium, Plastics, Ceramics or Nanoparticle Age in recognition of the influence that these technologically advanced materials have had on our modern life. Further developments in materials technology will no doubt see the production of new materials to meet the demands of our modern culture.

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 16.2.4. The more reactive metal acts as the reducing agent, and the metal ions of the other metal act as the oxidising agent.

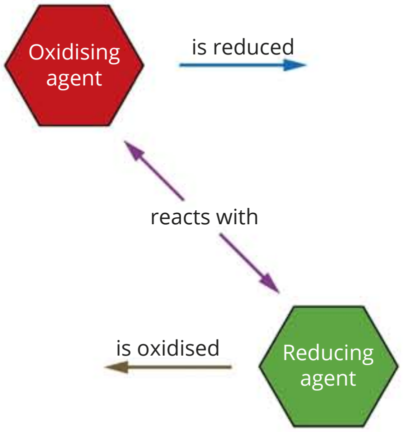


FIGURE 16.2.4 Predicting the reaction between an oxidising agent and a reducing agent.

A metal ion higher in the reactivity series (an oxidising agent) will react with a metal lower in the reactivity series (a reducing agent).

When a strip of copper wire is placed in a solution of silver nitrate as shown in Figure 16.2.5, 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 16.2.6. The overall redox reaction can be represented by the equation:

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

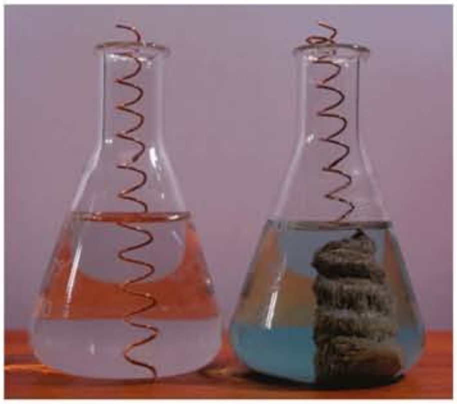


FIGURE 16.2.5 When a strip of copper wire is suspended in a solution of silver nitrate in the flask on the left, long crystals of silver metal start to form. In the flask on the right, the copper has displaced the silver from the solution.

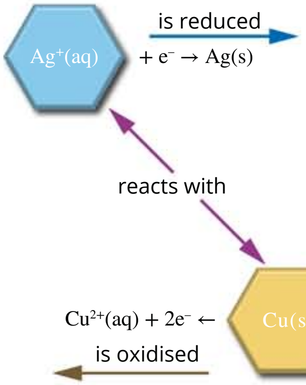


FIGURE 16.2.6 A spontaneous redox reaction occurs when copper is added to a solution of silver nitrate. Silver ions oxidise copper atoms.

Worked example 16.2.1

PREDICTING METAL DISPLACEMENT REACTIONS

Predict whether zinc will displace copper from a solution containing copper(II) ions and, if appropriate, write the overall equation for the reaction.

Thinking	Working
Locate the metal and the metal ions in the reactivity series.	Metals (reducing agents) are found on the right-hand side of the reactivity series and metal ions (oxidising agents) are on the left-hand side of the reactivity series. $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ $Sn^{4+}(aq) + 2e^{-} \rightarrow Sn(aq)$ $2H^{+}(aq) + 2e^{-} \rightarrow H_2(g)$ $Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)$ $Sn^{2+}(aq) + 2e^{-} \rightarrow Sn(s)$ $Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s)$ $Co^{2+}(aq) + 2e^{-} \rightarrow Co(s)$ $Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s)$ $Cr^{3+}(aq) + 3e^{-} \rightarrow Cr(s)$ $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$
Determine whether the metal is below (and to the right of) the metal ion in the table. If this is the case, there will be a reaction.	You can see from the reactivity series that Zn is on the right-hand side because it is a reducing agent and it is below Cu^{2+}, so there will be a reaction as shown in Figure 16.2.7.
Write the reduction reaction for the metal ion directly as it is written in the reactivity series, including states.	$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$
Write the oxidation reaction for the metal from the reactivity series, writing the metal on the left-hand side of the arrow (as a reactant). Include states.	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$
Combine the two half-equations, balancing electrons, to give the overall equation for the reaction.	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Worked example: Try yourself 16.2.1

PREDICTING METAL DISPLACEMENT REACTIONS

Predict whether copper will displace gold from a solution containing gold ions and, if appropriate, write the overall 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 16.2.7.

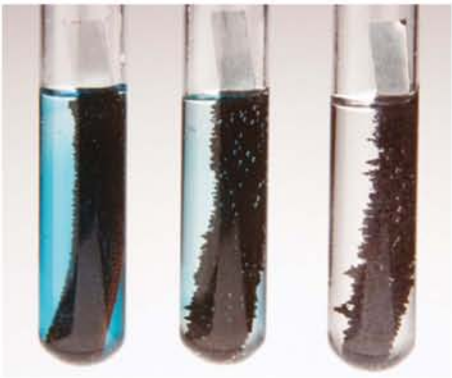


FIGURE 16.2.7 A brown deposit of copper metal is observed forming on the zinc and the blue copper(II) sulfate solution gradually becomes colourless as the concentration of Cu^{2+} ions decreases.

16.2 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 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 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 have inadvertently been left unlabelled. Name two metals that could be used to identify each solution.

16.3 Corrosion

The reactions that occur when metals corrode are redox reactions. The costs associated with corroding metals are substantial, especially since iron, which is particularly prone to corrosion in the presence of water and oxygen, is so widely used as a structural material for buildings, bridges, gas and water pipes and ships. The effect of corrosion in water pipes is evident in the pumping system shown in Figure 16.3.1.

In Australia, about $50 billion (approximately 3% of gross domestic product) is spent each year in an effort to prevent metals from corroding and replacing metal that has corroded. In spite of such efforts, steel structures continue to corrode, eventually producing the familiar orange-brown flakes known as rust, although corrosion prevention methods can slow down the rate of corrosion considerably.

This section will give you an opportunity to consider corrosion in terms of the causes and effects of an issue that relates to redox chemistry. In doing so, you will look at the redox reactions involved in corrosion both in the presence of water and in the absence of water.

FIGURE 16.3.1 Corrosion is causing water to leak in these pipes in a pumping system.

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 16.3.2 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; the rate of dry corrosion of iron is slow at room temperatures. When iron does corrode, it forms a coating that flakes off readily, leaving the metal underneath exposed to further corrosion.

FIGURE 16.3.2 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 16.3.3.

FIGURE 16.3.3 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.

Each of these observations gives us information about the factors that influence the rate of wet corrosion of iron. In general, corrosion is accelerated by:

- the presence of water
- impurities such as salt and acidic pollutants that dissolve in the water.

However, corrosion can be reduced when the iron is alloyed with certain other materials or when it has a protective coating. You will see this later when the methods of prevention of corrosion are discussed.

The wet corrosion process

Rust is a hydrated oxide of iron with the formula $Fe_2O_3.xH_2O$. 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 16.3.4.

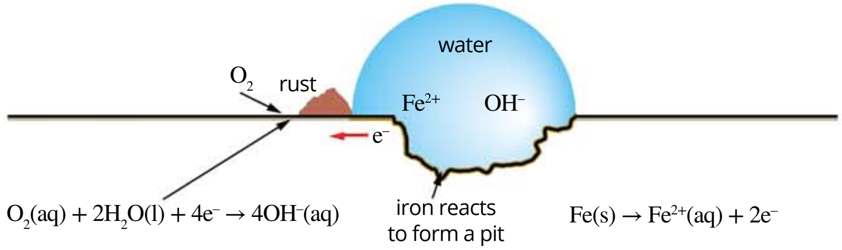


FIGURE 16.3.4 During wet corrosion, electrons are transferred through the iron from the area where oxidation occurs to the area where reduction occurs. Ions flow through the water droplets.

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 ($Fe_2O_3.xH_2O$), which is known as rust.

The porous rust easily flakes off the surface of the iron, exposing the iron underneath to further oxidation.

The wet corrosion of iron is accelerated if the water contains dissolved ions. This is particularly evident in coastal areas where iron objects are exposed to seawater. The presence of dissolved ions in the water increases its conductivity, which results in an increase in the rate of iron corrosion.

Prevention of corrosion

There are several ways to protect iron and steel structures against corrosion. These depend on the environment in which the structure is located, the design and intended use of the structure, and the relative costs of various protection measures.

The simplest way 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.

Iron can also be protected by alloying with small quantities of metals such as chromium, nickel, manganese or molybdenum to produce stainless steel. The atoms of the metals used to make the **alloy** are all bonded into the metallic lattice. These metals oxidise slightly in air, but the oxide coating produced is continuous and unreactive. This oxide layer protects the metal from further oxidation.

Iron and steel can also be coated with thin layers of less reactive metals in a process known as **electroplating**. The 'tin cans' used to package food are made from steel plated with tin. Tin is a much less reactive metal than iron and does not corrode greatly in the atmosphere. In addition to the tin coating, cans used for food, such as the ones shown in Figure 16.3.5, have a plastic liner to prevent contact between the food and any metal oxides that may be present.

FIGURE 16.3.5 These food cans are made from steel that has been plated with tin to prevent them corroding.

Electrochemical protection

Cathodic protection involves the use of a low-voltage, direct current (DC) power supply to give the iron being protected a negative charge. Because the iron is receiving electrons, oxidation is inhibited. Recall that oxidation is the loss of electrons.

The iron becomes the site of the reduction reaction, and is called the **cathode**. This method, represented in Figure 16.3.6, 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.

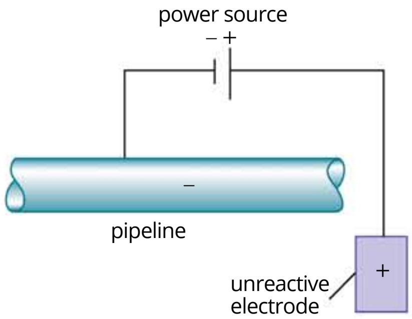


FIGURE 16.3.6 A pipeline carrying natural gas can be protected from corrosion if a direct current source is connected at intervals to give the pipe a negative charge.

Sacrificial protection also involves the iron acting as the cathode. A more easily oxidised metal, such as zinc, forms a region called the **anode** and is 'sacrificed' in order to protect the iron from corrosion. The more reactive metal loses electrons and forms metal cations in preference to the iron.

Iron that has been coated in zinc is known as galvanised iron and is used widely for roofs and sheds, as shown in Figure 16.3.7a. 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 16.3.7b depicts this process. The zinc slowly corrodes but the iron is protected for years.

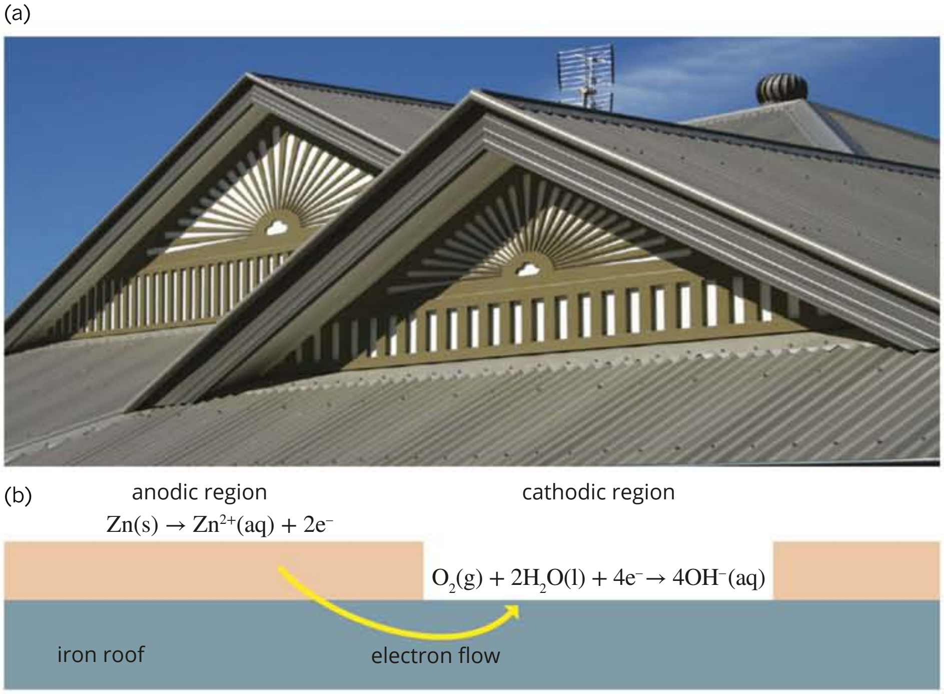


FIGURE 16.3.7 A galvanised iron roof is a common sight in Australia. The zinc coating is oxidised in preference to the iron, protecting the structural role of the iron.

FIGURE 16.3.8 These aluminium sacrificial anodes are attached to the underwater steel structures of offshore gas platforms to protect them against corrosion.

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 16.3.8).

16.3 Review

SUMMARY

- Dry corrosion refers to the oxidation of a metal by oxygen gas.
- Wet corrosion involves both oxygen gas and water.
- 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 ($Fe_2O_3.xH_2O$).
- 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 near 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 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

16

KEY TERMS

alloy
anode
cathode
cathodic protection
conjugate redox pair
direct corrosion
displace
dry corrosion
electroplating
half-equation
metal displacement reaction
oxidant
oxidation
oxidised
oxidising agent
reactivity series
redox reaction
reduced
reducing agent
reductant
reduction
sacrificial anode
sacrificial protection
spontaneous redox reaction
wet corrosion

Introducing redox reactions

1 Consider the following half-equations and the overall equation for the reaction between sodium metal and a solution of silver ions.

$Na(s) \rightarrow Na^+(aq) + e^-$
$Ag^+(aq) + e^- \rightarrow Ag(s)$

$Na(s) + Ag^+(aq) \rightarrow Na^+(aq) + Ag(s)$

Which one of the following sets of statements correctly describes this redox reaction?

A Na(s) is the oxidising agent, $Ag^+(aq)$ is the reducing agent, sodium metal is reduced.
B Na(s) is the reducing agent, $Ag^+(aq)$ is the oxidising agent, sodium metal is reduced.
C $Na^+(aq)$ is the oxidising agent, Ag(s) is the reducing agent, sodium metal is oxidised.
D Na(s) is the reducing agent, Ag+(aq) is the oxidising agent, sodium metal is oxidised.

2 Magnesium reacts with nickel(II) ions according to the following equation:

$$Mg(s) + Ni^{2+}(aq) \rightarrow Mg^{2+}(aq) + Ni(s)$$

Which one of the following is the correct set of conjugate redox pairs for this reaction?

A $Mg^{2+}(aq)/Mg(s)$ and $Ni^{2+}(aq)/Ni(s)$
B $Ni(s)/Mg^{2+}(aq)$ and $Ni^{2+}(aq)/Mg(s)$
C $Mg(s)/Ni(s)$ and $Ni^{2+}(aq)/Mg^{2+}(aq)$
D $Mg(s)/Ni^{2+}(aq)$ and $Ni(s)/Mg^{2+}(aq)$

3 Which one of the following alternatives describes what happens when sodium and oxygen react?

A Each sodium atom gains one electron.
B Each sodium atom loses one electron.
C Each oxygen atom gains one electron.
D Each oxygen atom loses one electron.

4 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 $Zn^{2+}(aq) + Mg(s) \rightarrow Zn(s) + Mg^{2+}(aq)$

5 Define oxidation and reduction in terms of the transfer of:

a oxygen **b** electrons.

6 Identify the conjugate redox pairs in the following reaction:

$$Zn(s) + Co^{2+}(aq) \rightarrow Zn^{2+}(aq) + Co(s)$$

7 Identify the following half-equations as involving either oxidation or reduction.

a $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$
b $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
c $O_2(aq) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
d $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

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 In these redox reactions, which species have been oxidised and which have been reduced?

a $Cu^{2+}(aq) + Mg(s) \rightarrow Cu(s) + Mg^{2+}(aq)$
b $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$
c $PbO(s) + CO(g) \rightarrow Pb(s) + CO_2(g)$
d $Ca(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2(g)$
e $Pb^{2+}(aq) + Fe(s) \rightarrow Pb(s) + Fe^{2+}(aq)$

10 When zinc reacts with a solution of hydrochloric acid, hydrogen gas is produced.

a What has been oxidised in this reaction?
b Write a half-equation for the oxidation reaction.
c What has been reduced in this reaction?
d Write a half-equation for the reduction reaction.
e Identify the oxidising agent.
f Identify the reducing agent.
g Write an overall equation for this redox reaction.

The reactivity series of metals

You may need to refer to the reactivity series of metals to answer Questions 11–16.

11 List the following in order of increasing reducing strength.

Mg, Ag, Ni, Sn, Li, Cu

12 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.

13 If a piece of zinc metal is added to solutions of the following compounds, will a reaction be expected? If so, write a fully balanced chemical equation for the reaction.

a $AlCl_3$

b $AgNO_3$

c $SnCl_2$

d $CuSO_4$

14 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.

15 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.

16 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.

Corrosion

17 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.

18 Deep sea divers sometimes report that the metal on vessels they find on the seabed does not appear to have been corroded. Which one of the following might contribute to the lack of corrosion?

A Deep sea creatures eat iron oxide.

B A lack of light prevents corrosion from occurring.

C There is little oxygen dissolved in the water near the seabed.

D The concentration of dissolved salt in the sea decreases with increasing depth.

19 Consider the following products that are made during the wet corrosion of iron. Put them in the correct order in which they are made: $Fe(OH)_3(s)$, $Fe_2O_3.xH_2O$, $Fe(OH)_2(s)$, $Fe^{2+}(aq)$ and $OH^-(aq)$.

20 Explain the term 'cathodic protection' of iron.

21 Why is it usually not necessary to protect structures made of copper from corrosion?

22 The iron in galvanised iron nails is protected from corrosion by a coating of zinc. Explain why a coating of tin instead of zinc would not be appropriate protection for iron nails.

23 Steel garden furniture rusts much more readily near the seaside than inland. Explain why.

Connecting the main ideas

24 Construct a concept map that shows the links between the following terms:

oxidising agent, reducing agent, electrons, oxidation, reduction

25 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?

26 Consider the following information relating to metals, R, S and T, and solutions of their salts, $Q(NO_3)_2$, 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.

27 Would elements from the following groups be more likely to be oxidised or reduced when they take part in chemical reactions with the other group? Give reasons for your answers.

Group A: sodium, calcium and magnesium

Group B: sulfur, oxygen and chlorine

28 The insides of food cans are protected from corrosion by a coating of tin. Explain why:

a a tin layer protects the can from corrosion

b zinc would be unsuitable for coating the inside of a food can

c the contents of cans that are dented may be dangerous to use.

UNIT 2 • Area of Study 1

REVIEW QUESTIONS

How do substances interact with water?

Multiple-choice questions

1 Which of the following statements about water is not correct?

A Water molecules are polar and so water is a good solvent.
B Water has a high latent heat value and so it is a good coolant.
C Water expands on freezing and so lakes are covered with a layer of ice in very cold climates.
D Water has a low specific heat capacity and so large bodies of water moderate temperatures on Earth.

2 Which one of the equations below best represents table sugar ($C_{12}H_{22}O_{11}$) dissolving in water?

A $C_{12}H_{22}O_{11}(s) + H_2O(l) \rightarrow C_{12}H_{23}O_{11}^{+}(aq) + OH^{-}$
B $C_{12}H_{22}O_{11}(s) + H_2O(l) \rightarrow C_{12}H_{21}O_{11}^{-}(aq) + H_3O^{+}(aq)$
C $C_{12}H_{22}O_{11}(s) \xrightarrow{H_2O(l)} C_{12}H_{22}O_{11}(aq)$
D $C_{12}H_{22}O_{11}(s) \xrightarrow{H_2O(l)} C_{12}H_{22}O_{11}(l)$

3 Which one of the following describes the types of bonds broken in the solute and formed with water when hydrogen chloride dissolves?

	Bonds broken	Bonds formed
A	Covalent	Hydrogen and dipole–dipole
B	Dipole–dipole	Covalent and ion–dipole
C	Dipole–dipole	Hydrogen and dipole–dipole
D	Covalent	Covalent and ion–dipole

4 Addition of which one of the following substances to copper(II) sulfate will not result in the formation of a precipitate?

A $BaCl_2(aq)$
B $NH_4Cl(aq)$
C $Na_2CO_3(aq)$
D Zn(s)

5 Which one of the following solutions would have the highest pH?

A Lemon juice
B 1.0 M hydrochloric acid
C 1.0 M sodium hydroxide
D 1.0 M ammonium ions

6 Which one of the following represents a concentrated solution of a weak acid?

A 6.0 M CH_3COOH
B 0.01 M CH_3COOH
C 6.0 M HCl
D 0.01 M HCl

7 Which one of the following is the conjugate base of OH^-?

A H_2O
B O^{2-}
C H_3O^+
D NaOH

8 Which one of the following can act as either a Brønsted–Lowry acid or base in aqueous solutions?

A HS^-
B NH_4^+
C CO_3^{2-}
D CH_4

9 Which of the following acids can be classified as polyprotic in water?

I CH_3COOH
II H_2SO_3
III NH_4^+

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

10 Consider the following statements, which compare 20.00 mL of a 0.10 mol L^{-1} solution of nitric acid with 20.00 mL of a 0.10 mol L^{-1} solution of ethanoic acid.

I Both solutions are of the same strength.
II The pH of the nitric acid solution will be higher.
III The electrical conductivity of the nitric acid solution will be higher.
IV Both solutions will require the same volume of 0.10 mol L^{-1} NaOH for neutralisation.

Which two of the above statements are correct?

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

11 Beakers A and B both contain nitric acid. The pH of the acid in beaker A is 3 whereas the pH of the acid in beaker B is 1. From this information, what can be deduced about the concentration of hydrogen ions in beaker A?

A It is three times that in beaker B.
B It is one-third that in beaker B.
C It is a hundred times that in beaker B.
D It is one-hundredth of that in beaker B.

12 A solution of NaOH has a pH of 13 at 25°C. What mass, in g, of sodium hydroxide is present in 500 mL of this solution?

A 2.0×10^{-12}
B 0.050
C 2.0
D 4.0

13 Since the mid 1700s, the pH of the world's oceans has changed from 8.2 to 8.1. Which of the following substances is the main cause for this change?

A CO_2
B SO_2
C H_2SO_4
D $CaCO_3$

14 Which of the species below is the strongest reductant?

A Ag
B Ag^+
C Mg
D Mg^{2+}

15 Which one of the following is not a redox reaction?

A $2Fe^{3+}(aq) + Sn^{2+}(aq) \rightarrow 2Fe^{2+}(aq) + Sn^{4+}(aq)$
B $Mg(s) + O_2(g) \rightarrow 2MgO(s)$
C $2Na(s) + 2H_2O(l) \rightarrow H_2(g) + 2NaOH(aq)$
D $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

16 Which of the following species would not be expected to react with each other to a great extent?

A Cu(s) and $Mg^{2+}(aq)$
B Fe(s) and $Al^{3+}(aq)$
C Mg(s) and $Fe^{2+}(aq)$
D Cu(s) and $Ag^+(aq)$

17 Consider the following equation:

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$

Which one of the following statements is correct about this reaction?

A H_2SO_4 is acting as a strong acid.
B $MgSO_4$ is a conjugate base.
C H^+ is acting as an oxidising agent.
D Mg is acting as an oxidising agent.

18 Metal X was added to a solution of lead nitrate ($Pb(NO_3)_2$). A reaction occurred and a precipitate of lead was produced. On the basis of this result, which one of the following can be deduced?

A Lead metal must be more reactive than metal X.
B Metal X must be able to react with hydrochloric acid to release hydrogen gas.
C Metal X must be able to react with a solution of $Mg(NO_3)_2$ to produce a precipitate of Mg.
D Lead metal must be able to react with a solution of $X(NO_3)_2$ to produce a precipitate of X.

19 Which of the following statements about a reducing agent is/are correct?

I A reducing agent is reduced in a reaction.
II A reducing agent causes another substance to be reduced.
III A reducing agent takes electrons away from another substance.

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

20 Nickel metal reacts with copper(II) ions according to the following equation:

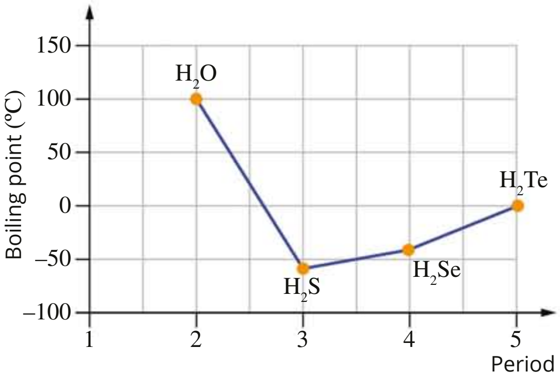
$Ni(s) + Cu^{2+}(aq) \rightarrow Ni^{2+}(aq) + Cu(s)$

Which one of the following statements about this reaction is correct?

A Ni(s) is oxidised and $Cu^{2+}(aq)$ is the oxidising agent.
B Ni(s) is reduced and $Cu^{2+}(aq)$ is the oxidising agent.
C Ni(s) is oxidised and $Cu^{2+}(aq)$ is the reducing agent.
D Ni(s) is reduced and $Cu^{2+}(aq)$ is the reducing agent.

Short-answer questions

21 The following graph shows the boiling points of the group 16 hydrides.



Explain the following.

a The boiling point of H_2S is so much lower than that of H_2O.
b The boiling point of H_2S is also lower than that of H_2Se.

22 The specific heat capacity of some common substances are listed in the table below.

Substance	Specific heat capacity ($J\ g^{-1}\ °C^{-1}$)
Water	4.18
Ethanol	2.4
Copper	0.39

a Calculate the amount of heat energy, in J, required to increase the temperature of 250.0 g of water from 18°C to 100°C.

b How much energy would be required to raise the temperature of an equal mass of copper by the same amount?

c If the same amount of energy as in part **b** is used to heat 250.0 g ethanol, what would the temperature rise of the ethanol be?

d Explain why water has a high heat capacity.

e Give one use for water based on its high heat capacity.

23 The specific heat capacity of water is 4.18 $J\ g^{-1}\ °C^{-1}$ and the specific heat capacity of liquid hexane (C_6H_{14}) is 2.29 $J\ g^{-1}\ °C^{-1}$.

a What is measured by the specific heat capacity of a substance?

b Explain, in terms of bonding, why the specific heat capacity of water is so much higher than that of hexane. Your answer should include a diagram showing the structure of two water molecules with the bond types within each molecule and between the two molecules clearly labelled.

c 100 g of water and 100 g of hexane are both at a temperature of 20.0°C. The same amount of heat is applied to each liquid. The temperature of the water rises to 32.0°C. To what temperature does the hexane rise?

24 One of the important properties of water is that it is an excellent solvent.

a Describe the structural features of the water molecule that allow it to be a solvent for a variety of compounds.

b Describe one way in which the solvent properties of water are important in a biological context.

c Explain why absolutely pure water is not found in nature.

25 Small amounts of solid magnesium chloride and liquid ethanol are dissolved in separate beakers of water.

a **i** Write an equation for the dissolving process of magnesium chloride in water.

ii What type of bonds need to break in the solid magnesium chloride in order for it to dissolve?

iii What bonds are formed when magnesium chloride dissolves in water?

b **i** Write an equation for the dissolving process of ethanol (C_2H_5OH) in water.

ii What type of bonds need to break in the liquid ethanol in order for it to dissolve?

iii What bonds are formed when ethanol dissolves in water?

c Which solution would you expect to be the better conductor of electricity? Justify your answer.

26 Write fully balanced chemical equations to represent each of the following reactions.

a Hydrochloric acid reacts with zinc powder.

b Dilute nitric acid reacts with a solution of calcium hydroxide.

c Dilute sulfuric acid reacts with a sodium carbonate solution.

d A piece of solid copper reacts with a solution of silver nitrate.

27 Write ionic equations for the reaction between:

a solutions of barium nitrate and potassium sulfate

b dilute sodium hydroxide and dilute nitric acid

c dilute hydrochloric acid and magnesium carbonate solution

d zinc metal and copper(II) sulfate solution.

28 **a** Define the term 'strong acid'.

b Give the formula of a substance that is polyprotic.

c HCO_3^- is an amphiprotic ion. Write chemical equations to show it acting in water as:

i a base

ii an acid.

d Give the formula of the conjugate acid of H_2O.

29 **a** Calculate the pH of each of the following at 25°C.

i 100 mL solution of 0.050 M $Ca(OH)_2$

ii 400 mL solution of 0.125 M nitric acid that has been diluted by the addition of 100 mL of water

iii 65.0 mL solution of hydrochloric acid that was prepared by dissolving 2.45 g of hydrogen chloride in water

b Calculate the mass of HNO_3 present in 300 mL of nitric acid with a pH of 0.050.

30 An experiment was conducted to compare the conductivity of three solutions, A, B and C. Each solution had the same concentration. The results are shown in the table below.

	pH	Litmus paper test	Conductivity (relative units)
A	?	Turns blue litmus paper red	3
B	1.5	Turns blue litmus paper red	6
C	10.5	Turns red litmus paper blue	3

a Which solution (A, B or C) is most likely to be an aqueous sodium hydroxide solution? Give a reason for your choice.

b Which solution (A, B or C) contains the strongest acid? Give an explanation for your answer.

c Give an estimation for the pH of solution A. Give a reason for your choice.

d Determine the hydrogen ion concentration in:

- **i** solution B
- **ii** solution C.

31 The pH of three different acids is given below.

Acid	Concentration in mol L^{-1}	pH
Nitric acid (HNO_3)	0.010	2.0
Propanoic acid (C_2H_5COOH)	0.010	3.4
Sulfuric acid (H_2SO_4)	0.010	1.7

The three acids have the same concentration.

a Explain why propanoic acid has the highest pH of the three.

b Explain why sulfuric acid has the lowest pH of the three.

32 Some excess potassium chloride solution is added to a solution containing 3.15 g of lead(II) nitrate. A white precipitate forms.

a Write a full chemical equation for the formation of the precipitate.

b Write an ionic equation for the formation of the precipitate.

c For this reaction, give the name of the:

- **i** precipitate
- **ii** spectator ions.

d Assume there was sufficient potassium chloride to react with all of the lead(II) nitrate.

- **i** Calculate the amount, in mol, of lead(II) nitrate that reacted.
- **ii** Calculate the mass of precipitate that would form.

33 Iron is an important structural material in our society and the prevention of its corrosion is expensive.

The half-equations for the reaction resulting in iron corrosion are given below:

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

a Write an overall equation for this reaction.

b Identify the oxidising agent and the reducing agent.

c A moist iron nail corrodes readily.

- **i** If a small piece of zinc metal is wrapped around only one part of the nail, corrosion is prevented. Explain why.
- **ii** If tin is used instead of zinc, the nail needs to be completely coated with the tin to prevent corrosion. Explain why.

34 The following equation represents the overall ionic redox equation that occurs between solutions of hydrogen peroxide (H_2O_2) and sodium bromide (NaBr):

$H_2O_2(aq) + 2H^+(aq) + 2Br^-(aq) \rightarrow 2H_2O(l) + Br_2(aq)$

a **i** Give the half-equation for the oxidation component of this reaction.

- **ii** Give the half-equation for the reduction component of this reaction.

b A redox reaction can also occur between hydrogen peroxide and silver metal, Ag(s), to produce silver ions, $Ag^+(aq)$.

Deduce the overall ionic redox equation for this reaction.

35 Consider the following chemical equations:

I $Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$
II $Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$
III $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$
IV $Fe(NO_3)_3(aq) + 3NaOH(aq) \rightarrow Fe(OH)_3(s) + 3NaNO_3(aq)$
V $HCOOH(aq) + H_2O(l) \rightarrow HCOO^-(aq) + H_3O^+(aq)$
VI $2Br^-(aq) + Cl_2(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$
VII $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

a **i** Which two reactions can be classified as acid–base reactions?

- **ii** Explain why each of your selected reactions is considered to be an acid–base reaction.
- **iii** For either of the two reactions selected, identify one acid–base conjugate pair.

b **i** From the list, select two reactions that can be classified as oxidation–reduction reactions.

- **ii** Explain why each of your selected reactions is considered to be a redox reaction.
- **iii** For either of the two reactions selected, identify one conjugate redox pair.

c **i** From the list, select two reactions that can be classified as precipitation reactions.

- **ii** Explain why each of your selected reactions is considered to be a precipitation reaction.
- **iii** Identify the spectator ions in one of the precipitation reactions.

CHAPTER

17

Water sample analysis

Water is needed for all living things; where there is no water, there is no life. In this chapter you will learn about where water exists on Earth and how much of the water is available for us to drink. You will learn about the main sources of drinkable water and which one poses the most risk.

Water is an exceptional solvent for a large variety of substances. However, the solvent properties of water do cause problems. Because water dissolves many chemicals readily, it can be easily contaminated. The quality of the water available for drinking, agriculture and other uses is vitally important to humans. In this chapter you will also investigate the procedures used for taking water samples in order to test the levels of contaminants in water supplies.

Key knowledge

- Existence of water in all three states at Earth's surface, including the distribution and proportion of available drinking water
- Sampling protocols, including equipment and sterile techniques for the analysis of water quality at various depths and locations
- The definition of a chemical contaminant and an example relevant to a selected water supply

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17.1 The availability of drinking water

FIGURE 17.1.1 The Pont du Gard is an aqueduct in France built by the Romans in the first century. It stands 49 metres high and was 50 km long. The aqueduct carried water from a spring to the town of Nimes.

In Australia, we expect clean drinking water to come out of the taps in all homes, but this is not always the case in other parts of the world. To ensure the availability of high-quality drinking water, a large infrastructure is required to supply a town or city.

The Romans were one of the earliest civilisations to develop systems for the transport of clean water to the residents of their cities. Figure 17.1.1 shows an aqueduct, or structure made to transport water, built in the first century to supply water to the town of Nimes in France.

In this section, you will learn about the distribution of the water available on Earth and the main sources of drinking water.

WATER SOURCES ON EARTH

Water is found on Earth in three states of matter (gas, liquid and solid), and it readily changes from one state into another. The **water cycle** shown in Figure 17.1.2 involves the continuous movement of water between the land, oceans, streams and atmosphere. Solar energy is the primary energy source for the cycle.

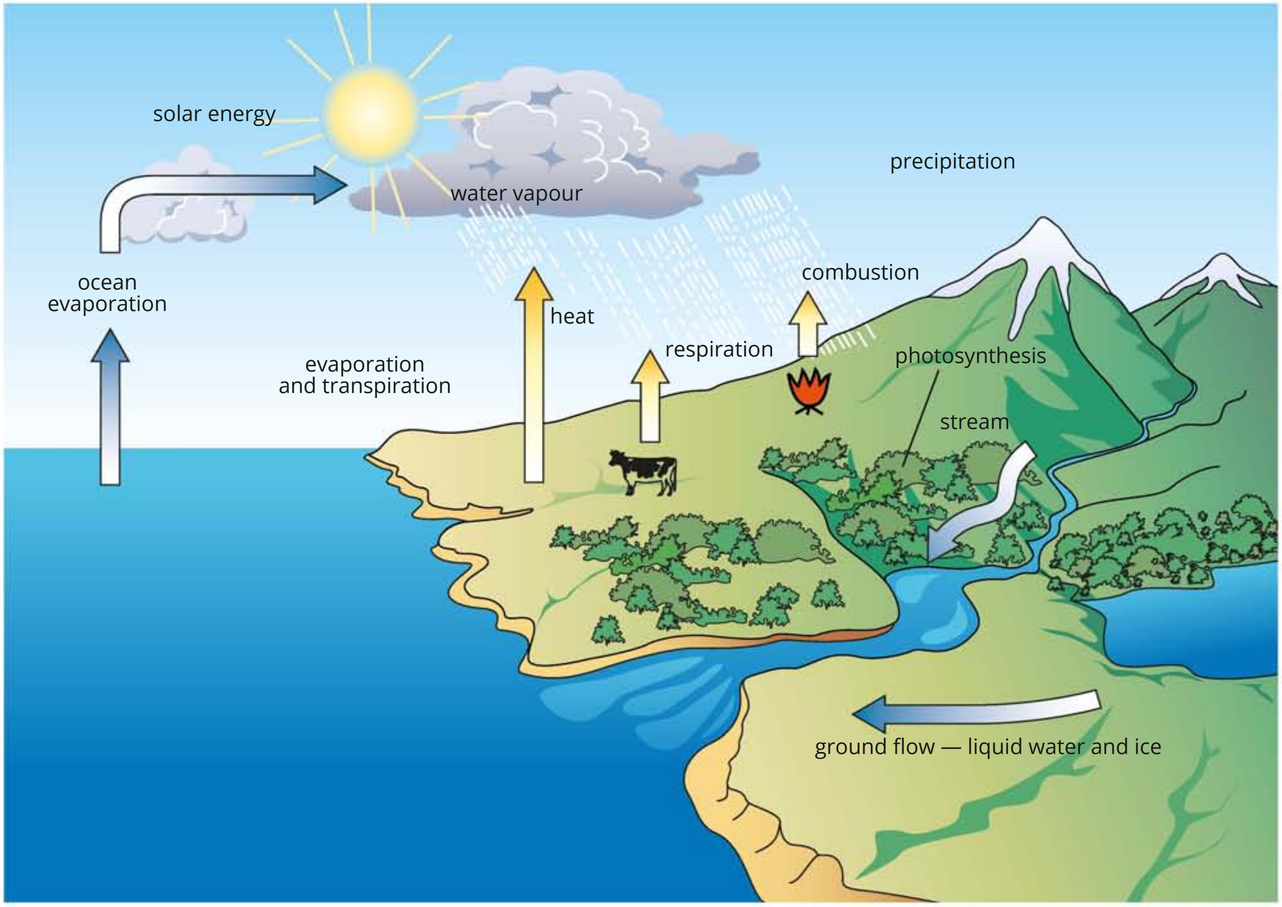


FIGURE 17.1.2 The water cycle illustrates how water is moved around the Earth through evaporation, condensation and precipitation.

The water cycle involves three main processes.

- Heat from the Sun causes water to evaporate from the oceans, lakes and streams.
- Water vapour in the air is transported around the globe until it condenses to form clouds.
- The water precipitates as rainwater, or occasionally as ice crystals in hail or snow, and falls to the ground.

Human activities such as the combustion of fossil fuels, which produce steam, also contribute to the water cycle.

Table 17.1.1 shows how water is distributed on the planet.

TABLE 17.1.1 The distribution of water on Earth

Location of water	State of matter	Volume (km^3)
Oceans	Liquid	1 300 000 000
Ice caps and glaciers	Solid	24 000 000
Groundwater	Liquid	23 000 000
Ground ice and **permafrost**	Solid	300 000
Lakes	Liquid	180 000
Soil moisture	Liquid	17 000
Atmosphere as water vapour	Gas	13 000
Rivers	Liquid	2100

The volumes in Table 17.1.1 are approximate but, from these figures, the total volume of water on Earth is over 1.3 billion km^3.

Despite the large quantities of water, there is a limited supply of fresh water on our planet. Figure 17.1.3 shows that only 2.5% of the water on Earth is drinkable and most of this water is not accessible as it is locked in icecaps, glaciers or the soil.

About 40% of the world's population lives in areas where water is scarce and that number will grow to nearly 50% by 2025. Australia has close to 5% of the land mass of the world but has only 1% of the water carried by the world's rivers.

Australia is the driest inhabited continent and has extremely variable rainfall. It has hundreds of large dams and thousands of farm dams that can hold a lot of water so that Australians can be prepared for periods of drought. Since Australia is also very flat and hot, most of the rain that falls evaporates before it can enter rivers and reservoirs.

CHEMFILE

Great Artesian Basin

The **Great Artesian Basin** is located within Australia. It has the following key features.

- It is the largest **artesian basin** (underground water supply) in the world.
- It covers an area of over 1 700 000 km^2. It underlies nearly a quarter of the Australian continent.
- In some places, the basin is up to 3000 m deep.
- The temperature of the water in the basin has been recorded to be anywhere from 30°C to 100°C.
- It provides a reliable source of **groundwater** for a very large part of inland Australia.

Traditionally, the water could be readily accessed as it flowed to the surface under natural pressure. However, in the last century, government bodies have set up initiatives to try to maintain stores of water within the basin.

FIGURE 17.1.4 The Great Artesian Basin provides water for stock and the human population for a large area of inland Australia.

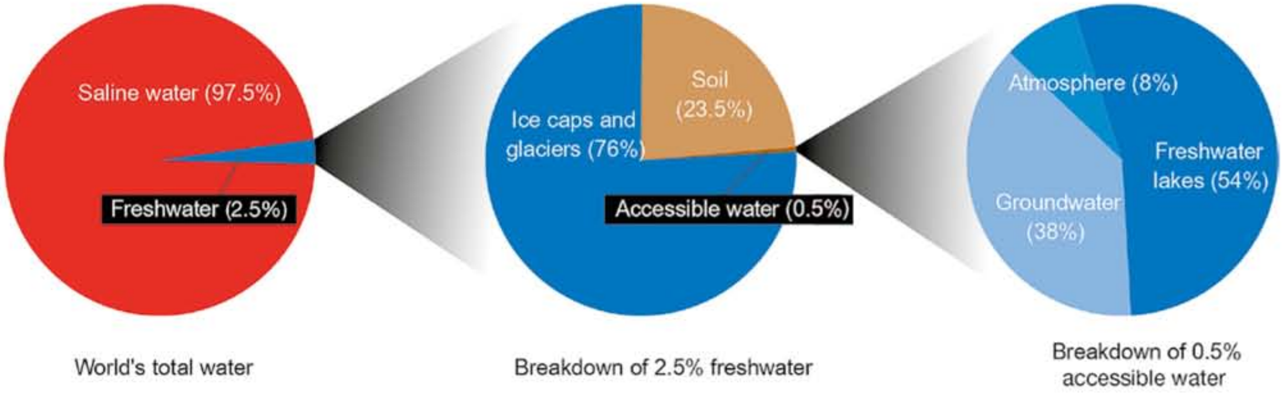


FIGURE 17.1.3 Distribution of water on Earth. Only 2.5% of the water on Earth is drinkable.

POTABLE WATER

Obtaining clean drinking water, or **potable water**, has been a challenge for people living in communities for thousands of years.

Major sources of drinking water

Drinking water in Australia is obtained from a variety of sources. The main sources are:

- reservoirs filled by run-off from rivers and streams
- water obtained directly from rivers and lakes
- groundwater
- **recycled water**
- **desalinated seawater**.

In most of Australia's major cities, water comes from reservoirs built on rivers in protected areas. These reservoirs are able to provide the population with safe, clean water. Water from such sources needs only minor treatment before being released for consumption. Reservoirs like the one shown in Figure 17.1.5 are surrounded by protected land, classifying them as **protected catchments**. They are often located in national parks and forests with limited access to ensure the quality of the water is very high.

FIGURE 17.1.5 The Silvan Resevoir stores water from the Upper Yarra, Thomson and O'Shannassy reservoirs for Melbourne's water supply. Note the surrounding protected land.

However, in some parts of inland Australia, and in some other countries in the Asia–Pacific region, water comes from sources other than protected catchments. In some cases, water is taken directly from rivers and lakes that may be subject to contamination from run-off from farms and urban areas. Drinking water may also be obtained from groundwater, which is often referred to as **bore water** in Australia. Such sources may contain levels of contamination that require a more complex purification process than for water from protected catchments.

Table 17.1.2 shows the major sources of drinking water in some Australian towns and cities.

TABLE 17.1.2 Sources of drinking water in Australia

City or town	Main water source
Alice Springs, inland Northern Territory	Groundwater
Adelaide, South Australia	Torrens and Murray rivers
Bourke, inland New South Wales	Darling River
Broome, coastal Western Australia	Groundwater
Melbourne , Victoria	Reservoirs
Mildura, inland Victoria	Murray River
Birdsville, inland Queensland	Groundwater
Hobart, Tasmania	Derwent River

Drinking water in Victoria

Most Victorians obtain their drinking water from a mains water supply, which is called **reticulated water**. The water is piped from a reservoir and is controlled by a local water authority. Where this supply is not available, drinking water may be obtained from:

- rainwater tanks
- bores
- dams
- rivers and creeks.

The water from the mains supply is tested rigorously and is of the highest quality and poses the lowest risk of contamination. The risk of contamination from different water sources can be seen in Figure 17.1.6.

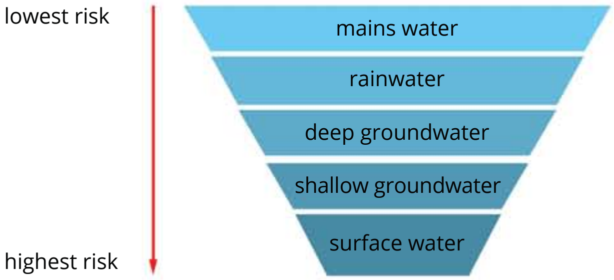


FIGURE 17.1.6 Different sources of drinking water present different risks of contamination.

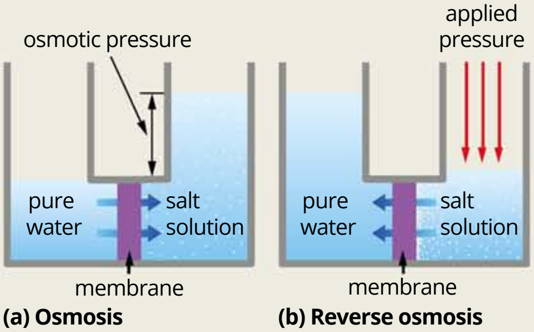
EXTENSION

Victorian desalination plant

Fresh water is a relatively scarce commodity on Earth, whereas seawater is plentiful. Seawater contains about 3.5% dissolved salts and is not suitable for either drinking or agriculture. **Desalination** involves the removal of dissolved salts from seawater to obtain fresh water. The Victorian desalination plant at Wonthaggi produces drinking water from seawater in this way.

Osmosis is the natural tendency of water to move from a region of low salt concentration to one of higher salt concentration. If salt water and fresh water are separated by a **semipermeable membrane**, water molecules, but not the dissolved ions, can pass through it. The water molecules will move through the membrane from the freshwater side to the saltwater side.

This natural tendency can be reversed if pressure is applied to the saltwater side of the semipermeable membrane. This process is called **reverse osmosis** and is used by the Victorian desalination plant. The processes of osmosis and reverse osmosis can be seen in Figure 17.1.7.



(a) Osmosis **(b) Reverse osmosis**

FIGURE 17.1.7 Reverse osmosis can be used to obtain fresh water from seawater. The blue arrows in the diagram represent the movement of water molecules through the semipermeable membrane.

The difficulty and expense of reverse osmosis is associated with making suitable membranes that will not rupture under the high pressures used.

A number of reverse osmosis plants were built in Australia during the extended drought of the first decade of this century. They can be found in Victoria, Western Australia, South Australia, New South Wales and Queensland.

The Victorian desalination plant at Wonthaggi shown in Figure 17.1.8 was completed in December 2012. It has the capacity to produce 150 billion litres of water a year and expand production to 200 billion litres of water a year. To this date, the Victorian Government has not ordered any water from the plant and so it has not delivered a single litre of water.

FIGURE 17.1.8 Desalination plant at Wonthaggi, Victoria.

CHEMFILE

Monitoring water quality

The Environment Protection Authority (EPA) Victoria monitors water quality around the state. Recent cases include an:

- investigation into the cause of the death of fish at the council reserve in Kilmore
- enforceable undertaking between Goulburn Valley Water and EPA Victoria for the water authority to improve its environmental performance after storing industrial waste without the required licences
- investigation into possible chemical contamination of a waterway that may have contributed to the death of fish at Three Mile Creek in Wangaratta.

FIGURE 17.1.9 A scientist collecting water samples for analysis.

How water is collected to test its quality (Figure 17.1.9) will be looked at more closely in the next section of this chapter.

17.1 Review

SUMMARY

- Most of the water on Earth is in liquid form and contained in the oceans.
- Only 2.5% of all the water on Earth is drinkable, but just 0.5% of all the water on Earth is drinkable and accessible.
- Drinking water can be obtained from a variety of sources including:
  - rivers flowing through protected catchments
  - directly from rivers and lakes
  - groundwater
  - rainwater collected from a roof and stored in tanks
  - desalinated seawater.
- Reservoirs, which are fed by rivers, are the main source of household water in Australian cities.

KEY QUESTIONS

1. Which water source has the highest risk of contamination? Explain why.
2. Where does reticulated water come from?
3. Why is only 0.5% of water on Earth available for drinking?
4. Why does Australia store more water per person than any other country?

17.2 Water quality

In 2012, Chinese newspapers reported that 54% of China's drinking water was too polluted to drink. Just two years later, the situation in the country had worsened as the percentage of polluted drinking water rose to 60%. About 60 000 people die each year in China from diseases caused by water pollution, such as cholera, dysentery and diarrhoea.

The quality of the drinking water around the world varies enormously. Most of the water in Australia is of high quality but there have been instances where this is not the case.

This section explores the **chemical contaminants** that can be found in drinking water and how samples are obtained for analysing water quality.

CHEMICAL CONTAMINANTS

You will remember from Chapter 13 that water can dissolve many different types of substances. This can cause problems when unwanted or toxic solutes pollute water supplies. The dissolved materials may end up in rivers, reservoirs or groundwater, and therefore in Australia's water supplies.

As a result, water supplies may be subject to pollution caused by human activity. Although chemical contamination of water supplies is not common in Australia, it can happen (Figure 17.2.1). Contamination can occur because of:

- run-off from farms and cities
- run-off from industrial and mining wastes
- lead used in solder in copper water pipes.

FIGURE 17.2.1 Pollution can be caused by seepage of heavy metals and other contaminants into aquifers (water-bearing rock).

Chemical contaminants are elements or compounds that may be harmful if consumed in drinking water. They can be naturally occurring or synthetic. The main types of chemical contaminants are:

- **heavy metals**
- pollutants from fertilisers
- organic pollutants.

Heavy metal contamination

Heavy metals, such as mercury and lead, can contaminate drinking water and have severe health effects. These effects include cancer, organ and nervous system damage, and, in the most extreme cases, death. Unfortunately, young people are even more susceptible to the effects of heavy metals, and permanent brain damage can be the consequence of exposure to heavy metals.

The quality of drinking water around Australia is governed by local water authorities and is generally high. However, some rural communities do not have access to the same quality of drinking water as city residents do. As a result, there are guidelines in place for the levels of heavy metals that are permissible in Australian drinking water, which are shown in Table 17.2.1.

TABLE 17.2.1 Australian Drinking Water Guidelines values for heavy metals

Heavy metal	Guideline value (mg L^{-1})
Arsenic	0.01
Cadmium	0.002
Copper	2
Chromium	0.05 as chromium(VI)
Lead	0.01
Mercury	0.001

Example of contamination: mining

In 2013, it was discovered that one-third of Tasmania's town water supplies did not meet the national standards for heavy metals. The residents of five towns in the north-west of Tasmania were told not to drink the water due to contamination. In particular, the Tamar River (Figure 17.2.2) was polluted by effluent and the heavy metals zinc, cadmium and lead. The issue for most towns was unusually high concentrations of zinc, cadmium and lead resulting from nearby mining operations.

FIGURE 17.2.2 The Tamar River in Tasmania has been polluted by effluent, including the heavy metals zinc, cadmium and lead.

Example of contamination: water pipes

Lead-based solder was once used to join copper water pipes. As a result of corrosion, the lead can be released into water flowing through the pipes. In 1993 in Perth, Western Australia, a study showed that some households had higher than acceptable levels of heavy metals. Table 17.2.2 shows the percentage of houses in Perth with unacceptable heavy metals levels.

TABLE 17.2.2 Heavy metal levels in Perth

Heavy metal	Households with unacceptable levels (%)
Lead	5
Copper	12
Cadmium	2

To minimise this potential problem, Australian standards were introduced in 1998 to limit the amount of lead in solder to no more than 0.1% by weight.

WATER SAMPLING

To ensure high water quality and to test for contamination in water supplies, water samples are regularly collected for analysis. The results may be compared against water quality standards. This determines the water's suitability for its intended use and, if necessary, the treatment required to purify the water.

There are protocols for obtaining water samples to ensure that the samples are collected in a consistent manner and with the correct equipment. There are many different methods for obtaining water samples depending upon whether the samples are collected close to shore, from boats (Figure 17.2.3) or from bridges (Figure 17.2.4).

In a large dam or reservoir, it may be necessary to take samples from different depths. When comparing samples over time, samples need to be taken from the same location and in the same manner on each occasion, making it especially important to follow established protocols.

When collecting water samples for testing, it is important to consider the following questions.

- Which chemical is to be analysed and why is the testing to take place?
- What health risks are associated with the sampling?
- What equipment is required, and are **sterile** containers needed?
- What sample size is required for the selected test?
- What method is to be used to record the measurements?
- Where should the samples be taken and at what depths should the samples be taken?
- How will a representative sample be obtained?
- What are the labelling, storage and transport requirements for the sample?

FIGURE 17.2.3 Sampling water from a boat.

Protocols for water sampling

The containers used for sampling should not react with the sample. To assure the quality of the sample, the:

- container can be rinsed with the sample before the final sample is taken
- container should be cleaned before taking another sample
- water used for cleaning the container can be tested to ensure there is no contamination between samples.

If the water is to be tested for bacteria and other microorganisms, it is important that the container be sterile.

Sampling methods and equipment

The method used to avoid contamination of a water sample depends on where the water is being sampled from, and the conditions under which the sample is taken. Some sampling methods are outlined in Table 17.2.3.

FIGURE 17.2.4 Sampling water from a bridge.

TABLE 17.2.3 Sampling methods for collecting water samples

Conditions	Sampling method
Sample taken from a well-mixed body of water	Sampling near the surface is sufficient to obtain a representative sample. A sample should be taken about 10 cm below the surface and away from the water's edge.
Sample taken from water contaminated by **sediment** (solid particles)	A sample should be drawn into the sample container by suction to avoid including the sediment.
Sample taken from a river	A sample should be taken upstream from where the person taking the sample stands.

EPA Victoria has published water-sampling protocols, which detail:

- the type of container
- how to sample and transport the sample
- how to preserve the sample
- the maximum holding time for the sample.

An extract from the protocols is shown in Table 17.2.4.

TABLE 17.2.4 EPA Victoria guidelines for measuring mercury and lead contaminants in water

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period (days)	Additional notes
Mercury	Fluoropolymer or acid-washed borosilicate glass	500	Immediately acidify the unfiltered sample to pH < 2	28	Add 5 mL of 12 M HCl or bromine monochloride (BrCl) to preserve the sample.
Lead	Acid-washed polyethylene or acid-washed glass	500	Acidify with nitric acid to pH 1–2	28	Acid-washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations.

Sampling depths

To determine the depth at which a sample should be taken, the temperature is initially measured at every metre of depth.

- If the temperature is consistent, it can be assumed that the water is thoroughly mixed and a sample is taken halfway down.
- If there is a temperature variation, then a sample is taken in the middle of each temperature region.

When the water being sampled is more than 2 metres deep or samples are required from different depths, a **Van Dorn sampler** (Figure 17.2.5) can be used. This sampler can be lowered horizontally and pulled sideways before the sample is taken. Van Dorn samplers are made of a transparent polymer and are attached by a rope to the surface. After the sampler is raised to the surface, the water is drained and placed in a sterile sample bottle. The Van Dorn sampler is very useful when there are distinct layers in the water, such as in a deep lake or reservoir.

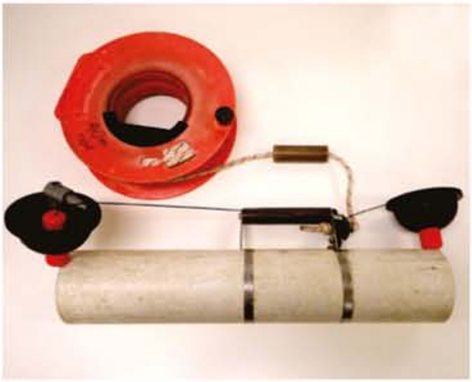


FIGURE 17.2.5 A Van Dorn sampler consists of a polymer tube with caps at each end.

Sampling locations

To develop a true picture of the water quality in a body of water, you need to take samples from many different locations.

For example, a water-quality monitoring program in the Tamar Estuary in Tasmania took samples from 20 sites divided into five zones, as shown in the map in Figure 17.2.6. The sites ranged from Launceston to where the lower estuary discharges into Bass Strait. The samples were taken monthly at specific depths and all samples were taken on the same day.

FIGURE 17.2.6 Sampling sites in the Tamar Estuary, Tasmania.

17.2 Review

SUMMARY

- Contamination of water supplies comes from farms, industry, mines and through the soil.
- Types of chemical contaminants include:
  - heavy metals
  - pollutants from fertiliser
  - organic pollutants.
- Protocols exist for sampling water for the analysis of water quality.
- All protocols need to consider:
  - the reason for testing
  - the chemical to be analysed
  - health risks associated with the sampling
  - specific requirements for the chemical being tested
  - selection of equipment and sample size
  - recording results and taking representative samples
  - labelling and storage requirements.

KEY QUESTIONS

1 The EPA Victoria has published water-sampling methods for collecting water samples to analyse for specific metals. By referring to the sampling protocols in Table 17.2.4 on page 438, select which one of the following is not relevant for collecting water samples to analyse for mercury.

A The use of a container made of borosilicate glass

B The volume of the container

C The temperature of the sample during preservation

D The maximum holding time for the sample

2 What is the correct protocol for taking a water sample from a river?

3 In a large body of water, the temperature of water should be measured at every metre of depth before taking samples. What is the reason for doing this?

Chapter review

KEY TERMS

aquifer
artesian basin
bore water
chemical contaminant
desalinated seawater
desalination
Great Artesian Basin
groundwater
heavy metal
osmosis
permafrost
potable water
protected catchment
recycled water
reticulated water
reverse osmosis
sediment
semipermeable membrane
sterile
Van Dorn sampler
water cycle

The availability of drinking water

1 Copy and complete the following diagram relating to drinking water and water quality.

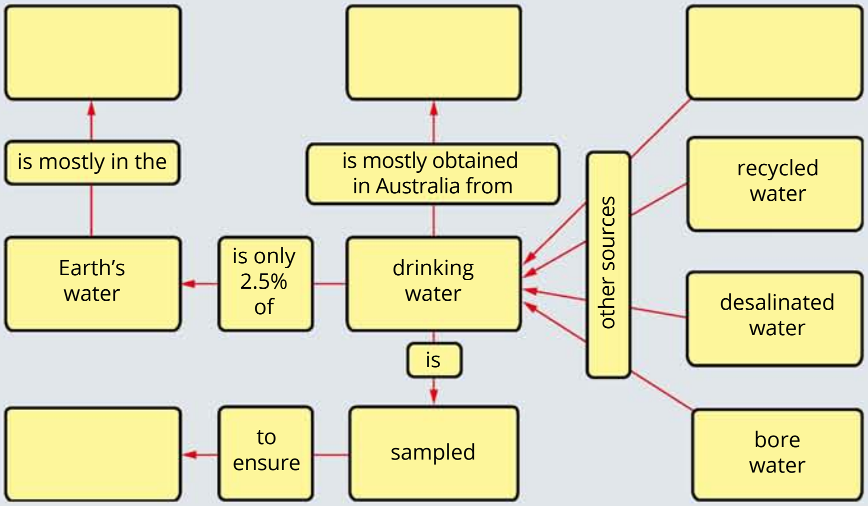


FIGURE 17.3.1 Concept map on water quality.

2 Where is most of the drinkable water found on Earth?
- **A** Ice
- **B** Rivers
- **C** Groundwater
- **D** Bore water

3 What is the drinking water that comes from groundwater called?

4 What is the source of drinking water for most Australians and why?

5 Arrange the following sources of water on Earth in order from highest volume to lowest volume: oceans, groundwater, rivers, soil moisture, ground ice and permafrost, lakes, ice caps and glaciers, atmosphere as water vapour

Water quality

6 Imagine that you are an environmental scientist and have been asked to develop a water-sampling program for a large reservoir. The quality of the water is to be tested over a month. What are some of the matters that should be addressed before starting your program?

7 Which one of the following factors does not need to be considered when sampling water for analysis?

- **A** Temperature
- **B** Depth
- **C** Distance from the shore
- **D** Humidity

8 A water sample was tested for heavy metals. The results are shown in Table 17.3.1. Classify which of the concentrations are above and which are below the Australian Drinking Water Guidelines acceptable levels (Table 17.2.1 on page 436).

TABLE 17.3.1 Heavy metals in a water sample

Heavy metal	Concentration (mg L^{-1})
Arsenic	0.009
Cadmium	2.2×10^{-4}
Copper	1.9
Lead	0.1
Mercury	0.9×10^{-2}

9 Give a possible source of error in each of the following steps in sampling water from a lake.

- **a** Determine sampling location
- **b** Collect sample
- **c** Transfer sample to a container
- **d** Store sample
- **e** Transport sample

10 Why has EPA Victoria developed protocols for sampling water?

Connecting the main ideas

11 Describe some of the important ways in which water is used in industry and how these might affect water quality.

CHAPTER 18

Analysis for salts in water

As you discovered in Chapter 13, water is a very good solvent for a wide variety of polar molecules and ionic salts. As a result of water's solvent properties, all water systems contain some dissolved salts. Their presence can be attributed to a number of factors such as natural processes, pollution, farming and industrial activities.

In this chapter you will examine the ways in which salts can enter the water system and the methods used by scientists to test water to determine salinity levels. You will also look at a number of methods used to test water samples for the presence of metal contaminants and other ions.

Key knowledge

- Sources of salts found in water (these may include minerals, heavy metals, organometallic substances)
- The use of electrical conductivity to determine the salinity of water samples
- The application of mass–mass stoichiometry to gravimetric analysis to determine the mass of a salt in a water sample
- The application of colorimetry and/or UV–visible spectroscopy, including the use of a calibration curve, to determine the concentration of coloured species (ions or complexes) in a water sample
- The application of atomic absorption spectroscopy (AAS), including the use of a calibration curve, to determine the concentration of metals or metal ions in a water sample (excluding details of instrument)

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18.1 The source of salts in water

Figure 18.1.1 shows a dry section of Lake Eyre, a very large inland salt lake in South Australia. On the rare occasions when the lake contains water, the salt concentration in the water is very high. When the lake dries up, the salts are deposited on the lake bed. The high concentration of salts in the water in Lake Eyre is an extreme example of **salinity**.

Sodium chloride (NaCl) is referred to as salt but, in the context of soil and water supplies, the term 'salt' refers to any ionic compounds present. In this chapter you will examine ways in which these salts come to be in the water system. The sources of the salts found in water can include minerals, heavy metals and organometallic substances. This section will also describe one of the most common ways in which the salt concentration is determined.

FIGURE 18.1.1 Lake Eyre is Australia's lowest natural point at approximately 15 metres below sea level. Salt deposits on the dry bed are a result of the extreme salinity levels in this region.

SALTS FROM MINERALS

Salts are naturally present in the water system. As part of the water cycle, water runs through soil and rocks, dissolving solid **mineral** deposits and transporting these salts into lakes, rivers, creeks and other bodies of water. The centre of Australia was once submerged under the ocean, so the presence of salt in Lake Eyre should not be a surprise.

FIGURE 18.1.2 The action of water dissolving and redepositing minerals has led to these limestone formations and caves.

The region near Buchan in Gippsland, Victoria, was also submerged under the ocean millions of years ago. During that time, the remains of marine organisms containing calcium carbonate ($CaCO_3$) accumulated there. These layers of calcium carbonate deposits eventually formed limestone. The spectacular caves throughout the region are a result of underground rivers cutting through limestone rock. In Figure 18.1.2 you can see the formations that are the result of the dissolving and redepositing of limestone by rainwater over time as it passes through the caves.

There are many other examples of regions in Victoria with high mineral concentrations, including:

- Hepburn: Hepburn is famous for its mineral water springs. Tourists bathe in the hot pools that contain high levels of minerals. The ions present in the water include Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Cl^- and HCO_3^-.
- Wimmera mineral sands: The sandy soil in the Wimmera region of north-west Victoria contains significant levels of zircon and titanium minerals. Iluka Mines operates in this region to extract these valuable minerals.
- Pittong clay mine: Levels of clay minerals in the soil near Pittong in Central Victoria are very high and are mined for commercial use.

Salts from human activity

Human activity can increase salt levels in water. In most cases the addition of these salts is considered a form of pollution and results from various industries and processes such as mining, agriculture, domestic sources and sewage treatment plants.

In many countries, governments monitor and regulate the levels of dissolved salts and other contaminants in waterways.

Mining

Mining industries can use large volumes of water to process the materials they are extracting. Some of this water, still containing various ions, may be discharged back into local waterways.

Agriculture

Most farms use fertilisers to improve the yield of crops. When it rains, some of this fertiliser dissolves and may be transported to the waterways through run-off. Ammonium nitrate (NH_4NO_3), ammonium sulfate ($(NH_4)_2SO_4$) and superphosphate ($Ca(H_2PO_4)_2$) are common fertilisers used in Australia that can contribute to the build-up of excess nutrients in waterways such as rivers and lakes.

Domestic sources

Until recently, most detergents contained softening agents made from phosphate compounds. Therefore, the discharge from washing machines and sinks added metal cations and anions, such as phosphate, to the water system. Phosphate is a nutrient for plants and leads to excessive algae growth in waterways, which is known as algal blooms. In Figure 18.1.3, you can see the effect of high levels of phosphates in water. The growth of algal blooms due to excess nutrients leads to a significant problem known as **eutrophication**.

FIGURE 18.1.3 Eutrophication due to algal blooms can result from high concentrations of phosphate in the water.

Sewage treatment plants

All cities have treatment plants to process effluent (sewage) and grey water (non-sewage water waste from homes and businesses). Although this water is treated to remove harmful contaminants, the water discharged from the treatment plants may contain a variety of ions similar to those from domestic sources.

There are many different ways in which human activity contributes to the salt content of waterways. This increase in salt content can have harmful effects on the environment.

Heavy metal salts

Definitions of **heavy metals** vary, but they are usually described as metals with a high density that have a toxic effect on living organisms. Cadmium, lead, chromium, copper and mercury all fit this description of heavy metals. Some metalloids, including arsenic, are also commonly included in lists of heavy metals due to their high toxicity. Figure 18.1.4 compares the densities of some heavy metals and lighter, non-toxic elements such as aluminium and magnesium. Some scientists regard aluminium ions in solution as toxic.

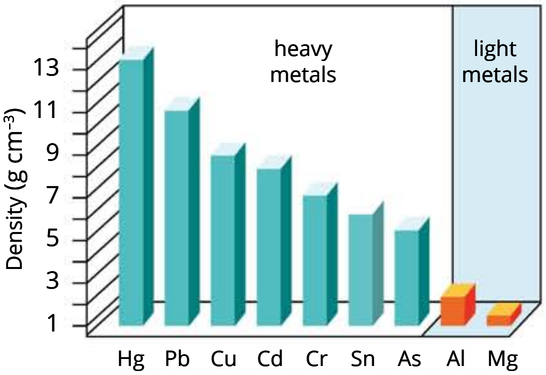


FIGURE 18.1.4 A comparison of the relative densities, in g cm^{-3}, of a number of toxic heavy metal elements with the lighter elements aluminium and magnesium. Tin is considered a heavy metal to a lesser extent due to its lower toxicity levels.

Heavy metals occur naturally within the Earth's crust. Their salts can dissolve into rivers and groundwater and so make their way into drinking water supplies. Usually the concentrations of heavy metals from these natural sources are very low. However, heavy metals are often used in industry, and various human activities can result in elevated levels of heavy metals in the environment.

Heavy metal salts can be a threat to human health. The high affinity of the ions for thiol (–SH) groups in proteins and enzymes can distort the overall three-dimensional shape of these molecules. The change in shape results in a loss of biological activity and the organism suffers adverse effects. There have been many examples in which elevated levels of heavy metals in particular environments have led to illness and death in communities, so government agencies monitor the levels of heavy metal salts very closely. Table 18.1.1 lists some heavy metal pollutants, their sources and the effects they can have on human health.

TABLE 18.1.1 Health effects and sources of a number of heavy metals

Heavy metal pollutant	Source	Effects
Copper	• Copper pipes	• Anaemia • Liver and kidney damage • Stomach and intestinal irritation
Lead	• Lead pipes • Batteries • Leaded petrol • Paints • Ammunition	• Negatively affects haemoglobin production • Damage to kidneys, gastrointestinal tract, joints and reproductive system • Can lower IQ levels in young children
Cadmium	• Smelting • Improper disposal of rechargeable batteries	• Kidney failure • Liver disease • Osteoporosis
Nickel	• Power plants • Waste incinerators • Improper disposal of batteries	• Decreased body weight • Damage to the heart and liver
Zinc	• Mining • Smelting • Steel production	• Anaemia • Damage to nervous system and pancreas
Arsenic	• Natural deposits in the ground • Industry • Agricultural processes	• Carcinogenic • Stomach pain • Numbness • Blindness
Mercury	• Improper disposal of batteries, fluorescent light bulbs, thermometers and barometers • Various industrial processes • Burning of fossil fuels	• Tremors • Gingivitis • Spontaneous abortion • Damage to the brain and central nervous system

Heavy metal ions are released into the environment in two main ways: through human activity directly, or as a result of reaction with water in the atmosphere. Heavy metal compounds can be released directly into waterways through waste from industries such as metal processing and mining. Other potential sources of contamination from heavy metals include leachate from landfill sites and agricultural run-off.

Combustion of fuels and wastes containing heavy metals can release the ions into the atmosphere where they can interact with water molecules. Rain can then take the dissolved salts into soils, rivers and groundwater.

Problems caused by heavy metals in the environment can be made worse when they increase in concentration in a food chain. The build-up of heavy metals in higher-order predators is often referred to as **bioaccumulation**, and is illustrated in Figure 18.1.5.

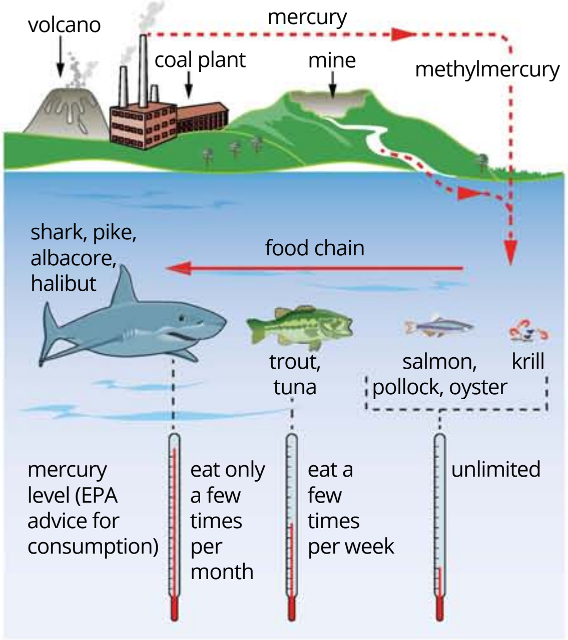


FIGURE 18.1.5 As living organisms have no way of removing heavy metals, such as mercury, from their cells, the concentration of heavy metals can be seen to increase in species higher up the food chain.

Heavy metals are not biodegradable; once released into the environment they will persist and accumulate.

Government authorities provide guidelines for maximum heavy metal levels in water supplies and monitor these levels closely. Only specified low levels of heavy metals are permissible in drinking water. Table 18.1.2 is from the Australian Drinking Water Guidelines and shows the permissible levels of some heavy metals.

One method of removing heavy metals from a contaminated water supply is by the use of precipitation reactions. You were introduced to precipitation reactions in Chapter 13. You can use solubility rules introduced there to select appropriate reagents that will result in the formation of a solid precipitate that contains the heavy metal ion.

The process involves adding a soluble compound that will lead to the heavy metal ion forming an insoluble compound that precipitates from the solution. The precipitate can then be removed by filtration. An example of this process is the addition of calcium hydroxide ($Ca(OH)_2$) to contaminated water to form a precipitate of a heavy metal hydroxide.

The precipitated, insoluble heavy metal salts are no longer toxic. Heavy metals are only toxic to living organisms when present as cations in water-soluble compounds or as **organometallic compounds**.

Heavy metal elements are only toxic when present as cations in water-soluble compounds or as organometallic compounds.

TABLE 18.1.2 Australian Drinking Water Guidelines for the levels of heavy metals, in mg L^{-1}, considered safe for drinking water supplies

Heavy metal	Australian Drinking Water Guidelines* (mg L^{-1})
Arsenic	0.01
Cadmium	0.002
Copper	2
Chromium	0.05 as Cr(VI)
Lead	0.01
Mercury	0.001

*The definition of the health-related guideline value is the concentration that, based on present knowledge, does not result in any significant risk to the health of the consumer over a lifetime of consumption.

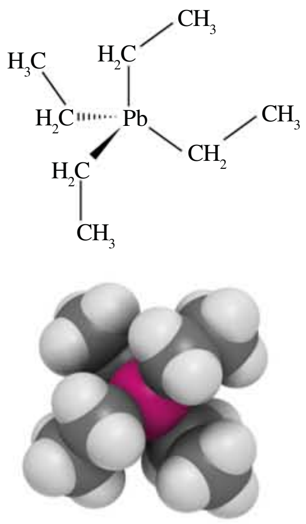


FIGURE 18.1.6 Two different structural representations of tetraethyl lead. This compound has four ethyl groups (–CH_2CH_3) bonded to a lead atom in the centre of the molecule.

ORGANOMETALLIC COMPOUNDS

Another source of heavy metal ions in water systems is the use and disposal of organometallic compounds. Organometallic compounds are substances with at least one carbon–metal bond. They are usually synthetic substances that are used in industry as catalysts or reagents in chemical processes.

An example of an organometallic compound used in industry is tetraethyl lead ($Pb(C_2H_5)_4$) shown in Figure 18.1.6. You can see this molecule has four bonds between a lead atom and the carbon atom of an ethyl group. Tetraethyl lead was added to petrol in Australia for many years to improve the smoothness of combustion in car engines. It is now banned because lead levels near busy roads were affecting the health of local residents. The lead emissions from the cars could even enter nearby waterways. The toxicity of tetraethyl lead is a consequence of the toxic lead it contains.

To be considered an organometallic compound, there must be at least one direct bond between the metal atom or ion and a carbon atom. If the metal is very electropositive, this bond may be very polar, almost ionic.

Another example of an organometallic compound is methylmercury. It is an organometallic cation with the formula CH_3Hg^+. In methylmercury, a methyl group is bonded to a mercury(II) ion. Methylmercury combines with anions to form organometallic salts such as methylmercury chloride and methylmercury hydroxide. Methylmercury compounds are formed in some industrial processes, such as the production of ethyne, but they are also formed when compounds containing mercury are burnt. Methylmercury compounds are more toxic than mercury itself because they can be easily transported around the human body in the same way as proteins.

CHEMISTRY IN ACTION

Lasting impact of heavy metals

The levels of heavy metals in waterways are closely monitored because even amounts as small as 24.8 ppm (24.8 mg L^{-1}) can be deadly. The wide-ranging and long-term effects of heavy metal poisoning were clearly shown in Japan in the 1950s. A factory in the small fishing village of Minamata had been discharging toxic waste containing methylmercury into the local bay. As mercury compounds are non-biodegradable, the toxic mercury compounds built up in the aquatic organisms living in the bay. The main diet of the people of Minamata consisted of seafood caught in the contaminated bay.

The first indication of a problem was the erratic behaviour of the local cats that were seen to be 'dancing' down the streets before collapsing and dying. This strange behaviour was a direct result of mercury poisoning that causes neurological disorders and eventually death.

Neurological symptoms were also seen in the local population, with many residents suffering irreversible brain and organ damage. Many people died as a result of the high levels of mercury they unknowingly ingested. Originally referred to as 'Minamata disease', the neurological effects were eventually determined to be the direct result of mercury poisoning. The Minamata area residents still struggle with highly toxic levels of mercury to this day. The accumulated mercury levels in the people also led to the development of a number of congenital disorders in children born to parents suffering from Minamata disease. Figure 18.1.7 shows a young boy receiving physiotherapy to treat the effects of mercury poisoning.

FIGURE 18.1.7 A young boy in Japan receives physiotherapy for the ravaging effects of mercury poisoning.

HARD WATER

Hard water is a term used to describe water that requires a lot of soap to obtain a lather or froth. **Hardness** in water is caused by the presence of some metal ions, mainly calcium, magnesium and iron. These metal ions are due mainly to the presence of dissolved minerals and interfere with the washing action of soaps and some detergents.

Hard water also causes deposits to form on the inside of kettles and water pipes. These deposits can lead to the eventual blocking of the pipes (Figure 18.1.8).

FIGURE 18.1.8 Accumulation of limescale in pipes is a result of the precipitation of soap scum due to the calcium and magnesium ions present in hard water. Eventually, the crystalline deposits can become so severe they block the flow of water.

Table 18.1.3 outlines the composition of metropolitan reserve water supplies in five Australian capital cities in μg g^{-1}. The data shows why Melbourne's water is considered to be **soft water**, while water in Perth and Adelaide can be described as hard water.

TABLE 18.1.3 The composition of five metropolitan reserve water supplies (μg g^{-1})

Metal ions	ADWG standard*	Adelaide	Brisbane	Melbourne	Perth	Sydney
Na^+ and K^+	180	82–106	43	10	61–95	16–22
Ca^{2+}		16–28	23	4.5	5	1.5–9.7
Mg^{2+}		13–20	14	1.5	7–12	5.9–6.2
Fe^{2+}	0.3	0.018	0.01	0.05	0.06	0.01–0.03
Cl^-	250	141–182	63	12.5	105–166	28–35
Total dissolved solids	500	412	273	55	380	112–130
Total hardness (as $CaCO_3$)	200	148	116	18	90	55–61

*Australian Drinking Water Guidelines (ADWG) of maximum permissible levels in drinking water

One of the essential ingredients in soap is the compound sodium stearate ($C_{17}H_{35}COONa$). When dissolved in water, soap provides the stearate ion ($C_{17}H_{35}COO^-$) which can act as a dirt remover. The metal ions in hard water react with this ion to produce a precipitate, removing the stearate ions from solution and reducing the amount of lather produced (Figure 18.1.9). The reaction can be described using the following equation:

$$2C_{17}H_{35}COO^-(aq) + Ca^{2+}(aq) \rightarrow Ca(C_{17}H_{35}COO)_2(s)$$

The formation of this precipitate means that extra soap must be used for washing to achieve the same effect. The precipitate also contributes to the formation of an unwanted 'soap scum', which should be cleaned from baths and showers as part of regular household cleaning chores.

FIGURE 18.1.9 Metal ions such as calcium and magnesium in hard water react with stearate to form a precipitate that reduces the lathering ability of soaps and detergents.

Modern laundry detergents contain anions that will combine with the calcium ions and magnesium ions to form insoluble compounds so that these ions do not react with the stearate ions. One example is the carbonate ion, added in the form of sodium carbonate (washing soda). Until 2014, phosphate ions were also added to laundry detergents, but they have been phased out in Australia due to their ability to contribute to eutrophication of natural water resources.

CHEMFILE

Australian laundry detergents become phosphate free

Most Australian laundry detergents became phosphate free by 2014, as major companies agreed to phase out the environmentally damaging ion from their products.

Major supermarkets such as Coles, Woolworths and Aldi also agreed to stop selling environmentally damaging detergents.

FIGURE 18.1.10 Phosphates have been phased out of Australian laundry detergents.

Zeolites are widely used as a replacement to phosphates. Zeolites are aluminosilicate minerals with large numbers of small pores with diameters smaller than 2 nm. As a consequence, they have extremely high surface areas.

MONITORING WATER QUALITY

In Australia, water authorities are required to provide water suitable for drinking purposes. This involves regular monitoring of water quality from catchment areas and throughout the various stages of treatment, storage and delivery. Monitoring includes checking the level of various solutes in water and making sure that acceptable levels are maintained.

Aspects of water quality that are monitored usually include:

- the concentration of common ions such as Na^+, Ca^{2+}, K^+, Fe^{3+}, Cl^-, SO_4^{2-} and HCO_3^-
- **turbidity**, which is a measure of the cloudiness of water due to suspended solids
- **pH**, which is a measure of acidity
- hardness
- nutrients such as nitrates and phosphates.

TESTING FOR SALINITY

One of the most common methods for testing salinity levels of water samples is to measure the **electrical conductivity (EC)** of the sample. Electrical conductivity is the degree to which a specified material conducts electricity. If two electrodes in a circuit containing a light globe and a battery are placed into a water sample, as shown in Figure 18.1.11, the intensity of the light emitted from the globe will provide an indication of the salinity level.

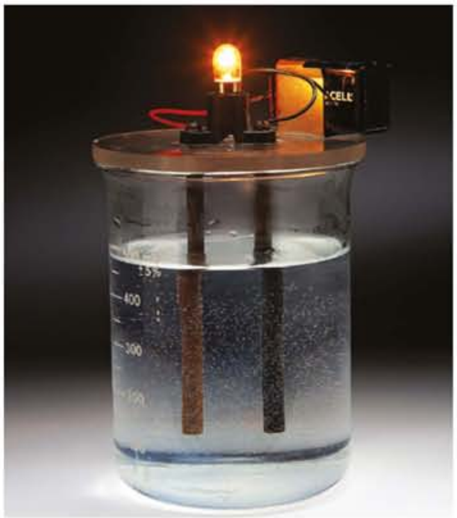


FIGURE 18.1.11 A simple circuit for detecting salinity. The brighter the light emitted from the globe, the greater the conductivity of the solution.

Pure water contains very few ions and is a poor conductor of electricity. As soluble salts are added to the water, the ion concentration increases, which in turn increases the conductivity of the solution. It is the flow of ions towards the electrodes that is responsible for the conductivity. Quantitative measurements can be taken if a meter is included in the circuit. Figure 18.1.12 shows how the increase in conductivity with increased ion concentration can be measured.

Pure water is a poor conductor of electricity. As the concentration of ions in solution increases so does the conductivity.

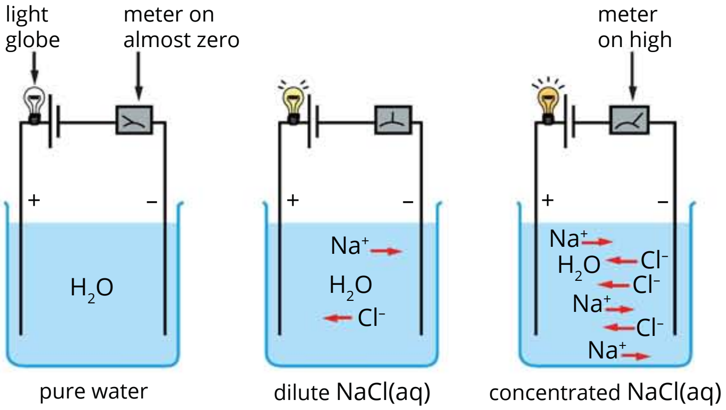


FIGURE 18.1.12 The conductivity of a salt solution depends upon the concentration of salt in the solution. The flow of current increases as the concentration of ions increases.

Figure 18.1.13 shows that at low salt concentrations, there is a direct relationship between the conductivity and concentration. A graph of conductivity against concentration of salt solutions is linear.

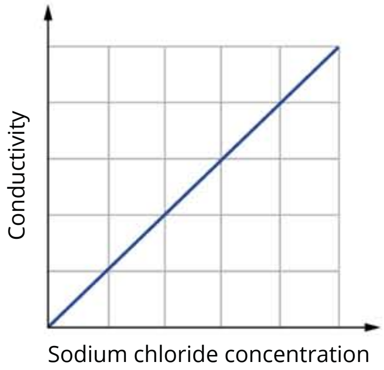


FIGURE 18.1.13 The conductivity of a salt solution increases with concentration. At low concentrations the relationship is considered to be a linear one.

Electrical conductivity is independent of the distance between the electrodes and is measured in units of microsiemens per centimetre, mS cm^{-1}. The electrical conductivity of a solution increases as the temperature of the solution increases, so to ensure consistency, readings for electrical conductivity are generally taken at 25°C and at a constant voltage.

Besides sodium chloride, there is usually a mixture of salts present in a water sample. The conductivity reading does not distinguish between the types of ions that are present, just the amount. When discussing water quality, the salinity level is referred to as the **total dissolved solids (TDS)**. The measured electrical conductivity can be converted to a TDS concentration by using the approximate relationship:

$$\text{TDS (in mg L}^{-1}\text{)} = \text{EC (in mS cm}^{-1}\text{)} \times k_c$$

where k_c varies between 0.55 and 0.8, depending on the salts present.

The value of k_c is usually taken as 0.6 in Victoria.

> The total dissolved solids in a water sample is given by the equation:
>
> $$\text{TDS (in mg L}^{-1}\text{)} = \text{EC (in mS cm}^{-1}\text{)} \times k_c$$

Typical guidelines for the salinity level of water for different uses are shown in Table 18.1.4.

TABLE 18.1.4 Salinity guidelines for water use

Electrical conductivity (EC) mS cm^{-1}	Water quality
0–800	Good drinking water, suitable for irrigation and livestock
800–2500	Unpleasant to drink; use in irrigation needs to be managed
2500–10 000	Not recommended for human consumption; suitable for salt-tolerant vegetation only
>10 000	Not suitable for any plants or animals

Handheld, portable salinity testing probes, such as the one shown in Figure 18.1.14, are widely used by agricultural experts and water authorities who want quick and reliable salinity estimates on the spot. Because these readings are often completed on-site, the probes are calibrated to account for differences in temperature.

FIGURE 18.1.14 Portable digital salinity meters such as this one usually self-adjust for temperatures other than 25°C.

18.1 Review

SUMMARY

- Pollution resulting from human activity is a source of salts in our water supplies. Activities include run-off from farms and cities, and release of chemicals from industries and mines.
- Heavy metals are metals with a high density, such as lead and mercury, which have a toxic effect on living things. Heavy metals are present in nature, but processes in some industries add to the levels of these metals in water supplies.
- Organometallic compounds are substances that contain at least one carbon–metal bond. Their use in industry and laboratories can lead to their presence in water systems.
- In some regions of Australia the high mineral levels in water leads to the water being described as 'hard'. This means it contains high levels of metal ions such as Ca^{2+}, Mg^{2+} and Fe^{2+}. Soaps do not function as effectively in hard water and they cause bathroom sinks, taps and drains to become blocked and permanently stained.
- Electrical conductivity is an effective way to measure the levels of salinity in water samples. The higher the concentration of ions in a solution, the higher the electrical conductivity.
- Electrical conductivity increases as the temperature of a solution increases, so readings are taken at 25°C.

KEY QUESTIONS

1 Define the term 'heavy metal' and provide an example.

2 List the ways in which toxic heavy metal levels make their way into waterways.

3 Which one of the following pairs of compounds contains only organometallic compounds?

A $Pb(C_2H_5)_4$ and CH_3Hg^+
B $Pb(C_2H_5)_4$ and HgH
C CH_3Hg^+ and $PbCr_2O_7$
D CH_3Hg^+ and HgF_4

4 The ionic compound sodium stearate ($C_{17}H_{35}COONa$) is the main cleaning agent in soap. In some Australian cities, the cleaning effectiveness of soap is reduced due to water hardness.

a Which ions in water contribute to hardness levels?

b Give an equation for the reaction of the stearate ion ($C_{17}H_{35}COO^-$) in hard water that reduces the lather in soaps.

5 Washing soda (Na_2CO_3) can be added to detergents to soften water. With the aid of an **ionic equation**, explain the action of the washing soda.

6 What does TDS stand for?

7 The electrical conductivity of a solution can be used to provide a measure of its salinity.

a Calculate the salinity level (TDS) from the following electrical conductivity readings of different water samples to mg L^{-1}. Assume that the readings were taken in Victoria.

EC (mS cm^{-1})	**Salinity level TDS (mg L^{-1})**
240	
3200	
12 000	

b Use the salinity guidelines in Table 18.1.4 on page 451 to describe each of the water samples in part **a** as fit or unfit for human consumption.

EC (mS cm^{-1})	**Fit or unfit to drink**
240	
3200	
12 000	

8 A variety of metal ions are found in low levels in a particular water supply. Classify these metal ions as either relatively safe or very toxic:
Na^+, Cu^{2+}, Pb^{2+}, Mg^{2+}, Cd^{2+}, Li^+, K^+, Hg^{2+}

18.2 Gravimetric analysis

In Chapter 13, you learned that water is an exceptional solvent for a large variety of substances. In this section, you will learn to calculate the amounts of reactants or products involved in chemical reactions that occur in solution. These reactions can involve **precipitation reactions**, such as that seen in Figure 18.2.1, as well as other types of reactions. Using your knowledge of the **mole** concept, you will be able to calculate the mass of products formed or reactants consumed.

This section will focus on calculations involving precipitation reactions to determine the amount of dissolved salts contained in a sample.

In the previous section, you learned that electrical conductivity can be used to measure the salinity level of a solution. This technique provides a measure for the total dissolved solids in a solution but it does not distinguish between the different salts that have contributed to the conductivity.

However, there are many instances in which you may want to know the concentration of a particular salt in a solution. For example, you might wish to determine the concentration of sodium chloride in a particular brand of soup. This section describes a technique called **gravimetric analysis** that can be used for this type of analysis.

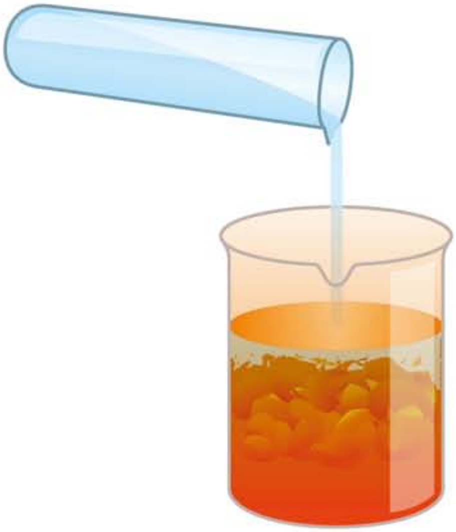


FIGURE 18.2.1 When colourless aqueous solutions of mercury(II) ethanoate and sodium iodide are mixed, they produce a red precipitate, mercury(II) iodide. The mass of the precipitate from this reaction can be used to determine the amount of mercury present in the original sample.

Gravimetric analysis is a technique that can be used to determine the amount of a particular salt present in a solution.

STOICHIOMETRY

In Chapter 5, you were introduced to the mole concept. Chemists can apply the mole concept to chemical reactions to determine the quantities of reactants involved or products formed. This is useful in industry, as manufacturers need to know the quantities of raw materials required to produce a predicted amount of product. Although particles such as atoms, ions and molecules are so small that they cannot be counted individually, the mole concept allows us to determine the number of individual particles by simply measuring their mass.

Calculations based on the mole are used to make these predictions. In this section, these calculations will be used for reactions involving the formation of precipitates.

The study of ratios of moles of substances is called **stoichiometry**. **Stoichiometric calculations** are based on the law of conservation of mass.

The total mass of all products is equal to the total mass of all reactants in a chemical reaction.

In a chemical reaction, the total number of atoms of each element in the reactants is always equal to the total number of each element in the products. The atoms are just rearranged to form new compounds.

Mole ratios

Consider the equation for the precipitation reaction that occurs when a solution of calcium chloride reacts with a solution of silver nitrate:

$$CaCl_2(aq) + 2AgNO_3(aq) \rightarrow 2AgCl(s) + Ca(NO_3)_2(aq)$$

The coefficients used to balance the equations show the ratios between the reactants and products involved in the reaction. The equation indicates that 1 mole of $CaCl_2$ reacts with 2 moles of $AgNO_3$ to form 2 moles of solid AgCl and 1 mole of $Ca(NO_3)_2$.

In more general terms, the amount, in mol, of $AgNO_3$ used will always be double the amount, in mol, of $CaCl_2$ used. The amount, in mol, of AgCl produced will be equal to the amount, in mol, of $AgNO_3$ used and double the amount, in mol, of $Ca(NO_3)_2$ produced.

You can use the coefficients of this reaction to write relationships that show the **mole ratios** of any two chemicals involved in the reaction:

$$\frac{n(AgNO_3)}{n(CaCl_2)} = \frac{2}{1}, \quad \frac{n(CaCl_2)}{n(AgCl)} = \frac{1}{2} \quad \text{and} \quad \frac{n(AgCl)}{n(AgNO_3)} = \frac{2}{2} = \frac{1}{1}$$

Stoichiometric calculations allow you to use the mole ratio established in a chemical equation to predict the amount of a product that will be formed or how much reactant will be used.

In the stoichiometric calculations that you will perform in this section, the moles or mass of one of the reactants or products will always be known (called the 'known chemical') and is used to determine the moles or mass of one of the other reactants or products involved in the reaction (called the 'unknown chemical'). You can write the relationship between the known and the unknown chemicals using ratios:

$$\frac{n(\text{unknown chemical})}{n(\text{known chemical})} = \frac{\text{coefficient of unknown chemical}}{\text{coefficient of known chemical}}$$

When carrying out any stoichiometric calculation, you must always clearly state the mole ratio you are working with.

Worked example 18.2.1

USING MOLE RATIOS

Solutions of copper(II) sulfate and sodium hydroxide are mixed together, forming 0.40 mol of solid copper(II) hydroxide. How many moles of sodium hydroxide reacted in this reaction?

Thinking	Working
Write a balanced equation for the reaction.	$CuSO_4(aq) + 2NaOH(aq) \rightarrow Cu(OH)_2(s) + Na_2SO_4(aq)$
Determine the number of moles of the 'known substance'. The known substance is the one you are provided information about in the question.	$n(Cu(OH)_2) = 0.40$ mol
Find the mole ratio: mole ratio = $\frac{\text{coefficient of unknown chemical}}{\text{coefficient of known chemical}}$ The 'unknown' substance is the one whose number of moles you are required to calculate.	$\frac{n(NaOH)}{n(Cu(OH)_2)} = \frac{2}{1}$
Calculate the number of moles of the unknown substance using: $n(\text{unknown}) = n(\text{known}) \times (\text{mole ratio})$	$n(NaOH) = 0.40 \times \frac{2}{1}$ $= 0.80$ mol

Worked example: Try yourself 18.2.1

USING MOLE RATIOS

Solutions of lead(II) nitrate and potassium iodide are mixed together, forming 0.30 mol of solid lead(II) iodide. How many moles of potassium iodide reacted in this reaction?

Mass–mass stoichiometry

When you carry out a reaction in the laboratory, you will measure quantities of chemicals in grams, not moles. For this reason, most calculations will require you to start and finish with mass rather than moles of a substance. To calculate the number of moles of the known substance from a mass, you can use the relationship:

$$\text{number of moles} = \frac{\text{mass (in g)}}{\text{molar mass (in g mol}^{-1}\text{)}}$$

This can be written as:

$$n = \frac{m}{M}$$

To calculate a final answer as a mass, this formula is rearranged:

$$m = n \times M$$

Calculating the mass of a salt in solution from a precipitation reaction

Stoichiometry can be combined with your knowledge of precipitation reactions to find the amount of a salt in a solution.

When analysing for salts in samples using precipitation reactions, knowledge of the solubility rules is important.

There are several steps involved in calculating the mass of a salt in a water sample, based on the mass of a **precipitate** produced in a precipitation reaction.

1 Write a balanced equation for the reaction.

2 Calculate the number of moles of the precipitate from its mass, using the formula $n = \frac{m}{M}$.

3 Use the mole ratios in the equation to calculate the number of moles of the salt in solution.

4 Calculate the mass of the salt using $m = n \times M$.

Figure 18.2.2 provides a flow chart that summarises this process. Worked Example 18.2.2 will help you to understand these steps.

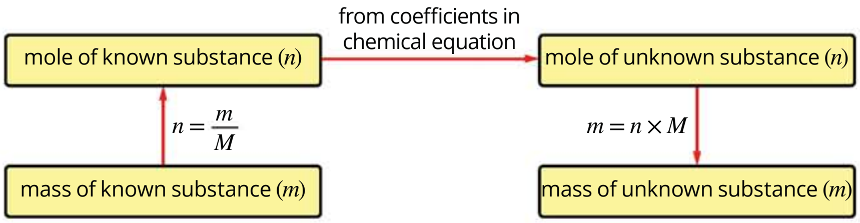


FIGURE 18.2.2 A flow chart for mass–mass stoichiometric calculations is helpful when trying to solve these problems.

Worked example 18.2.2

MASS–MASS STOICHIOMETRIC PROBLEMS

When solutions of potassium iodide and lead(II) nitrate are mixed, a precipitate of lead(II) iodide is formed. Calculate the mass of potassium iodide required to precipitate a mass of 1.46 g of lead(II) iodide.

Thinking	**Working**
Write a balanced equation for the reaction.	$2KI(aq) + Pb(NO_3)_2(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$
Calculate the number of moles of the known substance (the precipitate): $n = \frac{\text{mass } (m)}{\text{molar mass } (M)}$	$n(PbI_2) = \frac{1.46}{461.0}$ $= 0.00317$ mol
Calculate the mole ratio: $\text{mole ratio} = \frac{\text{coefficient of unknown}}{\text{coefficient of known}}$	$\text{mole ratio} = \frac{n(KI)}{n(PbI_2)} = \frac{2}{1}$
Calculate the number of moles of the unknown substance: $n(\text{unknown}) = n(\text{known}) \times (\text{mole ratio})$	$n(KI) = 0.00317 \times \frac{2}{1}$ $= 0.00633$ mol
Calculate the mass of the unknown substance: $m = n(\text{unknown}) \times \text{molar mass}$	$m(KI) = 0.00633 \times 166.0$ $= 1.05$ g

Worked example: Try yourself 18.2.2

MASS–MASS STOICHIOMETRIC PROBLEMS

A reaction between solutions of sodium sulfate and barium nitrate produces a precipitate of barium sulfate with a mass of 2.440 g. Calculate the mass of sodium sulfate required to produce this precipitate.

GRAVIMETRIC ANALYSIS OF A SALT

As you have seen above, by selecting a solution that will form a precipitate with the ion you wish to test for, you can use precipitation reactions to determine the mass of some salts in solutions. This is an example of gravimetric analysis. The aim of forming a precipitate is to separate one of the ions of the salt being analysed from other ions present in solution.

For example, the concentration of barium ions in a solution containing both barium and sodium ions can be determined by adding sodium sulfate solution (Figure 18.2.3). The sodium ions will remain in solution but a precipitate of barium sulfate is formed, which can be separated from the solution and dried. The mass of the precipitate may then be used to calculate the barium ion concentration in the initial solution.

Gravimetric analysis can be used to determine the salt content of a number of samples as long as a suitable precipitating agent can be found. Regardless of the salt being tested for, the steps in the process remain the same. Figure 18.2.4 shows the typical laboratory steps in a gravimetric analysis.

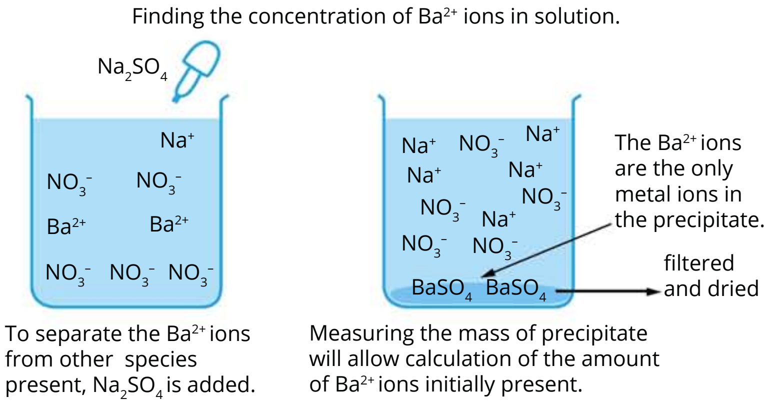


FIGURE 18.2.3 The principle of gravimetric analysis: Ba^{2+} ions in a solution are separated from Na^+ ions and NO_3^- ions by precipitation. The precipitate is then collected and dried so that the initial mass of Ba^{2+} can be determined using stoichiometry.

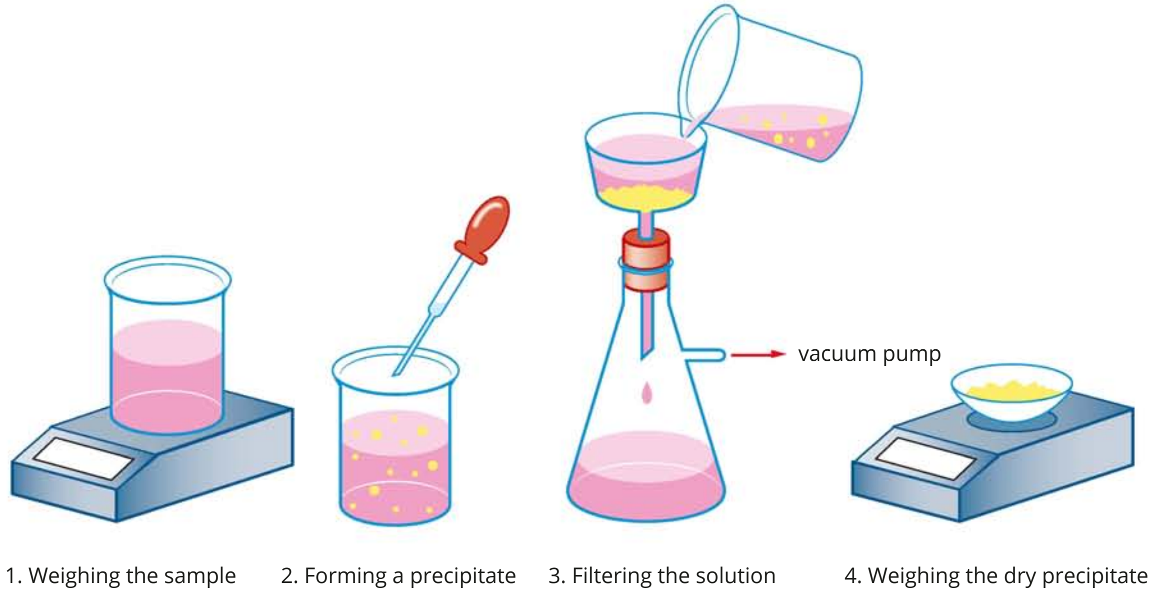


FIGURE 18.2.4 Laboratory procedure for gravimetric analysis.

The steps in this process are listed below.

1 Prepare your sample solution (this includes dissolving a solid sample if required).

2 Add the precipitation solution in sufficient (excess) amounts to cause complete precipitation of the ion being analysed.

3 Collect the precipitate by filtration and wash it carefully to ensure that no soluble components are trapped in it.

4 Dry the precipitate carefully to ensure that the mass obtained is not higher than it should be. The precipitate is usually heated, cooled and weighed repeatedly until its mass is constant. This ensures that all water has been removed.

When conducting a gravimetric analysis, the filtrate obtained after filtering the precipitate is often tested with additional precipitating agent to ensure that all of the ions of interest have been precipitated from the sample.

Note that the precipitate must be stable when heated. The number of moles of the precipitate cannot be accurately calculated if decomposition occurs and the precipitate is not a pure compound.

Uses of gravimetric analysis

Gravimetric analysis is one of the techniques used by chemists to analyse substances for their composition or concentration. It is inexpensive and can be used for a range of common inorganic substances.

Because of its versatility and the relative ease with which it is conducted, gravimetric analysis has been used for analysis in a variety of industries. Gravimetric analysis can be used to determine the salt content of foods, the sulfur content of ores and the level of impurities in water. Since the introduction of modern instruments, gravimetric analysis has usually been replaced by faster, automated techniques. However, it is still used to check the accuracy of analytical instruments.

Gravimetric analysis is not appropriate for the analysis of all salts. For example, it is not suitable for insoluble salts, nor is it suitable for salts such as sodium nitrate for which all compounds of both the anion and the cation are soluble.

Only salts that can form a stable precipitate are suitable for gravimetric analysis.

Figure 18.2.5 shows a simplified version of the steps in a gravimetric analysis to determine the amount of sulfur in a sample of iron sulfide (fool's gold). You should note that gravimetric analysis is not always a direct technique. The **analyte** being tested may be first subjected to a chemical reaction to convert it to a form suitable for precipitation. For example, this occurs in the analysis of iron sulfide in which the sulfide ions are converted to sulfate ions as part of the procedure.

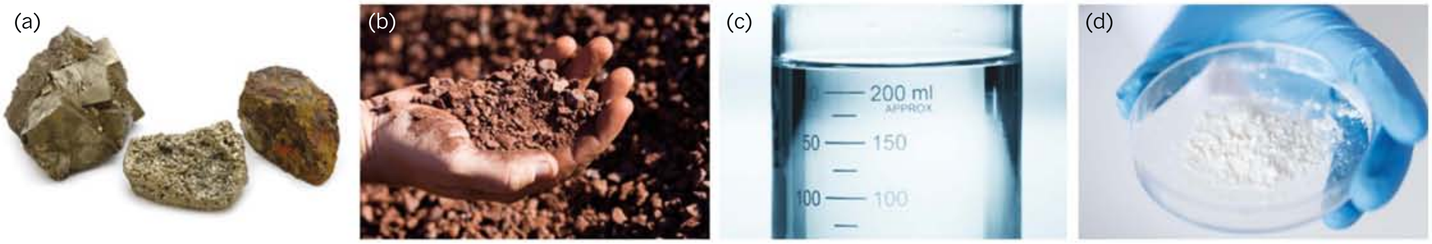


FIGURE 18.2.5 Analysis of sulfur in iron sulfide ore by gravimetric analysis. (a) A sample of ore is (b) crushed, (c) dissolved in nitric acid to convert the sulfide ions to sulfate ions and (d) precipitated as barium sulfate.

Worked example 18.2.3

GRAVIMETRIC ANALYSIS

The silver chloride precipitate collected from a 7.802 g sample of peanut butter has a mass of 0.112 g. What is the percentage of sodium chloride in the peanut butter, assuming all chloride ions are present as sodium chloride?

Thinking	Working
Write a balanced equation for the precipitation reaction.	$NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
Calculate the number of moles of precipitate using: $n = \frac{m}{M}$	$n(AgCl) = \frac{m}{M}$ $= \frac{0.112}{143.4}$ $= 0.000781$ mol
Use the balanced equation to find the mole ratio of the 'known' and 'unknown' substances. The 'known substance' is the one for which you are provided information about in the question; the 'unknown substance' is the one whose mass you are required to calculate.	mole ratio $= \frac{n(NaCl)}{n(AgCl)}$ $= \frac{1}{1}$
Calculate the number of moles of unknown substance.	$n(NaCl) = n(AgCl) = 0.000781$ mol
Calculate the mass of unknown substance in the sample.	$m(NaCl) = n \times M$ $= 0.000781 \times 58.5$ $= 0.0457$ g
Calculate the percentage mass of the unknown substance in the 7.802 g of sample.	$\%\ NaCl = \frac{0.0457}{7.802} \times 100$ $= 0.586\%$

Worked example: Try yourself 18.2.3

GRAVIMETRIC ANALYSIS

Water discharged from a mining plant contains silver ions present as silver nitrate ($AgNO_3$). Excess potassium chromate (K_2CrO_4) solution is added to a 50.0 g sample of water to precipitate the silver as silver chromate. The precipitate is heated to remove any water to produce 1.32 g of silver chromate (Ag_2CrO_4).

Calculate the percentage mass of silver in the water supply. (The molar mass of Ag_2CrO_4 is 331.7 g mol^{-1}.)

18.2 Review

SUMMARY

- A balanced equation shows the ratio of the amount, in mol, of reactants used and products formed in the reaction.
- Given the quantity of one of the reactants or products of a chemical reaction, such as in a precipitation 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 given substance.
  3. Use the mole ratios of reactants and products in the balanced equation to calculate the amount, in mol, of the required substance.
  4. Use the appropriate formula to determine the required quantities of the required substance. Formulas are:

$$m = n \times M$$

$$c = \frac{n}{V}$$

- Precipitation reactions can be used to determine the amount of a salt in a solution of a sample. This process is known as gravimetric analysis.
- In gravimetric analysis the:
  - precipitation solution is added in sufficient (excess) amounts to cause complete precipitation of the ion being analysed
  - precipitate is filtered and dried to constant mass, to ensure all water is removed
  - mass of precipitate is used to calculate the number of moles of the original salt in solution, and hence the composition of the sample can be found.
- Gravimetric analysis can be used to determine the amount of salt in food, impurities such as sulfur in ores, or the level of impurities in water.
- Gravimetric analysis is cheap and simple to perform but has largely been replaced by faster instrumental methods.

KEY QUESTIONS

1 Which one of the following reactions is most likely to be part of a gravimetric analysis?

A $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

B $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$

C $AgNO_3(aq) + LiBr(aq) \rightarrow AgBr(s) + LiNO_3(aq)$

D $2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$

2 Answer true or false to each of the following statements.

a All salts can be analysed by gravimetric analysis.

b A poorly dried precipitate will lead to a high result.

c A precipitate should be washed before it is dried.

d Precipitates should be dried at high temperatures to ensure that all water is removed.

e A precipitate needs to be stable when heated.

3 There are a number of points during a gravimetric analysis where poor practice can affect the overall result. Match each of the issues listed below with their likely impact on the final result.

Poor practice initially displayed	Impact
Precipitate is not dried to constant mass.	Mass of the precipitate is high due to the presence of impurities.
Precipitate is not washed with deionised water.	The composition of the precipitate is not consistent.
Precipitate is left on the sides of the flask.	Mass of the precipitate is high due to the presence of water.
Precipitate decomposes when heated.	Precipitate is pure but its measured mass is lower than it should be.

4 A 5.64 g precipitate of calcium phosphate is obtained when a solution of sodium phosphate is added to a solution of calcium nitrate. The equation for the reaction is:

$$3Ca(NO_3)_2(aq) + 2Na_3PO_4(aq) \rightarrow Ca_3(PO_4)_2(s) + 6NaNO_3(aq)$$

What mass of calcium nitrate was required to produce this precipitate?

5 The sodium chloride concentration in a solution used as eye drops is determined by adding a solution that causes the precipitation of the chloride ions as silver chloride.

- **a** Suggest a solution containing an ionic compound that could be added to cause the precipitation of the chloride ions as silver chloride.
- **b** Write an equation for the formation of the precipitate.
- **c** Determine the required mole ratio for this reaction.

6 The mass of aluminium nitrate in a solution is determined by adding sodium carbonate solution to precipitate the aluminium as aluminium carbonate. The equation for the reaction occurring is:

$$2Al(NO_3)_3(aq) + 3Na_2CO_3(aq) \rightarrow Al_2(CO_3)_3(s) + 6NaNO_3(aq)$$

In a particular reaction, 4.68 g of precipitate is obtained.

- **a** Calculate the moles of aluminium carbonate produced.
- **b** Determine the required mole ratio for the reaction.
- **c** Calculate the mass of aluminium nitrate that reacted.

7 The reaction between mercury(II) ethanoate and sodium iodide is represented by the following equation.

$$Hg(CH_3COO)_2(aq) + 2NaI(aq) \rightarrow HgI_2(s) + 2NaCH_3COO(aq)$$

A precipitate of mass 4.82 g is formed when sodium iodide is added to a solution of mercury(II) ethanoate.

$$M(Hg(CH_3COO)_2) = 318.7 \text{ g mol}^{-1}; M(HgI_2) = 454.4 \text{ g mol}^{-1}$$

Calculate the mass of mercury(II) ethanoate that reacted to produce this precipitate.

8 The calcium content of a sample of hard water is determined gravimetrically through the precipitation of insoluble calcium carbonate.

List the steps required to carry out this analysis in the correct sequence.

18.3 Calculations involving excess reactants

In the previous section, you calculated the amount of product that could be formed given the amount of one reactant. You were also able to calculate the amount of a second reactant that would be required, given the amount of the first. In chemistry, once you know the mass of a reactant that is completely consumed in a chemical reaction, you can use that information to determine the amount of any other component based on the 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, to determine which reactant will be the limiting factor in the reaction.

STOICHIOMETRY PROBLEMS INVOLVING EXCESS REACTANTS

When two reactants are mixed to create 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. However, it is more likely, that they are not present in exactly the right mole ratio. In this case, one of the reactants will be used up before the other and some of the other reactant will be left over at the end of the 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 18.3.1, a complete skateboard is made up of one deck and four wheels.

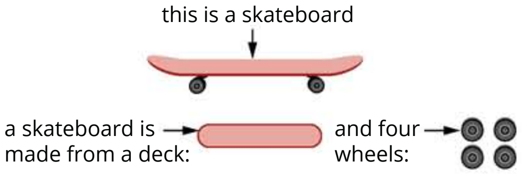


FIGURE 18.3.1 In order to make a complete skateboard, you must always use one deck and four wheels. This sets up the basic formula for a skateboard.

Now consider the situation shown in Figure 18.3.2. If you were given two decks and ten wheels, how many complete skateboards can you make from these materials?

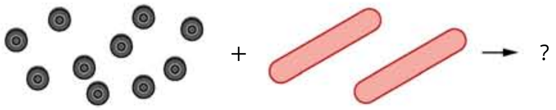


FIGURE 18.3.2 When provided with ten wheels and two skateboard decks, how many complete skateboards can be made?

The answer is that you could make two complete skateboards and there would be two wheels left over (Figure 18.3.3).

FIGURE 18.3.3 When supplied with two decks and ten 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 at the end were in excess. Also, with the numbers 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 exact same ratio as that shown in the equation for the reaction.

When this happens, the reactant that is:

- completely consumed is the **limiting reactant**
- not completely consumed is the **excess reactant**.

In a chemical reaction the limiting reactant is completely used up.

Figure 18.3.4 shows three different scenarios for the reaction in which hydrogen gas and oxygen gas combine to form water, according to the equation:

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

Each of the diagrams provides examples to illustrate the concepts of limiting and excess reactants.

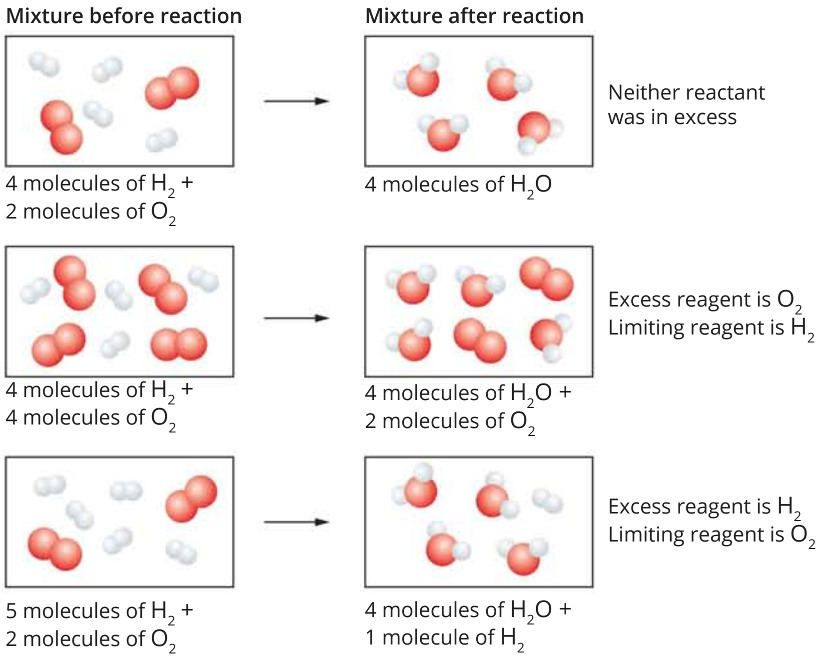


FIGURE 18.3.4 Different scenarios showing the concept of limiting reactant for the reaction $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$.

Note that in each of the examples shown in Figure 18.3.4, the amount of product:

- formed in these types of reactions is determined by the amount of the limiting reactant 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 reactant to determine the amount of product that will be formed.

Steps in solving stoichiometry problems involving excess reactants

When attempting to solve a limiting reactant problem in which you are required to work out the amount of product, there are three main steps.

1. Calculate the number of moles of each reactant.
2. Determine which reactant is in excess and therefore which is the limiting reactant.
3. Use the amount of limiting reactant to work out the amount of product formed.

Worked example 18.3.1

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 reactant?

Thinking	Working
Calculate the number of moles of each of the reactants in the equation using $n = \frac{m}{M}$ or $n = c \times V$ 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 reactant.	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 reactant (it will be completely consumed).

(b) What is the mass of precipitate formed?

Thinking	Working
Find the mole ratio of the unknown substance to the limiting reactant from the equation coefficients: $\text{mole ratio} = \frac{\text{coefficient of unknown}}{\text{coefficient of limiting reactant}}$	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 reactant: $n(\text{unknown}) = n(\text{limiting reactant}) \times \text{mole ratio}$	$n(Al(OH)_3) = n(Al(NO_3)_3) \times \frac{1}{1}$ $= 0.117 \times \frac{1}{1}$ $= 0.117$ 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 18.3.1

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 reactant?

(b) What is the mass of precipitate formed?

18.3 Review

SUMMARY

- If quantities of more than one reactant are given, the amount, in mol, of each reactant needs to be calculated.
- The limiting reactant needs to be determined; this will be the reactant that is consumed completely.
- The limiting reactant is used to predict the amount of product formed and the amount of the other reactant in excess.

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.

A Use mole ratios to determine which reactant is limiting.

B Calculate the number of moles of aluminium and oxygen.

C Calculate the mass of aluminium oxide that forms.

D Refer to the balanced equation.

E 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 product remaining at the end of the reaction.

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 M lead(II) nitrate solution reacts with 75.0 mL of 0.500 M potassium iodide solution, determine which reactant is in excess the mass of lead(II) iodide that forms.

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			

18.4 Determining salt concentration by colorimetry and UV–visible spectroscopy

In section 18.2, you learned how knowledge of precipitation reactions combined with stoichiometry can be used to determine the concentrations of salt solutions in the laboratory. Gravimetric analysis, like a titration (volumetric analysis) is a traditional form of chemical analysis that is relatively cheap and easy to perform. However, modern chemists have a range of chemical instruments at their disposal that can provide alternative methods of analysis. These methods are often faster and more accurate that traditional forms of analysis.

This section looks at how instruments called **colorimeters** and **UV–visible spectrophotometers** can be used to determine the concentration of a salt in solution. These instruments measure the interaction of light with solutions to determine the concentration of a solution. The intensity of the colour of a solution provides an indication of its concentration. Your eye can detect some differences in colour but the instruments studied in this section can measure their intensity accurately and use this to determine concentration.

SPECTROSCOPY

Light is a form of energy and is a type of **electromagnetic radiation**. Other forms of electromagnetic radiation are radio waves and X-rays. Visible light is only a small part of the range of different forms of electromagnetic radiation. The spread of the different types of radiation arranged according to their relative energies and wavelengths is referred to as the **electromagnetic spectrum** (Figure 18.4.1).

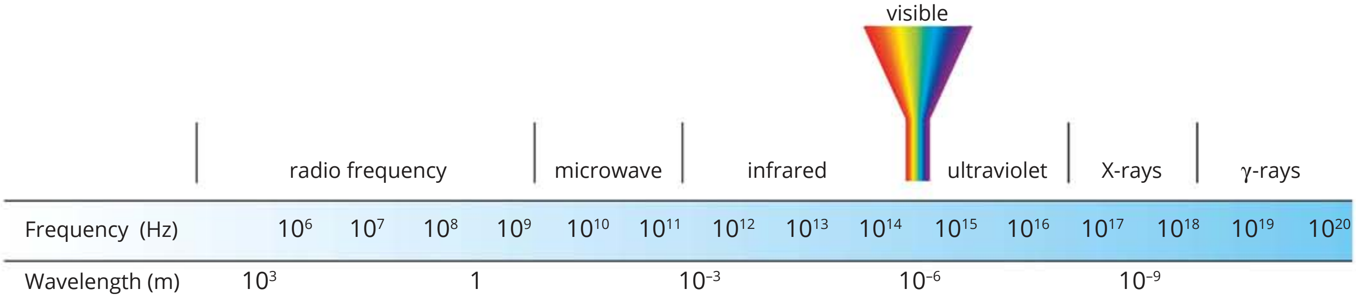


FIGURE 18.4.1 Visible light is only a small part of the electromagnetic spectrum. The spectroscopy techniques detailed in this chapter use radiation within the visible spectrum.

Electromagnetic radiation, such as light, can interact with atoms, and the nature of this interaction depends upon the energy of the electromagnetic radiation. In this section you will learn about an analytical technique called **spectroscopy**, which uses light and other radiation of the electromagnetic spectrum to give us information about the materials around us. The spectroscopic techniques that you will look at in this section will specifically deal with light within the visible region of the electromagnetic spectrum.

The visible region of light corresponds to the wavelengths between 400 and 700 nm on the electromagnetic spectrum.

When a substance absorbs visible light, it appears coloured. The colour observed is not the same as the colour of the light absorbed. The colour you see is actually due to reflected or transmitted light. For example, plant leaves contain chlorophyll. When you look at the leaves, they appear green because chlorophyll absorbs light in the purple and red ranges of the spectrum. Chlorophyll does not absorb light in the green region of the spectrum, so this is reflected back into your eyes.

The observed colour and the absorbed colour are referred to as **complementary colours**.

Colorimeters and UV–visible spectrophotometers are instruments used to determine the concentration of solutions by measuring their **absorbance** of radiation in the ultraviolet and visible region of the spectrum. The more concentrated the solution, the more radiation it will absorb. Figure 18.4.2 shows solutions of potassium permanganate ($KMnO_4$) at two different concentrations. The solutions appear purple as they absorb light in the yellow–green region of the electromagnetic spectrum (570 nm) and transmit the remaining violet light.

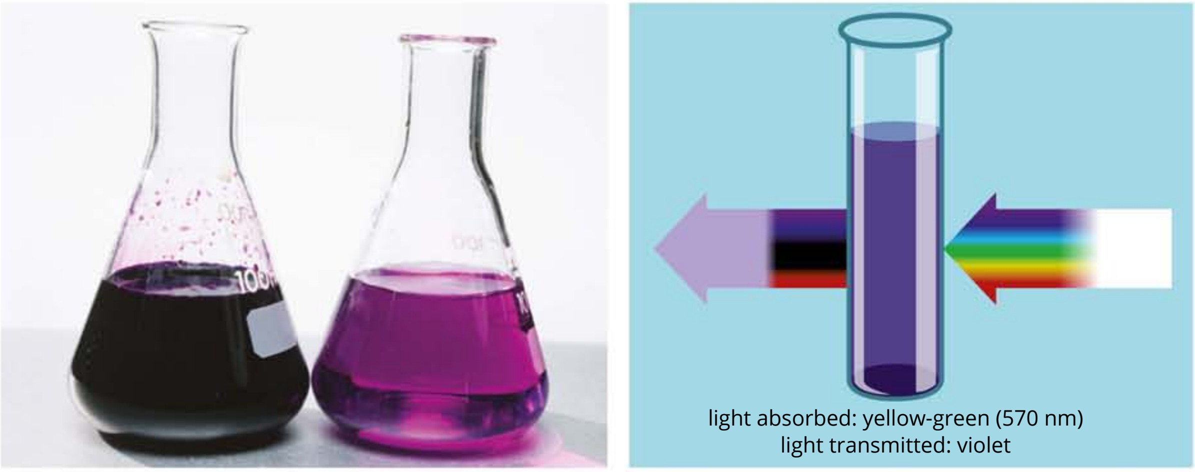


FIGURE 18.4.2 Two solutions of potassium permanganate ($KMnO_4$) appear purple because they absorb yellow–green light. The 0.001 M solution is lighter in colour than the 0.01 M solution because it absorbs less light.

The colour of a substance is due to the light that is reflected from its surface (for opaque objects) or transmitted through the substance (for transparent objects and solutions).

Colorimetry

Colorimetry is a technique that involves measuring the intensity of colour in a sample solution. Samples are often treated with a chemical compound in order to produce a coloured complex that can be analysed by colorimetry.

The construction of a colorimeter is shown in Figure 18.4.3. It consists of three main parts:

- a light source which produces light that is absorbed by the solution; this is passed through a filter to select a particular colour of light required for the analysis
- a glass, plastic or quartz cell to hold the sample
- an electronic detector to measure the absorbance of light that passes through the cell.

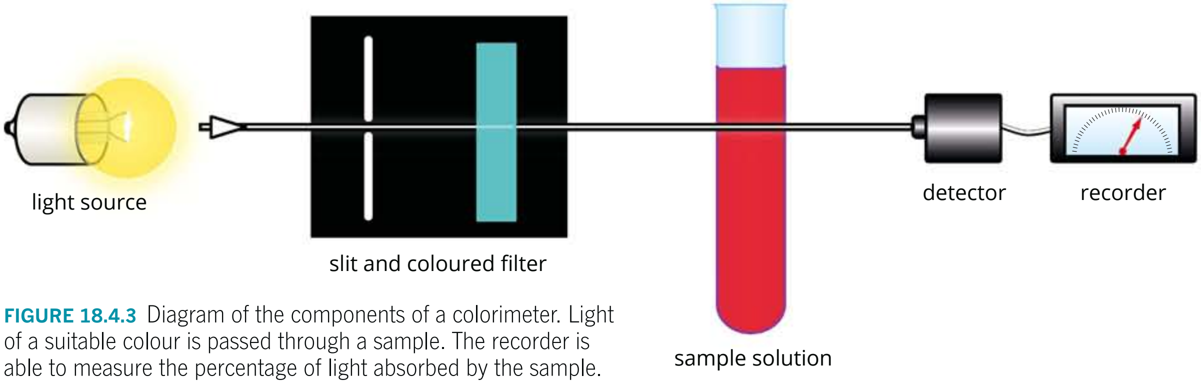


FIGURE 18.4.3 Diagram of the components of a colorimeter. Light of a suitable colour is passed through a sample. The recorder is able to measure the percentage of light absorbed by the sample.

The purpose of the filter is to select light of an appropriate colour that will be strongly absorbed by the sample. For example, since a chlorophyll solution absorbs strongly in the purple regions of the spectrum, a purple filter would be a good choice for chlorophyll analysis. The higher the concentration of chlorophyll, the higher the absorption of the purple light will be.

Table 18.4.1 shows the relationship between the colour of a solution and the selection of a filter for use in a colorimeter. Remember the colour absorbed by the sample is the complementary colour to the colour you observe.

TABLE 18.4.1 Colours of visible light and the complementary colours that are absorbed

Wavelength (nm)	Colour absorbed (colour of filter)	Colour observed
380–420	Violet	Green–yellow
420–440	Violet–blue	Yellow
440–470	Blue	Orange
470–500	Blue–green	Red
500–520	Green	Purple
520–550	Yellow–green	Violet
550–580	Yellow	Violet–blue
580–620	Orange	Blue
620–680	Red	Blue–green
680–780	Purple	Green

A handy way to remember complementary colours is to write the initials of the main colours in order of their decreasing wavelengths, as ROYGBV (red, orange, yellow, green, blue and violet), and then to write the initials again of the complementary colours directly below, this time starting from green.

R O Y G B V
G B V R O Y

Calibration curves

To determine the concentration of a substance in a solution using colorimetry, a series of **standard solutions** (solutions of accurately known concentration) of the substance must first be prepared and their absorbances measured.

For example, if you wished to test for nickel(II) sulfate, you would create a series of nickel(II) sulfate solutions of varying concentrations. Depending on the amount of nickel(II) sulfate you suspected to be in your sample, a suitable range of concentrations might be from 0.1 M to 0.5 M. Once your standard solutions are prepared, you can measure their absorbance at the selected wavelength. Table 18.4.2 shows a series of data typical for the absorbances of standard solutions of nickel(II) sulfate.

TABLE 18.4.2 Absorbance of standard solutions of nickel(II) sulfate

Nickel(II) sulfate concentration (M)	Absorbance
0.10	0.18
0.20	0.34
0.30	0.49
0.40	0.66
0.50	0.81

You can then construct a **calibration curve** from the data. A calibration curve is a plot of the absorbances of the standards against their concentration. Figure 18.4.4 shows the calibration curve created from the nickel(II) sulfate data in Table 18.4.2.

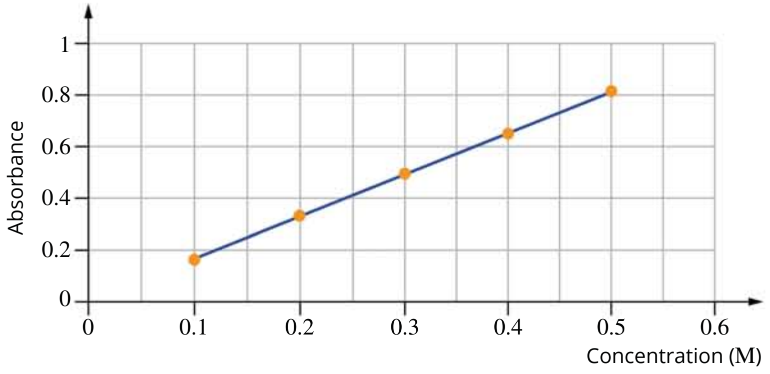
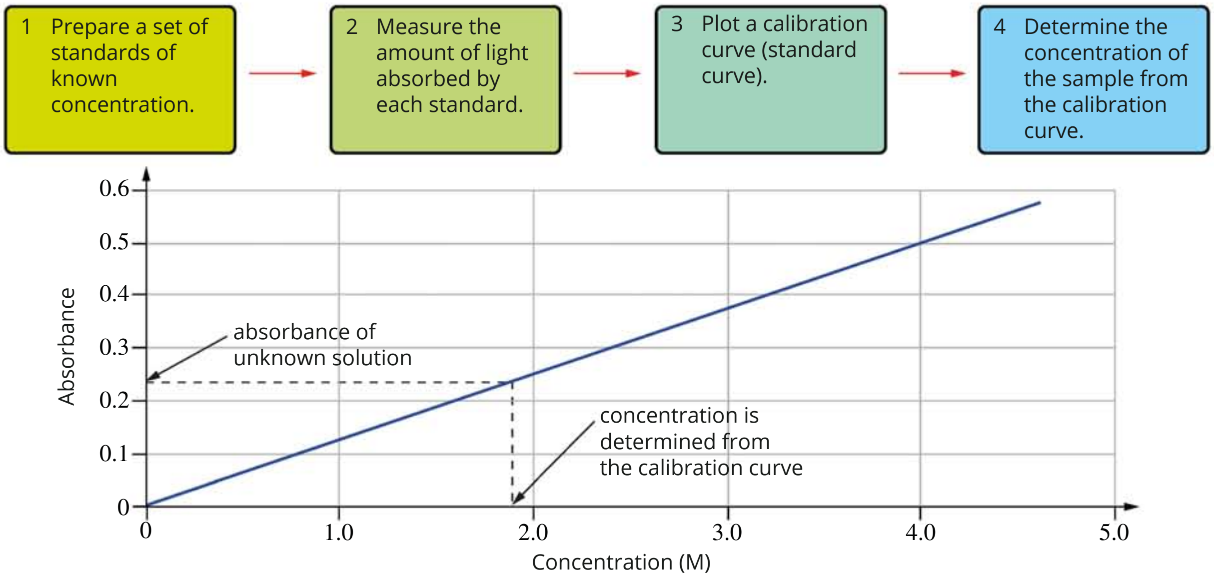


FIGURE 18.4.4 Calibration curve for nickel(II) sulfate.

If the absorbance of a solution of unknown concentration is now measured, the value can be used to determine the concentration from the calibration curve.

A calibration curve is constructed by measuring the absorbance of a series of solutions with accurately known concentrations and then plotting the results on a graph of absorbance versus concentration.

Figure 18.4.5 outlines the procedure that is followed when analysing a solution using colorimetry.



1. Prepare a set of standards of known concentration.
2. Measure the amount of light absorbed by each standard.
3. Plot a calibration curve (standard curve).
4. Determine the concentration of the sample from the calibration curve.

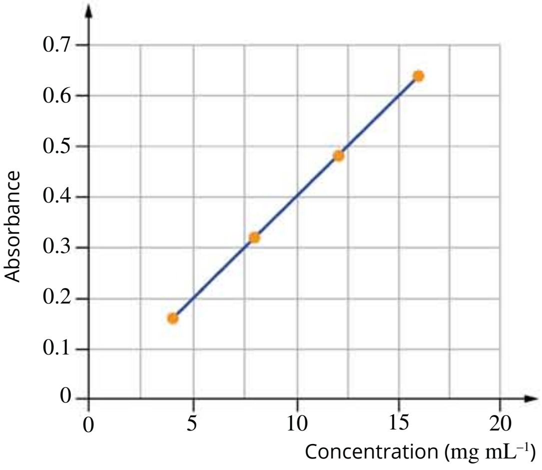
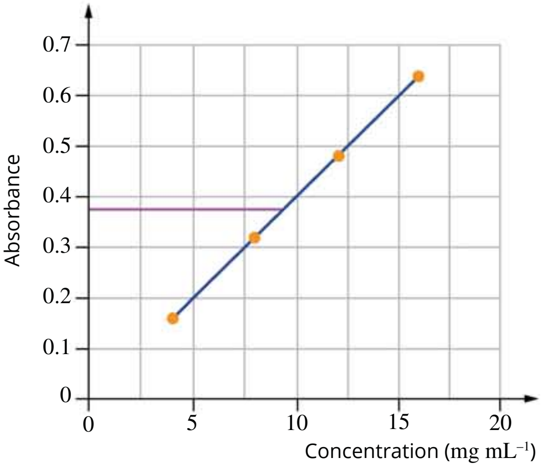
FIGURE 18.4.5 Procedure for the determination of concentration using a colorimeter.

Worked example 18.4.1

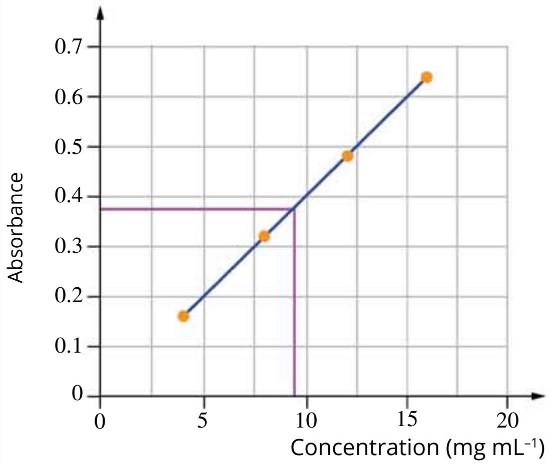
USING A CALIBRATION CURVE

The concentration of iron in dam water is determined by colorimetry. The absorbances of a series of standard solutions and a sample of dam water are shown in the table below. Determine the concentration of iron in the sample.

Concentration of Fe^{2+} (mg mL^{-1})	**Absorbance**
4.0	0.16
8.0	0.31
12.0	0.47
16.0	0.63
sample	0.38

Thinking	**Working**
Construct a calibration curve from the data above. Concentration will be on the horizontal axis.	
Mark where the absorption of the sample lies on the calibration curve by tracing a horizontal line to the curve.	 Plot the absorbance value of the unknown solution.

continued >

Draw a vertical line from the calibration curve to the *x*-axis.	
Determine the concentration of the sample by reading the concentration value for the unknown solution from the *x*-axis.	The concentration of Fe^{2+} in the dam water sample can be determined from the graph as 9 mg mL^{-1}.

Worked example: Try yourself 18.4.1

USING A CALIBRATION CURVE

Determine the lead level in a solution using the following colorimetry data.

Concentration of Pb^{2+} (mg L^{-1})	**Absorbance**
2.5	0.18
5.0	0.35
7.5	0.51
10.0	0.68
sample	0.60

UV–VISIBLE SPECTROSCOPY

A colorimeter is relatively simple and inexpensive, but its accuracy is limited. A UV–visible spectrophotometer, such as the one shown in Figure 18.4.6, is a more sophisticated instrument. A UV–visible spectrophotometer uses a **monochromator** rather than a filter to select light of an exact wavelength to be used in the analysis.

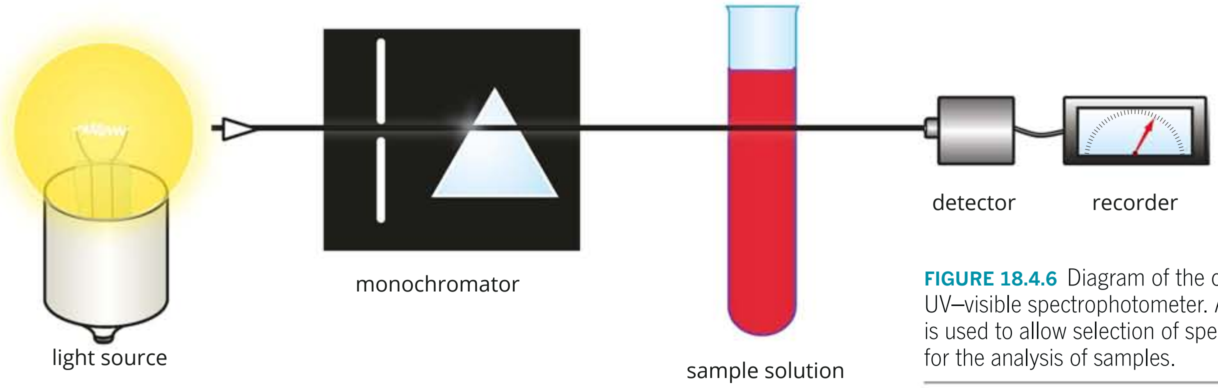


FIGURE 18.4.6 Diagram of the components of a UV–visible spectrophotometer. A monochromator is used to allow selection of specific wavelengths for the analysis of samples.

When a UV–visible spectrophotometer is used, the solution to be tested can first be scanned across multiple wavelengths to select the best wavelength to use. Scanning involves varying the wavelength of light used and checking the absorbance of the sample. Figure 18.4.7 shows an example of a scan for a solution of the green plant pigment chlorophyll.

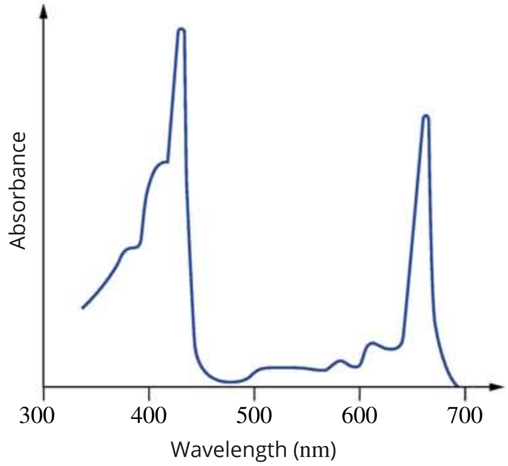


FIGURE 18.4.7 Scan of a green chlorophyll solution showing absorbance maxima at around 450 and 650 nm.

The scan shows strong absorbance at wavelengths of around 450 and 650 nm, which correspond to purple and red light respectively. The measurements of absorbance for the standard solution and sample would be conducted at one of these two wavelengths. In practice, the wavelength at which other compounds in the solution do not absorb strongly would be chosen.

In UV–visible spectroscopy, the best wavelength for analysis of a sample is where maximum absorbance occurs without interference from other components in the sample. This is not always at the wavelength at which the sample absorbs most strongly.

Metal complexes

Solutions containing Fe^{2+} ions do not absorb very strongly in the ultraviolet or visible part of the spectrum. If the Fe^{2+} ions are oxidised to Fe^{3+} and potassium thiocyanate (KSCN) is added to the solution, a bright red solution forms, as seen in Figure 18.4.8. This highly coloured red solution can be analysed using either a colorimeter or UV–visible spectrophotometer.

The reaction shown in Figure 18.4.8 is represented by the equation:

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

$FeSCN^{2+}$ is an example of a **metal complex** in which metal ions are bound to molecules or negative ions. Transition metals in particular can form complexes, such as $FeSCN^{2+}$, many of which are brightly coloured and suited to analysis with a colorimeter or UV–visible spectrophotometer.

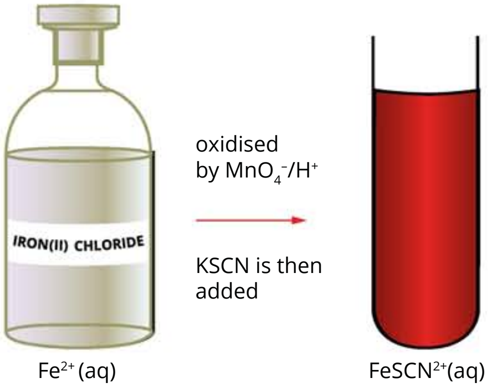


FIGURE 18.4.8 A pale yellow solution containing Fe^{2+}(aq) is oxidised to form Fe^{3+}(aq) ions. When KSCN is added, a blood-red solution of $FeSCN^{2+}$(aq) ions forms.

Some metal ions may need to be converted into highly coloured metal complexes to be analysed using UV–visible spectroscopy or colorimetry.

The analysis of a sample using colorimetry or UV–visible spectroscopy can be summarised in the following steps.

1. If the metal ion to be analysed is not strongly coloured, a metal complex may need to be formed.
2. Select the wavelength or filter to be used for the analysis. This will correspond to the wavelength of light absorbed most strongly by the sample.
3. Measure the absorbance of a series of standard solutions of accurately known concentration at the selected wavelength.
4. Plot a calibration curve of absorbance (y-axis) versus concentration (x-axis) for the standard solutions.
5. Measure the absorbance of the sample solution and determine the concentration from reading the corresponding value from the calibration curve.
6. Account for any dilutions that may have been carried out during your sample preparation to calculate the final concentration.

Uses of colorimetry and UV–visible spectroscopy

Colorimeters and UV–visible spectrophotometers are used in many and varied fields. These instruments can determine the concentrations of lead in urine, blood sugar levels, cholesterol levels, levels of haemoglobin in blood and phosphates in water. Portable colorimeters, such as the one shown in Figure 18.4.9a, are now available to make on-site testing easier.

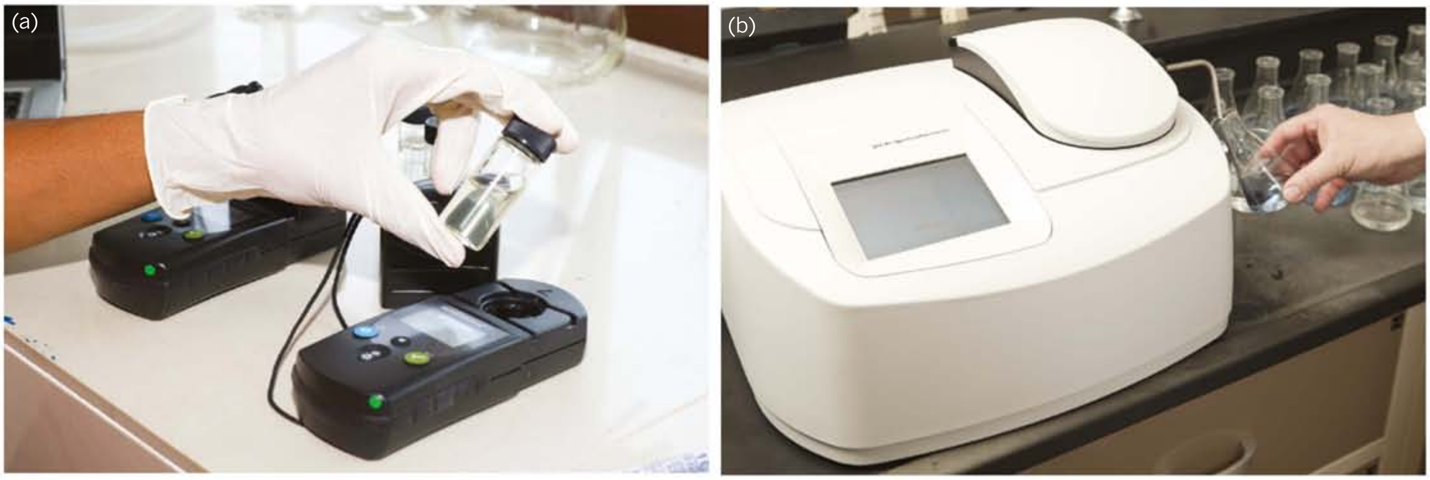


FIGURE 18.4.9 (a) A portable colorimeter. A solution sample is inserted into this unit in a small plastic cell. (b) A laboratory UV–visible spectrophotometer.

Further examples of the use of colorimetry or UV–visible spectroscopy are:

- measurement of chromium levels in a workplace: a worker carries a pump and PVC filter unit for a set period of time. The pump samples the air around the worker and solids in the air are collected on the filter paper. Chromium can be extracted from the filter paper and converted to yellow chromate ions (CrO_4^{2-}) before analysis.
- determining phosphate levels in waterways: phosphate ions can be harmful to the environment as they cause **eutrophication**. Ammonium molybdate and tin(II) chloride can be added to water samples containing phosphates, forming a dark-blue complex called molybdenum blue, which can then be used for spectroscopic analysis.

18.4 Review

SUMMARY

- Radiation from each part of the electromagnetic spectrum can be described in terms of its frequency, wavelength and energy. Different colours of light have different frequencies, wavelengths and energies.
- Some solutions containing metal ions absorb light in the visible and ultraviolet regions of the spectrum. Colorimeters and UV–visible spectrophotometers can be used to determine the concentration of metal ions in these solutions.
- A metal complex consists of a metal ion bonded to molecules or anions. The solutions of many metal complexes are suited to analysis by colorimetry or UV–visible spectroscopy.
- The amount of light absorbed by a solution is related to the concentration of the solution.
- Calibration curves are prepared by measuring the absorbance of a series of standard solutions of known concentration. The absorbance readings are then plotted against concentration. The concentration of a solution can be determined by plotting its absorbance on the calibration curve and reading off the corresponding concentration.
- A colorimeter uses a filter to select the colour of light to be used (Figure 18.4.3 on page 466). The light chosen for the analysis should be complementary to the observed colour of the solution.
- A UV–visible spectrophotometer uses a monochromator in place of a filter (Figure 18.4.6 on page 470). This allows a specific wavelength to be chosen.
- A scan across a range of wavelengths is used to determine the wavelength that offers the best absorbance for a particular solution.
- A UV–visible spectrophotometer can usually provide more accurate results than a colorimeter but it is more expensive. Both instruments offer a means of determining the concentration of salts in a solution.

KEY QUESTIONS

1 Two samples of copper(II) sulfate solution with concentrations of 0.080 M and 0.30 M were analysed using a spectrophotometer.

  a Which sample would allow the most amount of light to pass through to the detector?

  b Which sample would show the strongest absorption of light?

2 Why would red light, rather than blue light be used in a colorimeter to measure the concentration of a blue-coloured copper(II) sulfate solution?

3 The absorption spectrum of a commercial dye is shown in Figure 18.4.10. The colour chart under the graph shows the colour of each region of the spectrum. What colour is the dye?

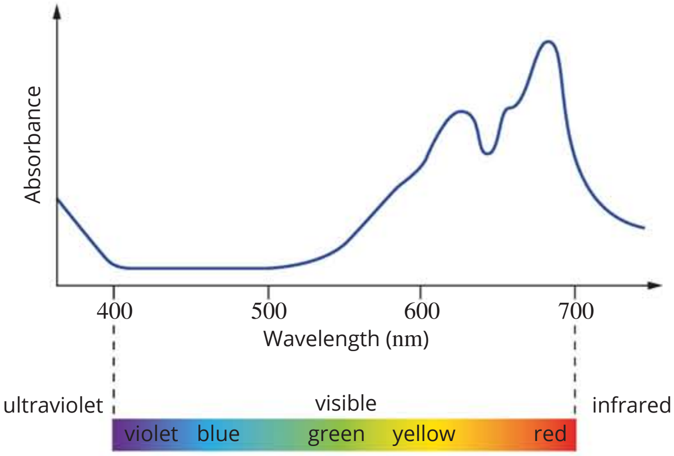


FIGURE 18.4.10

4 A colorimeter is used to analyse the concentration of iron(II) ions (Fe^{2+}) in the water in a tank. The calibration curve in Figure 18.4.11 is obtained from measuring the absorbance of a series of standards.

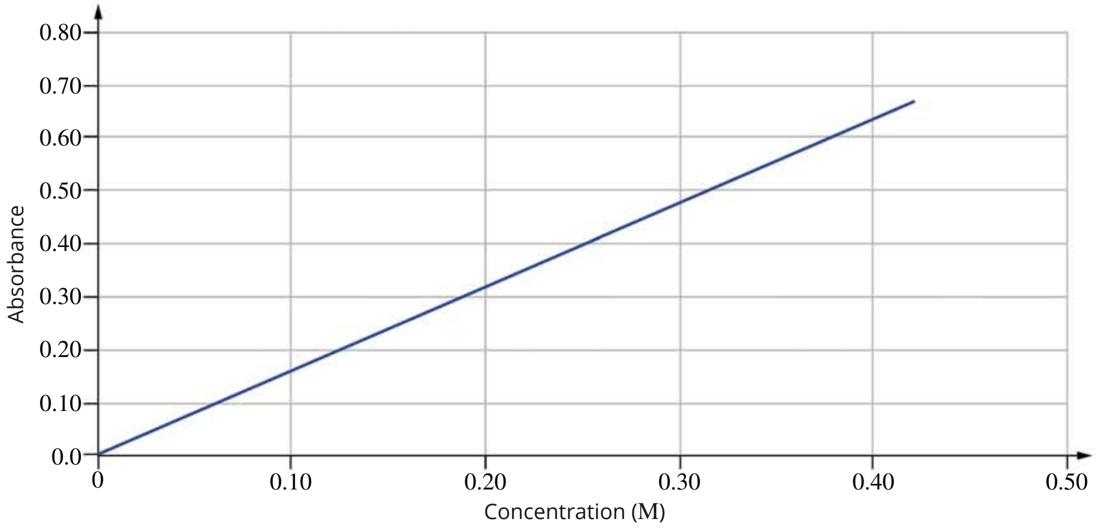


FIGURE 18.4.11

The iron solution is diluted from 5 mL to 20 mL before its absorbance is measured to be 0.24.

- **a** What is the concentration of Fe^{2+} in mol L^{-1} of the Fe^{2+} solution analysed in the colorimeter?
- **b** What is the concentration of Fe^{2+} in the original tank water sample?
- **c** Fe^{2+} ions are generally too pale to be analysed by spectrophotometry directly. Outline the process for preparing Fe^{2+} ions for analysis through the formation of a metal complex.

5 What are the complementary colours to the observed colours of the following solutions?

Solution colour	Complementary colour
Green	
Purple	
Orange	
Green–yellow	
Blue–green	

6 The concentration of copper(II) ions in industrial waste water was analysed by colorimetry. The absorbance values from a series of standards and the waste water are provided below.

Concentration (mg L^{-1})	Absorbance
50	0.12
100	0.23
150	0.36
200	0.48
250	0.58
Waste water sample	0.42

- **a** Use the values provided to construct a calibration curve for the analysis of Cu^{2+}.
- **b** Using the calibration curve you created in part **a**, determine the concentration of copper(II) ions in the waste water.

7 Potassium dichromate forms an orange-coloured solution, as shown in Figure 18.4.12. Provide a description of how you would use colorimetry to determine the concentration of potassium dichromate in this solution.

FIGURE 18.4.12

8 The absorption spectrum of chlorophyll is shown in Figure 18.4.7 on page 471.

- **a** At what wavelengths is there maximum absorbance of light?
- **b** What wavelength would you select if you were required to determine the concentration of chlorophyll in a leaf extract using UV–visible spectroscopy? Provide an explanation for your answer.

18.5 Determining concentration by atomic absorption spectroscopy

You will be familiar with the colourful effects that are created in fireworks displays. Small quantities of different metal compounds are incorporated in fireworks to produce different colours. For example, in Figure 18.5.1, strontium compounds have produced the eye-catching scarlet colour and sodium compounds have produced the yellow. If you have ever spilt salt into the flame of a gas stove, you might have noticed this same yellow colour in the flame.

FIGURE 18.5.1 Metal compounds incorporated into fireworks are responsible for the colours in this display.

In this section, you will examine how the emission and absorption of light by metals can be used to determine the concentration of salts in solution.

FLAME TESTS

Chemists use the fact that some metals produce particular colours when they are heated as a convenient and simple method of analysis. The metallic elements present in a compound can often be determined just by inserting a sample of the compound into a non-luminous Bunsen burner flame, as shown in Figure 18.5.2.

Each metal ion produces a characteristic colour. This means that the metal in an unknown sample can be identified by comparing the flame colour with the known characteristic colours produced by metals. Some examples of the flame colours produced by metals can be seen in Figure 18.5.3.

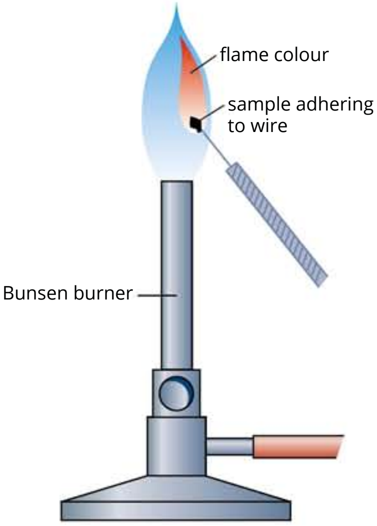


FIGURE 18.5.2 Performing a flame test. A moist wire has been dipped in the sample and then placed in the flame. A fine spray of solution from a spray bottle could be used instead.

FIGURE 18.5.3 The colour of the flame is determined by the different metal compounds present and can be used to identify these metals. The flame colours shown here are for (from left to right): barium (yellow–green), lithium (crimson), strontium (scarlet), sodium (yellow), copper (green) and potassium (lilac).

TABLE 18.5.1 Characteristic flame colours of some metal ions

Metal	Flame colour
Sodium	Yellow
Strontium	Scarlet
Copper	Green
Barium	Yellow–green
Lithium	Crimson
Calcium	Red
Potassium	Lilac

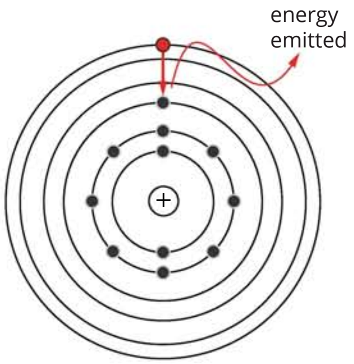


FIGURE 18.5.5 An excited electron quickly returns to a lower energy level, emitting electromagnetic energy in the form of light of a particular wavelength.

Because each flame colour is unique, you can use the flame colour produced to qualitatively identify a metal ion in an unknown sample. Table 18.5.1 shows some of the flame colours that can be used to identify the presence of metals in a flame test.

It is important to note that only a small number of metals produce flame colours by this process. Although the exact colour produced by each metal is unique, simple flame tests can result in a level of uncertainty when trying to decide between different shades of similar colours such as scarlet (strontium), crimson (lithium) and red (calcium).

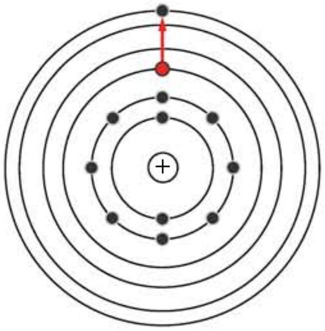


FIGURE 18.5.4 Energy from a flame can promote an electron in an atom to a higher energy level.

You will recall from section 1.5 that electrons are arranged in atoms in different energy levels. Electrons in energy levels close to the nucleus have the lowest energies and experience the strongest attraction to the nucleus. When placed in a flame, an electron can jump up to a higher energy level if it absorbs energy that corresponds exactly to the difference in energy between the lower energy level and the higher energy level (Figure 18.5.4).

Atoms with electrons in higher energy levels are unstable, so the **excited electrons** quickly return to lower energy levels. Figure 18.5.5 shows that the energy absorbed by the electrons is emitted as light as they return to a lower energy level. When electrons are located in the lowest energy shells possible, this is known as the **ground state**.

Some of the energy emitted from the transitions of electrons falls within the region of the electromagnetic spectrum corresponding to visible light (Figure 18.5.6). This emitted light is what you observe as the coloured flame in a flame test. The different colours observed correspond to specific wavelengths of light.

The colour of the light emitted from a sample is dependent on its energy. Red light has a lower energy than blue light.

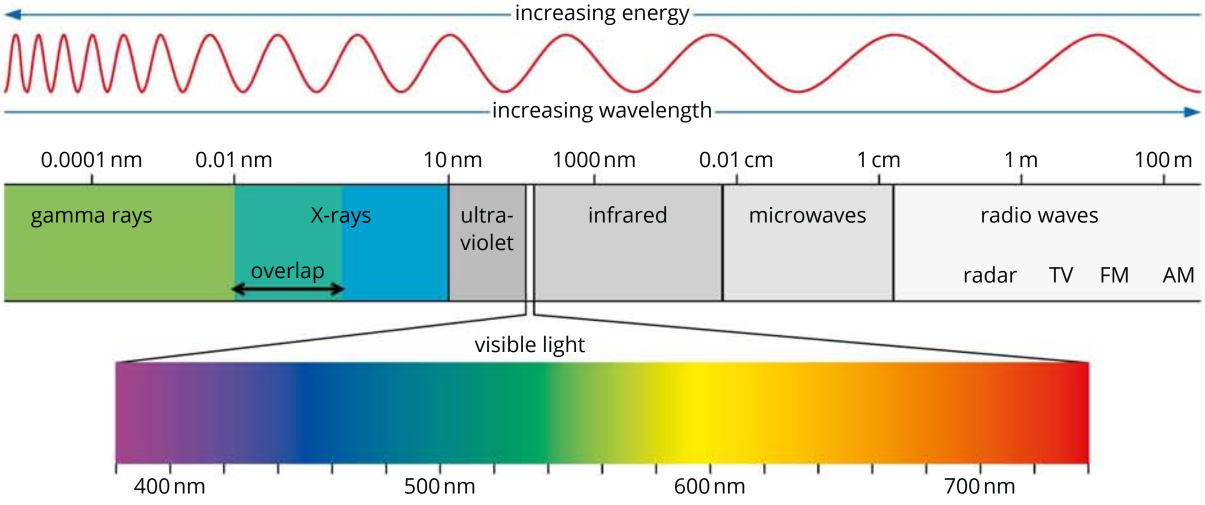


FIGURE 18.5.6 When excited electrons return to a ground state from a flame test, the emitted energy falls within the region of the electromagnetic spectrum that corresponds to visible light.

ATOMIC EMISSION SPECTROSCOPY

Flame tests provide only limited information about the likely elements present in a sample. As mentioned previously, only a few elements give a coloured flame in a Bunsen burner, and the colours of some are similar. In impure samples, a faint colour may be masked by a stronger one.

An atomic emission spectrometer is an apparatus that can be used to determine the metal ions present in a sample (Figure 18.5.7). By making two changes to the flame test technique, the reliability and usefulness of flame colour identification is greatly improved.

- Using a hotter flame ensures that sufficient energy is available to excite electrons in a wider range of elements.
- Passing the light through a prism separates the different energies in the light emitted by a heated sample into a series of coloured lines called a **line spectrum** or an **emission spectrum.**

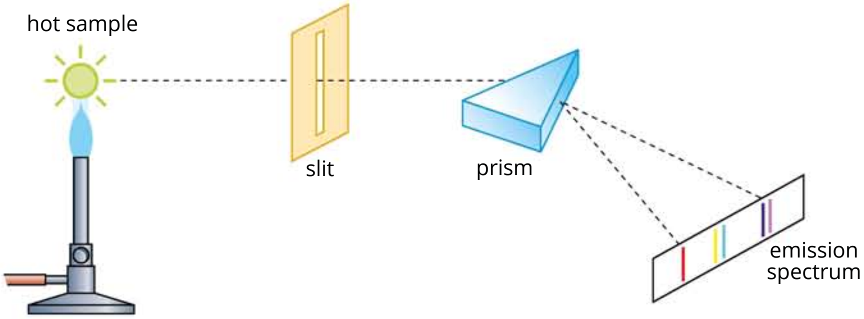


FIGURE 18.5.7 Essential components of an atomic emission spectrometer. The prism splits the emitted light into each of the component wavelengths, creating a line spectrum that is unique to the sample being tested.

When the light emitted from an excited atom is viewed through a spectrometer, it is much easier to see how the colour produced is unique. Because each element has a different number of protons in the nucleus and a unique electron configuration, the energy transitions that the electrons undergo as they move from the ground state to an excited state are also unique. Therefore, no two elements have energy levels of exactly the same energy, so a spectrum is characteristic of a particular element. It may be used as a 'fingerprint' to identify the elements present in a substance. The emission spectra of calcium, sodium, mercury and cadmium are shown in Figure 18.5.8 as examples. You can see how the spectra consist of distinct lines corresponding to the different colours emitted by the atoms.

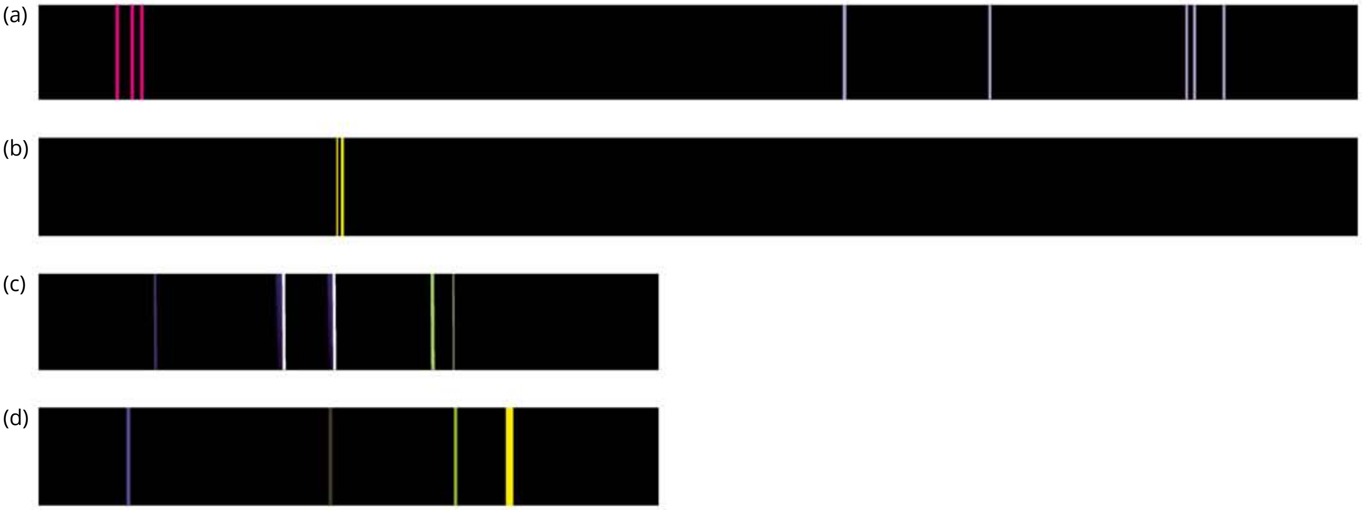


FIGURE 18.5.8 The emission spectrum of (a) calcium, (b) sodium, (c) mercury and (d) cadmium. The spectral lines are indicative of the different energies of light emitted in the visible region.

CHEMISTRY IN ACTION

How do we know what stars are made of?

The light produced by stars can be viewed through a spectroscope to produce an emission spectrum just like that seen for the light from a flame test. The Hubble space telescope, which is responsible for many of the well-known images of our universe, is equipped with a spectrograph. This allows astronomers to analyse the emission spectra of stars and determine what they are made of.

The brightest star in our night sky is Sirius, a binary white star in the constellation Canis Major, approximately 6.8 light-years away from Earth. Figure 18.5.9 shows Sirius as seen in the southern sky and its corresponding emission spectrum. The dark lines in the spectrum are absorption lines that correspond to the wavelengths of light absorbed by elements present in the outer gas layers of the star.

FIGURE 18.5.9 The star Sirius, in the constellation Canis Major, as seen in the southern sky. The emission spectrum obtained from the light emitted by Sirius can be used to work out the elements the star is made up of.

The position of the absorption lines in the spectrum match the position of lines observed for the colours emitted by different elements. Comparison of the spectrum obtained for a star with the spectra of known elements allows astronomers to identify the elements in the star.

Figure 18.5.10 shows the emission spectrum of 13 different stars. Each of these contains the characteristic lines representative of the absorption spectrum of hydrogen (the major component of most stars). The remaining dark lines correlate to other elements that are present in the outer layers of the star; these include calcium, sodium and iron, to name a few.

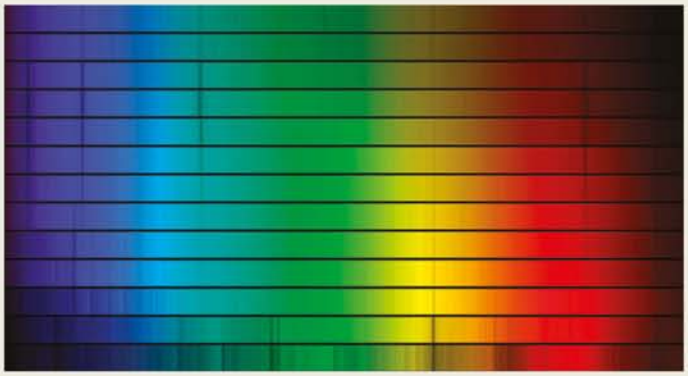


FIGURE 18.5.10 The emission spectra of 13 different stars. Astronomers collated the spectral data from the observable stars in the universe and classified them according to 13 types. Each of these spectra shows distinct absorption lines corresponding to the absorption pattern for hydrogen.

Astronomers have created a classification system for the stars in our universe based on their emission spectra. Spectral information is one of the most powerful tools we have to investigate the stars that exist light-years away from Earth.

ATOMIC ABSORPTION SPECTROSCOPY

In the early 1950s, the Australian scientist Alan Walsh was working on the measurement of small concentrations of metals at the CSIRO. During this time he developed the technique of **atomic absorption spectroscopy** (**AAS**), which is now used widely for detecting the presence of most metals and determining their concentration.

How AAS works

Alan Walsh's breakthrough was to recognise that atoms will absorb light if the energy of the light is exactly equal to the energy required to promote an electron from its ground state energy level to a higher energy level. As every element absorbs light of different energies (and hence different wavelengths), the amount of light absorbed by a sample at a specific wavelength can be used to determine the concentration of that element.

Unlike emission spectroscopy, AAS measures the amount of light *absorbed* by the sample.

Figure 18.5.11 gives a simplified depiction of how an atomic absorption spectrometer works.

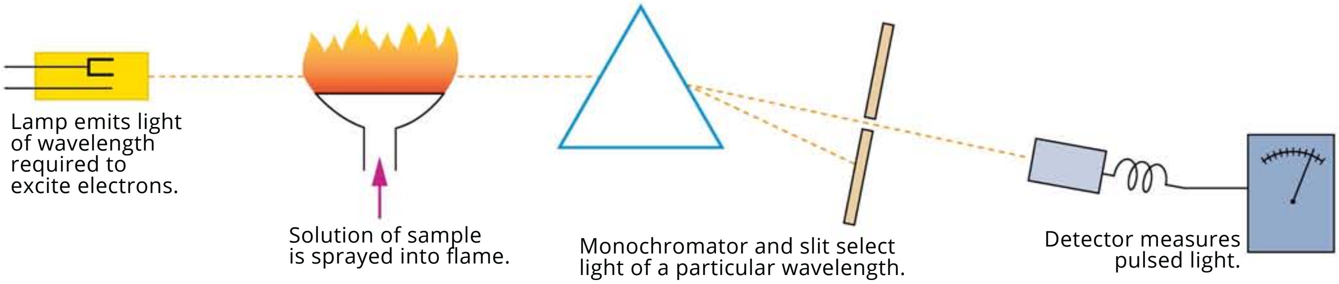


FIGURE 18.5.11 Schematic diagram of the inner workings of an atomic absorption spectrometer.

The light absorbed at a specific wavelength by a sample can be determined by the following process.

1. A hollow source cathode lamp emits different wavelengths of light that are absorbed by the metal being analysed. The lamp must be made with a filament of the metal being analysed.
2. A solution of a sample is sprayed into the flame to create an atomic vapour.
3. A monochromator is used to select a wavelength of light for analysis.
4. A detector measures the amount of light that reaches it, and a computer determines the amount of light that has been absorbed by the sample.

Calibration curves

Atomic absorption spectroscopy can be used to simply detect the presence of most metals; however, it is more often used to determine the concentration of a metal in a sample. The absorbance measured for a sample can be related to the concentration of the metal being analysed by using a calibration curve.

To construct a calibration curve, you must first create a series of standard solutions of the metal ion, and then measure their absorbance by AAS. A calibration curve is then constructed by plotting the concentrations of the standard solutions against the absorbance of each solution, as shown in Figure 18.5.12 on page 480.

As the concentration of the metal in the sample increases, the amount of light absorbed by the sample increases.

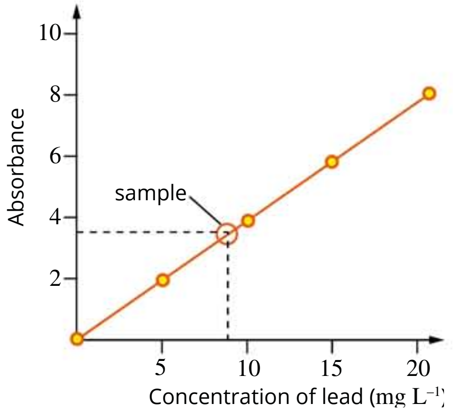


FIGURE 18.5.12 The AAS calibration curve that shows the relationship between the absorbance of light and the concentration of lead in a sample.

Because the amount of light that is absorbed by the sample is proportional to the amount of metal present, the relationship between concentration and absorbance is a linear one.

Once constructed, the calibration curve can be used to determine the concentration of the metal being analysed in the unknown sample. The absorbance of the unknown sample is measured and the corresponding concentration value can be read from the graph.

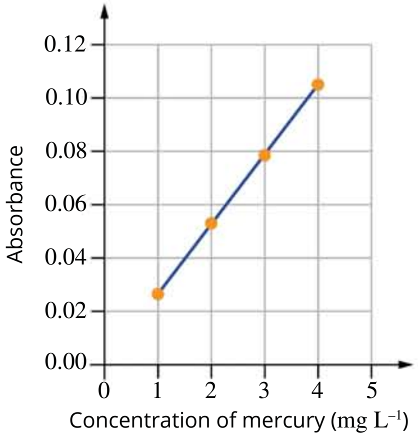
As you learned in Chapter 14, there are many different units for concentration. For simplicity, concentration will be measured in mg L^{-1} in the following examples, but it is important to always check the concentration unit specified on the *x*-axis of the calibration curve when answering questions involving AAS. In the example in Figure 18.5.12, the unit mg L^{-1} refers to the mass of metal (in mg) in every litre of the solution being analysed.

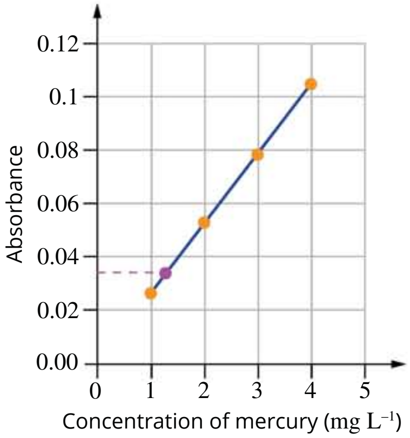
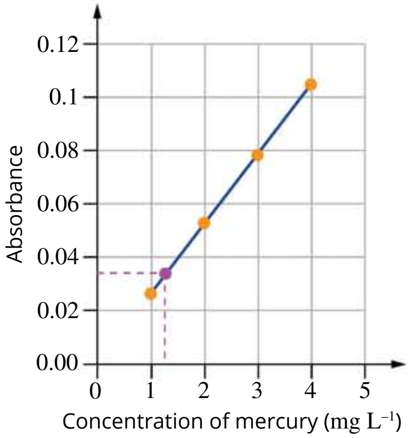
Worked example 18.5.1

USING A CALIBRATION CURVE TO DETERMINE CONCENTRATION

Determine the concentration of mercury in a sample, given the data in the following table.

Concentration of mercury (mg L^{-1})	Absorbance
1.0	0.026
2.0	0.053
3.0	0.078
4.0	0.105
Sample	0.036

Thinking	Working
Construct a calibration curve using concentrations of the standard solutions and their absorbance.	

Mark where the absorption of the sample lies on the calibration curve. This can be done by finding the absorption of the sample on the *y*-axis and moving horizontally right until you reach the calibration curve and marking that point.	
Determine the concentration of the sample by reading off the graph on the *x*-axis at the point where the sample's absorption lies on the calibration curve.	 The sample's absorption is 0.036. The concentration of mercury for the sample can be read off the graph as 1.2 mg L^{-1}.

Worked example: Try yourself 18.5.1

USING A CALIBRATION CURVE TO DETERMINE CONCENTRATION

Determine the concentration of sodium in a sample, given the data in the following table.

Concentration of sodium (mg L^{-1})	**Absorbance**
20	0.041
40	0.080
60	0.121
80	0.159
Sample	0.104

AAS TODAY

Approximately 60 years after Alan Walsh developed AAS, the technique is still used by many modern-day chemists. It is a very good tool for analysing the concentration of metals in a wide variety of samples, including water, urine, blood, soil, fish and other foods. AAS is capable of detecting 68 different metallic elements, and is sensitive enough to detect metals present in concentrations of less than 1 mg L^{-1}. Figure 18.5.13 shows an analytical chemist using an atomic absorption spectrometer to analyse the concentration of potassium in a sample.

FIGURE 18.5.13 An analytical chemist uses AAS to determine the concentration of metals in food samples.

AAS is a very sensitive technique for the detection of metals, but it can only be used to detect one element at a time.

EXTENSION

ICP–AES analysis

Even with the use of very hot flames (a mixture of oxygen and ethyne gas gives the hottest flame, up to 3100°C), there are still many elements that cannot be analysed by AAS or give a poor response.

FIGURE 18.5.14 An ICP atomic emission spectrometer.

Modern instruments, such as that seen in Figure 18.5.14, can analyse most elements by using an energy source called inductively coupled plasma (ICP) in combination with atomic emission spectroscopy (AES). Instead of a flame to excite the atoms, the ICP generates very high temperatures of up to 10 000°C to create a **plasma**, a state of matter containing charged particles. At these temperatures, virtually all the atoms in the sample are excited and are able to emit electromagnetic radiation as an emission spectrum as they return to their ground state.

There are several advantages of using ICP-AES over AAS. ICP-AES:

- can be used to identify most elements
- is suitable for almost all concentrations
- can rapidly identify many elements present in a sample at the same time, as the emission spectrum is resolved by comparison with a computerised database of spectral lines (analysis of 70 elements together takes just two minutes), whereas AAS can determine only one element at a time.

18.5 Review

SUMMARY

- An atom in which the electrons are in their lowest possible energy state is said to be in its ground state.
- When an element is heated, electrons may absorb energy and move into higher energy levels (shells). The atom is described as being excited.
- When the electrons move back to lower energy levels, they emit electromagnetic radiation, such as light, with specific energies; each element emits light with a unique set of energies called an emission spectrum.
- Flame tests are performed by inserting a sample in a non-luminous Bunsen burner flame.
- Flame tests can be used to detect the presence of a small number of metal elements.
- The accuracy of flame tests is hampered by our ability to detect small differences in colours.
- Emission spectra are unique for each element and represent each of the energy transitions within an element as a series of different-coloured lines.
- The technique of atomic absorption spectroscopy (AAS) is based on the ability of electrons to absorb energy as they move between energy levels.
- AAS can be used to accurately determine the concentration of most metals in samples of water and other substances.
- The AAS technique involves the construction of a calibration curve to relate the concentration of the metal to the absorbance measured.

KEY QUESTIONS

1 Select words from the following list to complete the sentences below. Not all of the words provided are required.

protons, higher, transition, electrons, lower, let out, emit, excited

When a sample containing copper is heated in the flame of a Bunsen burner, the flame turns a green colour. This is because the __________ in the copper atoms absorb energy and move to _________ energy levels and then _______ light that corresponds to a green colour as they return to ___________ energy levels.

2 Explain what an emission spectrum is.

3 Match each component of an AAS with its corresponding description.

Component	Description
Flame	Selects a specific wavelength of light
Hollow source cathode lamp	Measures the amount of light
Computer	Produces light with wavelengths that are absorbed by the metal being analysed
Monochromator	Where the sample is sprayed and light is absorbed
Detector	Converts the amount of light detected into the amount of light absorbed by the sample

4 Which one of the following best describes the elements that can be analysed by AAS?

A All elements
B All metal elements
C Most metal elements
D Most non-metal elements

5 **a** Plot a calibration curve using the absorbance readings of the standard solutions containing potassium given below.

Concentration of potassium (mg L^{-1})	Absorbance
0.0	0.01
2.0	0.08
4.0	0.15
6.0	0.21

b Use the calibration curve you created in part **a** to determine the concentration of potassium, in mg L^{-1}, in a sample solution that gives an absorbance of 0.17.

Chapter review

18

KEY TERMS

absorbance
analyte
atomic absorption spectroscopy (AAS)
bioaccumulation
calibration curve
colorimeter
complementary colours
electrical conductivity (EC)
electromagnetic radiation
electromagnetic spectrum
emission spectrum
eutrophication
excess reactant
excited electron
gravimetric analysis
ground state
hard water
hardness
heavy metals
ionic equation
limiting reactant
line spectrum
metal complex
mineral
mole
mole ratio
monochromator
organometallic compounds
pH
plasma
precipitate
precipitation reaction
salinity
soft water
spectroscopy
standard solution
stoichiometric calculations
stoichiometry
total dissolved solids (TDS)
turbidity
UV–visible spectrophotometer

The source of salts in water

1 Maintaining fresh supplies of water is a major concern in society. Mercury, phosphate and ammonium ions all contribute to the salts present in waterways. The concentration of these ions is monitored and controlled.

a Human activity can increase the concentration of these ions in water. Provide three examples of human activities that lead to the increase in the amount of salts in waterways.

b How can heavy metal ions, such as mercury, be removed from water samples?

2 Complete the following passage about electrical conductivity by filling in the gaps.

Salt solutions will conduct electricity due to the presence of _______________. The higher the concentration of the ions, the _______________ the electrical conductivity. Conductivity readings are taken at a standard temperature of _________________. Electrical conductivity readings _____________ be used to identify the actual metal ions present in a natural water sample.

3 Which one of the following solutions will have the highest electrical conductivity?

A 0.001 M KCl
B 0.1 M $LiNO_3$
C 0.1 M CH_3COOH
D 0.1 M NH_3

4 Tetraethyl lead is an organometallic compound. Give an example of another organometallic compound and explain what makes these substances 'organometallic'.

Gravimetric analysis

5 For each amount given, calculate the amounts, in mol, of the other reactants and products required for a complete reaction according to the following equation:

$3Ca(NO_3)_2(aq) + 2Na_3PO_4(aq) \rightarrow Ca_3(PO_4)_2(s) + 6NaNO_3(aq)$

$Ca(NO_3)_2$	Na_3PO_4	$Ca_3(PO_4)_2$	$NaNO_3$
27 mol			
	0.48 mol		
		0.18 mol	
			2.4 mol

6 A student is given solutions of lead(II) nitrate, copper(II) chloride and barium hydroxide.

  a Name the precipitates that could be formed by mixing together pairs of these solutions. You may need to refer to a solubility table.

  b Write full and ionic equations for each of these reactions.

7 When solutions of iron(II) sulfate and potassium hydroxide are mixed, the reaction that occurs can be represented as:

$$FeSO_4(aq) + 2KOH(aq) \rightarrow Fe(OH)_2(s) + K_2SO_4(aq)$$

Complete the following expressions based on this equation. The first one has been done for you.

$$n(KOH) = \frac{2}{1} \times n(Fe(OH)_2)$$

$$n(FeSO_4) = \frac{(\quad)}{(\quad)} \times n(KOH)$$

$$n(KOH) = \frac{(\quad)}{(\quad)} \times n(K_2SO_4)$$

$$n(Fe(OH)_2) = \frac{(\quad)}{(\quad)} \times n(FeSO_4)$$

8 The silver content of a silver alloy is determined by dissolving a sample in nitric acid and precipitating the silver ions as silver chloride. A precipitate of 0.169 g is obtained from a sample with a mass of 0.693 g.

Find the percentage by mass of silver in the alloy.

9 A chemist determined the salt content of a sausage roll by precipitating chloride ions as silver chloride. If an 8.45 g sample of sausage roll yielded 0.636 g of precipitate, calculate the percentage of salt in the food. Assume that all the chloride is present as sodium chloride.

10 Water pollution can result from phosphate added to washing powders to improve the stability of their suds. The phosphorus in a 2.0 g sample of washing powder is precipitated as $Mg_2P_2O_7$. The precipitate weighs 0.085 g.

  a What is the percentage by mass of phosphorus in the washing powder?

  b Suppose you were in charge of an advertising campaign to promote the washing powder. Would you advertise the percentage of phosphorus or phosphate in the product? Explain.

11 The barium concentration in a solution can be determined by precipitating the barium ions from the solution as barium sulfate and measuring the mass of the precipitate. The result obtained in a particular experiment is higher than it should be. What are some experimental errors that could lead to a high result?

Calculations involving excess reactants

12 In three separate experiments, different amounts of carbon and oxygen were reacted together 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			

13 Sodium can react with oxygen gas to form sodium oxide. The equation for this reaction is:

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$

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 is produced in the reaction?

14 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.

15 4.40 g of P_4O_6 and 3.00 g of I_2 are mixed and allowed to react according to this equation:

$$5P_4O_6(s) + 8I_2(g) \rightarrow 4P_2I_4(s) + 3P_4O_{10}(s)$$

a Which reactant is in excess and by how much, in g?

b What mass of the P_2I_4 forms?

c What mass of P_4O_{10} forms?

d What is the total mass of all the products? (Hint: Compare this with the mass of the reactants.)

Determining salt concentration by colorimetry and UV–visible spectroscopy

16 Label the parts of the diagram of a UV–visible spectrometer in Figure 18.6.1.

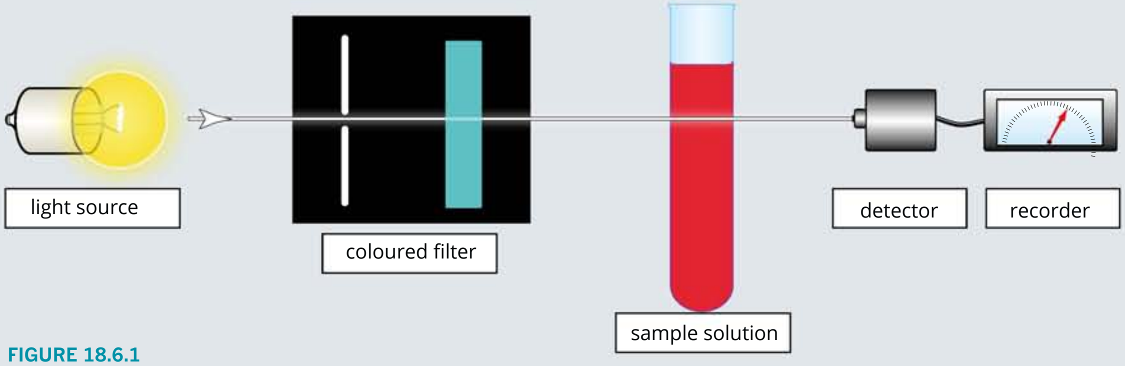


FIGURE 18.6.1

17 A scan of a blue-coloured copper(II) sulfate solution in a UV–visible spectrophotometer produces the spectrum shown in Figure 18.6.2.

a The scan shows the strongest absorption at what wavelength?

b What colour of light is the solution absorbing?

c What colour would you observe the solution to be?

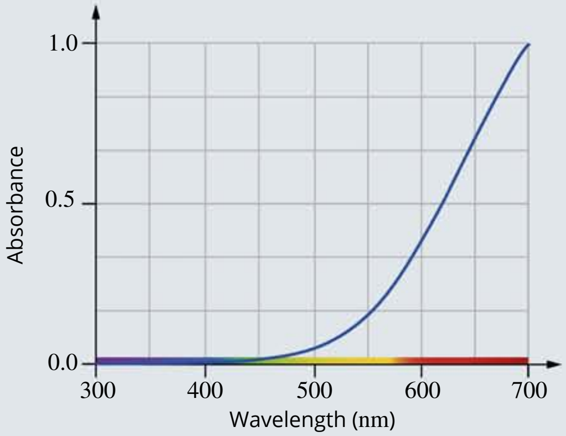


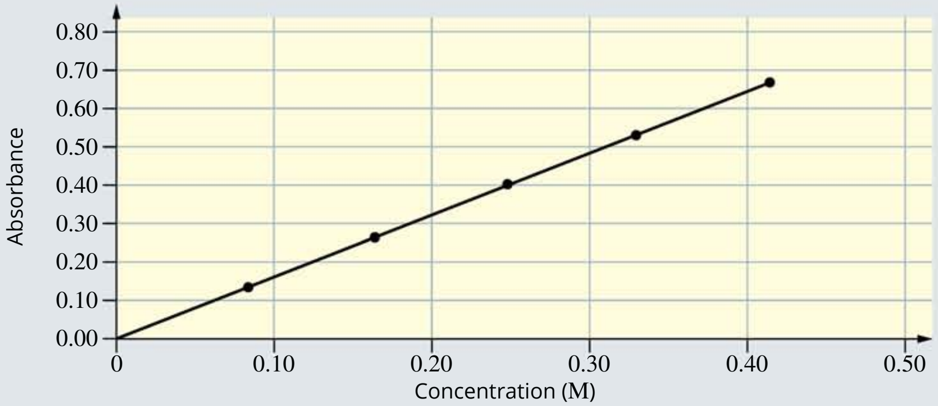
FIGURE 18.6.1

18 Match each component of a UV–visible spectrophotometer or colorimeter with its function.

Component	Function
Detector	Selects a range of wavelengths of light
Filter	Provides ultraviolet and visible light of all wavelengths
Light source	Transparent container that holds the sample
Monochromator	Measures the intensity of light
Sample cell	Displays the absorbance measurement
Recorder	Allows selection of light of a particular wavelength

19 The phosphate content of a detergent may be analysed by UV–visible spectroscopy. In one analysis, a 0.250 g sample of detergent powder was dissolved in water and the solution made up to 250 mL. The solution was treated to convert any phosphate present to a blue-coloured molybdenum phosphorus compound. The absorbance of the solution at a wavelength of 600 nm was measured as 0.17.

The absorbances of five standard phosphate solutions were measured in a similar fashion and the calibration graph below was obtained.



- **a** What is the concentration of phosphorus in the 250 mL detergent solution?
- **b** Determine the percentage by mass of phosphorus in the detergent powder.
- **c** Why was a wavelength of 600 nm selected for this analysis?

20 Label each of the following statements as true or false.

- **a** All visible light has the same wavelength.
- **b** A blue solution does not absorb blue light.
- **c** A purple solution will absorb green light.
- **d** All green solutions absorb the same quantity of purple light.

Determining concentration by atomic absorption spectroscopy

21 Figure 18.5.2 on page 475 shows a flame test being performed.

- **a** What colour would the flame be if copper were present in the sample?
- **b** Before performing the test, it is necessary to heat the wire strongly for several minutes. Why?
- **c** Why would copper wire be unsuitable for use in flame tests?
- **d** Why are flame tests not used for qualitative analysis by modern chemists?

22 Why does an emission spectrum contain a number of lines of different colours?

23 The basis of the operation of an AAS instrument is that metal atoms can absorb light of certain energies. Where in the instrument does that absorption occur?

24 Compare the analytical techniques of AAS and UV–visible spectroscopy. In what way are they:

a similar?

b different?

25 The absorbances of a set of solutions of known concentrations of lead were measured by AAS and are recorded in the table below.

Concentration of lead (mg L^{-1})	Absorbance
0	0.008
10	0.059
20	0.107
30	0.155
40	0.206

a Draw a calibration graph using this data.

b From the calibration curve, determine the concentration, in mg L^{-1}, of lead in a sample solution that gives an absorbance of 0.135.

Connecting the main ideas

26 Match each analytical technique with a feature of the technique.

Technique	Feature
Electrical conductivity	The mass of a precipitate is used to determine the concentration of a salt.
Atomic emission spectroscopy	A monochromator allows complementary light of an exact wavelength to be used.
Colorimetry	Ions flow between electrodes in a solution.
UV–visible spectrophotometry	A filter is used to select a range of wavelengths of visible light.
Gravimetric analysis	A sample is injected into a flame.

27 A solution contains an equal number of moles of aluminium sulfate and sodium sulfate. Barium nitrate is added to precipitate all the sulfate ions as barium sulfate. The mass of barium sulfate obtained is 3.76 g.

a Complete the equations for the two precipitation reactions occurring.

$Al_2(SO_4)_2(aq) + 3Ba(NO_3)_2(aq) \rightarrow$

$Na_2SO_4(aq) + Ba(NO_3)_2(aq) \rightarrow$

b Calculate the number of moles of sulfate ions in the solution.

c Calculate the number of moles of aluminium sulfate and the number of moles of sodium sulfate in the solution before the barium nitrate was added.

28 Gravimetric analysis can be used to determine the mass of Fe^{2+} in a solution. The iron ions can be precipitated from solution by adding a solution of NaOH. The precipitate is filtered, washed and heated until it forms iron(III) oxide.

a What is the chemical formula of iron(III) oxide?

b How many moles of iron were present in the solution if 2.4 moles of iron(III) oxide is formed?

c Will the presence of sodium ions in the solution interfere with the analysis?

29 The Fe^{2+} concentration in a water sample can be determined by colorimetry. The Fe^{2+} ions are first converted to Fe^{3+} ions and a solution of SCN^- ions is added to produce a deep red solution.

a What colour filter should be used for this analysis?

b What will be the mole ratio for the number of moles of Fe^{3+} determined and the number of moles of Fe^{2+} in the original solution?

c What steps must be conducted in order to determine the concentration of Fe^{2+} in the sample?

d What type of lamp would be used to analyse a sample from the Fe^{2+} solution using atomic absorption spectroscopy (AAS)?

CHAPTER

19

Analysis for organic compounds in water

Modern society uses large quantities of organic compounds such as crude oil, pesticides and plastics. These chemicals can end up in the environment in a number of different ways, including from human activity, and can be harmful to living things. For example, an explosion at an oil rig will have a huge environmental impact in the weeks and months following the event. Toxic smoke and crude oil are released into the water, which is the natural habitat for many living things.

This chapter will examine a number of ways in which chemicals such as crude oil end up in the environment. You will also learn how an instrumental technique called a high-performance liquid chromatography, or HPLC, can be used to measure levels of soluble organic contaminants.

Key knowledge

- Sources of organic contaminants in water (may include dioxins, insecticides, pesticides and oil spills)
- The application of high-performance chromatography (HPLC), including the use of a calibration curve and retention time to determine the concentration of a soluble organic compound in a water sample (excluding details of instrument)

19.1 Organic contaminants in water

The worker in Figure 19.1.1 is spraying **fungicide** on trees to destroy fungi that were slowly strangling the trees. At first glance, this looks like a triumph for science, as the trees will be saved. However, some of the fungicide could make its way into local water supplies. If the spray kills fungi, it could also affect other organisms that it comes into contact with.

This section will examine different ways in which organic contaminants enter the water system.

FIGURE 19.1.1 A worker sprays trees with a fungicide.

ORGANIC CONTAMINANTS

You learned about some of the many families of organic compounds in Chapter 9. We make use of organic chemicals in many aspects of our daily lives. Cooking oils, transport fuels, pharmaceuticals, paints and polymers are examples of organic chemicals used in large quantities. These organic chemicals can enter water systems as pollutants.

The nature of the pollutants in particular regions and countries varies, depending on local industries, regulations and climate. Sources of pollutants include:

- industrial waste. Many industrial processes release water back into local creeks and rivers. For example, in the 1900s many companies in Melbourne released **effluent** into the Yarra River. Regulations governing this practice have been gradually tightened and, in 2012, the last remaining company had its licence to release effluent into the Yarra revoked
- illegal dumping. There are instances of companies releasing waste into water systems illegally
- households and schools. Some households are not aware of, or don't care about, the chemicals that should not be added to waste water. However, schools are required to comply with the strict regulations that apply to the hazardous chemicals used during science classes. Organic chemicals that are insoluble in water should be collected and disposed of by professional waste management companies
- leakage from storage facilities
- farming practices. Modern agriculture uses a range of pesticides and fertilisers, which can enter local water systems.

CHEMISTRY IN ACTION

DDT

DDT (dichlorodiphenyltrichloroethane), as shown in Figure 19.1.2, was first synthesised in Germany in 1874. However, it was the Swiss scientist Paul Hermann Muller who brought it to prominence in 1939 when he recognised the potential of DDT as an **insecticide**.

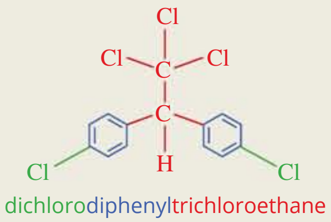


FIGURE 19.1.2 The structure of DDT.

DDT was used extensively during World War II to control disease-carrying mosquitoes. It was so effective that malaria and dengue fever were eliminated in some countries. After the war, DDT was widely used in agriculture and Muller was awarded the 1948 Nobel Prize in Physiology or Medicine.

As spectacular as was the rise in popularity of DDT, its fall has been even more spectacular. In 1972, the United States became the first country to ban the agricultural use of DDT and Australia followed suit in 1987. There were three main reasons for this ban.

- In countries where mosquitoes had not been completely eradicated, mosquito numbers started to increase as the mosquitoes became DDT resistant.
- Scientists became aware of the impact of DDT on the health of animals and humans. Studies showed that numbers of birds of prey such as the peregrine falcon and bald eagle in North America were falling. The inability of these birds to breed or to lay eggs with solid shells was linked to the high content of DDT in their systems.
- Once DDT is added to the environment, it remains active for a long time. It has a **biological half-life** of eight years. This means it takes eight years for the concentration to drop to half of its initial value. In each subsequent eight years, the concentration halves again.

PERSISTENT ORGANIC POLLUTANTS (POPS)

DDT is just one example of an organic contaminant in the environment. The term ‘POP’ is used to describe such chemicals—**persistent organic pollutants (POPs)**. POPs are substances that are toxic to living things. The word ‘persistent’ is included in this term because it takes a long time for these molecules to break down to less harmful products.

Concerns about the impact of POPs on the environment led to the 2001 Stockholm Convention at which the Governing Council of the United Nations Environmental Program issued guidelines to reduce or restrict the use of the 12 most used POPs, or the so called ‘Dirty Dozen’. Table 19.1.1 describes some of these chemicals.

TABLE 19.1.1 Five chemicals identified as significant persistent organic pollutants by the Stockholm Convention in 2001

Chemical	Use	Comment
Aldrin	Insecticide	Colourless white crystals once used to kill insects in the soil and to protect wooden structures
Chlordane	Pesticide; termiticide	A white solid once sprayed on crops such as corn and citrus to kill insects
DDT	Insecticide	Used to control mosquitoes and fleas
Dioxins	Industrial chemicals	Formed as by-products of the combustion of organic chemicals
Polychlorinated biphenyls (PCBs)	Industrial chemicals	Used as coolants and lubricants in industrial equipment

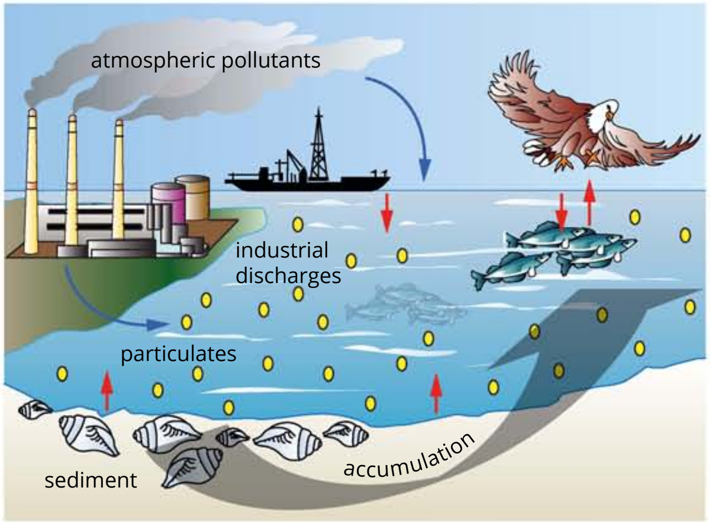


FIGURE 19.1.3 The eagle is at the top of this food chain and is likely to have higher levels of contaminants than the foods it eats.

Impact of POPs in the environment

When released into the air, POPs disperse and can travel long distances and eventually deposit on land and surface water. They do not easily dissolve in water, so they attach themselves to particles and settle in sediment. Aquatic animals consume these particles. They are difficult for the body to break down.

Bioaccumulation occurs when the concentration of a substance in an organism exceeds the background concentration of that substance. Figure 19.1.3 shows how contaminants are progressively transferred through a food chain.

Impact of POPs on humans

Humans, like the eagle in Figure 19.1.3, are at the top of their food chain. The POPs in the plants and animals you eat accumulate in your body. Most POPs are non-polar molecules, so they are deposited in fatty tissue. Their stability means they remain in the body for a long time.

The impact of POPs on humans varies with different chemicals, but they are generally linked with:

- damage to the nervous system
- damage to the reproductive system
- cancer
- allergies
- birth defects.

CHEMFILE

Fiskville CFA training facility

In 2015, Victoria's Monash University released a study concluding that the Country Fire Authority (CFA) training centre in Fiskville, near Ballarat, was the site of a cancer cluster. The study examined the cancer and death rates among the 606 people who had worked at the site between 1971 and 1999. In this group there were 69 cancer cases, which is significantly above the national average.

Investigations will continue to confirm if the high incidence of cancer can be attributed to exposure to organic chemicals, foams and contaminated recycled water during training drills similar to the drill shown in Figure 19.1.4. Several million dollars have been spent trying to remove all traces of contaminants from the facility but the long-term future of the site is uncertain.

FIGURE 19.1.4 Fire-fighting training drills could result in exposure to a range of organic chemicals. Concerns date back to 1971 and centre on the chemicals used to fight fires at the CFA facility in Fiskville.

PESTICIDES

The term **pesticide** includes all chemicals that are used to kill or control pests. Some pesticides are POPs and may be present in the run-off from crops and orchards that have been sprayed. As a result, these chemicals may be found in waterways. Some of the categories covered by the term 'pesticide' are shown in Table 19.1.2.

TABLE 19.1.2 Examples of pesticides

Pesticide	Purpose	Comment
Defoliant	Causes leaves and foliage to drop from a plant	Agent Orange is a mixture of **herbicides** used during the Vietnam War to clear forest areas
Fungicide	Kills fungi	Fungi include blight, mildew and moulds
Herbicide	Kills weeds and other plants	Some are designed to kill all plants, others to kill specific weeds
Insecticide	Kills insects and arthropods	May target the insect or its eggs or larvae
Pheromone	Biochemical used to disrupt the mating of insects	Chemical used to change the sexual behaviour of animals
Rodenticide	Controls mice and rats	Often works by thinning the blood of rats to cause internal bleeding

The yields of crops are vastly increased if pests are removed. However, it is important that an awareness of the health impact of the pesticides is also factored in to their use. Once ingested by humans, pesticides have a similar effect to those of the POPs.

The images in Figure 19.1.5 illustrate some uses of pesticides that have varying impacts on the environment.

FIGURE 19.1.5 (a) A crop-dusting plane can quickly disperse different pesticides over crops. (b) Bees communicate by producing pheromones. Research chemists can artificially produce these compounds and spray them on to crops to either attract or repel bees. (c) A village in Madagascar is sprayed with DDT to eradicate fleas. Fleas are linked to the transfer of a range of potentially fatal diseases, such as bubonic plague. (d) Spraying an orchard to protect fruit from pests. Insects landing on the fruit are killed before they can lay eggs.

DIOXINS

Dioxin is the term given to a family of chemical compounds that contain chlorine atoms and a particular carbon–oxygen framework. The structure of the most common dioxin is shown in Figure 19.1.6. It is the arrangement of atoms around the two middle oxygen atoms that makes this compound a dioxin. The toxicity and slow breakdown of dioxins is the reason for their inclusion in the list of serious POPs.

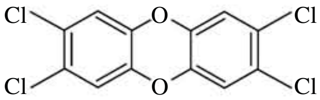


FIGURE 19.1.6 Chemical structure of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. This is a complex structure so it is simplified in this formula by omitting the carbon atoms that are present at each corner of the two hexagons and the hydrogen atoms bonded to those carbons on each side of the molecule.

Although dioxins can be produced from natural processes, they are mainly unwanted by-products of manufacturing processes such as metal smelting and paper production. They are also produced when toxic waste **incinerators** are used to dispose of medical and municipal waste. Even polyvinyl chloride (PVC) plastic added to backyard fires can produce dioxins.

Many developed countries use toxic waste incinerators like the one shown in Figure 19.1.7. These incinerators operate at higher temperatures (about 1000°C) than normal incinerators. The elevated temperature results in a higher level of decomposition of the toxic material added. The gases emitted pass through scrubbing towers but some dioxins may still be released into the atmosphere where rain and wind patterns lead to the dioxins reaching our waterways.

FIGURE 19.1.7 Toxic waste incinerators release toxic material into the atmosphere.

Although dioxins may only be present in the environment in low levels, their toxicity is high. They are linked to liver problems and, unfortunately, they are easily transferred to a foetus through the placenta or to infants through breast milk.

Expensive chemical equipment is required to test for dioxins and each form of dioxin has to be tested separately. Typical levels of dioxins considered safe are less than 0.00000003 mg L^{-1}.

OIL SPILLS

When a reserve of crude oil is found off-shore under the seabed, a platform is built over the area to be drilled. Pipelines are installed and used to transport the oil to refineries for further processing. Oil spills during the drilling process or transportation are another way in which organic contaminants can get into the waterways.

Cleaning up oil spills

Oil and water don't mix. If an oil spill occurs, usually the crude oil floats on the water, forming a characteristic slick. Figure 19.1.8 shows physical barriers called booms being stretched out on the water to stop the spread of the oil. They serve to protect the shoreline and to allow time for some of the constituents of the oil to evaporate.

FIGURE 19.1.8 Booms are used to protect the coast from an oil spill.

The composition of crude oil varies with the source, but it usually contains a mix of alkanes. The smaller alkane molecules will often evaporate when trapped in these booms.

Dispersants can be sprayed on the oil to break up the slicks. The dispersants work like detergent on the slick. This improves the 'look' of the area, but can lead to further damage from oily sludge sinking to the bottom of the ocean.

Sometimes biological agents are used. These come usually in the form of added fertiliser that is sprayed onto the oil. The fertiliser fosters the growth of particular microorganisms that can feed on the oil and break it down to simpler molecules.

FIGURE 19.1.9 Effects of oil spills on wildlife and habitat.

Impact of oil spills

Oil spills can affect plants and animals in many ways, sometimes for many years after the spill itself. Typical impacts include:

- oil coatings on animals. The feathers on birds and the fur on animals such as seals perform a role in protecting and insulating the animal. A coating of oil can destroy this mechanism
- animal poisoning. Spilled oil can harm living things because its chemical constituents are poisonous. Oil can enter animals through both **ingestion** and **inhalation**
- disruption of food chains. Many small animals, such as insects and frogs, are smothered in oil spills. Without them, the food supply of larger species is jeopardised
- damage to plants, weeds and marshes. These plants are a source of food and shelter for animals
- reproduction of species. Fish eggs and other larvae cannot survive in oil
- dispersant damage. Dispersant agents sprayed onto oil to break up large oil slicks are toxic to animals.

The images shown in Figure 19.1.9 highlight how plants and animals are affected by oil spills.

CHEMFILE

Gulf of Mexico oil disaster

The Deepwater Horizon was a nine-year-old oil rig operating for BP in the Gulf of Mexico. On 20 April 2010, the Deepwater crew was drilling into the ocean floor more than 1.5 kilometres below the surface when methane rising into the drilling rig ignited and exploded. Helicopters and boats rescued the survivors. Eleven of the 126 crew members were never found. The rig itself sank two days later as a result of the damage caused by the explosion.

Meanwhile, below the surface of the ocean, oil from the well was gushing into the waters of the Gulf of Mexico. It took three months for the well to be capped. Here are some statistics about the world's worst oil spill.

- Over 87 days, more than 800 million litres of crude oil flowed into the Gulf of Mexico.
- Two million metres of booms, or water barriers, were used to collect and absorb oil.
- BP will pay a US\$18.7 billion fine, in addition to clean-up costs and settlements as a result of the spill.

The images in Figure 19.1.10 record the environmental impact of the Gulf of Mexico oil spill and the work done by thousands of volunteers to help clean up beaches and care for animals.

Unfortunately, the Gulf of Mexico disaster is just one of many major oil spills that have occurred around the world, ranging from the aftermath of the Gulf War in the Middle East, to oil tanker groundings, to pipeline breaks. Australia's worst oil spill occurred in 2009 when a ship called the MV *Pacific Adventurer* was caught in a cyclone along the Queensland coast. Almost 230 tonnes of crude oil were spilt off the Sunshine Coast and Moreton Bay in Queensland.

FIGURE 19.1.10 (a) Volunteers scooping up oil. More than 30 000 people responded to the spill, cleaning up beaches and caring for animals. (b) Oily sludge reached beaches around the Gulf of Mexico. (c) More than 8000 animals, such as birds, turtles and mammals, were reported dead in the six months after the spill, including many that were on endangered species lists. (d) An oily slick moves towards the Florida coast in the United States; 25 000 kilometres of coastline in Texas, Louisiana, Mississippi, Alabama and Florida were affected.

19.1 Review

SUMMARY

- Modern society uses large volumes of organic compounds such as crude oil, pesticides and plastics. Although these chemicals are beneficial, they may have harmful side effects to health or cause environmental damage.
- The term ‘POP’, or persistent organic pollutant, refers to toxic organic contaminants that are slow to degrade.
- Many POPs are carcinogenic and many affect the nervous and reproductive systems of living things. They often accumulate in fats as they are not soluble in water. Levels can be higher in organisms that are high in a food chain.
- Dioxins are formed as a product of the incineration of organic compounds containing chlorine. They can also be produced in heavy industries such as metal smelting and paper production.
- Better guidelines and less toxic alternatives have reduced global emissions of most POPs since the Stockholm Convention in 2001.
- The frequent incidence of oil spills makes them a source of organic contamination.

KEY QUESTIONS

1 Select the substances that are classed as POPs.

A DDT
B Dioxins
C Heavy metals
D Minerals
E Crude oil

2 Select the three medical adverse effects linked to the intake of POPs.

A Cancer
B Radiation levels
C Diabetes
D Nervous system damage
E Birth defects
F Arthritis

3 Which one of the following organic compounds is most likely to form a dioxin when burnt in an incinerator?

A Sugar
B PVC
C Petrol
D Ethanol

4 Select the most likely place for dioxins to be found in humans.

A Urine
B Stomach
C Blood
D Fat tissue

5 Which of the following is a property of crude oil?

A Non-flammable
B Insoluble in water
C High density
D Colourless

6 Select the correct words to complete this paragraph about dioxins. (Some words are not used.)

storage
water supplies
ingestion
sulfur
nitrogen
urine
positive
insoluble
soluble
fat
the stomach
limited
adverse
burning
chlorine

Dioxins can be formed from the ________________ of organic chemicals containing ______________ atoms. The dioxins can end up in _________________. They are usually ___________________ in water, so they become attached to plants or sediments. When consumed by an animal they are usually stored in _____________. They can have _________________ effects on your health.

7 The materials required for a school chemistry experiment are listed below. Select the three chemicals that should be retained for disposal by a professional waste management company.

A Methanol
B Ethanol
C Cyclohexane
D Cyclohexene
E Ethanoic acid
F Chloroethane

19.2 Principles of chromatography

Chromatography is a technique used to separate the **components** in a mixture. It can be used for both **qualitative** and **quantitative analysis** to identify numerous inorganic and organic substances such as contaminants in water, toxic gases in air, impurities in food, and drugs present in blood.

In this section, you will learn about the underlying principles of **chromatography** and about two simple forms of the technique called **paper chromatography** and **thin-layer chromatography**.

HOW CHROMATOGRAPHY WORKS

All methods of chromatography have a:

- **stationary phase**
- **mobile** (moving) **phase**.

You can perform a simple chromatography experiment by dipping the end of a stick of chalk into water-soluble black ink and then standing the chalk in a beaker containing a small amount of water, as seen in Figure 19.2.1.

FIGURE 19.2.1 The pattern of bands produced when this stick of chalk is dipped in black ink and then placed in water is called a chromatogram.

As the water carries the ink up the chalk, you will see that the ink separates into bands of different colours. Each band contains one of the substances present in the ink mixture. The pattern of bands or spots is called a **chromatogram**.

In this simple chalk-and-ink exercise, the stationary phase is the chalk and the mobile phase is the water.

As the components in the ink are swept upwards over the stationary phase by the solvent, they undergo a continual process of **adsorption** onto the solid stationary phase, followed by **desorption** and dissolving into the mobile phase. The ability of the components to stick to the stationary phase will depend upon the polarity of the stationary phase and the component molecules. Similarly, the attraction of the components to the solvent molecules is determined by their polarity.

The rate of movement of each component depends mainly upon how:

- strongly the component adsorbs onto the stationary phase
- readily the component dissolves in the mobile phase.

CHEMFILE

Colour writing

While studying the coloured materials (pigments) in plants, Russian botanist Mikhail Tsvet (Figure 19.2.2) developed the separation technique known as chromatography. The word chromatography means 'colour writing'. It is a way by which a chemist can separate the components in mixtures.

FIGURE 19.2.2 Mikhail Tsvet was the inventor of chromatography.

Passionate about botany, Tsvet discovered that different pigments appeared as different coloured bands. In 1903, chlorophyll and xanthophyll were the only known plant pigments. Tsvet produced chromatograms similar to the one shown in Figure 19.2.3 and discovered two forms of chlorophyll and eight other pigments.

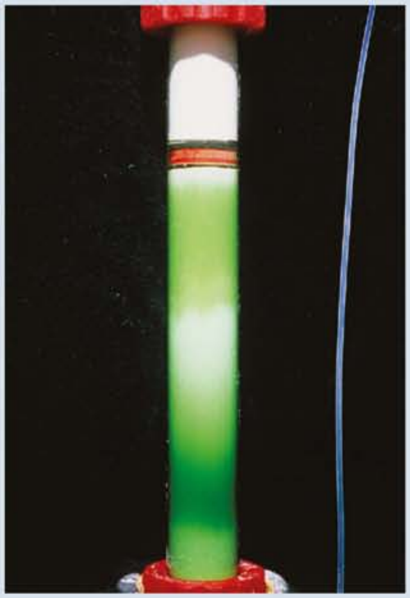


FIGURE 19.2.3 Chromatogram of a plant sample similar to the chromatograms obtained by Mikhail Tsvet.

Chromatography is such an important technique that two Nobel prizes have been awarded for research based mainly on this analytical method.

The components separate because they undergo these two processes to different degrees. In the example involving the chalk and ink shown in Figure 19.2.1 on page 497, the blue dye in the ink is more soluble in the mobile phase than the red dye, and bonds less strongly than the red dye with the stationary phase. The blue dye in the ink has moved faster up the piece of chalk than the red dye, resulting in their separation.

Water, the mobile phase, is a polar solvent. The blue dye moves more quickly with the water up the stationary phase than the red dye, indicating that the blue dye is more polar than the red dye.

PAPER AND THIN-LAYER CHROMATOGRAPHY

In the laboratory, paper chromatography is performed on high-quality absorbent paper, similar to filter paper, as the stationary phase. Thin-layer chromatography (TLC) is very similar to paper chromatography. In this case the stationary phase is a thin layer of a fine powder, such as alumina (aluminium oxide), spread on a glass or plastic plate. Both techniques are useful for qualitative analysis.

Paper and thin-layer chromatography in practice

In both paper and thin-layer chromatography, a small spot of the solution of the sample to be analysed is placed on one end of the chromatography paper or plate.

The position of this spot is called the **origin**. The paper or plate is then placed in a container with solvent. The origin must be a little above the level of the solvent so that the components can be transported up the paper or plate and not dissolve into the liquid in the container. As the solvent rises up the paper or plate, the components of each sample separate, as shown in Figure 19.2.4.

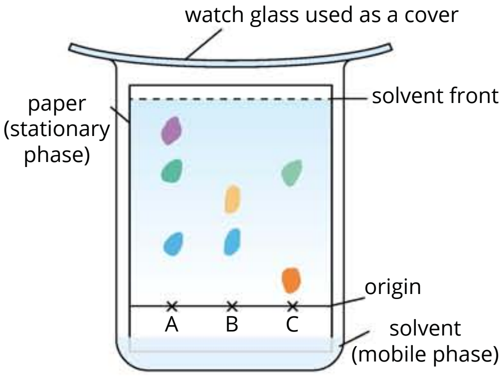


FIGURE 19.2.4 Paper chromatography of three different food colours (A, B and C).

Identifying the components of a mixture

The components in a mixture can be identified by chromatography in one of two ways:

1 by including standards of known chemicals on the same chromatogram as the unknown sample

2 by calculating the **retardation factor (R_f)** of the sample.

Method 1: Using standards

In this method, you need to know what chemicals might be present in the sample. For example, if you wish to find out whether a vitamin tablet contains vitamins A and D, a sample of the vitamin tablet can be placed alongside samples of each of vitamins A and D on the same chromatogram. If spots from the tablet sample move the same distance from the origin as the spots from the pure samples, then the tablet is likely to contain the vitamins.

The sample and standards are 'run' on the same chromatogram because the distances moved from the origin will depend on the distance moved by the solvent front. The further the solvent front is allowed to travel, the further the spots travel.

Method 2: Calculating R_f values

Another way of identifying the components of a mixture is by comparing the distance they travel up the stationary phase to the distance travelled by the solvent front. This is expressed as a retardation factor, R_f, for a component:

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

You can see from the chromatogram in Figure 19.2.5 that:

- R_f values will always be less than one
- the component most strongly adsorbed onto the stationary phase moves the shortest distance and has the lowest R_f value.

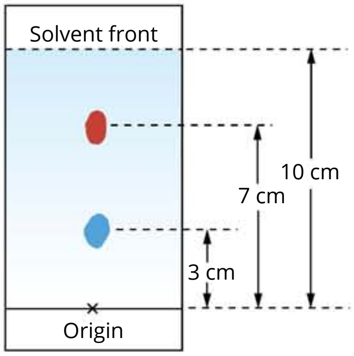


FIGURE 19.2.5 A chromatogram of a sample that consists of two components. The distances from the origin enable R_f calculations.

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

In this method, the distance moved by the solvent front is no longer critical as the proportion of the distance moved from the origin (the R_f value) stays the same provided the conditions under which the chromatogram is obtained are the same.

This means the R_f values of unknown spots can be compared against a table of R_f values of common materials. However, changes in the temperature, the type of stationary phase, the amount of water vapour around the paper or plate and the type of solvent will all change the R_f value for a particular chemical.

Worked example 19.2.1

CALCULATING R_f VALUES

Calculate the R_f value of the red component in Figure 19.2.5.

Thinking	Working
Record the distance the component has moved from the origin and the distance the solvent front has moved from the origin.	Distance from origin of red component = 7 cm Distance from origin of solvent front = 10 cm
$R_f = \frac{\text{distance of component from origin}}{\text{distance of solvent front from origin}}$	$R_f \text{ (red component)} = \frac{7}{10}$ $= 0.7$

Worked example: Try yourself 19.2.1

CALCULATING R_f VALUES

Calculate the R_f value of the blue component in Figure 19.2.5 on page 499.

In chromatograms of plant pigments and food dyes, the components can be seen easily; however, most compounds are colourless and must be made visible. Many organic compounds fluoresce and appear blue when viewed under ultraviolet light. For other compounds, the chromatogram can be sprayed with a chemical that reacts to form coloured or fluorescent compounds. Ninhydrin reacts with amino acids to give blue and brown coloured compounds.

The choice between paper and thin-layer chromatography depends upon the sample being analysed. Table 19.2.1 lists the advantages of each method.

TABLE 19.2.1 A comparison of paper and thin-layer chromatography

Paper chromatography	Thin-layer chromatography
Cheap	Detects smaller amounts
Little preparation	Better separation of less polar compounds
More efficient for polar and water-soluble compounds	Corrosive materials can be used
Easy to handle and store	A wide range of stationary phases is available

For a particular combination of stationary phase and mobile phase, many different chemicals may have similar R_f values. Paper and thin-layer chromatography are only a guide to the identity of a chemical. Further testing using **high-performance liquid chromatography (HPLC)** or **gas chromatography (GC)** may be required to confirm the identity of a chemical. Section 19.3 will introduce you to HPLC and how it can be used to determine the presence and concentration of organic compounds in water.

19.2 Review

SUMMARY

- Chromatography is a technique commonly used to separate and identify the components in a mixture.
- Paper and thin-layer chromatography are simple forms of this technique.
- All chromatographic techniques involve a mobile phase and a stationary phase.
- Components separate during chromatography as a consequence of how strongly they adsorb to the stationary phase and desorb back into the mobile phase.
- Components in a mixture have differing affinities for the mobile and stationary phases.
- In paper and thin-layer chromatography, the components in a mixture are identified by comparison with known standards and determination of R_f values.

KEY QUESTIONS

1 Paper chromatography is used to separate the pigments in a plant leaf. A spot of each pigment is placed on a sheet of chromatography paper and the chromatogram is run inside a closed jar that is partly filled with ethanol. Which one of the following options is the mobile phase in this instance?

A Pigments
B Ethanol
C Paper
D Ethanol vapour in the closed jar

2 Match each term with its correct description.

Term	Description
Adsorption	The breaking of the attraction between a substance and the surface to which the substance is adsorbed
Desorption	The components of a mixture undergo adsorption to this phase
Components	The different compounds in the mixture, which can be separated by chromatography
Polar molecule	The attraction of one substance to the surface of another
Mobile phase	A molecule that acts as a dipole; it has one or more polar covalent bonds, with the charge being distributed asymmetrically
Stationary phase	The solvent that moves over the stationary phase in chromatography

3 An extract from a plant was analysed by thin-layer chromatography with a non-polar solvent. The chromatogram obtained is shown in Figure 19.2.6. Table 19.2.2 gives the R_f values of some chemicals commonly found in plants measured under the same conditions.

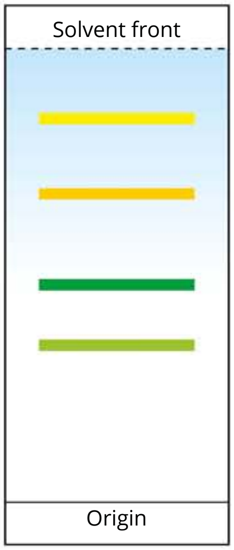


FIGURE 19.2.6 Plant extract chromatogram.

TABLE 19.2.2 R_f values of some plant materials

Chemical	R_f
Xanthophyll	0.67
β-Carotene	0.82
Chlorophyll a	0.48
Chlorophyll b	0.35
Leutin	0.39
Neoxanthin	0.27

a Measure and record the distance from the origin to the centre of each band, and the distance of the solvent front from the origin.
b Calculate the R_f value of each band.
c Compare R_f values for the bands with the R_f values in Table 19.2.2 and name the chemicals present in the extract.
d If water had been used as the solvent, would the chromatogram be likely to have a similar appearance? Explain.

4 Phenacetin was once an ingredient in analgesic drugs, but it is not used now because it causes liver damage. It is soluble in chloroform. A chemist wishes to analyse a brand of analgesic by thin-layer chromatography to determine whether it contains phenacetin. Outline the steps in the analysis. (Assume that a sample of pure phenacetin is available to the chemist.)

19.3 High-performance liquid chromatography

In section 19.2, you learned the principles of chromatography and how both paper and thin-layer chromatography can be used to separate the components in a mixture.

In these techniques, a liquid mobile phase is used to carry the components of the mixture past a solid stationary phase. The components undergo a continual process of adsorption to the stationary phase and desorption back into the mobile phase. The components of a mixture undergo the processes of adsorption and desorption to different degrees, so the components separate as they move past the stationary phase.

In this section, you will learn about another chromatographic technique, known as **column chromatography**, which operates in a similar way to paper and thin-layer chromatography. Column chromatography is the basis for a modern analytical technique, high-performance liquid chromatography (HPLC), which is highly sensitive and capable of detecting miniscule amounts of a compound.

COLUMN CHROMATOGRAPHY

Figure 19.3.1 shows the chromatographic technique of column chromatography, which can be used to separate the components of a mixture.

The solid stationary phase is packed into a glass column. The sample mixture is applied carefully to the top of the packed solid, and a solvent, which acts as the mobile phase, is dripped slowly onto the column from a reservoir above. A tap at the bottom of the column allows the solvent, which is called the **eluent**, to leave the column at the same rate as it enters it at the other end. Figure 19.3.2 shows how column chromatography can be used to separate and collect different components in a black ink.

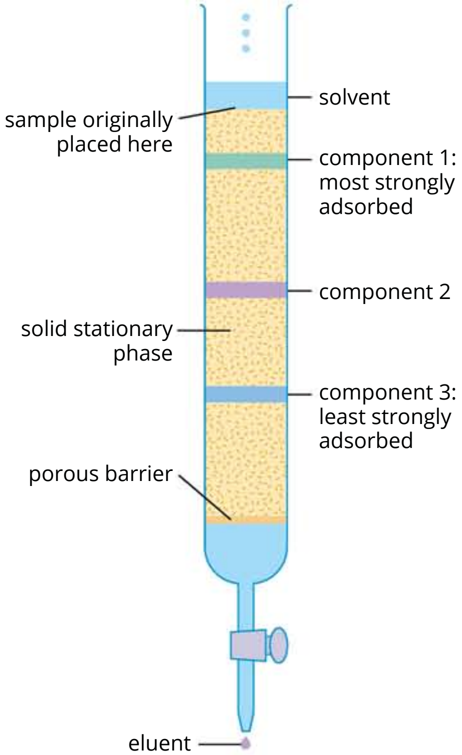


FIGURE 19.3.1 Column chromatography is used to separate the components in a mixture.

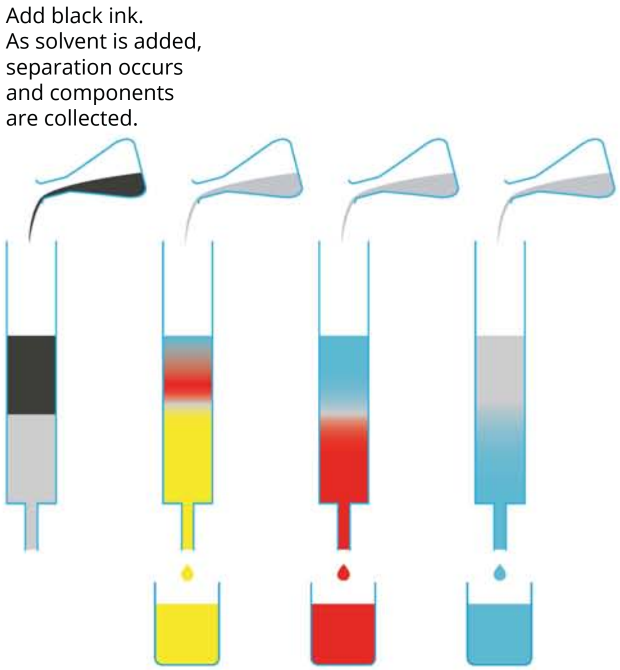


FIGURE 19.3.2 Column chromatography can be used to separate and collect the components in black ink. The yellow dye in the ink is more soluble in the mobile phase and adsorbs less strongly to the stationary phase than the red and blue dyes. The yellow dye in the ink moves faster through the column than the red and blue dyes, resulting in separation of the dyes.

HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

High-performance (or high-pressure) liquid chromatography (HPLC) is an instrumental chromatographic technique based on column chromatography that allows scientists to perform extremely sensitive analyses of a wide range of mixtures. It is commonly used for the separation and identification of complex mixtures of similar compounds, such as contaminants that are soluble in water, drugs in blood and hydrocarbons in oil samples.

HPLC is now used routinely for environmental, pharmaceutical and industrial analyses. For example, it can be used to analyse for the presence and concentration of dioxins, insecticides, pesticides and oil spills in water. It is also used to determine the presence of pesticides in food or to detect the presence of drugs in blood.

Figure 19.3.3 shows the apparatus used for HPLC. The basic principles of HPLC are the same as for column chromatography described earlier. There are two main differences between simple column chromatography and HPLC.

- The particles in the solid used in the HPLC column are often 10–20 times smaller than those used in column chromatography, allowing more frequent adsorption and desorption of the components, giving much better separation of similar compounds.
- The small particle size used in HPLC creates a considerable resistance to the flow of the mobile phase and so the solvent is pumped through the column under high pressure.

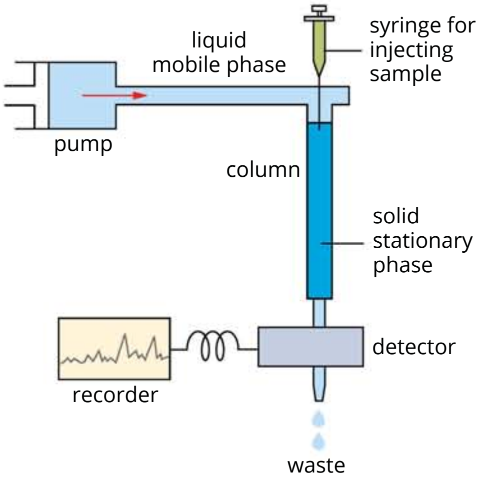
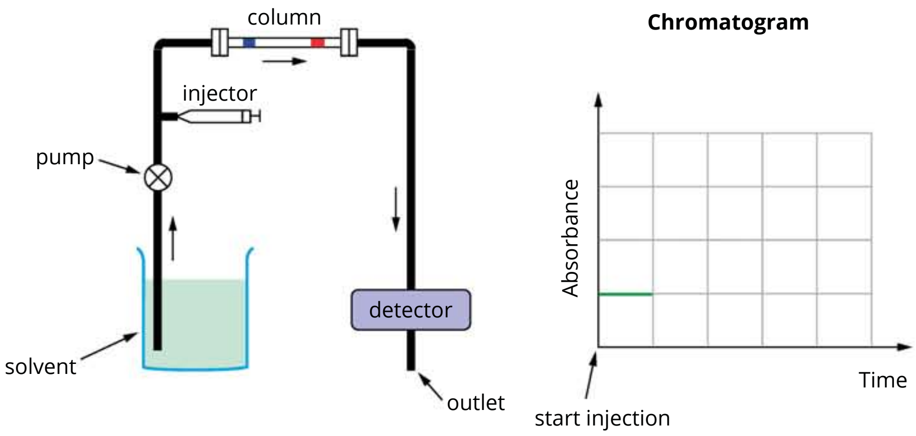


FIGURE 19.3.3 The construction of a high-performance liquid chromatograph.

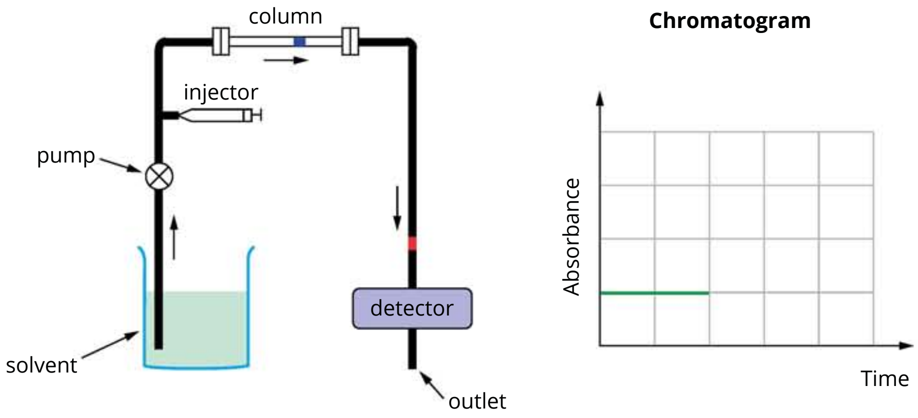
A range of solids is available for use in HPLC columns, some with chemicals specially bonded to their surfaces to improve the separation of particular classes of compounds.

In HPLC, the components are usually detected by passing the eluent stream through a beam of ultraviolet (UV) light. Many organic compounds absorb UV light, so when an organic compound passes in front of the beam of light, a reduced signal is picked up by a detector. The amount of light received by the detector is recorded on a chart that moves slowly at a constant speed or sent to a computer. The resulting trace is called a chromatogram. Each component forms one peak in the chromatogram.

Figure 19.3.4 indicates how the chromatogram is produced as the components pass through the instrument.



After 1 minute



After 2 minutes

FIGURE 19.3.4 Separation of components of a sample using a high-performance liquid chromatograph.

Applications of HPLC

Chemists use HPLC in chemical analysis to answer two questions.

- What chemical is present in the sample (qualitative analysis)?
- How much of each chemical is present (quantitative analysis)?

Qualitative analysis

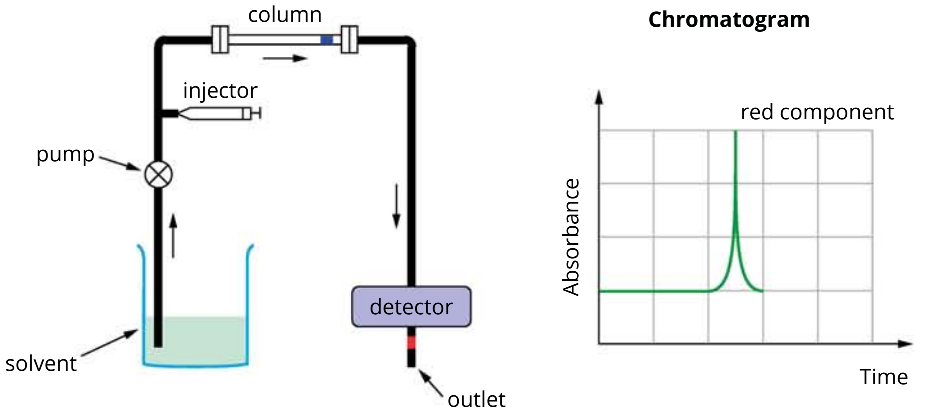
Qualitative analysis can be used to identify the components in a sample and determine its purity. A solution of a pure compound that is thought to be one of the components is injected into the HPLC under the same conditions. The chromatogram of the standard is then compared with the chromatogram of the sample.

The time taken for a component to pass through the HPLC column is called its **retention time (R_t)**, and is characteristic of the component for the conditions of the experiment. It is analogous to the R_f value determined for paper and thin-layer chromatography.

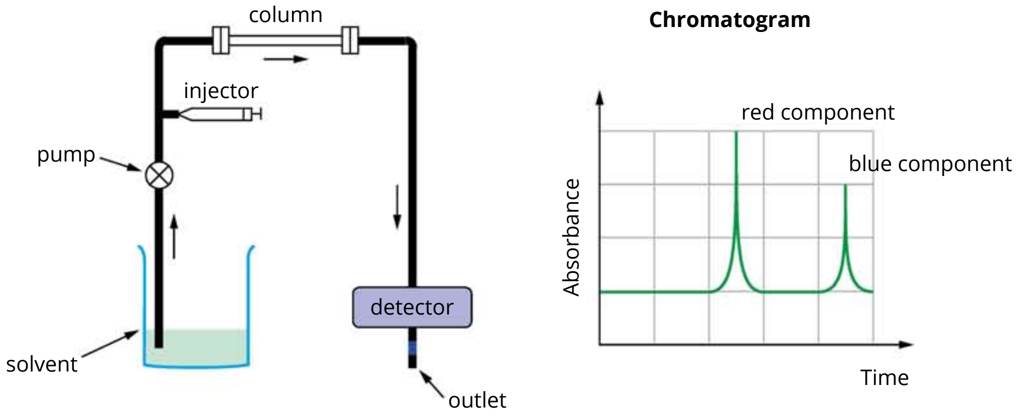
The same compound will have the same retention time if the conditions (temperature, mobile phase, stationary phase, flow rate, pressure etc.) remain the same.

Retention times are used to identify the components associated with the peaks on a chromatogram.

After 3 minutes



After 5 minutes



Example: Detecting pesticides

Pesticides can be used to prevent mould in food such as the lettuce used in salads. HPLC can be used to test waste water samples from a farm for the presence of two pesticides: vinclozolin and carbendazin.

The high-performance liquid chromatogram of a water sample is shown in Figure 19.3.5. The two component pesticide peaks, marked 1 and 2, are identified by obtaining chromatograms of known pure compounds under exactly the same conditions as the sample.

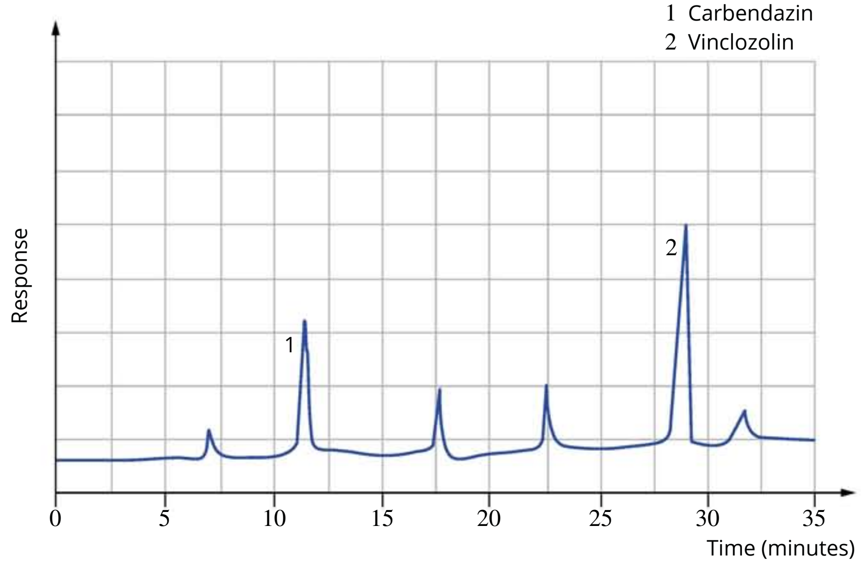


FIGURE 19.3.5 High-performance liquid chromatogram of a water sample from a farm.

A compound can also be identified by adding a known compound to the sample (a procedure called 'spiking'). The chromatogram in Figure 19.3.6 was produced when the water sample was spiked with carbendazin. Note that peak 1 is much bigger in the spiked sample. There are no extra peaks, indicating that carbendazin must have been component 1 in the sample.

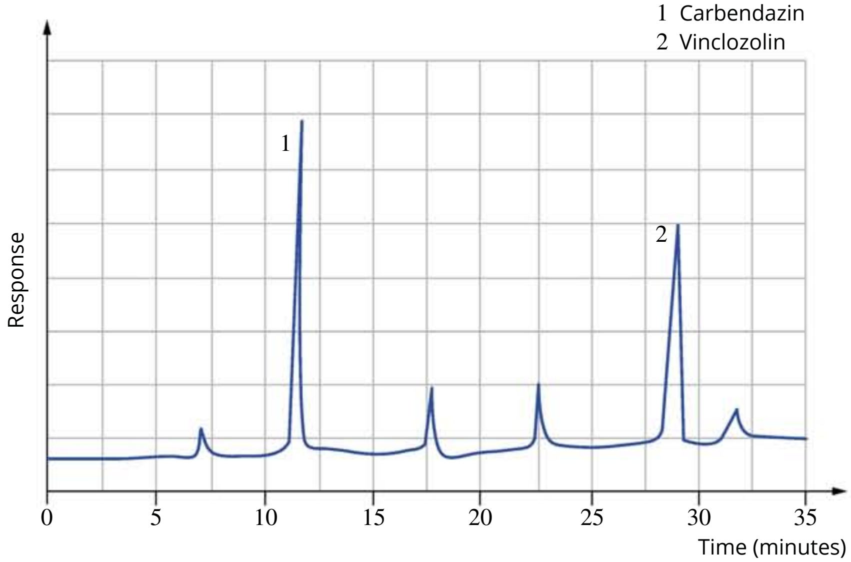


FIGURE 19.3.6 High-performance liquid chromatogram for a spiked water sample.

Quantitative analysis

To determine the concentration of an individual component in a mixture, its peak area is compared with the peak areas of samples of the same chemical at known concentrations. A solution with an accurately known concentration is called a **standard solution**.

By plotting the peak areas against the concentrations of the standard solutions, a calibration curve can be drawn and used to determine unknown concentrations.

Worked example 19.3.1 shows how HPLC can be used to find the concentration of a component in a mixture.

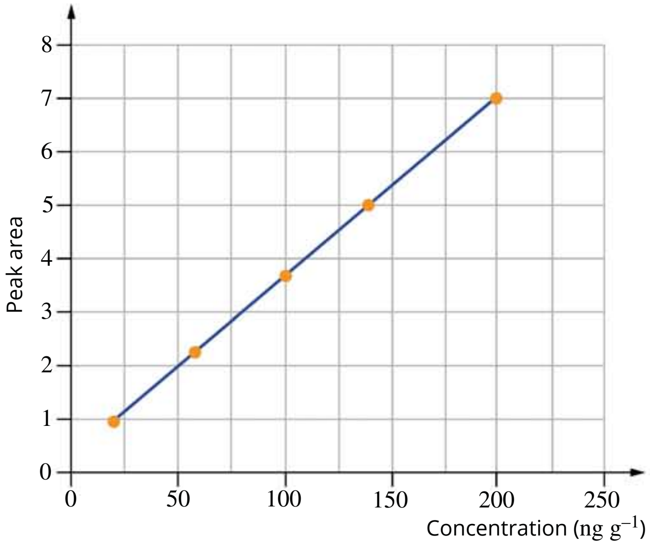
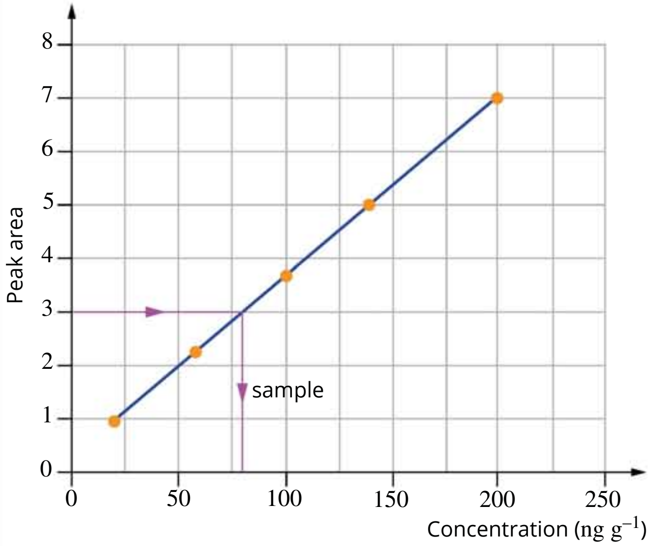
Worked example 19.3.1

CONCENTRATION OF A PESTICIDE

The concentration of the pesticide carbendazin in a sample of waste water from a farm was determined by HPLC. The chromatograms of a series of standards with accurately known concentrations of carbendazin were obtained under the same conditions as the sample.

The results from the chromatograms of the sample and the standards are shown in the following table. Determine the concentration of carbendazin in the sample of waste water.

	Peak area	**Concentration (ng g^{-1}) 1 ng = 10^{-9} g**
Standard 1	0.95	20
Standard 2	2.20	60
Standard 3	3.60	100
Standard 4	5.00	140
Standard 5	7.00	200
Sample	3.00	?

Thinking	**Working**
Construct a calibration graph by plotting peak area versus concentration.	
Mark where the peak area of the sample lies on the calibration curve by tracing a horizontal line to the curve and then a vertical line down to the *x*-axis.	
Determine the concentration of the sample by reading the concentration value for the unknown solution from the *x*-axis.	The concentration of carbendazin in the water sample is 80 ng g^{-1}.

Worked example: Try yourself 19.3.1

CONCENTRATION OF A PESTICIDE

Procymidone is a pesticide that is used to prevent disease in oranges. Tests have been performed by HPLC to determine the concentration of this pesticide in a sample of orange juice.

The chromatograms of a series of standards with accurately known concentrations of procymidone were obtained under the same conditions as the sample.

The results from the chromatograms of the sample and the standards are shown in the following table.

Determine the concentration of procymidone in the sample of orange juice.

	Peak area	**Concentration (mg kg^{-1})**
Standard 1	10	0.5
Standard 2	20	1.0
Standard 3	30	1.5
Standard 4	40	2.0
Standard 5	50	2.5
Sample	15	?

Information obtained from a high-performance liquid chromatogram:

- Retention time, R_t, is used to identify components in a mixture.
- The concentration of an individual component in a mixture can be determined by comparing its peak area with the peak areas of samples with known concentrations of the same chemical.

COMPARING CHROMATOGRAPHIC TECHNIQUES

In sections 19.2 and 19.3 you learned about different chromatographic techniques that can be used for analysis: paper or thin-layer chromatography and HPLC. What factors do chemists consider when choosing which technique to use in a particular situation?

The decision to use a particular technique depends on a number of factors, including the:

- properties of the components being separated
- amount of sample available for analysis
- concentration of the component in the sample
- sensitivity of the technique
- time taken for analysis
- cost of equipment.

Some of the important features of the different chromatographic techniques are listed in Table 19.3.1 on page 509. Chromatography is widely used for the drug testing of blood and urine samples, monitoring water and air pollution, and testing food quality.

TABLE 19.3.1 Features of different chromatographic techniques

Technique	Typical substances tested	Typical samples	Advantages	Disadvantages	Comments
Paper and thin-layer chromatography	Polar, water-soluble substances	Drug detection; dyes in foodstuffs	Very cheap, only basic laboratory equipment needed; easy to perform	Poor precision and accuracy	Samples need to be coloured or visible under UV light. Otherwise, samples can be made visible using stains.
High-performance liquid chromatography	Medium to high molecular mass organic compounds, e.g. pesticides, enzymes	Foods, drugs, biological samples	High sensitivity and precision; small sample size; readily automated	Moderately expensive instrument; trained technician needed to operate	Samples must be soluble in a suitable solvent.

CHEMFILE

Drug testing in sport

Since competitive sports began, some people have sought to gain an advantage by whatever means available. For example, athletes in ancient Greece and Rome consumed specially prepared lizard meat in the hope that it would improve their performance and give them a competitive edge.

Today, drug problems in sport usually result from the inappropriate use of therapeutic substances and manipulation of substances such as hormones and electrolytes that occur naturally in an animal's or athlete's system. In horse racing, the use of illegal 'go-fast' or 'stopper' drugs is now relatively rare because of their ease of detection by the combined analytical technique of gas chromatography–mass spectrometry, or GC–MS.

Gas chromatography is the most sensitive of the chromatographic techniques. It can detect as little as 10^{-12} g of a compound. The mobile phase is a gas and the stationary phase may be either a solid or a liquid.

The extreme sensitivity of gas chromatography makes it ideal for the analysis of trace contaminants in samples or for the detection of miniscule amounts of very potent compounds. Urine samples are routinely taken from athletes competing in major events to ensure that the athletes are not benefiting from the use of illegal, performance-enhancing drugs (Figure 19.3.7). These samples are analysed by gas chromatography. The combined technique, GC–MS, uses a mass spectrometer as the detector in the gas chromatography. In Unit 4, you will learn about how mass spectrometry is used to analyse organic compounds.

FIGURE 19.3.7 A chemist prepares samples from athletes for drug testing.

19.3 Review

SUMMARY

- High-performance liquid chromatography (HPLC) is a very sensitive technique used for qualitative and quantitative analysis.
- In HPLC, the mobile phase is liquid under pressure.
- In HPLC, retention time is used to identify components in a mixture.
- The concentration of an individual component in a mixture can be determined by comparing its peak area on a chromatogram with the peak areas of samples with known concentrations of the same chemical analysed under identical conditions as the mixture.

KEY QUESTIONS

1 The retention time can be used in HPLC to determine:
A the identity of the chemical
B the concentration of a chemical
C the amount of a chemical in a sample
D all of the above.

2 The concentration of a substance is most accurately determined in HPLC by measuring:
A peak area
B peak height
C retention time
D R_f value.

3 Use the following terms to complete the summary of column chromatography. Not all terms are used.

mobile desorb shortest
adsorb longest stationary

During column chromatography, the components of the sample ________________ onto the stationary phase and ________________ into the liquid mobile phase. A component that adsorbs most strongly to the ________________ phase and is least soluble in the ________________ phase would be expected to take the ________________ time to pass through the column.

4 Compounds A and B are equally soluble in water, but A is slightly more strongly adsorbed on silica powder. Compound C has a lower solubility in water than A and B. A sample containing A, B and C is mixed with water and injected into an HPLC instrument, which uses water as the solvent and silica as the stationary phase.
List the order of the components as they are likely to emerge from the column.

5 The ethanol content of waste water from a brewery can be analysed by HPLC. The peak areas produced from HPLC analysis of a sample of water and a number of standard solutions of ethanol are shown in the table.

	Ethanol (%)	Relative peak area
Water sample	?	5.6
Standard 1	0.2	1.6
Standard 2	0.4	3.2
Standard 3	0.6	4.8
Standard 4	0.8	6.4

a Construct a calibration curve of relative peak area against concentration of ethanol (%).
b Determine the percentage of ethanol in the water sample, correct to one decimal place.

Chapter review

KEY TERMS

adsorption
biological half-life
chromatogram
chromatography
column chromatography
component
desorption
dioxin
dispersant
effluent
eluent
fungicide
gas chromatography (GC)
herbicide
high-performance, or high-pressure, liquid chromatography (HPLC)
incinerator
ingestion
inhalation
insecticide
mobile phase
origin
paper chromatography
persistent organic pollutant (POP)
pesticide
qualitative analysis
quantitative analysis
retardation factor (R_f)
retention time (R_t)
standard solution
stationary phase
thin-layer chromatography

Organic contaminants in water

1 Which one of the following is not regarded as an organic contaminant in water?

A Calcium hydrogen carbonate
B Crude oil
C Pesticides
D Dioxins

2 Which part of the steak in Figure 19.4.1 is likely to contain the highest level of non-polar contaminant?

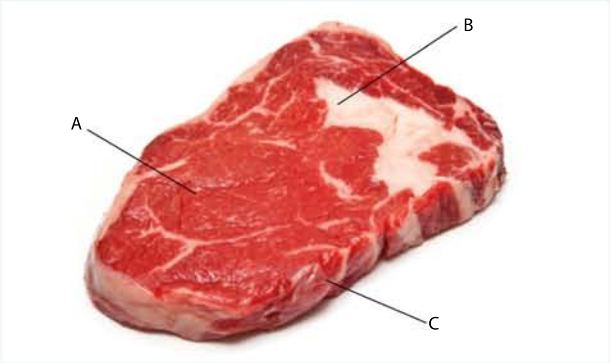


FIGURE 19.4.1

3 Although some dioxins are formed by natural processes, most are formed as a result of human activity. Sort the following into a sequence explaining how a dioxin might be formed and how it might find its way into the human body.

A Small fish consume plankton.
B Dioxins settle on marine plants in a reservoir.
C A fisherman takes his catch home.
D Contaminated waste is burnt in a waste incinerator.
E Plankton feed on marine plants.
F A family eats fish for dinner.
G Incinerator emissions are blown over water in a reservoir.
H A manufacturer produces PVC packaging for medical waste.

4 State whether the following are true or false.

a DDT kills mosquitoes.
b DDT degrades quickly in the environment.
c DDT is toxic to humans.
d It is illegal to use DDT in Australia.
e DDT is an ionic compound.

5 Rank each aquatic species from highest to lowest according to their likely level of contaminants.

- zooplankton
- large fish
- small fish
- whale
- aquatic plants

6 Which of the following elements is found in both DDT and dioxins?

A Oxygen
B Chlorine
C Nitrogen
D Sulfur

7 Use the following words to complete these sentences about pesticides.

dioxin
fungicide
herbicide
life-time
span
half-life
soluble
insoluble
meat
fat
bones

To kill fungi growing on a tree, the tree can be sprayed with a ________________. The chemical remains active even after the fungi have been killed. The term used to describe the time taken for 50% of the fungicide to degrade is known as the ________________ of the chemical. Some of the chemical may wash into streams and lakes. It will adhere to sediment or plants if it is ________________ in water. When animals swallow the chemical, it tends to accumulate in ________________.

8 The use of toxic waste incinerators can have an impact on the environment. Classify the following effects as ether beneficial or adverse effects.

- **a** Produces dioxins
- **b** Produces energy
- **c** Reduces landfill volume
- **d** Produces carbon dioxide

Principles of chromatography

9 Use the following terms to complete the sentences about paper chromatography. Words can be used more than once.

stationary
mobile
components
origin
phase
sample
above
below
phases

In paper chromatography, the paper acts as the ________________ phase. A small spot of a solution is placed at one end of the paper, called the ________________. The sample solution contains a number of different coloured compounds, the ________________. The paper is suspended so that the end with the spot is ________________ the surface of the solvent. The solvent or ________________ phase moves up the ________________ phase. Different coloured spots are observed at various places on the paper, due to the separation of different ________________.

10 **a** Use the terms ‘adsorbed’ and ‘absorbed’ correctly in each of the sentences below.

- **i** Water was ________________ by the towel as the wet swimmer dried himself.
- **ii** A thin layer of grease ____________________ onto the cup when it was washed in the dirty water.

b Explain the difference between the terms ‘adsorbed’ and ‘absorbed’.

11 The chromatogram of a dye is shown in Figure 19.4.2. Calculate the R_f values for each of the blue, purple and yellow components. Give answers to one decimal place.

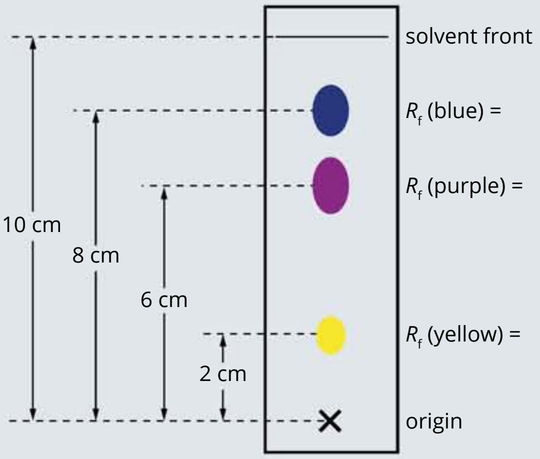


FIGURE 19.4.2 Chromatogram of a dye showing three components.

12 A sample of brown dye from a lolly is placed at the origin on a chromatography plate. The solvent front moves 9.0 cm from the origin. A blue component of the dye moves 7.5 cm and a red component 5.2 cm in the same time. Calculate the R_f values of the two components.

13 Consider the paper chromatogram of three food colours in Figure 19.2.4 on page 498.

- **a** Why must the level of the solvent be lower than the origin where spots of the mixture are originally placed?
- **b** Why are R_f values always less than one?
- **c** How many different components have been used to make colour A?
- **d** Which components present in colours B and C are also in colour A? Explain.
- **e** Which component of colour A is most strongly adsorbed on the stationary phase?
- **f** Calculate the R_f values of each component of colour C.

14 Thin-layer chromatography showed that the black dye used in a brand of writing ink contained blue, red, orange and yellow components. The R_f values of these substances in ethanol as solvent are 0.59, 0.32, 0.80 and 0.19, respectively.

- **a** How far apart would the blue and yellow components be after the solvent front had moved 8.0 cm from the origin?
- **b** When the red component had travelled 6.0 cm from the origin, how far would the orange component have travelled?
- **c** Sketch the chromatogram of the ink to scale after the solvent front had moved 15 cm from the origin.

15 Figure 19.4.3 shows a thin-layer chromatogram of amino acids in a medicine.

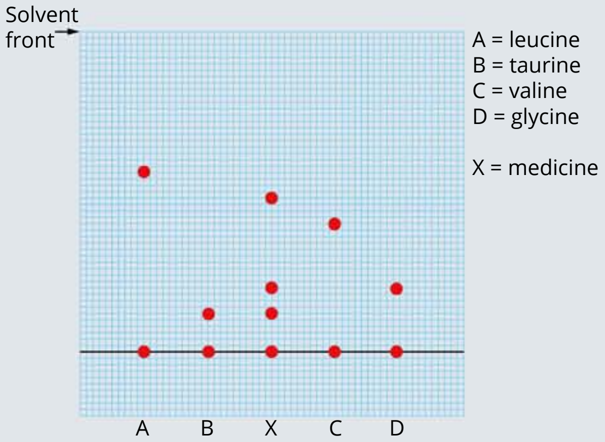


FIGURE 19.4.3 Thin-layer chromatogram of amino acids in a medicine.

- **a** Which amino acids are in the medicine?
- **b** Amino acids are colourless. What technique could be used to make the amino acid spots visible?

c Calculate the R_f value of taurine.

d Which amino acid is bonded least strongly to the stationary phase?

High-performance liquid chromatography

16 The components in a plant extract were separated by simple column chromatography. The mobile phase used was water and the column was packed with alumina powder. Use Figure 19.4.4 and the following terms to complete the sentences.

A
B
C

smaller
low
high
larger

used coarser alumina powder
increased the column length
decreased the column length

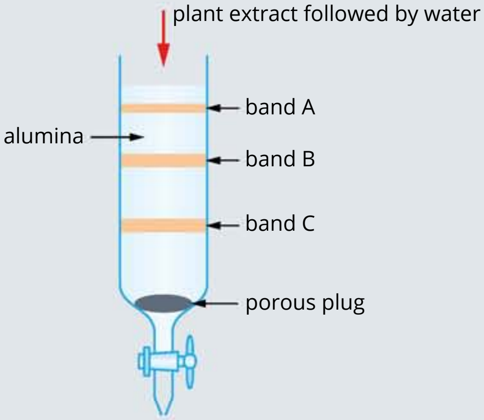


FIGURE 19.4.4 Column chromatography of a plant extract.

The component most strongly adsorbed to the stationary phase is band ________________.

As band B begins to emerge from the column, it appears to separate into two bands. These two components would be more successfully separated if you ________________.

HPLC differs from column chromatography because the particles in the stationary phase are ________________ and ________________ pressure is applied to the mobile phase.

17 Why is it necessary to measure the peak areas produced by a number of standard solutions when performing quantitative analysis using an HPLC instrument?

A HPLC does not directly produce measures of concentration.

B A graph of the actual number of standard solutions against the peak area can then be drawn.

C To ensure peak areas remain constant throughout the analysis.

D The less standard solutions used, the more accurate the graph will be.

18 Which one of the following is the basis for the operation of HPLC?

A Interaction of chemicals with both mobile and stationary phases

B Movement of chemicals through a column using a carrier gas

C Passage of chemicals through a heated column under pressure

D Small molecules becoming trapped in gaps between solid particles in a packed column

19 A chemist working for an environmental agency wishes to analyse the levels of a herbicide in a country stream using HPLC. Sort the following steps in the analytical process into the correct order.

A Measure the herbicide peak areas from the chromatograms of the standard solutions and the stream water sample.

B Obtain chromatograms of the stream water and of standard solutions of the herbicide.

C Construct a calibration curve and mark the herbicide peak area from the stream water sample on it.

D Use R_t values to identify the herbicide peak on the chromatogram of stream water.

E Determine the herbicide concentration in the stream water sample.

20 A herbal tea extract was analysed by HPLC. The chromatogram obtained is shown in Figure 19.4.5.

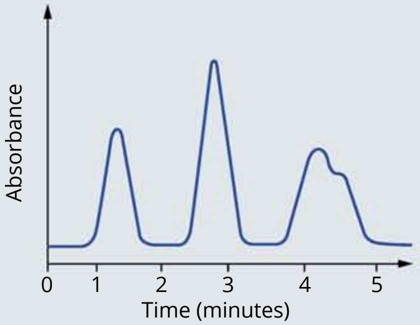


FIGURE 19.4.5 Chromatogram of a herbal tea extract.

a Explain what information chemists can obtain from this chromatogram.

b How many components are evident?

c Briefly explain how the components are separated by the HPLC technique.

Connecting the main ideas

21 A chemist working for a local council wishes to analyse the composition of a river where children swim. It is thought the water might contain high levels of dioxins.

Which one of the following statements concerning the analysis of this water is correct?

A Paper chromatography would allow determination of the concentration of dioxins present but not their identity.

B The results obtained from HPLC would provide identification and accurate concentrations of the dioxins present.

C HPLC can identify the dioxins present but not their concentration.

D Paper chromatography would be suitable for identifying the dioxins and measuring their concentration.

22 The maximum level of exposure to dioxin in water in the United States is 3.0×10^{-8} mg L^{-1}. Calculate the maximum mass of dioxin permitted in:

a 1 mL of water

b a 600 mL bottle of water

c a 750 ML reservoir (ML = megalitre = 10^6 L).

23 Each chromatography technique has disadvantages associated with it. Complete the table using the options provided to indicate the problem or problems associated with each technique. Options may be used more than once.

A Requires relatively large amounts of solvents to operate

B Difficult or impossible to obtain quantitative data

C Expensive equipment needed

D Samples must be able to be dissolved in solvent

Technique	**Problem**
Paper or thin-layer chromatography	
High-performance chromatography (HPLC)	

24 It is common for crude oil to leak or spill from an oil well. Explain the likely sequence of events that occur once oil leaks from an offshore oil rig. Include a discussion of the properties of crude oil that influence the nature of an oil spill.

25 The organophosphorus insecticide parathion has been widely used in mosquito-prone areas. An empty drum of the insecticide was found close to a major reservoir. The EPA was asked to analyse the water to determine whether it was a threat to human health. Levels above 0.01 mg L^{-1} in water are a threat to human health. Parathion has an LD_{50} value (lethal dose to 50% of test animals exposed to this concentration) of 8 mg kg^{-1}.

Parathion standards in water of 0 ppm, 10 ppm, 20 ppm and 30 ppm parathion were prepared and analysed by HPLC, as shown in Figure 19.4.6. An undiluted sample of the reservoir water was run on the column under the same conditions.

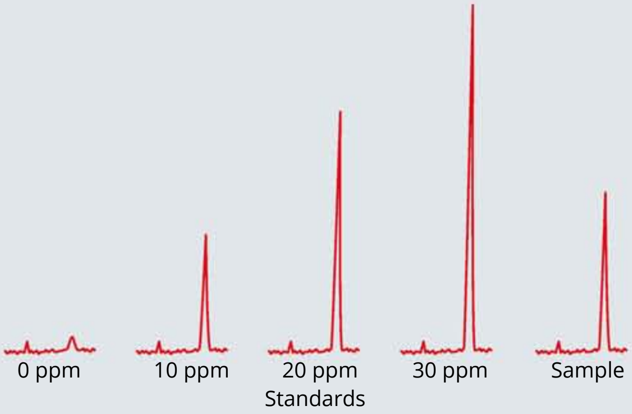


FIGURE 19.4.6 Chromatograms produced for suspected contaminated water sample and parathion standards.

a Complete the table below.

Standard	**Peak height (cm)**
Standard 0 ppm parathion	
Standard 10 ppm parathion	
Standard 20 ppm parathion	
Standard 30 ppm parathion	
Reservoir water	

b Construct a calibration curve for the analysis of parathion.

c Determine the concentration of parathion in the water sample. (Assume that peak height is a measure of the concentration of the insecticide.)

d Is the reservoir water within the legal limits for safe drinking? Support your answer with a calculation.

e What volume of water would a laboratory mouse, mass 150 g, need to drink to reach the LD_{50} dose?

CHAPTER 20

Volumetric analysis

There are many situations in which a chemist may want to find the amount of a substance in solution, such as the amount of a chemical present in industrial or mining wastes, the composition of antacid tablets or the acidity of polluted rainwater.

This chapter begins by examining the natural and artificial sources of acids and bases found in water. It then describes a method used for the analysis of acids and bases in water. The method is called volumetric analysis, and involves chemical reactions between substances in aqueous solution.

Volumetric analysis requires the measuring of accurate volumes using specialised pieces of glassware. This chapter looks at the equipment and techniques of volumetric analysis, as well as the calculations involved. It concludes by considering the issues of accuracy of measurements and sources of error in volumetric analysis.

Key knowledge

- Sources of acids and bases found in water (may include dissolved carbon dioxide, mining activity and industrial wastes)
- Volume–volume stoichiometry (solutions only) and application of volumetric analysis, including the use of indicators, calculations related to the preparation of standard solutions, dilution of solutions and use of acid–base titrations to determine the concentration of an acid or a base in a water sample

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20.1 Sources of acids and bases in water

You will recall from Chapter 15 that pure water has a pH of 7 at 25°C, which is described as neutral. You may expect that the water in rainwater, oceans and mountain streams would be neutral. However, this is not the case. Unpolluted rainwater has a pH between 5.5 and 6, and rainwater falling near large cities and industrial areas is much more acidic.

Water in even the most pristine, unpolluted rivers and lakes has a pH value anywhere between 6.5 and 8.5. Domestic, agricultural and industrial wastes discharged into rivers can further affect the pH.

In this section, you will use your understanding of acid–base and redox chemistry to learn about natural and artificial sources of acids and bases in water.

NATURAL ACIDITY OF RAIN AND RIVER WATER

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) in the following reaction:

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

Carbonic acid is a weak acid and only donates a proton to a limited extent to form hydrogen carbonate 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, NO_2 and SO_2 in the atmosphere only make a minor contribution to the natural acidity of rainwater.

CHEMFILE

Effects of natural acidity of rainwater

The slightly acidic nature of rainwater is responsible for the chemical weathering of rocks. Naturally acidic rainwater is responsible for the formation of limestone caves. Limestone consists of calcium carbonate ($CaCO_3$). Calcium carbonate reacts with the acidic rainwater to form a solution of calcium hydrogen carbonate:

$$H_3O^+(aq) + CaCO_3(s) \rightarrow Ca^{2+}(aq) + HCO_3^-(aq) + H_2O(l)$$

Over thousands of years, caves form where the calcium carbonate has been chemically eroded. An interesting feature of limestone caves is the spectacular formations of stalactites and stalagmites, as can be seen in Figure 20.1.1.

Stalactites are formed when water containing calcium hydrogen carbonate gathers on the roof of caves. Over time the water evaporates and a small speck of solid calcium carbonate is formed:

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

The calcium carbonate deposits build up gradually, forming the stalactite.

A similar reaction takes place when drops of water containing calcium hydrogen carbonate fall to the cave floor. As the calcium carbonate deposits build up, a pillar or stalagmite is formed.

FIGURE 20.1.1 Stalactites and stalagmites in limestone caves grow at a rate of 0.13 mm per year. Columns are formed when stalactites and stalagmites join up. The colouring is due to iron salts leached from the surrounding rocks.

pH of water in rivers and lakes

The pH of unpolluted river water is between 6.5 and 8.5. As with rainwater, the acidic pH is due to carbon dioxide dissolved in the water. If the river also flows over limestone, then a small amount of calcium carbonate dissolves. The carbonate ions react with water, forming hydroxide ions. This results in water having a pH value greater than 7. This process is represented by the following equations:

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

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

The pH of water in rivers and lakes depends upon the relative extent of the reactions of water with carbon dioxide and with calcium carbonate.

ACID RAIN

Since the Industrial Revolution, human activity has produced a much greater quantity of 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 20.1.2. This is known as **acid rain**.

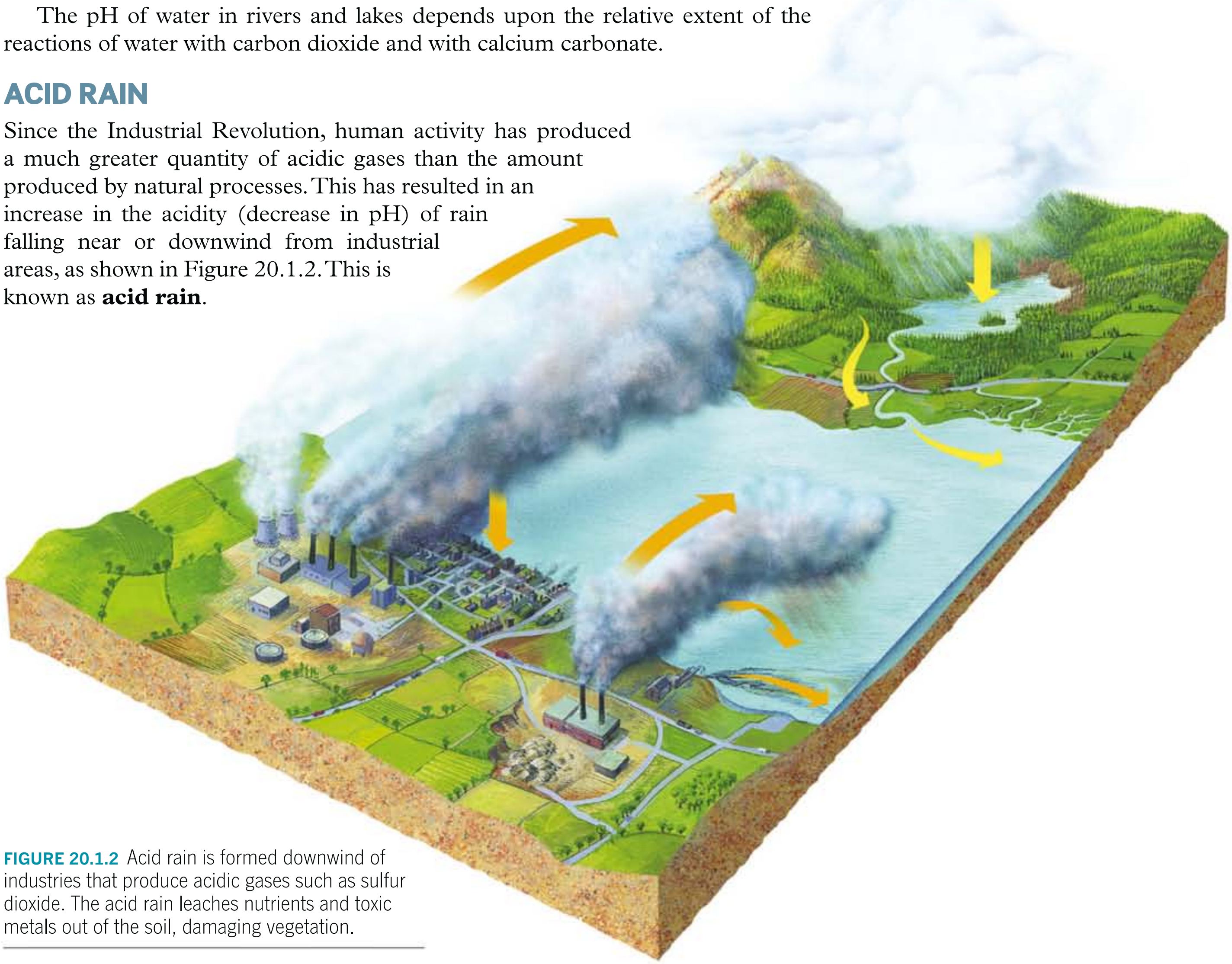


FIGURE 20.1.2 Acid rain is formed downwind of industries that produce acidic gases such as sulfur dioxide. The acid rain leaches nutrients and toxic metals out of the soil, damaging vegetation.

The 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.

The sulfur dioxide is converted to sulfuric acid via 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 the smelting of ores containing metal sulfides, have produced localised acid rain in Australia. Fortunately, smelters are often located in remote areas that have little rainfall. The production of nitrogen oxides occurs mainly in cities due to greater traffic concentrations.

Stricter government regulations and international treaties aimed at reducing the emissions of sulfur dioxide and nitrogen oxides have been adopted. These regulations have decreased the concentration of these gases over recent years.

Effects of acid rain

The lower pH of acid rain has a number of undesirable environmental effects.

- Aquatic environments are upset when the pH of the water drops below 5.5, resulting in the death of many species of aquatic plants and animals (Figure 20.1.3).

FIGURE 20.1.3 Aquatic plants and animals are killed when the pH falls too low.

- Acid rain leaches minerals such as calcium and magnesium. These soil minerals are essential to plant growth. Toxic aluminium ions are also leached from the soil in the following reaction:

  $$Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(aq)$$

  These aluminium ions damage the roots of trees and block the transportation of water. This can kill plant species and are a contributing cause of the forest dieback typical of acid rain-affected areas (Figure 20.1.4).

FIGURE 20.1.4 These trees in Grayson Highlands National Park, Virginia, USA, have been damaged by acid rain.

- Metal fittings and limestone used in buildings are corroded by acid rain, as can be seen in Figure 20.1.5. How the calcium carbonate in the stone reacts with the sulfuric acid in acid rain is shown in the following reaction:

  $$CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$$

  The calcium sulfate ($CaSO_4$) formed is commonly known as gypsum. Gypsum is a soft, slightly water-soluble material.

FIGURE 20.1.5 The cavities in this limestone wall have been corroded by acid rain.

ACID MINE DRAINAGE

Iron pyrite (FeS_2) was extracted from the open-cut Brukunga mine in South Australia between 1955 and 1972. The pyrite ore was used to manufacture sulfuric acid, which was then used to make superphosphate fertiliser. **Acid mine drainage**, a pollutant from the mine, containing a corrosive and toxic mixture of sulfuric acid and heavy metal ions, seeped into a nearby stream (Figure 20.1.6).

FIGURE 20.1.6 Acid mine drainage from the disused Brukunga mine site.

This pollution seriously affected aquatic life and made the water unsuitable for farming and human consumption. Although mining operations at the Brukunga mine ceased in 1972, acid drainage from the mine site continues to affect water quality. Chemical and biological monitoring of the acid mine drainage, neutralisation of acid wastes, the removal of toxic metals and ongoing mine-site remediation works continue to this day.

Chemistry of acid mine drainage

Acid drainage occurs during the mining process when sulfide ores, such as iron pyrite (FeS_2) (Figure 20.1.7), are exposed to oxygen and water.

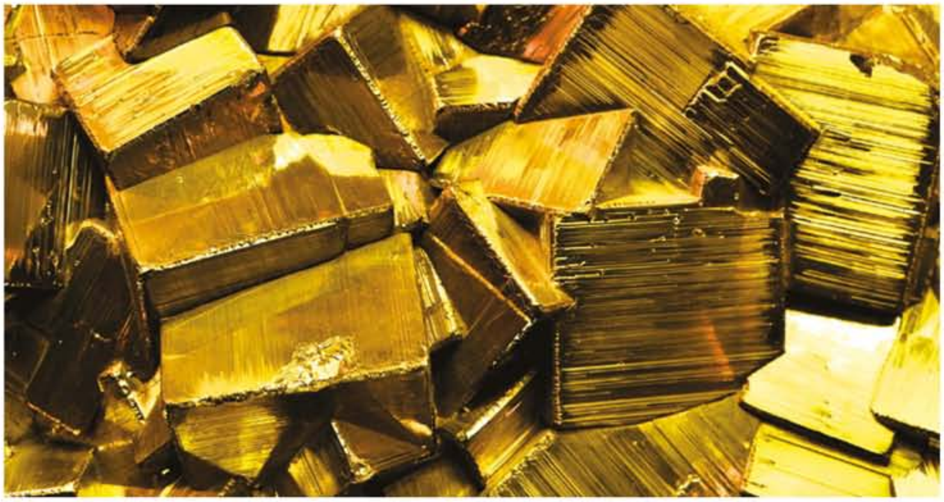


FIGURE 20.1.7 Crystals of iron pyrite (FeS_2). The bronze-coloured crystals are sometimes mistaken for gold, hence the common name of fool's gold.

A complicated series of reactions results in the formation of sulfuric acid, (H_2SO_4) and a suspension of iron(III) hydroxide ($Fe(OH)_3$). These reactions can be summarised as follows:

$$4FeS_2(s) + 15O_2(g) + 14H_2O(l) \rightarrow 4Fe(OH)_3(s) + 8H_2SO_4(aq)$$

The iron(III) hydroxide produced has a characteristic colour and stains the water orange-red, as can be seen in Figure 20.1.8.

FIGURE 20.1.8 The pool of red-coloured water at this mine site is typical of the effects of acid mine drainage.

The acidic water from mines leaches metals such as aluminium, cadmium, copper, manganese and zinc when it comes in contact with minerals that contain these elements. These metals are toxic to aquatic plants and animals, and make the water unfit for human consumption, recreation and farming.

Figure 20.1.9 summarises the effects of acid mine drainage.

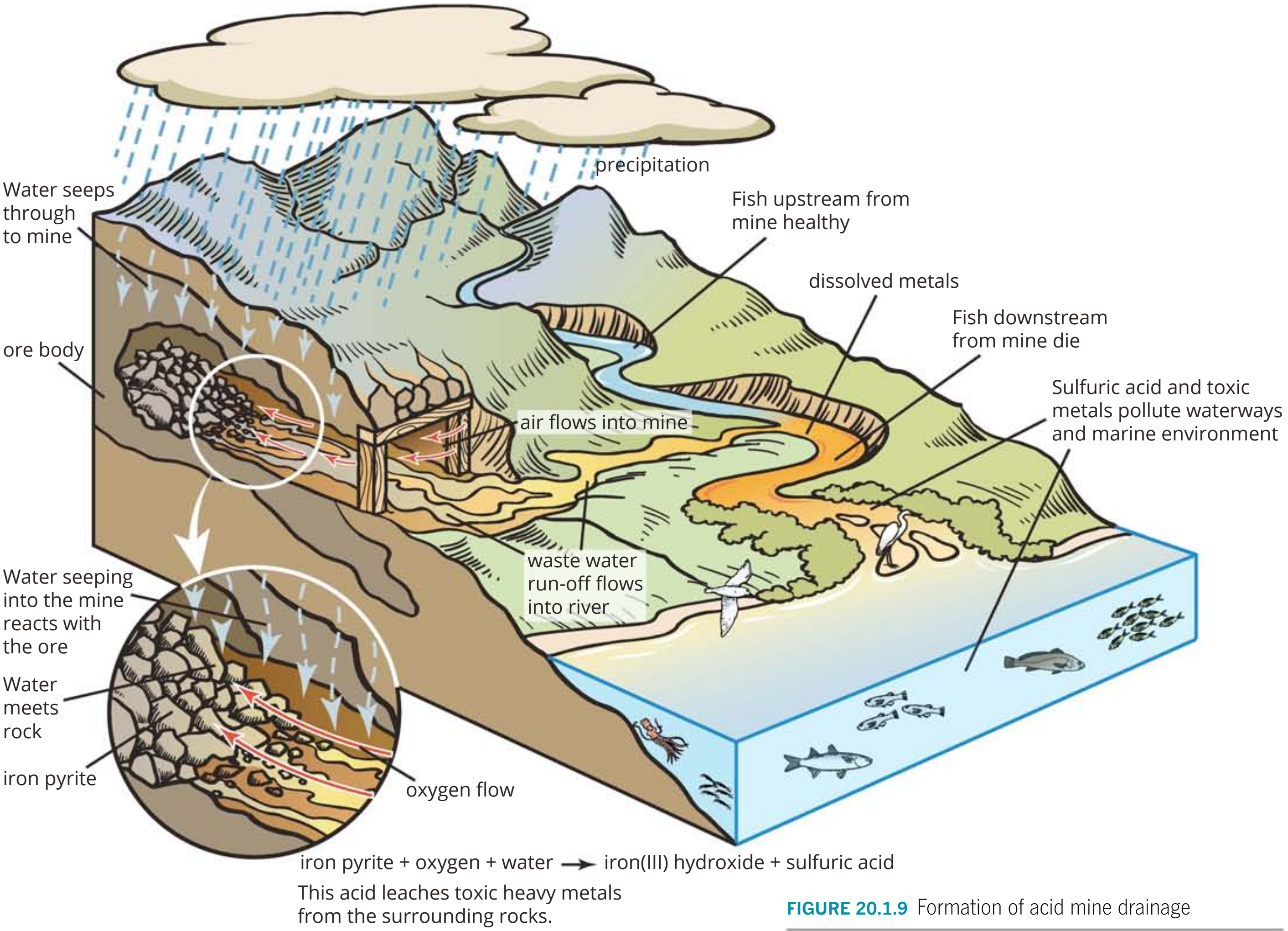


FIGURE 20.1.9 Formation of acid mine drainage

Environmental effects of acid mine drainage

- Aquatic life can only exist within a limited pH range. The combined effects of low pH and toxic metals, such as cadmium and copper, leached into the water can kill aquatic life.
- The fine suspension of iron(III) hydroxide found in acid mine drainage decreases the penetration of light through the water. Low light decreases the rate of photosynthesis. Photosynthesis produces oxygen; therefore, low photosynthesis results in a reduction of dissolved oxygen. The iron(III) hydroxide also coats the surfaces of plants, further reducing photosynthesis.
- The iron(III) hydroxide coats the gills of fish, reducing their ability to absorb dissolved oxygen from the water.
- Use of water downstream for drinking, industry and agriculture is affected.

20.1 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.
- In some rivers, the water is basic due to the reaction of dissolved carbonate ions from limestone with water.
- Acid mine drainage is caused by the oxidation of sulfur (found in coal or metal ores) to sulfuric acid.
- Toxic heavy metal ions are leached from ores by acidic wastes produced by mines.

KEY QUESTIONS

1. What is the name of the compound that reacts with river water to raise its pH?
2. What is the source of nitrogen oxides and what effect do they have on the pH of rainwater?
3. Balance the equation for the formation of acid mine drainage.

$$4FeS_2(s) + \_O_2(g) + \_H_2O(l) \rightarrow \_Fe(OH)_3(s) + 8H_2SO_4(aq)$$

4. Write a balanced ionic equation for the reaction between sulfuric acid in acid rain and the limestone found in many statues and buildings.

20.2 Standard solutions

FIGURE 20.2.1 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.

In the previous section, you studied the causes of acidity in rainwater and in the water in rivers and lakes as a result of human activity. Chemists monitor the health of waterways by analysing the concentration of chemicals such as acids and heavy metals in the water.

Volumetric analysis is a common technique used by analytical chemists and it will be the focus of the remaining sections in this chapter. 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 20.2.1.

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
- be inexpensive.

Examples of primary standards are:

- bases: anhydrous sodium carbonate (Na_2CO_3) and sodium borate ($Na_2B_4O_7.10H_2O$).
  (The term **anhydrous** indicates there is no water present in the compound.)
- acids: hydrated oxalic acid ($H_2C_2O_4.2H_2O$) and potassium hydrogen phthalate ($KH(C_8H_4O_4)$).

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 20.2.2.

FIGURE 20.2.2 (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 20.2.3) 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 standard flask is filled so that the bottom of the meniscus is level with the graduation line on the neck of the flask (Figure 20.2.4). Your eye should be level with the line to avoid **parallax errors**.

To prepare a standard solution from a primary standard, you need to dissolve an accurately known amount of the substance in deionised water to produce a solution of known volume. The steps in this process are shown in Figure 20.2.5.

The molar concentration of the standard solution is then found 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:

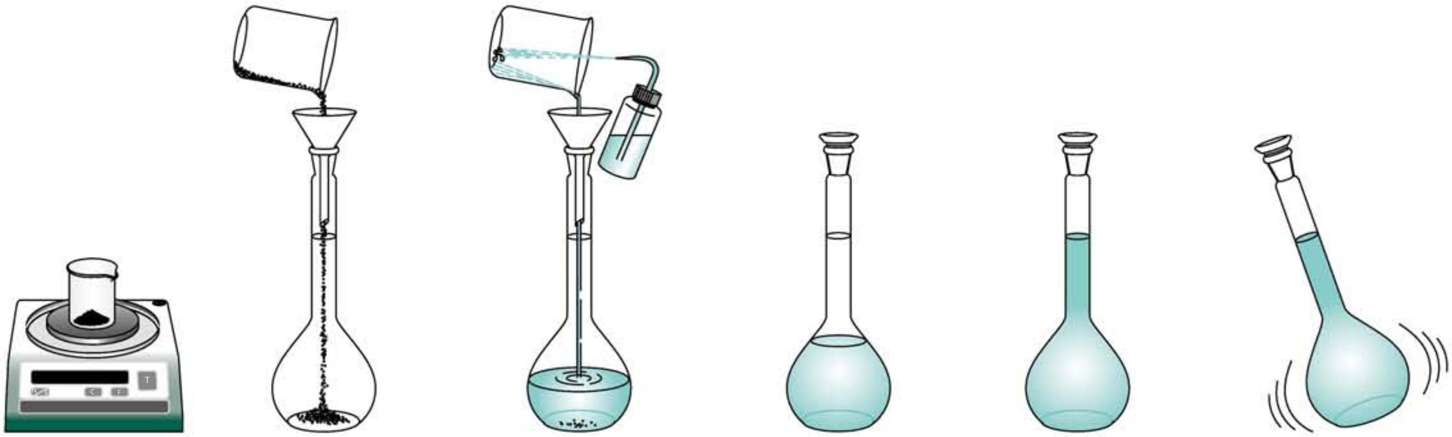
- strong bases, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH), absorb water and react with carbon dioxide in the air
- many hydrated salts, such as hydrated sodium carbonate ($Na_2CO_3.10H_2O$), lose water to the atmosphere over time.

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) or $KH(C_8H_4O_4)$(aq). This is done by titration, which is discussed in the next section of this chapter.

FIGURE 20.2.3 Volumetric flasks of various sizes are used to prepare standard solutions.

FIGURE 20.2.4 This close-up view of the neck of a standard flask shows the bottom of the meniscus level with the graduation line.



Weigh the pure solid on a 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, stopper and swirl vigorously to dissolve the solid. → 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 viewed at eye level. → Stopper and shake the solution to ensure an even concentration throughout.

FIGURE 20.2.5 Preparing a standard solution from a primary standard.

Concentration of standard solutions

In Chapter 14, you looked at calculating the concentration of a solution and determining how much solute is required to prepare a solution of a specific concentration.

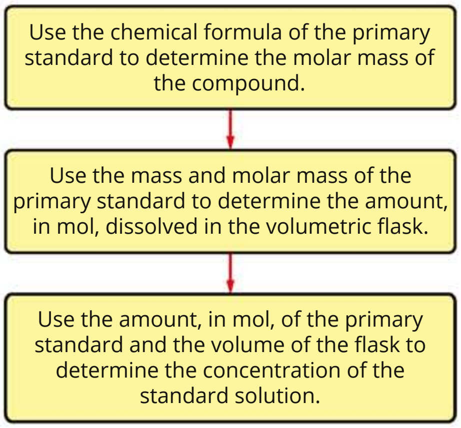


FIGURE 20.2.6 A summary of the steps used in the calculation of the concentration of a standard solution prepared from a primary standard.

Figure 20.2.6 summarises the steps involved in calculating the concentration of a standard solution from the accurately measured mass of a primary standard.

Worked example 20.2.1

CALCULATING THE CONCENTRATION OF A STANDARD SOLUTION PREPARED FROM A PRIMARY STANDARD

Calculate the concentration of a standard solution prepared from 29.22 g of sodium chloride (NaCl) dissolved in a 1.00 L volumetric flask.

Thinking	Working
Use the chemical formula to determine the molar mass (*M*) of the compound.	The molar mass (*M*) of NaCl is 23.0 + 35.5 = 58.5 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.	$n = \frac{29.22}{58.5}$ $= 0.502$ mol
Use the amount, in mol, to determine the concentration of the solution using the formula $c = \frac{n}{V}$.	$c = \frac{0.502}{1.00}$ $= 0.502$ M

Worked example: Try yourself 20.2.1

CALCULATING THE CONCENTRATION OF A STANDARD SOLUTION PREPARED FROM A PRIMARY STANDARD

Calculate the concentration of a standard solution prepared from 117.0 g of NaCl dissolved in a 500.0 mL volumetric flask.

20.2 Review

SUMMARY

- A substance is suitable for use as a primary standard if it:
  - is readily obtainable in a pure form
  - has a known chemical formula
  - is easy to store without deteriorating or reacting with the atmosphere
  - has a high molar mass to minimise the effect of errors in weighing
  - is inexpensive.
- A standard solution is a solution of an accurately known concentration.
- The concentration, in mol L^{-1}, of a prepared standard solution can be determined by measuring the mass of solid dissolved and the volume of solution prepared.

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 M standard solution.

20.3 Calculations involving acids and bases

In Chapter 15, you learned to predict the products for the reactions of acids with bases, carbonates or metals. In this section, you will learn how to calculate how much product is produced, or how much reactant is required in these reactions.

Being able to answer the 'how much' question has many useful applications, including determining:

- how much lime should be added to soil to increase its pH
- how much calcium carbonate should be used to neutralise hazardous acidic wastes from an industrial plant or a mine site
- how much phosphoric acid is in a cola drink
- how much stomach acid can be neutralised by an antacid tablet.

You will use your knowledge of the reactions of acids, your ability to write balanced chemical equations, and your understanding of the mole concept and mole relationships to answer 'how much' questions like these.

REACTING QUANTITIES OF ACIDS AND BASES

Calculations based on the reactions of acids usually involve determining the number of moles of a substance.

You will recall from earlier chapters that:

- the coefficients in a balanced chemical equation give the ratio in which substances react
- the amount of solid, in moles, can be calculated from the expression

  $n = \frac{m}{M}$

  where m is the mass in gram and M is the molar mass in g mol^{-1}
- the 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.

As you will see in the following worked examples, there are four main steps in solving calculation problems involving solutions of acids and bases:

1. Write a balanced equation for the reaction.
2. Calculate the amount, in mol, of the substance with known volume and concentration.
3. Use the mole ratio from the equation to calculate the amount, in mol, of the required substance.
4. Calculate the required volume or concentration.

The steps in a stoichiometric calculation can be summarised as shown in the flow chart in Figure 20.3.1.

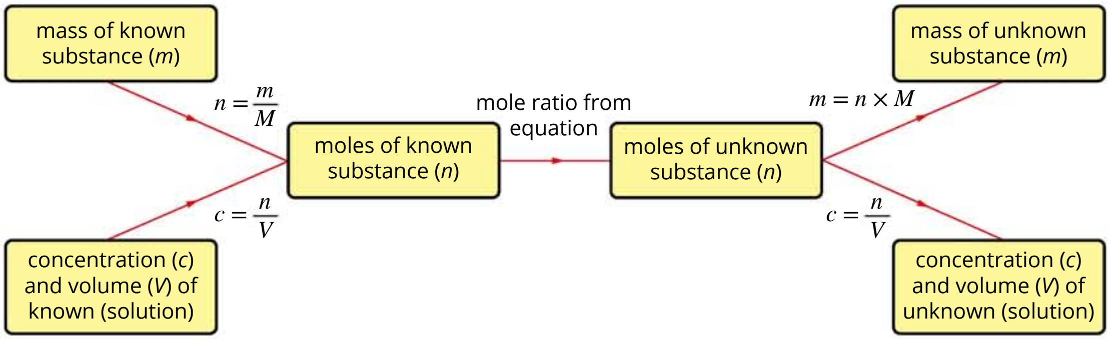


FIGURE 20.3.1 Flow chart for mass and solution calculations.

Worked example 20.3.1

A SOLUTION VOLUME–VOLUME CALCULATION

What volume of 0.100 M sulfuric acid reacts completely with 17.8 mL of 0.150 M potassium hydroxide?

Thinking	Working
Write a balanced full equation for the reaction.	$2KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$
Calculate the amount, in mol, of the substances with known volume and concentration.	The volume and concentration of potassium hydroxide solution are given, so you 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 or concentration required.	The volume of H_2SO_4 is found by using $n = cV$. $V(H_2SO_4) = \frac{n}{c}$ $= \frac{0.00134}{0.100}$ $= 0.0134$ L = 13.4 mL So 13.4 mL of 0.100 M H_2SO_4 will react completely with 17.8 mL of 0.150 M KOH solution.

Worked example: Try yourself 20.3.1

A SOLUTION VOLUME–VOLUME CALCULATION

What volume of 0.500 M hydrochloric acid (HCl) reacts completely with 25.0 mL of 0.100 M calcium hydroxide ($Ca(OH)_2$) solution? The salt formed in this acid–base reaction is calcium chloride.

STOICHIOMETRY PROBLEMS INVOLVING EXCESS REACTANTS

Reactants are not always mixed in stoichiometric amounts in acid–base reactions. There are occasions when one of the reactants, an acid or a base, is in excess. The issue of excess and limiting reactants was discussed in Chapter 18. The same principles for identifying whether or not an acid or a base is in excess in a reaction mixture apply.

- Calculate the number of moles of each reactant.
- Determine which reactant is in excess and which is the limiting reactant.
- Use the amount of limiting reactant to work out the amount of product formed or the amount of reactant in excess.

Worked example 20.3.2

SOLUTION STOICHIOMETRY: A LIMITING REACTANT PROBLEM

20.0 mL of a 1.00 M LiOH solution is added to 30.0 mL of a 0.500 M HNO_3 solution.
The equation for the reaction that occurs is:

$$HNO_3(aq) + LiOH(aq) \rightarrow LiNO_3(aq) + H_2O(l)$$

(a) Which reactant is the limiting reactant?

Thinking	**Working**
Calculate the number of moles of each of the reactants using $n = cV$.	$n(HNO_3) = 0.500 \times 0.0300$ $= 0.0150$ mol $n(LiOH) = 1.00 \times 0.0200$ $= 0.0200$ mol
Use the coefficients of the equation to find the limiting reactant.	The equation shows that 1 mole of HNO_3 reacts with 1 mole of LiOH. So the HNO_3 is the limiting reactant (it will be completely consumed).

(b) What mass of $LiNO_3$ will the reaction mixture contain when the reaction is complete?

Thinking	**Working**
Find the mole ratio of the unknown substance to the limiting reactant from the equation coefficients: $\frac{\text{coefficient of unknown}}{\text{coefficient of limiting reactant}}$	From the equation coefficients: $\frac{n(LiNO_3)}{n(HNO_3)} = \frac{\text{coefficient of } LiNO_3}{\text{coefficient of } HNO_3} = \frac{1}{1}$
Calculate the number of moles of the unknown substance using the limiting reactant: n(unknown) = n(limiting reactant) × mole ratio	$n(LiNO_3) = n(HNO_3) \times \frac{1}{1}$ $= 0.0150 \times \frac{1}{1}$ $= 0.0150$ mol
Calculate the mass of the unknown substance using: n(unknown) = n(limiting reactant) × molar mass	Molar mass of $LiNO_3$ = 68.9 g mol^{-1} $m(LiNO_3) = 0.0150 \times 68.9$ $= 1.03$ g

Worked example 20.3.2: Try yourself

SOLUTION STOICHIOMETRY: A LIMITING REACTANT PROBLEM

30.0 mL of a 0.100 M H_2SO_4 solution is mixed with 40.0 mL of a 0.200 M KOH solution. The equation for the reaction that occurs is:

$$H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$$

(a) Which reactant is the limiting reactant?

(b) What will be the mass of K_2SO_4 produced by this reaction?

20.3 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 given substances.
  3. Use the mole ratios of reactants and products in the balanced chemical equation to calculate the amount, in mol, of the required substance.
  4. Convert the amount, in mol, of the required substance to the quantity required in the question.

KEY QUESTIONS

1 A 0.100 M 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 M $Ca(OH)_2$ solution.

a Write a balanced equation for this reaction.

b What is the concentration of the nitric acid solution?

3 10.0 mL of a 0.200 M sulfuric acid solution is added to 16.0 mL of a 0.100 M sodium carbonate solution. The equation for the reaction is:

$$Na_2CO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l)$$

a Calculate the number of moles of H_2SO_4 in the acid solution.

b Calculate the number of moles of Na_2CO_3 in the sodium carbonate solution.

c Identify the limiting reactant and excess reactant.

d Calculate the amount, in mol, of excess reactant that remains unreacted.

4 18.26 mL of dilute nitric acid reacts completely with 20.00 mL of 0.09927 M 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.

20.4 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 20.4.1) contain bases such as magnesium hydroxide, sodium hydrogen carbonate and aluminium hydroxide to neutralise the acid secretions and relieve the discomfort.

To compare the effectiveness of antacids, you could design experiments to find out what volume of hydrochloric acid reacts with each brand. This would therefore allow you to determine which antacid is best at neutralising the acidic secretions.

In this section, you will learn about the experimental techniques that are used by chemists to perform such analyses involving acid–base reactions.

There are many situations in which a chemist may want to find the amount of a substance in solution. For example, the chemist 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.

FIGURE 20.4.1 The suitability of antacids can be assessed using acid–base reactions.

ACID–BASE TITRATIONS

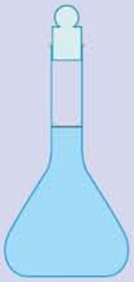
Volumetric equipment

Often the concentrations of acids and bases used in industry are unknown. The laboratory equipment shown in Table 20.4.1 is used to make precise measurements of mass and volume. These instruments, combined with calculations similar to those in the previous section 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 20.4.1 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:

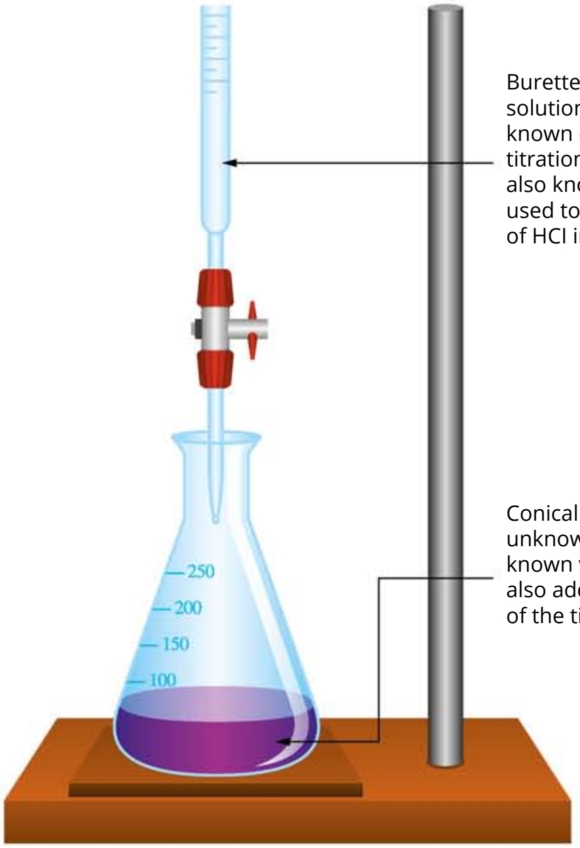
$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

The equivalence point occurs when exactly 2 mol HCl has been added for each 1 mol Na_2CO_3. This whole process is called a **titration**.

The reaction is complete when the equivalence point is reached. The concentration and volume of sodium carbonate (from the burette) required is now known, as is the volume of the aliquot of hydrochloric acid used. The concentration of the acid can now be calculated.

As both acid and base solutions are often colourless, an **indicator** is added to determine when the reaction is complete. (The indicator chosen should change colour when the solutions are neutralised.) 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 20.4.2 shows how the equipment listed would be used to complete the titration for the reaction of NaOH and HCl.



Burette containing a standardised solution of sodium hydroxide with a known concentration. Once the titration is complete, the volume is also known. This information can be used to calculate the concentration of HCl in the conical flask.

Conical flask containing HCl of unknown concentration but known volume. An indicator is also added to show the end point of the titration.

FIGURE 20.4.2 The equipment used in the titration of NaOH (in the burette) to determine the concentration of HCl (in the conical flask).

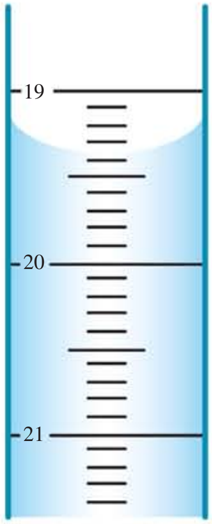


FIGURE 20.4.3 The burette is read from the bottom of the meniscus and the volume is estimated to the second decimal place. The volume measurement in this case is 19.38 mL.

Reading a burette scale

Burettes are usually calibrated in intervals of 0.10 mL. The volume of liquid in a burette is measured at the bottom of the meniscus of the liquid. The reading is estimated to the nearest 0.02 mL, as shown in Figure 20.4.3.

To minimise errors, the titration is repeated several times and the **average titre** is found. Usually three **concordant titres** (titres that are within 0.10 mL from highest to lowest of each other) are used to find this average.

The volume of one single drop from a burette is about 0.05 mL, so taking the average of three results assumes that the results will be no more than one drop over or one drop under the accurate titre.

Consider the titration data represented in Table 20.4.2.

TABLE 20.4.2 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 that gives an idea of the approximate end point. Titres 2, 4 and 5 are the concordant titres: they are within 0.10 mL from highest to lowest of each other. The difference between the highest and lowest readings is 19.86 – 19.78 = 0.08 mL, which is within the acceptable range for concordant results. The mean (average) titre is:

$$\frac{19.82 + 19.78 + 19.86}{3} = 19.82 \text{ mL}$$

Indicators

One of the characteristic properties of acids and bases is their ability to change the colour of certain chemicals called indicators. Some indicators, such as litmus, are extracted from plants; others are synthetic. One such synthetic indicator is methyl orange, which is red in solutions of strong acids and yellow in solutions of bases.

Other common laboratory indicators include bromothymol blue and phenolphthalein. The colours of indicators are usually intense and highly visible, even at low concentrations of the indicator in solution. As Figure 20.4.4 and Table 20.4.3 show, different indicators change colour over different pH ranges.

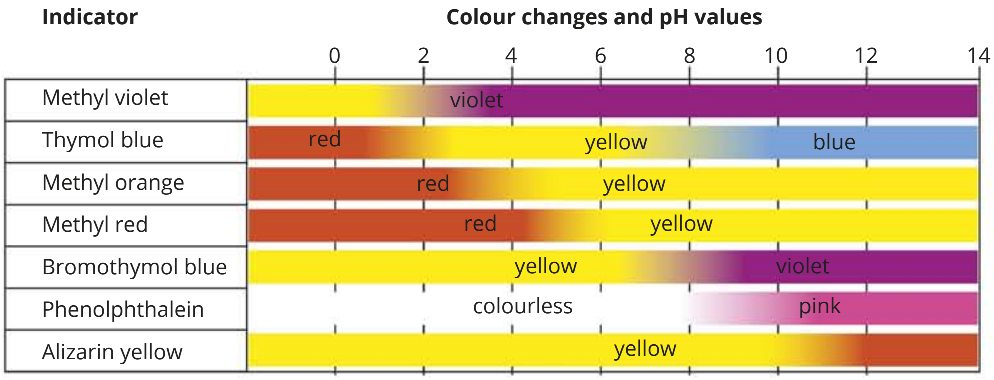


FIGURE 20.4.4 The colours of common indicators at different pH values.

TABLE 20.4.3 The pH ranges of a number of common acid–base indicators

Indicator	Colour of acid form	Colour of base form	pH range
Methyl orange	Pink	Yellow	3.2–4.4
Bromothymol blue	Yellow	Blue	6.0–7.6
Phenolphthalein	Colourless	Pink	8.2–10.0

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 20.4.5.

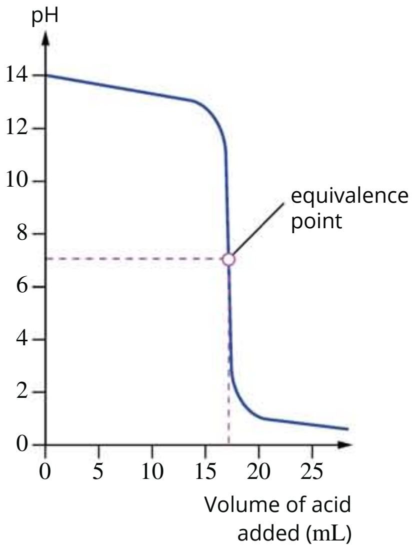


FIGURE 20.4.5 Titration curve for a strong acid being added to a strong base.

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 which changes between pH 6.0 and 7.6, one drop will cause a colour change. This is referred to as a sharp end point. Therefore, knowing the pH range of an indicator is an important tool to ensuring a sharp end point.

The volume of acid added at this point indicates the amount needed to react according to the balanced equation. This volume is the titre that is recorded for the titration.

For a reaction between a strong acid and a strong base, the pH at the equivalence point is 7. The equation for the reaction can be written as:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

Only $H_2O(l)$ and NaCl(aq) are present at the equivalence point, making the solution neutral.

Other indicators, including phenolphthalein (pH range 8.3–10.0), could be used for this titration because they would also produce a sharp end point for this reaction.

Figure 20.4.6 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.

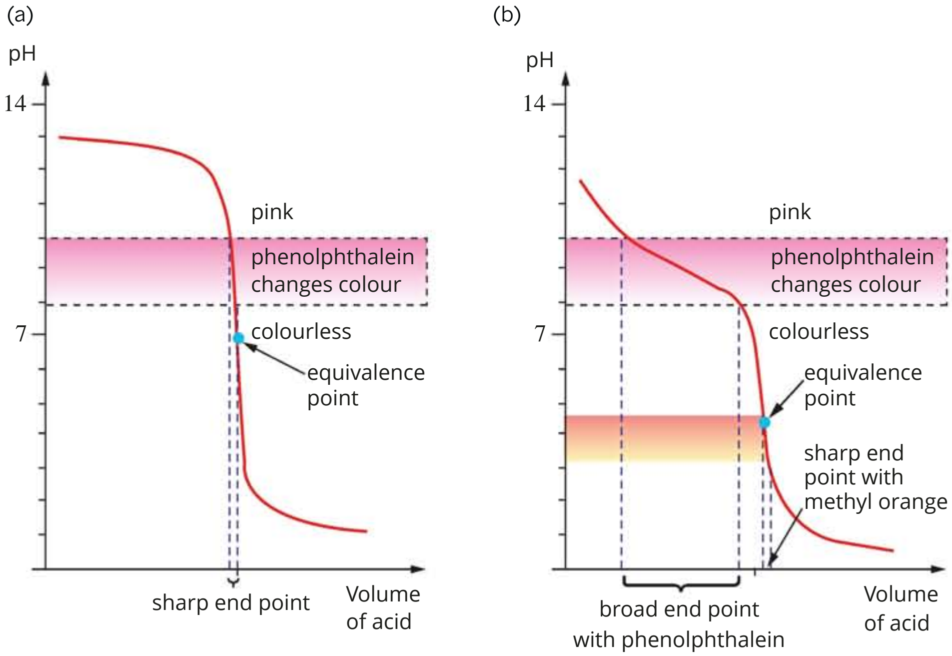


FIGURE 20.4.6 Titration curves showing the pH during a titration of (a) a strong base with a strong acid, and (b) a weak base with a strong acid. Phenolphthalein, which changes colour in the pH range 8.3–10.0, gives a sharp end point in (a) but a broad end point in (b). Methyl orange, which changes colour between pH 3.2 and 4.4, would be a more suitable indicator for the second titration.

20.4 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.
- Three concordant titres are usually obtained during volumetric analysis. Concordant titres lie within 0.10 mL from highest to lowest of each other.

KEY QUESTIONS

1 The titration curve in Figure 20.4.7 shows the change in pH as a solution of 0.10 M sodium hydroxide is added to a 20.00 mL solution of 0.10 M hydrochloric acid.

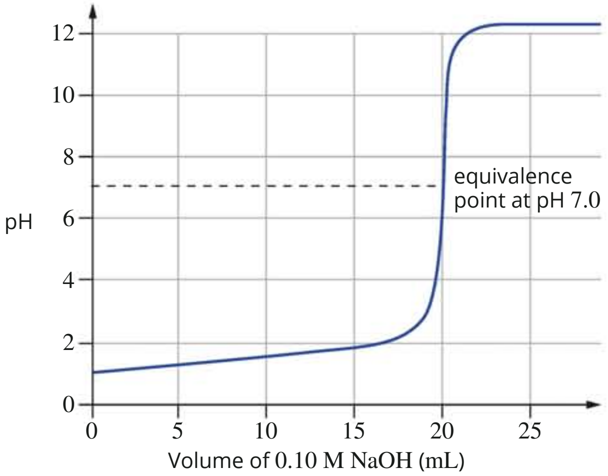


FIGURE 20.4.7

The titration is repeated using 0.20 M 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 Table 20.4.4. Use the indicator colour chart in Figure 20.4.4 on page 531 to find the colour of each solution after the indicator was added.

TABLE 20.4.4 Colour of indicator at pH 5

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.

20.5 Calculations in volumetric analysis

In the previous section, you learned about 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

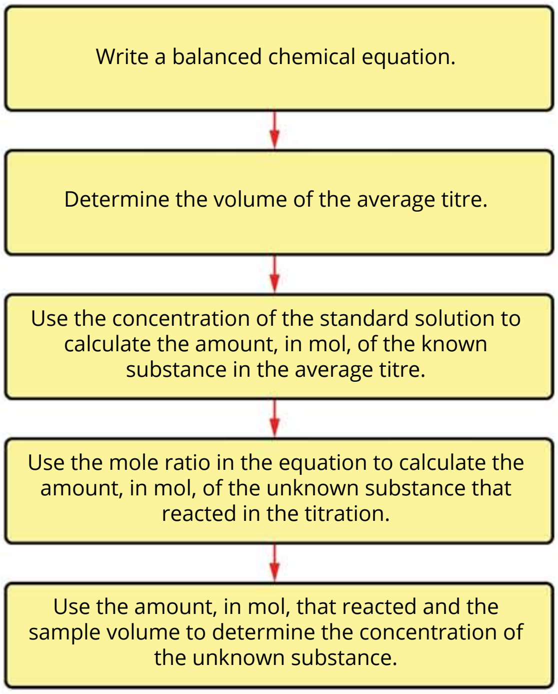
Consider the data gained in an acid–base titration in which the concentration of a dilute solution of hydrochloric acid was determined by titration with a standard solution of sodium hydroxide.

The data gained from the titration is summarised in Table 20.5.1.

TABLE 20.5.1 Sample data obtained from a volumetric analysis

Volume of aliquot of HCl	25.00 mL
Concentration of standard NaOH solution	1.00 M
Titre volumes of NaOH	25.05 mL, 22.10 mL, 22.00 mL, 22.05 mL

The concentration of hydrochloric acid is calculated by following a number of steps. These steps are summarised in the flow chart shown in Figure 20.5.1.



Write a balanced chemical equation.

Determine the volume of the average titre.

Use the concentration of the standard solution to calculate the amount, in mol, of the known substance in the average titre.

Use the mole ratio in the equation to calculate the amount, in mol, of the unknown substance that reacted in the titration.

Use the amount, in mol, that reacted and the sample volume to determine the concentration of the unknown substance.

FIGURE 20.5.1 This flow chart summarises the steps in the calculation of the concentration of an unknown substance using the data from a titration in which the standard solution was in the burette.

Worked example 20.5.1

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 M 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 as it is not concordant (i.e. it is not within a range of 0.10 mL from highest to lowest of the other titre volumes). $\text{Average titre} = \frac{22.10 + 22.05 + 22.00}{3}$ $= 22.05\ \text{mL}$
Calculate the amount, in mol, of the standard solution that was required to reach the end point.	$n(NaOH) = cV$ $= 1.00 \times 0.02205$ $= 0.02205\ \text{mol}$
Use the mole ratio in the equation to calculate the 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.	$c(HCl) = \frac{n}{V}$ $= \frac{0.02205}{0.02500}$ $= 0.882\ \text{M}$
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 M

Worked example: Try yourself 20.5.1

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 M 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 20.5.2.

TABLE 20.5.2 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 M
Volume of aliquot of Na_2CO_3 solution	20.00 mL

In this titration, 25.00 mL of concrete cleaner was diluted to 250.0 mL in a volumetric flask prior to taking a sample for titration. This means the **dilution factor** is $\frac{250.0}{25.00} = 10.00$. The undiluted concrete cleaner will be 10.00 times more concentrated than the concentration of the aliquot. This will be taken into account in the calculations.

The steps required to calculate the concentration of undiluted concrete cleaner are summarised in the flow chart shown in Figure 20.5.2.

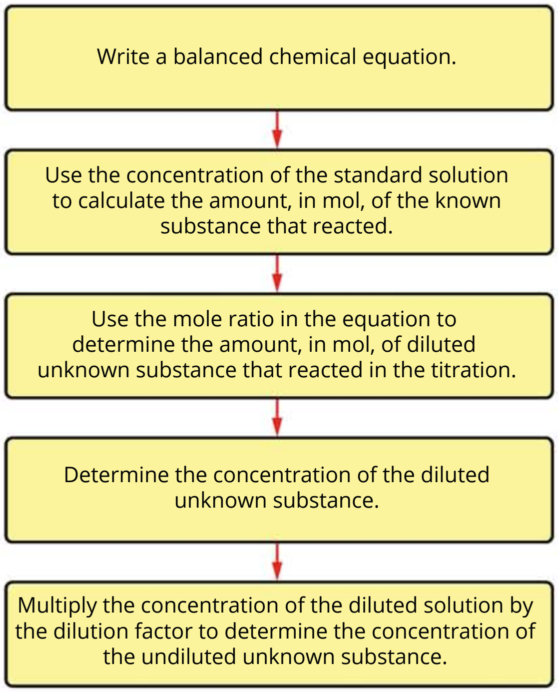


FIGURE 20.5.2 This flow chart shows the steps used in the calculation of the concentration of an unknown substance that has been diluted for use in a titration.

Worked example 20.5.2

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 M sodium carbonate solution was placed in a conical flask. Methyl orange indicator was added and the solution was titrated with the diluted cleaner. The indicator changed permanently from yellow to pink when 19.84 mL of the cleaner was added.

Calculate the concentration of hydrochloric acid in the concrete cleaner.

Thinking	**Working**
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.	$n(Na_2CO_3) = cV$ $= 0.4480 \times 0.02000$ $= 0.008960$ mol
Use the mole ratio in the equation to calculate the amount, in mol, of the diluted unknown solution that reacted in the titration.	$\frac{n(HCl)}{n(Na_2CO_3)} = \frac{2}{1}$ $n(HCl) = \frac{2}{1} \times n(Na_2CO_3)$ $= \frac{2}{1} \times 0.008960$ $= 0.01792$ mol
Calculate the concentration of diluted unknown solution reacting in the titration.	V(diluted HCl) = 0.01984 L $c(HCl) = \frac{n}{V}$ $= \frac{0.01792}{0.01984}$ $= 0.9032$ M
Multiply by the dilution factor to determine the concentration of undiluted concrete cleaner.	Dilution factor $= \frac{250.0}{25.00} = 10.00$ So undiluted $c(HCl)$ = diluted $c(HCl) \times 10.00$ $= 0.9032 \times 10.00$ $= 9.032$ M

Worked example: Try yourself 20.5.2

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 M sodium carbonate solution was placed in a conical flask. Methyl orange indicator was added and the solution was titrated with the diluted cleaner. The indicator changed permanently from yellow to pink when 18.68 mL of the cleaner was added.

Calculate the concentration of hydrochloric acid in the concrete cleaner.

Uncertainties

The accuracy with which the volumes of the aliquot and titre are measured in volumetric analysis depends on the calibration of the 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 20.5.3 compares accuracy and precision.

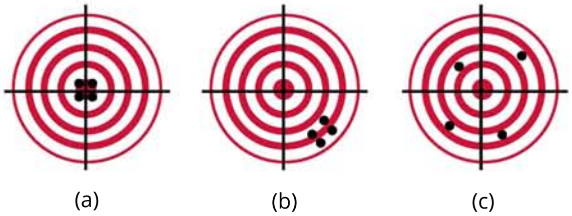


FIGURE 20.5.3 The holes in the targets illustrate the difference between accuracy and precision. Target (a) shows good accuracy and good precision. Target (b) illustrates poor accuracy but good precision, and target (c) shows both poor accuracy and poor precision. Analytical chemists aim to produce results that are both precise and accurate.

You can see that it is possible for a result to be precise but inaccurate.

Methods used for accurate quantitative analysis should be designed to minimise errors. Where errors cannot be avoided, any discussion of results should refer to the level of inaccuracy that may have accumulated. This requires an understanding of the different types of errors.

Types of errors

Mistakes

Mistakes are avoidable errors. Mistakes made during acid–base titrations could include:

- misreading the numbers on a scale
- mistakenly using a pipette of incorrect volume
- spilling a portion of a sample.

The effects of incorrectly rinsing volumetric glassware are detailed in Table 20.5.3.

TABLE 20.5.3 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 that can react and affect the results.

A measurement that involves a mistake must be rejected and not included in any calculations or averaged with other measurements of the same quantity. Mistakes are not generally referred to as errors.

Systematic errors

A **systematic error** produces a constant bias in a measurement that cannot be eliminated by repeating the measurement. Systematic errors that affect an acid–base titration could include:

- a faulty balance
- a 20.0 mL pipette that delivers 20.2 mL
- an unsuitable indicator being used
- 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 higher or lower than the true value.

Systematic errors are eliminated or minimised through calibration of apparatus and the careful design of a procedure. If the error cannot be eliminated an effort should be made to determine its size so that the error can be taken into account in calculations.

Random errors

Random errors follow no regular pattern. The measurement is sometimes too large and sometimes too small. Random errors in volumetric analysis could include:

- inherent uncertainty in the last value after the decimal place in the measurement of the mass of a primary standard on an analytical balance
- difficulty in judging where the meniscus sits on the line when measuring a volume using a pipette
- difficulty in judging the fraction between two 0.1 mL scale markings on a burette.

The effects of random errors can be reduced by taking multiple measurements of the same quantity, then calculating an average. In volumetric analysis, the average of three concordant titres is used to reduce random error.

20.5 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 an equal 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 M 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 M 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 M sodium carbonate solution was placed in a conical flask. Methyl orange indicator was added and the solution was titrated with the diluted cleaner. The indicator changed permanently from yellow to pink when 23.92 mL of the diluted cleaner had been added.

The equation for the reaction is:

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + 2H_2O(l)$$

Calculate the concentration of hydrochloric acid in the concrete cleaner.

Chapter review

20

KEY TERMS

accurate
acid mine drainage
acid rain
aliquot
anhydrous
average titre
burette
concordant titres
dilution factor
end point
equivalence point
indicators
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

Sources of acids and bases in water

1 Which one of the following minerals could potentially lead to acid mine drainage at the mine site where the mineral is mined?

A Haematite (Fe_2O_3)
B Iron pyrite (FeS_2)
C Magnetite (Fe_3O_4)
D Siderite ($FeCO_3$)

2 What are the main contaminants likely to be found in acid mine drainage from an iron pyrite mine?

3 What are the main gases that contribute to acid rain, and what are the sources of these gases?

4 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.

Standard solutions

5 Sodium borate ($Na_2B_4O_7.10H_2O$) 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}.

6 Calculate the concentration of a standard solution of hydrated oxalic acid ($H_2C_2O_4.2H_2O$) prepared by dissolving 25.21 g of hydrated oxalic acid in 250.0 mL of deionised water.

7 Calculate the mass of Na_2CO_3 required to make a 500 mL standard solution of 0.400 M Na_2CO_3.

Calculations involving acids and bases

8 What volume of 0.200 M KOH is required to react with 30.0 mL of 0.100 M HNO_3?

9 20.0 mL of a 1.00 M solution of HCl reacts with 16.0 mL of a 1.00 M of K_2CO_3 solution.

a Calculate the number of moles of HCl involved in the reaction.
b Calculate the number of moles of K_2CO_3 involved in the reaction.
c Identify the reactant that is in excess.
d By how much is this reactant in excess, in mol?

10 What volume of 0.100 M of NaOH is required to react with 20.00 mL of 0.200 M HCl?

11 15.0 mL of a 2.00 M LiOH solution is added to 25.0 mL of a 0.400 M HNO_3 solution. The equation for the reaction that occurs is:

$$HNO_3(aq) + LiOH(aq) \rightarrow LiNO_3(aq) + H_2O(l)$$

a Which reactant is the limiting reactant?
b What mass of $LiNO_3$ will the reaction mixture contain when the reaction is complete?

Volumetric analysis

12 Explain the use of each of the following pieces of equipment during a titration.

a Burette
b Pipette
c Standard flask

13 Explain the difference between the end point and the equivalence point of a titration.

14 Why is it important to select an indicator with an end point close to the equivalence point for the reaction?

Calculations in volumetric analysis

15 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.

16 A chemistry student is required to determine accurately 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?

17 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?

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 M 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.

UNIT 2 • Area of Study 2

REVIEW QUESTIONS

How are substances in water measured and analysed?

Multiple-choice questions

1 The approximate percentage of water on Earth that is both suitable for drinking and accessible is:

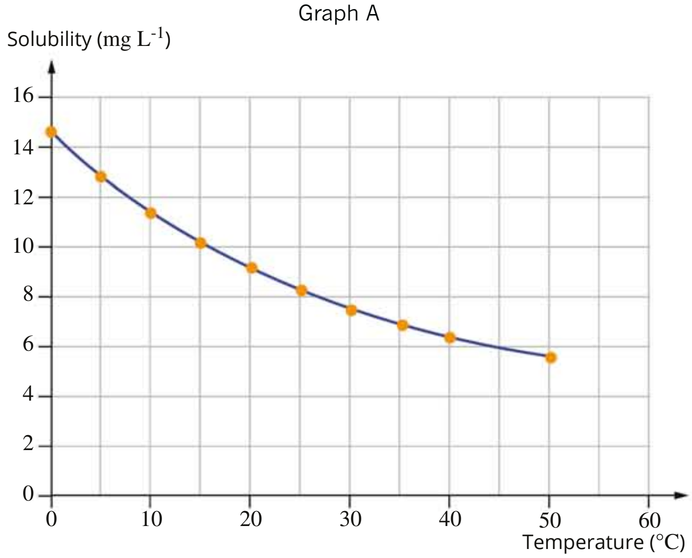
A 25
B 2.5
C 0.5
D 0.05

2 Which one of the following is not a possible source of heavy metal pollution in waterways?

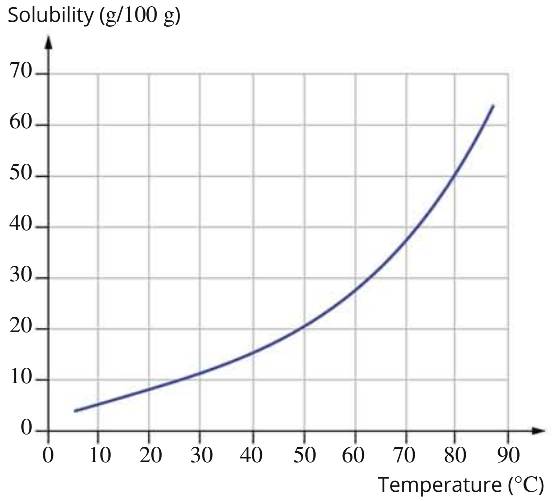
A Potassium from excessive use of fertilisers
B Arsenic from agricultural processes
C Cadmium from rechargeable batteries
D Lead from paints

3 Consider the shape of the following solubility curves.

Graph A



Graph B



Which one of the following alternatives correctly attributes the most likely shape of the solubility curve for the ionic solid potassium chlorate and the gas oxygen?

	Potassium chlorate	Oxygen
A	Graph A	Graph A
B	Graph A	Graph B
C	Graph B	Graph A
D	Graph B	Graph B

4 The solubility of ammonium chloride at 0°C is 28 g/100 g water and at 70°C it is 85 g/100 g water.

8.0 g of ammonium chloride is dissolved in 25.0 g water at 70°C. The solution is then cooled to 0°C. What mass of ammonium chloride, in grams, crystallises out, assuming a supersaturated solution does not form?

A None will crystallise.
B 1.0
C 7.0
D 8.0

5 0.540 g of aluminium reacts completely with a solution of sulfuric acid according to the following equation:

$2Al(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$

What volume of 1.10 M sulfuric acid is required for this reaction?

A 12.1 mL
B 18.2 mL
C 27.3 mL
D 56.6 mL

6 What volume of 3.0 M Na_2CO_3 is required to prepare 750 mL of 0.15 M solution?

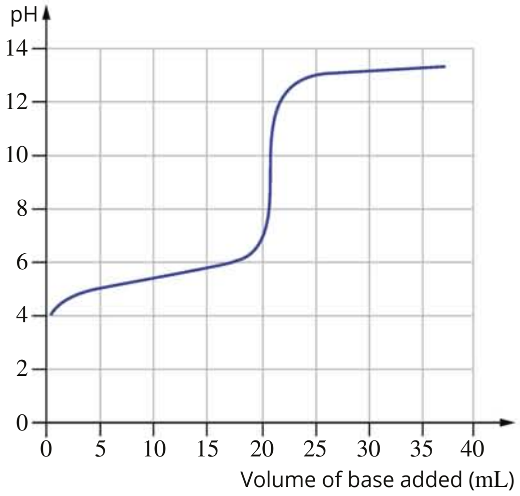
A 37.5 mL
B 45.0 mL
C 112.5 mL
D 250 mL

7 What volume of water, in mL, must be added to 20.0 mL of 0.50 M NaCl in order to change its concentration to 0.20 M?

A 30.0
B 50.0
C 200
D 500

The following information relates to Questions 8 and 9.

This acid–base titration curve shows the way pH changes when a base is added from a burette to a measured volume of acid. The concentration of both acid and base is 0.1 mol L^{-1}.



8 What can be deduced, from the shape of the curve, about the relative strength of the acid and the base?

A The acid is weak and the base is strong.
B The acid is strong and the base is strong.
C The acid is weak and the base is weak.
D The acid is strong and the base is weak.

9 Which one, or more, of the following indicators could be used for this titration?

	Indicator	pH range over which colour changes
I	Methyl orange	3.1–4.4
II	Methyl red	4.4–6.2
III	Bromothymol blue	6.0–7.6
IV	Phenolphthalein	8.3–10.0

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

10 A standard solution of HCl is titrated four times against some NaOH. The following titres are obtained: 21.05 mL, 20.75 mL, 20.65 mL, 20.75 mL.

The average titre is then calculated and used to determine the concentration of the NaOH. The correct value for the average titre is:

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

11 Which one of the following solutions will have the highest electrical conductivity?

A 0.01 M H_2CO_3
B 0.01 M NH_4Cl
C 0.01 M NaCl
D 0.01 M Na_2SO_4

12 Samples of water from a river at two different locations, X and Y, are collected for analysis. The electrical conductivity of the water taken at location X is 23.5 μS cm^{-1} and that of the water taken at location Y is 21.8 μS cm^{-1}.

Which one of the following alternatives is not a possible cause for this difference in electrical conductivity? Assume the temperature of X and Y is the same in options B, C and D.

A The water temperature at location location Y is much lower than that at location X.
B The sample taken at location Y was not stoppered and some of the water had evaporated before testing.
C Location X is much closer than Y to the mouth of the river where the river meets the ocean.
D The river at location X passes through an industrial area and some acidic wastes are dumped in the river at that point.

13 Unpolluted rainwater has a pH of 5.6. The main reason for this slight acidity is the presence of dissolved:

A hydrochloric acid
B sodium chloride
C oxygen
D carbon dioxide.

14 Cadmium is a metal used in photography, in nickel–cadmium batteries and solar cells, and for metal plating. Drinking water contaminated with cadmium can have harmful health effects. What is the concentration of cadmium, in ppb, in a reservoir containing 500 ML (1 ML = 10^6 L) of water if 1.75 kg of cadmium is discharged into it?

A 3.5
B 875
C 1750
D 3000

15 Excess silver nitrate ($AgNO_3$) is added to a 250.0 mL sample of river water. The precipitate of silver chloride (AgCl) was dried and weighed. Its mass was found to be 20.37 g. What is the concentration, in g L^{-1}, of chloride ions in the river water?

A 0.142
B 0.569
C 20.2
D 81.5

16 Which of the following, found in polluted water, can be quantitatively measured by atomic absorption spectroscopy (AAS)?

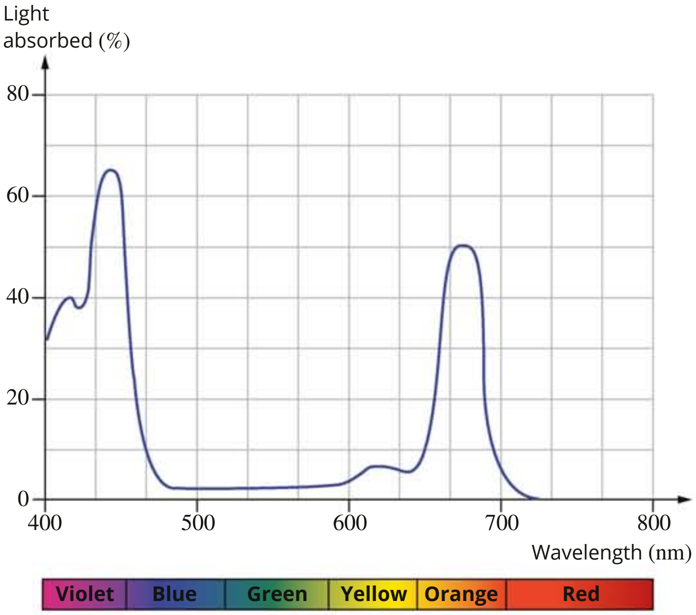
A Phosphates
B Dissolved oxygen
C Dioxins
D Arsenic

17 Which of the following analytical techniques is most appropriate for measuring the presence of hydrocarbons spilt into waterways?

A AAS
B HPLC
C UV–visible spectroscopy
D Gravimetric analysis

The following information relates to Questions 18 and 19.

The absorption spectrum of a coloured compound is shown below.



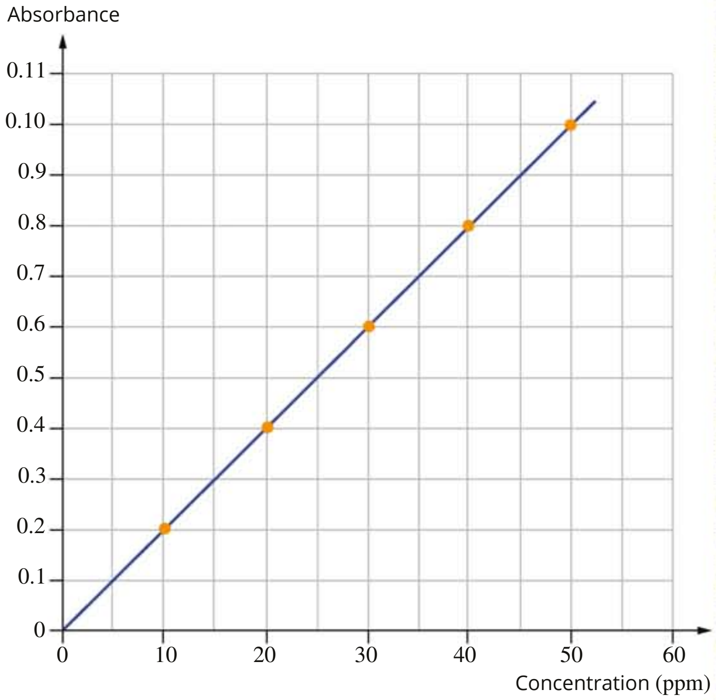
18 What is the best description of the colour of this compound?

A Violet
B Blue
C Green
D Orange-red

19 If the concentration of this compound were to be determined by UV–visible spectroscopy, which one of the following wavelengths, in nm, would be most suitable to use?

A 420
B 460
C 550
D 670

20 Dissolved calcium ions are responsible for the hardness of water. The concentration of calcium ions in a dam was determined by atomic absorption spectroscopy (AAS). The absorbance of several solutions of known concentration of calcium ions were measured and the results plotted as a calibration curve.



25.0 mL of the dam water is diluted to 100 mL with distilled water. The absorbance of the diluted solution, measured under the same conditions as the standards, is 0.30.

What is the approximate concentration, in ppm, of calcium in the dam water?

A 4
B 16
C 30
D 64

Short-answer questions

21 **a** Give a definition of a chemical contaminant.

b Give an example of a chemical contaminant in a body of water.

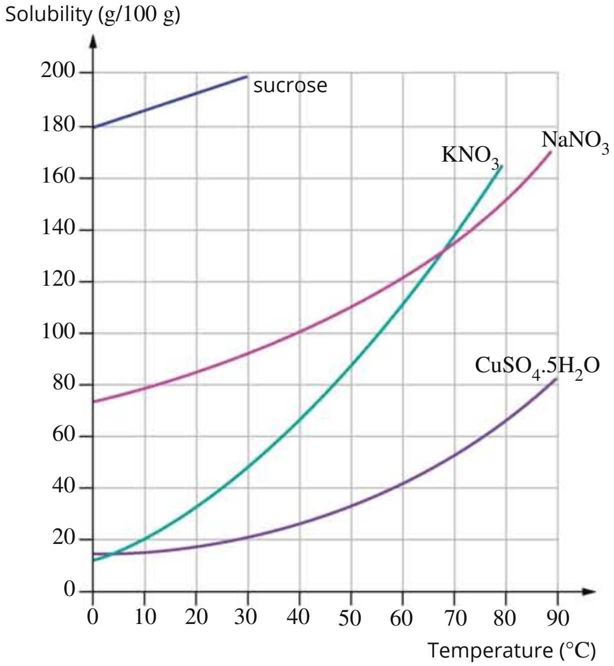
22 Provide concise explanations for each of the following.

a A glass of lemonade kept cold in the refrigerator tastes more ‘fizzy’ than one kept at room temperature.

b Large volumes of water, taken from a lake or river, are often used as coolants in industrial processes. As a result, the temperature of water is increased. Returning this water to the lake or river, while the water is still warm, sometimes leads to a change to the plants and animals living there.

c The electrical conductivity of a sample of water is indicative of its salinity.

23 Consider the following solubility curves.



a **i** What is the minimum mass of $NaNO_3$ that must be dissolved in 100 g of water to produce a saturated solution at 50°C?

ii What would be observed if the solution in part **i** were cooled to 20°C?

iii What mass of water must be added to 110 g of $NaNO_3$ to make a saturated solution at 10°C?

b What is the maximum amount of table sugar (sucrose) that can dissolve in a cup containing 200 g of water at 30°C?

c Three different solutions of KNO_3 are prepared by adding various masses of KNO_3 to 100 g of water. All three solutions are maintained at 50°C. The masses of KNO_3 contained in the solutions are 30 g, 80 g and 87 g.

i Use this information to clearly explain the difference between a saturated solution, an unsaturated solution and a supersaturated solution.

ii Describe a simple test that you could use to identify which solution is which.

iii Predict what would happen to each solution if it was cooled to 30°C.

d What mass of water must be added to 35 g of $CuSO_2.5H_2O$ to make a saturated solution at 27°C?

24 The solubilities of three different substances at 20°C and 80°C are given in the table below.

Substance	**Solubility in water (g/100 g water)**	
	20°C	**80°C**
Potassium sulfate	12.0	21.0
Sodium chloride	36	37
Graphite	Insoluble	Insoluble

a If 16.0 g of sodium chloride were mixed with 50 g of water, what mass of sodium chloride would dissolve at 20°C?

b If 9.0 g of potassium sulfate were mixed with 50 g of water, what mass of potassium sulfate would dissolve at:

i 20°C?

ii 80°C?

c If 1.5 g of graphite were mixed with 50 g of water, what mass of graphite would dissolve at 20°C?

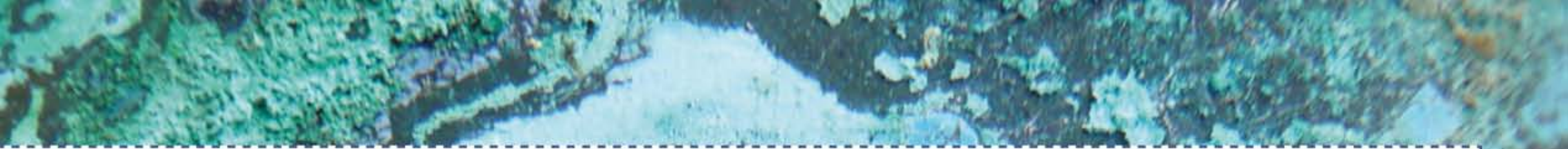
d What is the solubility of potassium sulfate at 20°C expressed in mol L^{-1}? The density of water at 20ºC is 1.00 g mL^{-1}. Assume that the volume of the solution is equal to the volume of water.

e You are given a mixture that contains 16.0 g of sodium chloride, 9.0 g of potassium sulfate and 1.5 g of graphite.

i Describe how you could obtain a pure sample of potassium sulfate and a pure sample of graphite from this mixture.

ii What is the maximum mass of potassium sulfate that could be obtained by this method?

f Use the data provided in the table above to explain why it would be difficult to obtain a pure sample of sodium chloride from the mixture.



25 You are given five solutions. They are not labelled but are known to be sodium carbonate, sulfuric acid, potassium nitrate, magnesium nitrate and copper(II) nitrate. You have been set the task to identify the solutions.

- **a** Predict what you would observe if a sample of each solution was added to a sample of each of the other four solutions. (If no observable reaction is predicted, write 'no change'.)
  - **i** Sodium carbonate and sulfuric acid
  - **ii** Sodium carbonate and potassium nitrate
  - **iii** Sodium carbonate and magnesium nitrate
  - **iv** Sodium carbonate and copper(II) nitrate
  - **v** Sulfuric acid and potassium nitrate
  - **vi** Sulfuric acid and magnesium nitrate
  - **vii** Sulfuric acid and copper(II) nitrate
  - **viii** Potassium nitrate and magnesium nitrate
  - **ix** Potassium nitrate and copper(II) nitrate
  - **x** Magnesium nitrate and copper(II) nitrate
- **b** Write a balanced ionic equation for each of the reactions predicted in part **a**.
- **c** Describe how the solutions can be identified by mixing each solution with each of the other four solutions.

26
- **a** A solution has a pH of 4. What is the concentration, in mol L^{-1}, of hydroxide ions in the solution at 25°C?
- **b** 100 mL of hydrochloric acid of concentration 0.0100 mol L^{-1} is added to 100 mL of sodium hydroxide of concentration 0.0120 mol L^{-1}. Both solutions are at 25°C.
  Calculate the pH of the resultant solution.

27 A solution of lead(II) nitrate is prepared by dissolving 9.80 g of solid lead(II) nitrate in water. The total volume of the solution formed was 50.0 mL.

- **a** Calculate the molar concentration of this solution.
- **b** The lead(II) nitrate solution is diluted by adding 30.0 mL of water. What is the new concentration of the solution?
- **c** The lead(II) nitrate solution is mixed with 50.0 mL of 0.650 M sodium iodide. A bright yellow precipitate forms.
  - **i** Write an ionic equation for the formation of the precipitate.
  - **ii** Calculate the mass of precipitate that forms.

28 To analyse the iron content of bore water, all of the iron ions in 1.30 L of bore water were first converted to $Fe^{3+}(aq)$ ions by oxidation. These were then reacted with excess OH^- to form a precipitate $Fe(OH)_3(s)$. The $Fe(OH)_3(s)$ was collected, dried then heated strongly so that it decomposed to produce $Fe_2O_3(s)$ and water.

- **a** Write an ionic equation for the precipitation of $Fe(OH)_3(s)$.
- **b** Write an equation for the production of $Fe_2O_3(s)$ from $Fe(OH)_3(s)$.
- **c** The mass of $Fe_2O_3(s)$ obtained was 1.095 g.
  - **i** Calculate the mass of iron in the 1.30 L of water.
  - **ii** Calculate the molar concentration of iron in the water.

29 A solution containing nickel(II) ions is green so its concentration could be determined using UV–visible spectroscopy.

- **a** Explain how a suitable wavelength is chosen to analyse the solution containing the nickel(II) ions.
- **b** Explain how the concentration of nickel(II) ions in the solution would be experimentally determined.

30 A student makes up a solution of 0.0500 M sodium hydrogen carbonate solution and uses it to determine the concentration of a hydrochloric acid solution.

- **a** Calculate the mass of sodium hydrogen carbonate required to make up 200.0 mL of 0.0500 M solution.
- **b** 20.00 mL of the sodium hydrogen carbonate solution is pipetted into a conical flask and titrated with the hydrochloric acid. An average titre was 35.05 mL of the hydrochloric acid solution.
  - **i** Write an equation for the reaction between hydrochloric acid and sodium hydrogen carbonate.
  - **ii** Calculate the concentration of the hydrochloric acid.

31 Many household cleaners contain ammonia (NH_3) as the active ingredient. An acid–base titration was performed in order to determine the concentration of ammonia in a commercially available cleaner.

10.00 mL of the cleaner is diluted to 100.0 mL with water in a volumetric flask. 20.00 mL of this diluted cleaner solution is placed in a dry conical flask and titrated against 0.0950 M hydrochloric acid using methyl orange as an indicator. The average of three concordant titres was 17.40 mL.

a Write an equation for the reaction between ammonia and hydrochloric acid.

b Calculate the molar concentration of ammonia in the cleaner.

c Calculate the mass, in grams, of ammonia in a 750 mL bottle of cleaner.

d Methyl orange is pink at pH lower than 3.1 and yellow at pH greater than 4.4. State the colour changes that would be observed in this titration.

e State whether each of the following changes to this titration procedure would lead to a higher, lower, or the same result for the concentration of ammonia in the cleaner. Give an explanation for your answer.

- **i** 20.00 mL of water was added to the 20.00 mL of diluted cleaner solution in the conical flask prior to titration.
- **ii** Phenolphthalein indicator was used instead of methyl orange. Phenolphthalein is colourless at pH less than 8.3 and pink at pH higher than 9.5.
- **iii** The conical flask was washed, then rinsed with the diluted cleaner solution before using it.

32 Succinic acid is one of the many acids present in wine. It is diprotic and has a molar mass of 118.1 g mol^{-1}.

In order to find the solubility of succinic acid in water, 10 g of succinic acid was thoroughly mixed with 100 mL of water in a beaker. The beaker was allowed to stand overnight at a constant temperature of 25°C in order to saturate the solution.

The next day, it was noted that there was some undissolved succinic acid in the bottom of the beaker. 20.00 mL samples of the succinic acid solution were titrated against 0.790 M NaOH using phenolphthalein indicator. The average of three concordant titres was 23.40 mL.

a Calculate the amount, in mol, of succinic acid in 20.00 mL of solution.

b Calculate the concentration of succinic acid in:

- **i** mol L^{-1}
- **ii** g L^{-1}
- **iii** %(m/v).

c The solubility of succinic acid at 25°C quoted in the literature is higher than that obtained in this experiment. Give a possible explanation for this difference.

33 The following method was used to determine the oxygen content of a body of water.

Five 300 mL bottles were completely filled with water at 20°C, each taken at a different location and a different depth of the body of water. The bottles were immediately stoppered.

To each bottle was added some manganese(II) sulfate solution, some alkaline sodium iodide solution and some concentrated sulfuric acid.

The resultant mixture was titrated with 0.0155 M $Na_2S_2O_3$. An average titre of 17.25 mL was obtained.

The sequence of reactions that occurred is complex; however, the overall equation for the reactions is:

$O_2(g) + 4S_2O_3^{2-}(aq) \rightarrow 2S_4O_6^{2-}(aq) + 2H_2O(l)$

a Calculate the concentration of oxygen in the water in:

- **i** mol L^{-1}
- **ii** ppm (assume that 1 litre of solution has a mass of 1 kg).

b At 20°C, the saturated concentration of oxygen in water is 9.2 ppm. Calculate the percentage saturation of oxygen in the water tested.

c Would you expect the saturated concentration of oxygen to be greater than, equal to or less than 9.2 ppm at 30°C?

d **i** Explain why the samples were collected at different locations and depths of the body of water.

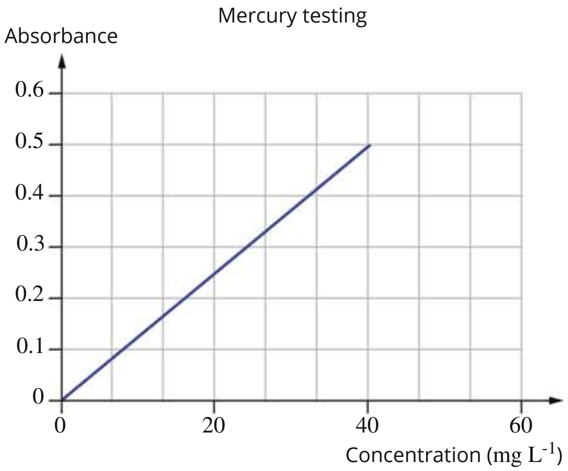
- **ii** Explain why the bottles were stoppered as soon as the water was collected.

34 Deep sea fish can build up high levels of mercury from contaminated water. A 3.0 g sample of fish is ground up and mixed with water. The mixture is made up to 100 mL with water. A sample of the solution is analysed by atomic absorption spectroscopy, giving an absorbance reading of 0.25.

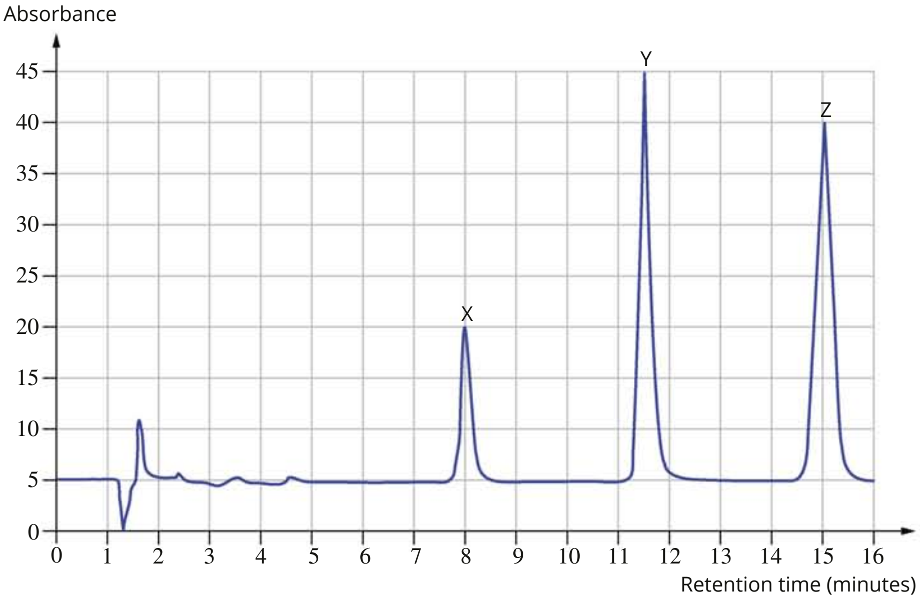
Use the following calibration curve to determine the:

a percentage mass of mercury in the fish

b concentration in ppm of mercury in the fish.



35 A sample of pond water was analysed for organic compounds X, Y and Z using an HPLC. The following chromatogram was obtained.



a What are some of the organic compounds that can find their way into waterways?

b **i** Which of the three compounds travelled through the HPLC column fastest? Explain your choice.

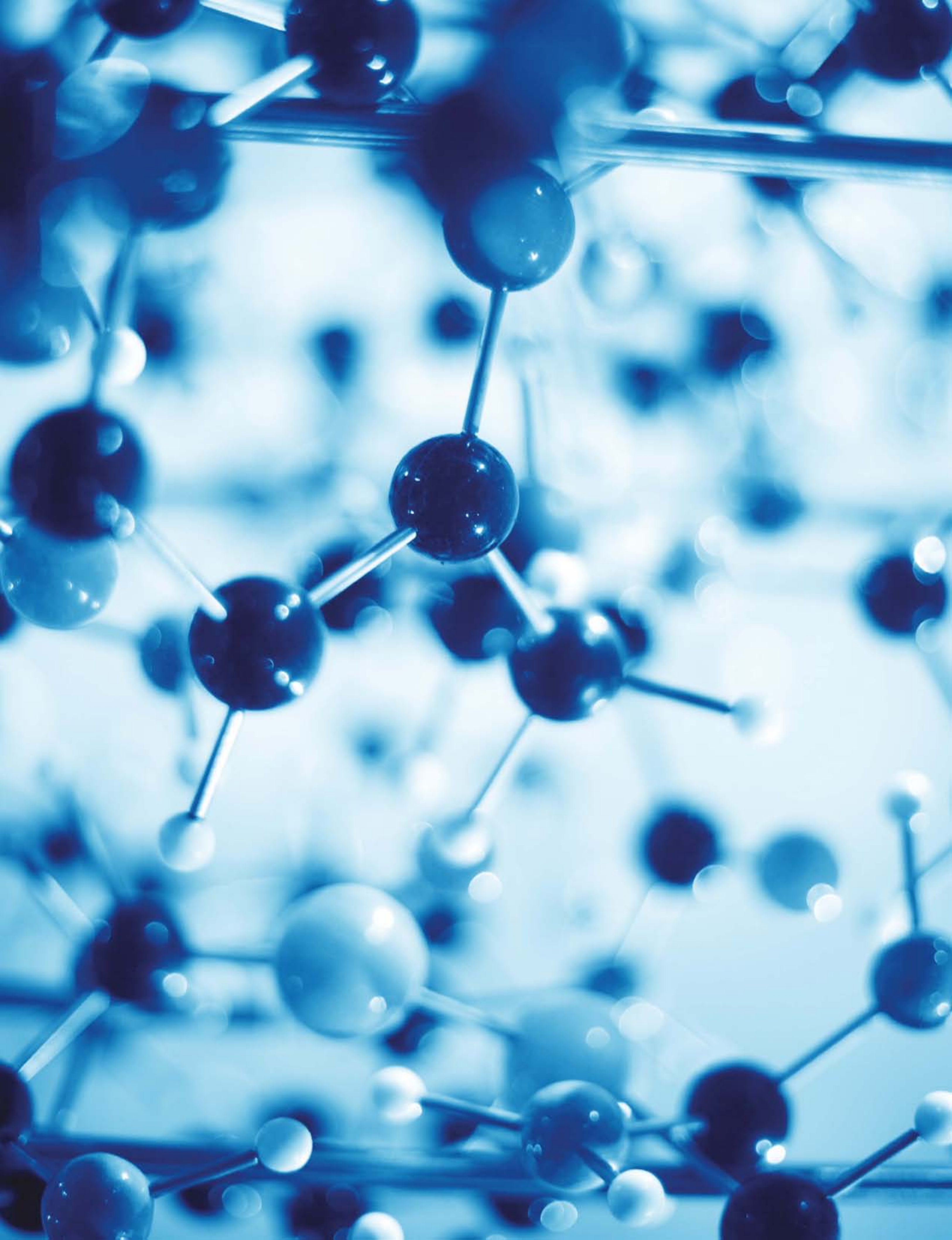
ii Which compound is present in the largest quantity? Explain your choice.

c The concentration of compound X needs to be determined.

i Explain why a calibration curve is required in order to determine the concentration of X.

ii Describe how you would prepare such a calibration curve.

d Another sample of water contained half of the concentration of X and Z but no Y nor any other compound. Sketch the predicted chromatogram for this sample of water.



CHAPTER

21 Practical investigation

Science is a practical subject. Most of what is known about how the world works is the result of practical investigations and from testing out ideas. In this chapter, you will learn how to design, plan and conduct investigations, including how to write a hypothesis and identify variables. You will also assess the validity, reliability and accuracy of results and research.

Finally, you will learn how to discuss your investigation and draw evidence-based conclusions in relation to your hypothesis and research question.

Key knowledge

- the chemical concepts specific to the investigation and their significance, including definitions of key terms, and chemical representations
- the characteristics of laboratory techniques of primary qualitative and quantitative data collection relevant to the investigation: sampling protocols; gravimetric analysis, acid-base titrations and/or pH measurement; precision, accuracy, reliability and validity of data; and minimisation of experimental bias
- ethics of and concerns with research including identification and application of relevant health and safety guidelines
- methods of organising, analysing and evaluating primary data to identify patterns and relationships including identification of sources of error and uncertainty, and of limitations of data and methodologies
- observations and experiments that are consistent with, or challenge, current chemical models or theories
- the nature of evidence that supports or refutes a hypothesis, model or theory
- options, strategies or solutions to issues related to water quality
- the key findings of the selected investigation and their relationship to solubility, concentration, acid/base and/or redox concepts
- the conventions of scientific report writing including chemical terminology and representations, symbols, chemical equations, formulas, units of measurement, significant figures and standard abbreviations

Key science skills

Develop aims and questions, formulate hypotheses and make predictions

- Determine aims, hypotheses, questions and predictions that can be tested
- Identify independent, dependent and controlled variables

Plan and undertake investigations

- Determine appropriate type of investigation: experiments (including use of controls and calibration curves); solving a scientific or technological problem; simulations; access to secondary data, including data sourced through the internet that would otherwise be difficult to source as raw or primary data through a laboratory or a classroom
- Select and use equipment, materials and procedures appropriate to the investigation, taking into account potential sources of error and uncertainty

Comply with safety and ethical guidelines

- Apply ethical principles when undertaking and reporting investigations
- Apply relevant occupational health and safety guidelines while undertaking

practical investigations, including following recommended protocols from safety data sheets

Conduct investigations to collect and record data

- Work independently and collaboratively as appropriate and within identified research constraints
- Systematically generate, collect, record and summarise both qualitative and quantitative data

Analyse and evaluate data, methods and scientific models

- Process quantitative data using appropriate mathematical relationships, units and number of significant figures
- Organise, present and interpret data using schematic diagrams and flow charts, balanced chemical equations, tables, graphs, percentages and calculations of mean
- Take a qualitative approach when identifying and analysing experimental data with reference to accuracy, precision, reliability, validity, uncertainty and errors (random and systematic)
- Explain the merit of replicating procedures and the effects of sample sizes in obtaining reliable data
- Evaluate investigative procedures and possible sources of bias, and suggest improvements
- Explain how models are used to organise and understand observed phenomena and concepts related to chemistry, identifying limitations of the models

Draw evidence-based conclusions

- Determine to what extent evidence from an investigation supports the purpose of the investigation, and make recommendations, as appropriate, for modifying or extending the investigation
- Draw conclusions consistent with evidence and relevant to the question under investigation
- Identify, describe and explain the limitations of conclusions, including identification of further evidence required
- Critically evaluate various types of information related to chemistry from journal articles, mass media and opinions presented in the public domain
- Discuss the implications of research findings and proposals

Communicate and explain scientific ideas

- Use appropriate chemical terminology, representations and conventions, including standard abbreviations, graphing conventions and units of measurement
- Discuss relevant chemical information, ideas, concepts, theories and models and the connections between them
- Identify and explain formal chemical terminology about investigations and concepts
- Use clear, coherent and concise expression
- Acknowledge sources of information and use standard scientific referencing conventions

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21.1 Designing and planning investigations

Taking the time to carefully plan and design a practical investigation before you begin will help you to maintain a clear and concise focus throughout. Preparation is essential.

It is important to have both a solid understanding of the theory behind your investigation and a detailed plan for the practical components of your investigation. In this section, you will learn about the key steps you should take when planning and designing a practical investigation.

DEVELOPING AIMS, HYPOTHESES AND PREDICTIONS

The research question, aim and hypothesis are interlinked. It is important to note that each of these can be refined as the planning of the investigation continues.

Research questions, aims and hypotheses

A **research question** is a sentence that seeks information. A question must end with a question mark ('?'). For example: 'What is the effect of increasing acid temperature on the rate of reaction between 1 g of magnesium and 10 mL of 0.1 M hydrochloric acid?'

An **aim** is a sentence summarising what will be investigated. For example: 'To determine the effect of acid temperature on the rate of reaction between 1 g of magnesium and 10 mL of 0.1 M hydrochloric acid'.

A **hypothesis** is a possible outcome of the experiment. It is based on previous knowledge on which you can make a prediction for the results of the experiment. For example: 'If the temperature of the acid increases, the rate of reaction will also increase.'

Formulating a question

Before you are able to formulate a hypothesis, you will need to formulate a question that you want to answer. This question will lead you to a hypothesis when you:

- are able to reduce the question to measurable **variables**
- can suggest a possible outcome of the experiment.

The question for your investigation must be related to an aspect of water quality. Some examples of questions you might study include the following.

- Is the **biological oxygen demand (BOD)** of water sampled from the Yarra River within acceptable limits?
- Is there a difference between the electrical **conductivity** of drinking water and the electrical conductivity of ground water at a specified location?
- What is the **pH** of commercially available mineral waters?

Knowing what resources you have available will also help you formulate a question. Available equipment may include thermometers, pH paper, pH meters, burettes, pipettes, volumetric flasks, conductivity meters, weighing balances and other common laboratory equipment.

Hypothesis

A hypothesis is a prediction, based on evidence and prior knowledge. It takes the form of a cause and effect.

Examples:

- An increase in water temperature will lead to a decrease in the pH of water.
- The electrical conductivity of ground water will be greater than that of drinking water.
- If water is filtered through a domestic water purifier, then its electrical conductivity will decrease.

- Sparkling mineral water will have a lower pH at room temperature than non-sparkling mineral water.

It is sometimes easier to write a hypothesis in which the prediction serves to disprove a question.

Examples:

- Increasing the water temperature will not have an effect on measured pH.
- The electrical conductivity of ground water and drinking water will be the same.
- Filtering water through a domestic water purifier will not affect its electrical conductivity.
- The pH of sparkling and non-sparkling mineral water will be the same at a given temperature.

Variables

A good scientific hypothesis can be tested through investigation.

There are three categories of variables.

- The **independent variable** is the variable that is changed by the researcher.
- The **dependent variable** is the variable that may change in response to a change in the independent variable. This is the variable that you will measure or observe.
- **Controlled variables** are all the variables that must be kept constant during the investigation. You should only test one variable at a time; otherwise, you cannot be sure that the changes in the dependent variable are the result of changes in the independent variable.

Completing a table like Table 21.1.1 will assist in evaluating your question, or questions.

TABLE 21.1.1 An example of the relationship between the investigation question, the variables and the hypothesis

Research question	Independent variable	Dependent variable	Controlled variables	Potential hypothesis
Does the use of a domestic water purifier cause a decrease in electrical conductivity of water?	Type of water purifier	Electrical conductivity of water	Water source, type of sampling container, temperature, humidity	If water is filtered through a domestic water purifier, then its electrical conductivity will decrease.

Qualitative and quantitative variables

Variables are either **qualitative** or **quantitative**, depending on whether or not they can be measured. Figure 21.1.1 shows examples of variables belonging to both types.

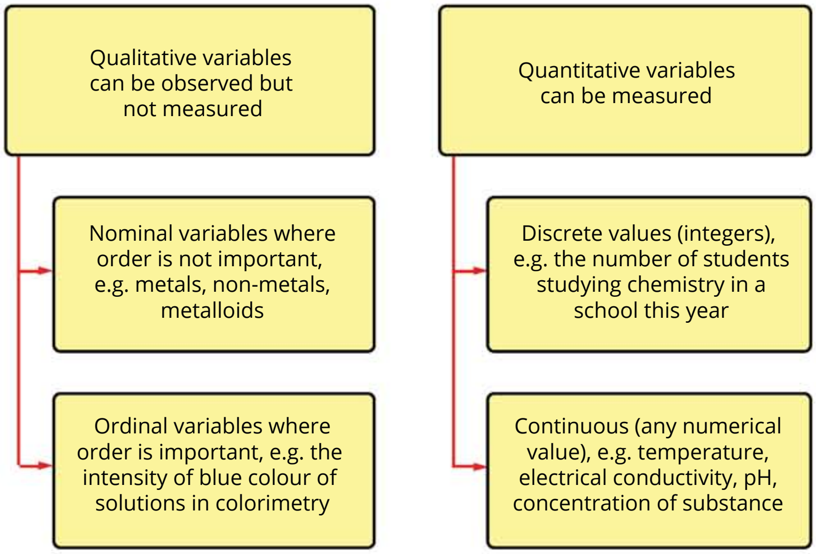


FIGURE 21.1.1 A description of qualitative and quantitative variables can be broken down further.

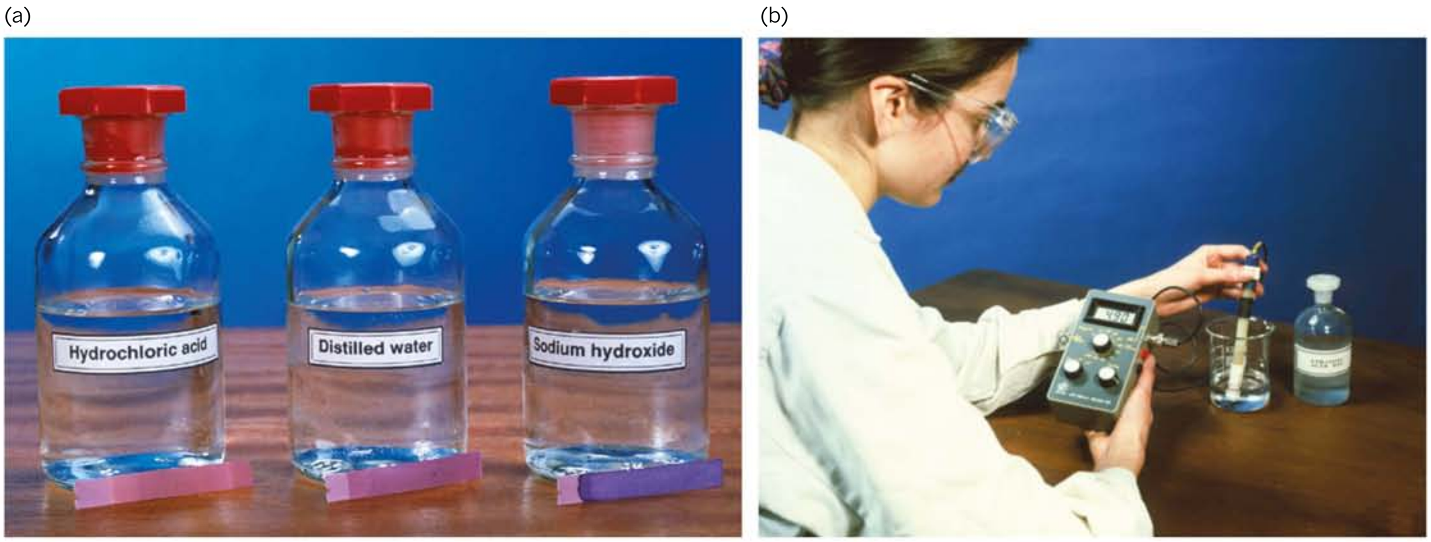


FIGURE 21.1.2 Determining whether a solution is acidic or basic can be qualitative or quantitative. (a) Litmus paper gives a qualitative observation indicating the nature of the solution. (If the paper turns purple, the solution is basic; if the paper turns pink, the solution is acidic.) (b) A calibrated pH meter gives a quantitative measurement indicating the nature of the solution (pH < 7, the solution is acidic; pH > 7, the solution is basic.)

Defining the aim of the investigation

The aim is the key step required to test your hypothesis. The aim should relate directly to the variables in the hypothesis, describing how each will be measured. The aim does not need to include the details of the method. Table 21.1.2 provides an example of a hypothesis, the variables to be measured and the aim of an investigation into the electrical conductivity of water.

TABLE 21.1.2 The relationship between hypothesis, variables and aim

Hypothesis	Variables	Aim
If water is filtered through a domestic water purifier, then its electrical conductivity will decrease.	Independent variable: type of water purifier Dependent variable: electrical conductivity	To measure and compare the electrical conductivity of water samples before and after filtering through different domestic water purifiers

Writing the methodology

The methodology of your investigation is a step-by-step procedure that a reader can follow. As outlined below, a successful method is valid, reliable and accurate.

Validity

Validity refers to whether an experiment or investigation is testing the set hypothesis and aims.

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.

To ensure validity, carefully determine the:

- independent variable (the variable that you will change) and how you will change it
- dependent variable (the variable that you will measure)
- controlled variables (the variables that must remain constant) and how you will maintain them.

Reliability

Reliability refers to the consistency of the results when the experiment is repeated many times. Maintain your investigation's reliability by:

- defining the control
- ensuring there is sufficient replication of the experiment.

Control

The **control** is an identical experiment carried out at the same time but the independent variable is not changed. The control is a basis for comparison with the experiment and helps to support a hypothesis.

Replication

It is also important to determine how many times the experiment needs to be replicated.

Repeat each reading at least three times. Record each measurement and then average the three measurements.

Accuracy and precision

If repeated measurements of the same quantity give values that are in close agreement, the measurement is said to be **precise**.

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**.

Reasonable steps to ensure the accuracy of your investigation may include considering the:

- unit in which you will measure the independent and dependent variables
- instrument that you will use to measure the independent and dependent variables.

The precision of glassware used used in chemistry experiments varies. Table 21.1.3 shows some typical uncertainties of laboratory glassware.

TABLE 21.1.3 Typical uncertainties of laboratory glassware

Type of laboratory glassware	Typical uncertainty
10 mL measuring cylinder	10.0±0.1 mL
20 mL pipette	20.00±0.03 mL
50 mL burette	50.00±0.02 mL
250 mL volumetric (standard) flask	250.0±0.3 mL

Data analysis

Before you begin your experiment you should consider the data that you will collect.

Table 21.1.4 provides an example of the data to be collected and analysed in an experiment, and the things you should consider.

A table of results for the experiment measuring the pH of commercially available mineral waters is shown in Table 21.1.5.

Sometimes methods need to be changed. If so:

- record everything
- be prepared to make changes to your approach
- note any difficulties you encounter and the ways you overcame them. What were the failures and successes? List these as you work, including all tests performed, to ensure you have a well-written report.

TABLE 21.1.4 Types of variables and the ways in which they could be measured and used within an example research investigation

Research question: What is the pH of commercially available mineral waters?	
List the independent variable (the variable that you will change in the experiment). Is the variable quantitative or qualitative?	The independent variable is the name and brand of commercially available mineral water (qualitative).
List the dependent variable. This is the variable that you will measure. What equipment will you use to measure it?	A calibrated pH meter connected to a computer will be used to measure pH. The pH meter has an uncertainty of ±0.1 pH units.
List the variables that you will control. What will you do to control these variables?	All mineral waters will be stored in a temperature-controlled environment where the air temperature will be maintained at 20°C. The temperature of each will be measured with an ethanol-filled glass thermometer. The uncertainty of the thermometer is ±0.1°C.

TABLE 21.1.5 Results table indicating the pH of three different mineral waters (X, Y and Z)

Brand and volume of commercial mineral water	Date	pH	Temperature (°C)
X 1 L		6.7	22.3
Y 1 L		6.4	22.3
Z 1 L		6.4	22.3
Uncertainty of equipment		±0.1	±0.1

COMPLYING WITH ETHICAL AND SAFETY GUIDELINES

Everything we do involves some risk. A **risk assessment** is performed to identify, assess and control hazards. Always identify the risks and control them to keep everyone safe.

To identify risks, think about the:

- activity that you will be carrying out
- equipment or chemicals that you will be using.

Figure 21.1.3 shows a flow chart of how to consider and assess the risks involved in a research investigation.

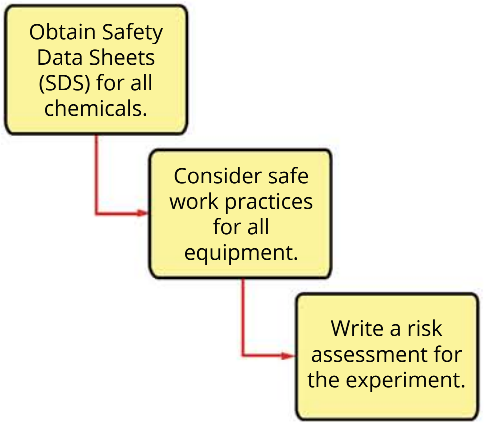
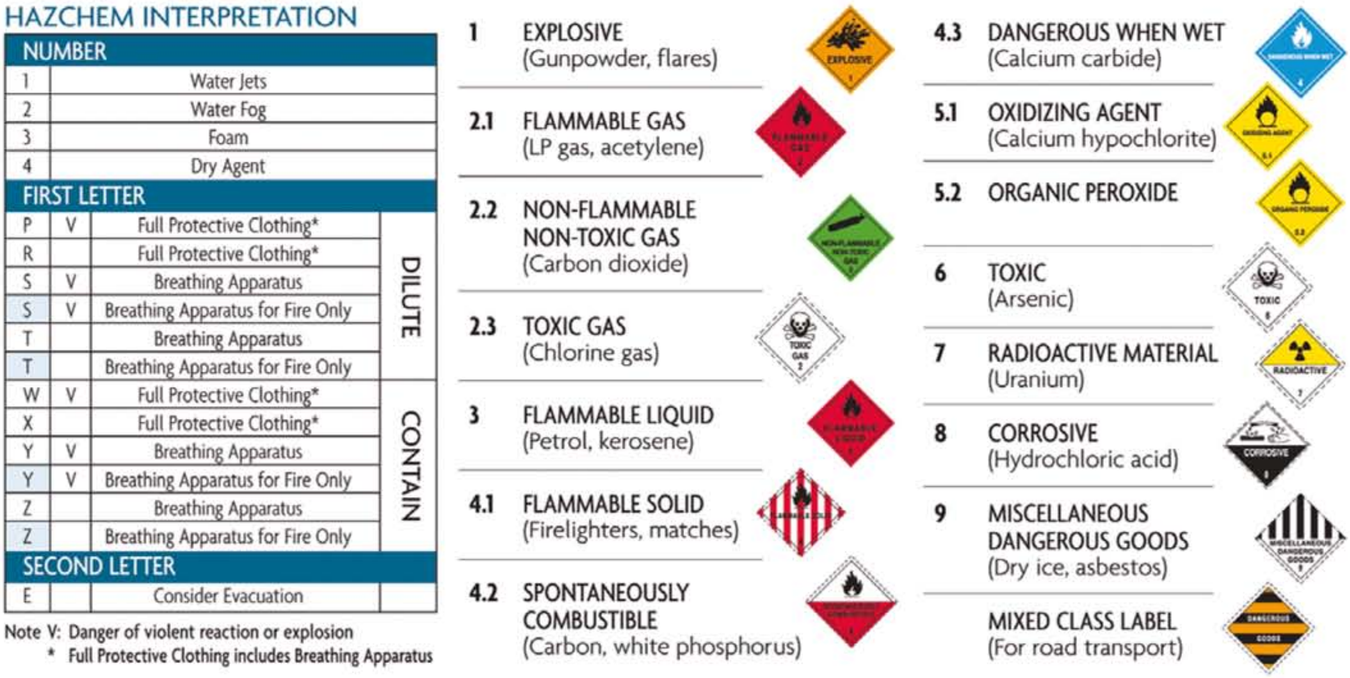


FIGURE 21.1.3 Steps involved in identifying risks.

Chemical codes

The chemicals at school or at the hardware shop have a warning symbol on the label. These are **chemical** (HAZCHEM) **codes**. Some common codes and their meanings are shown in Figure 21.1.4. Trucks that carry chemicals display hazard symbols, as shown in Figure 21.1.5.

Safety Data Sheets



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*	
S	V	Breathing Apparatus	
S	V	Breathing Apparatus for Fire Only	
T		Breathing Apparatus	
T		Breathing Apparatus for Fire Only	
W	V	Full Protective Clothing*	CONTAIN
X		Full Protective Clothing*	
Y	V	Breathing Apparatus	
Y	V	Breathing Apparatus for Fire Only	
Z		Breathing Apparatus	
Z		Breathing Apparatus for Fire Only	
SECOND LETTER			
E		Consider Evacuation	

Note V: Danger of violent reaction or explosion
* Full Protective Clothing includes Breathing Apparatus

1	EXPLOSIVE	(Gunpowder, flares)
2.1	FLAMMABLE GAS	(LP gas, acetylene)
2.2	NON-FLAMMABLE NON-TOXIC GAS	(Carbon dioxide)
2.3	TOXIC GAS	(Chlorine gas)
3	FLAMMABLE LIQUID	(Petrol, kerosene)
4.1	FLAMMABLE SOLID	(Firelighters, matches)
4.2	SPONTANEOUSLY COMBUSTIBLE	(Carbon, white phosphorus)
4.3	DANGEROUS WHEN WET	(Calcium carbide)
5.1	OXIDIZING AGENT	(Calcium hypochlorite)
5.2	ORGANIC PEROXIDE	
6	TOXIC	(Arsenic)
7	RADIOACTIVE MATERIAL	(Uranium)
8	CORROSIVE	(Hydrochloric acid)
9	MISCELLANEOUS DANGEROUS GOODS	(Dry ice, asbestos)
	MIXED CLASS LABEL	(For road transport)

FIGURE 21.1.4 HAZCHEM signs.

FIGURE 21.1.5 Trucks transporting hazardous substances such as flammable liquids have hazard symbols attached.

Each chemical substance has an accompanying document called a **Safety Data Sheet (SDS)** (Figure 21.1.6), previously 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).

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

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 21.1.6 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.

FIGURE 21.1.7 It is important to wear appropriate personal protective equipment as identified in a risk assessment.

Protective equipment

Everyone who works in a laboratory should wear items that help keep them safe. This is called personal protective equipment (PPE) (Figure 21.1.7) and includes:

- safety glasses
- closed-toe shoes
- disposable gloves when handling chemicals
- a disposable apron or a lab coat if there is risk of damage to clothes
- ear protection if there is risk to hearing.

A fume cupboard should be used when toxic or corrosive gases are being handled or produced.

21.1 Review

SUMMARY

- A research question is a statement defining what is being investigated.
- An aim is a statement describing in detail what will be investigated.
- A hypothesis:
  - is a prediction of the outcome of an experiment, based on previous knowledge
  - often takes the form of a proposed connection between two or more variables in a cause-and-effect relationship.
- A practical investigation determines the relationship between variables, measuring the results.
- The three types of variables are:
  - independent—the variable that is controlled by the researcher (the one that is selected and changed)
  - dependent—the variable that may change in response to a change in the independent variable, and is measured or observed
  - controlled variables—all the variables that must be kept constant during the investigation.
- Quantitative variables are measured; qualitative variables are observed but cannot be measured.
- An investigation or experiment should be valid, reliable and accurate.
  - Validity refers to whether an experiment or investigation is in fact testing the set hypothesis and aims.
  - Reliability refers to the consistency of the results when the experiment is repeated many times.
  - Accuracy refers to the ability to obtain the correct measurement using the correct instrument.
- Ethical and safety considerations must be of the highest priority at all times during a practical investigation.
  - Safety Data Sheets need to be obtained for all chemicals used.
  - Safe work procedures outline how to use equipment safely.
  - A risk assessment should be conducted prior to commencing the investigation.
  - Appropriate protective equipment including personal protective equipment should be used according to the risk assessment.

KEY QUESTIONS

1 For each of the following hypotheses, select the dependent variable.

a If water is filtered through a domestic water purifier, then its electrical conductivity will decrease.

b The concentration of lead in water will be higher in storm water close to an industrial site than in drinking water.

c The electrical conductivity of water from the Gippsland Lakes in Victoria will be greatest where ocean water can mix with lake water.

d The pH of commercially available sparkling mineral water will be lower than commercially available non-sparkling mineral water.

2 Give the meaning of the term ‘hypothesis’, using the terms ‘variables’ and ‘evidence’.

3 A student wanted to find out at what pH mussel shells begin to dissolve.

a What would be the independent variable for the experiment?

b What would be the dependent variable?

c What would be an appropriate way of measuring quantitatively the dissolution of mussel shells?

d What variables would need to be controlled in the student’s experiment?

21.2 Conducting investigations and recording and presenting data

Once you have planned your practical investigation, the next step is to undertake the experimental part. As with the planning stages, there are key steps to keep in mind to maintain high standards and minimise errors while carrying out your investigation.

This section will focus on the best methods of conducting a practical investigation using an analysis of water quality as an example. You will look at how to generate, record and process data. Finally, you will look at how you will present it to your audience.

CONDUCTING INVESTIGATIONS TO COLLECT AND RECORD DATA

For an investigation to be scientific, you must be objective and systematic. Ensuring that you are familiar with your method before you begin will help you to do so.

As you work, keep asking yourself questions. Is there any **bias** in the work in any way? If changes are made, how will it affect the study? Will your investigation still be valid for your aim and hypothesis?

It is essential that during your investigation, you record the following in your logbook:

- dates of all entries
- all quantitative and qualitative data collected
- the methods used to collect the data
- any unexpected event that may have affected the quality or validity of your data.

Raw data is what you collect and record as you do the experiment. This will need to be processed in a manner that makes it easy to read in the presentation of your investigation.

During experiments scientists constantly take notes and track any changes they make in an experimental method to ensure the method could be followed by somebody else and that the results are accurate.

IDENTIFYING ERRORS

Most practical investigations have errors associated with them. As shown in Figure 21.2.1, there are many different types of errors that can occur. You will also remember looking at these in Chapter 20.

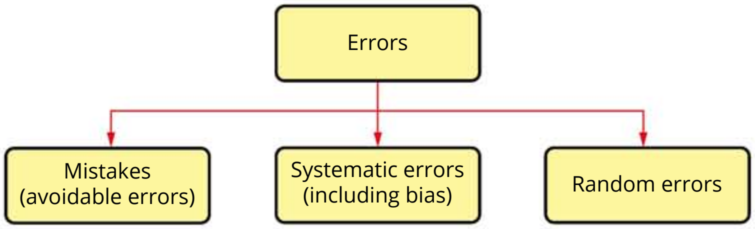


FIGURE 21.2.1 Types of errors that can be made in an experiment.

Mistakes

Mistakes are avoidable errors. Mistakes made during water quality analysis could include:

- misreading the numbers on a scale
- not labelling a sample adequately
- 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. Mistakes are not generally referred to as errors.

Systematic errors

A **systematic error** produces a constant bias in a measurement that cannot be eliminated by repeating the measurement. Systematic errors that affect water quality analysis could include:

- a balance used in gravimetric analysis that has not been **calibrated**, for example to weigh a precipitate
- a 20.0 mL pipette that delivers 20.2 mL **aliquots**
- an unsuitable indicator being used in a **titration**
- 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 too high or too low as a result. These lead to bias. Examples of bias are shown in Figure 21.2.2.

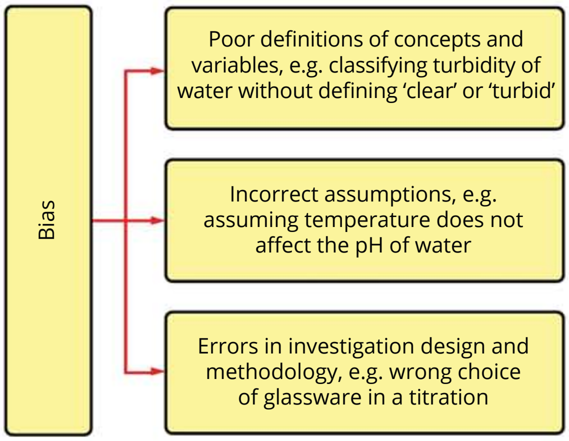


FIGURE 21.2.2 Types and examples of bias in an analysis of water quality.

Random errors

Random errors follow no regular pattern. The measurement is sometimes too large and sometimes too small. Random errors in water quality analysis could include:

- error in estimating the position of a needle between divisions on a scale
- temperature fluctuations during the measurement of pH or conductivity.

The effects of random errors can be reduced by taking multiple measurements of the same quantity, then calculating an average. For example, **concordant titres** are always obtained in a titration in an effort to reduce random errors.

TECHNIQUES FOR REDUCING ERROR

Designing the method carefully, including selection and use of equipment, will help reduce errors. Once you have chosen the appropriate equipment, it is necessary to calibrate the equipment to increase the accuracy of any measurements. To increase precision, include a larger sample size.

Equipment

To minimise errors, check the precision of the equipment that you intend to use. Pipettes, burettes and volumetric flasks have greater precision than using a beaker to measure volumes of liquids. However, you must still use all equipment correctly to reduce error.

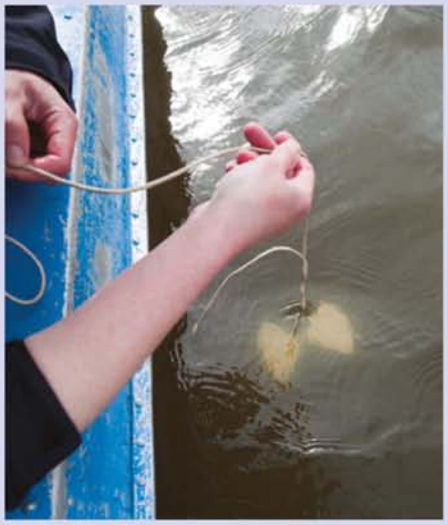
For example, when using a pipette and/or volumetric flask, ensure that you look at the bottom of the meniscus on the calibration line. To avoid parallax error, ensure that you take measurements at eye level, as shown in Figure 21.2.3.

FIGURE 21.2.3 It is important to read the bottom of the meniscus at eye level in order to avoid parallax error. This student is showing how you can use a piece of white card (or a tile) to improve the contrast between the solution and the scale.

Other equipment used for water analysis

Table 21.2.1 lists the types of equipment used for water analysis.

TABLE 21.2.1 Types of equipment used for measuring water quality

Parameter	Considerations	Equipment
Conductivity	Electrical conductivity is a measure of the total level of dissolved salts in a water sample. The greater the conductivity, the greater the concentration of total dissolved salts.	Portable conductivity meters can be used qualitatively (indicates relative conductivity), or quantitatively using a data-logging conductivity probe attached to a computer, as shown in Figure 21.2.4.  **FIGURE 21.2.4** Analysing a stream for electrical conductivity.
Turbidity	Turbidity is a measure of the clarity of water. Highly turbid water contains more suspended particles (such as clay, silt, plankton etc.) than clear water. Less light can penetrate turbid water, thereby reducing photosynthesis and concentration of **dissolved oxygen**.	Turbidity can be measured using a **Secchi disk.** (The depth at which the disk is no longer visible is taken as a measure of the transparency of the water, as seen in Figure 21.2.5.) Alternatively, a sample can be inserted into a turbidity meter connected via **data-logging equipment** to a computer.  **FIGURE 21.2.5** A Secchi disk is lowered into water to measure the depth at which the disk is no longer visible. This is a measure of the relative turbidity of a sample.

Calibration

Some equipment, such as pH meters and weighing balances, need calibrating before use. By using calibrated equipment, you can be more certain that your measured values are accurate.

Sampling size

In general, the larger the sample of water that is taken for analysis, the more precise the measured values will be. However, you will be limited by the size of the container that you can transport back to school.

For example, if you need to measure 10 mL of a liquid, a measuring cylinder will afford more accurate and precise readings than a 100 mL measuring cylinder.

Record the precision of the equipment that you intend to use.

Table 21.2.2 lists typical precision for water-testing equipment.

Often glassware and equipment have information that indicates its precision. Figure 21.2.6 shows where this can be found on a pipette.

TABLE 21.2.2 Precision of water-testing equipment and glassware

Equipment	Typical precision
pH meter	±0.1
50 mL burette	±0.02
20 mL pipette	±0.03

FIGURE 21.2.6 Record the uncertainty for glassware and instruments in your logbook. This pipette can dispense an aliquot of 25.00 mL ± 0.03 mL.

RECORDING AND PRESENTING QUANTITATIVE DATA

Consider how you will present the data that you collect. Prepare a table in which to record your data.

Presenting raw data in tables

Table 21.2.3 shows an example of how to present raw data in a table.

TABLE 21.2.3 Analysis of Yarra River water and how it could be recorded

Title: Analysis of Yarra River water

Location	Date and time	Temperature (°C) (±0.1)	pH (±0.1)	Conductivity (mS m^{-1}) (±1)	Turbidity (NTU) (±2)	Dissolved oxygen (DO) (mg L^{-1}) (±0.1)	Biological oxygen demand (BOD) (mg L^{-1}) (±0.1)
A		10.4	6.5	72	5	11.8	0.9
B		9.2	6.6	73	10	11.4	0.7
C		9.5	6.4	77	10	10.9	0.9
D		9.9	6.5	75	10	11.3	1.0

Table 21.2.3 includes:

- a descriptive title
- column headings (including the unit)
- aligned figures (align the decimal points)
- the independent variables (location and date/time) listed towards the left-hand side of the table
- the uncertainty of each measurement.

PROCESSING DATA

Calculating the mean

Table 21.2.4 shows an example of **mean** (average) values of water temperature with uncertainty.

TABLE 21.2.4 Mean water temperature of the Murray River in winter

Average water temperature of the Murray River at Yarrawonga, 2014	
Month	**Mean water temperature (°C) (±2)**
June	10
July	9
August	8

The mean value for June was calculated from raw data given by the results in Table 21.2.5.

TABLE 21.2.5 Water temperature readings from different dates in June

Date	Water temperature (°C) (±1)
19 June	9
20 June	8
21 June	9
22 June	10
23 June	11
24 June	12
25 June	11

The mean value is calculated by finding the sum of the daily values and dividing by the number of days, as shown below.

$$(9 + 8 + 9 + 10 + 11 + 12 + 11) \div 9 = 10^\circ\text{C}$$

However, the mean on its own does not provide an accurate picture of the results.

Uncertainty

For your results to be presented in an accurate way, the mean must be accompanied by the uncertainty. In other words, the mean must be accompanied by a description of the **range** of data obtained.

Uncertainty is sometimes calculated by:

$$\text{uncertainty} = (\text{maximum value} - \text{minimum value}) \div 2$$

According to the data in Table 21.2.5, in June, the maximum water temperature was 12°C and the minimum water temperature was 8°C. The uncertainty can be calculated by:

$$(12 - 8) \div 2 = 2$$

Mode and median

Other statistical measures that can be used, depending on the data obtained, are:

- **mode**—the value that appears most often in a data set. This measure is useful to describe qualitative or **discrete** data (e.g. the mode of the values 0.01, 0.01, 0.02, 0.02, 0.02, 0.03 and 0.04 is 0.02).
- **median**—the median is the 'middle' value of an ordered list of values (e.g. the median of the values 5, 5, 8, 8, 9, 10 and 20 is 8). The median is used when the data is spread. Data can often become spread; for example, due to the presence of **outliers**, making the mean unreliable.

Graphs

It is easier to observe trends and patterns in data in graph form rather than in table form.

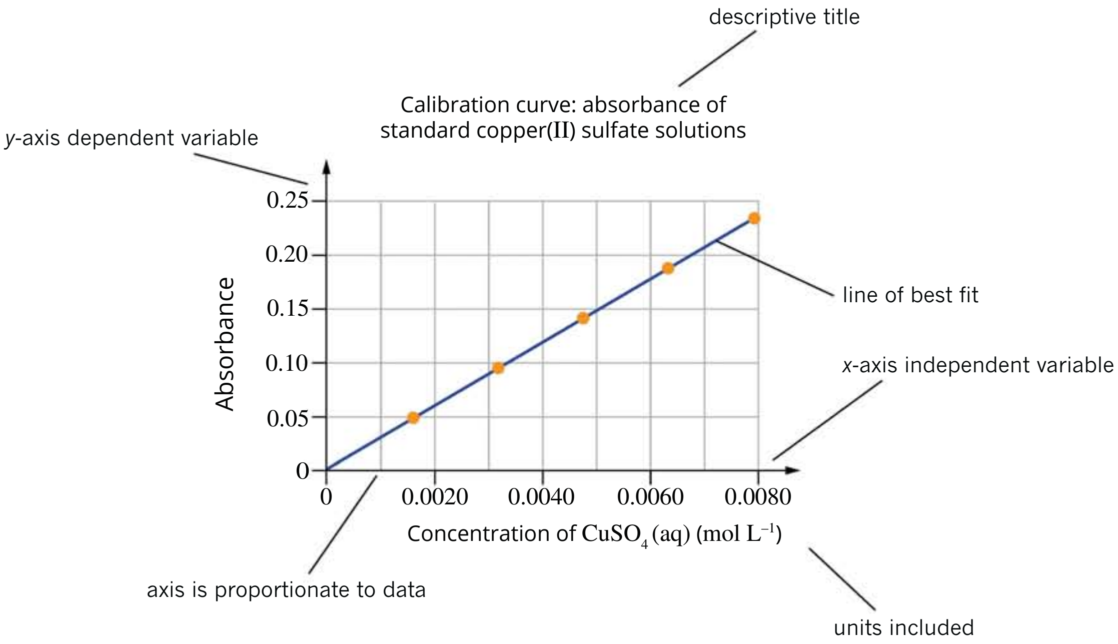


FIGURE 21.2.7 A graph is a better way to observe trends and patterns in data form.

A scatter graph, such as Figure 21.2.7, is used when two variables are being considered and one variable is dependent on the other. The independent variable is plotted along the x-axis and the dependent variable is plotted along the y-axis. When an appropriate line of best fit is fitted to the data points, the graph should show the relationship between the two variables.

Outliers

Sometimes when you collect data, there may be one point that does not fit the trend. An outlier is often caused by a mistake when measuring or recording data.

The graph shown in Figure 21.2.8 on page 566 is a **calibration curve** for determining the concentration of phosphate in a water sample. The data point that does not fit the trend of the other data points is an outlier. A mistake may have occurred when preparing that particular phosphate standard solution. In this case, show the data point, but do not use this point when drawing a line of best fit.

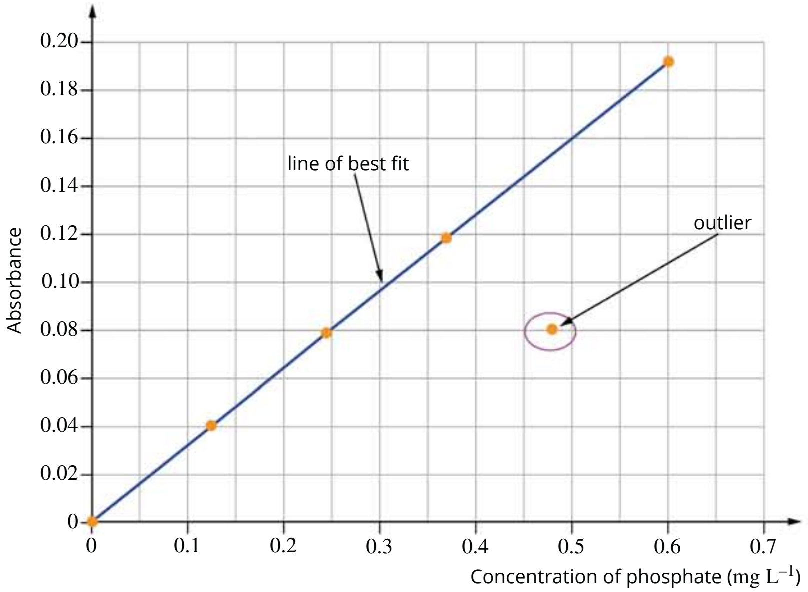


FIGURE 21.2.8 The graph is a calibration curve for determining the concentration of phosphate in a water sample.

Table 21.2.7 lists the types of graphs used for various examples.

TABLE 21.2.7 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	Constructing a calibration curve in colorimetry
Line graph	With 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	Turbidity of water at various locations, as shown in Figure 21.2.9
Pie diagrams	When summarising qualitative data; to display proportions	Relative proportion of different pesticides in a sample of water

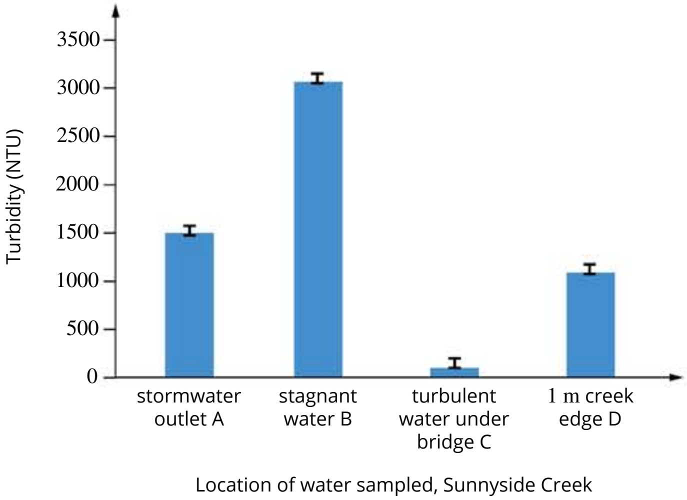


FIGURE 21.2.9 A bar graph can be used to compare data. This graph shows the measured turbidity of water samples taken from various locations along Sunnyside Creek.

21.2 Review

SUMMARY

- Record all information objectively in your logbook, including data and method during an investigation.
- Be aware of potential errors when conducting an investigation, including:
  - mistakes—are avoidable
  - systematic errors—errors that are consistent and will occur again if the investigation is repeated in the same way
  - random errors—errors that occur in an unpredictable manner and are generally small.
- Reduce errors by:
  - selecting appropriate equipment
  - properly calibrating equipment
  - using equipment correctly
  - using a larger sample.
- Tables are often an efficient way in which to record raw data.
- Processed data can be presented in tables, flow charts, diagrams or graphs.
- Tables allow the presentation of more detail, while graphs allow trends to be shown more clearly.
- To present data accurately, the mean and its uncertainty should be included.
- Scatter graphs are useful when showing quantitative data where one variable is dependent on another variable.
- Line graphs are useful for presenting continuous quantitative data.
- Bar graphs are useful for comparing data.
- Pie diagrams are useful for showing proportional data.

KEY QUESTIONS

1 A titration was carried out by a student during a research investigation. These titres were recorded: 18.34 mL, 17.34 mL, 17.38 mL, 17.84 mL and 17.44 mL. Which three are concordant titres?

2 Which of the following would not cause an error in measuring the turbidity of a sample?

A The presence of air bubbles in the water sample

B Using a control with distilled water

C Dirty fingermarks on the sample container inserted into the turbidity sensor

D Putting the water sample in an opaque container, then inserting this into the turbidity sensor

3 Identify whether each error is a mistake, a systematic error or a random error.

a A pipette that should have dispensed aliquots of 25.00 ± 0.03 mL actually dispensed aliquots of 25.87 ± 0.03 mL.

b A student misread the value of the burette for the second titration.

c A sample of sodium carbonate powder was weighed three times with the following results: 1.5791 g, 1.5792 g and 1.5790 g.

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 What kind of statistical measurement is most affected by an outlier: mean, median or mode?

21.3 Discussing investigations and drawing evidence-based conclusions

The final part of your investigation involves summarising your findings in an objective, clear and concise manner for your audience.

In this section, you will learn how to discuss your investigation and draw evidence-based conclusions in relation to your hypothesis and research question.

EXPLAINING RESULTS IN THE DISCUSSION

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

The key sections of the discussion are:

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

Consider the message you want to convey to the audience when writing your discussion. Statements need to be clear and concise. At the conclusion of your discussion, the audience must understand the context, results and implications of your investigation.

ANALYSING AND EVALUATING DATA

In the discussion, the findings of your investigation need to be analysed and interpreted. The following factors should be looked at and discussed.

- State whether a pattern, trend or relationship was observed between the independent and dependent variables.
- Describe what kind of pattern it was and specify under what conditions it was observed.
- Were there **deviations** in the data? If so, these should be noted and explained.
- Identify any limitations in the data you have collected. Would a greater sample or further variations in the independent variable 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 trend line, as shown in Figure 21.3.1.

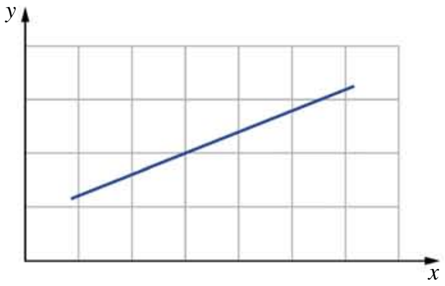
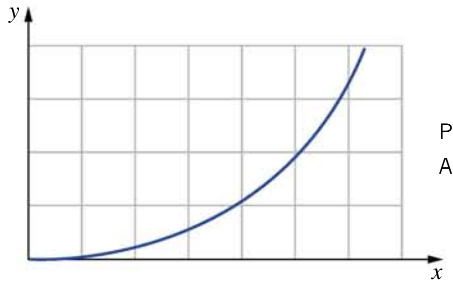


FIGURE 21.3.1 Trend line for variables that change in direct response to each other.

- Variables that change non-linearly in proportion to each other produce a curved trend line, as shown in Figure 21.3.2.



Positive non-linear relationship
As *x* increases, *y* increases non-linearly.

FIGURE 21.3.2 Variables that change in response to each other in a non-linear way.

- When there is an inverse relationship, one variable increases as the other variable decreases (see Figure 21.3.3).

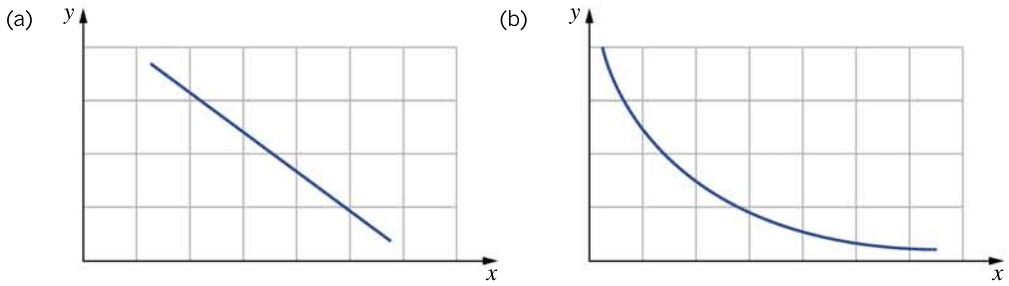


FIGURE 21.3.3 An inverse relationship in which one variable decreases in response to the other variable increasing. It may be (a) direct or (b) non-linear.

- When there is no relationship between two variables, one variable will not change even if the other changes. A graph in which there is no relationship can be seen in Figure 21.3.4.

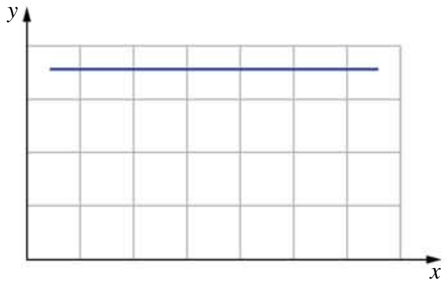


FIGURE 21.3.4 When two variables show no relationship, there is no trend in the graph.

Remember that your results may be unexpected. This does not make the investigation a failure. However, you must be able to relate your findings to the hypothesis, aims and method.

EVALUATING THE METHOD

It is important to discuss the limitations of your method. You can do this by:

- evaluating the method
- identifying issues that could affect validity, accuracy, precision and reliability of data
- state sources of systematic and random errors
- recommend improvements to the investigation if it is to be repeated.

The more times an experiment is repeated, the more reliable the results are. Limited time and resources to repeat your experiment may make your results less reliable. Your control group is important to the reliability of your experiment. This will help you work out if you have overlooked a variable and may explain unexpected results.

DISCUSSING RELEVANT CHEMICAL CONCEPTS

You need to be able to explain your results in relation to chemical ideas, concepts and theories. Doing this will allow you to explain your hypothesis.

For example, if you were studying the impact of dissolved carbon dioxide on the pH of sparkling mineral water, you could include the information in Table 21.3.1 in your discussion.

TABLE 21.3.1 Examples of how to include chemical concepts in your discussion

Key ideas	Example
Definitions of key terms	'pH', 'dissolved carbon dioxide' and 'sparkling' mineral water
The function of added carbon dioxide	In order to create 'sparkling' water
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 your hypothesis

You now need to be able to discuss whether your data supports or refutes your hypothesis.

Ask yourself questions relating to your hypothesis and the literature regarding chemical concepts as shown in Figure 21.3.5.

Ensure you discuss the broader implications of your findings. Implications are the bigger picture. Outlining them for the audience is an important part of the investigation.

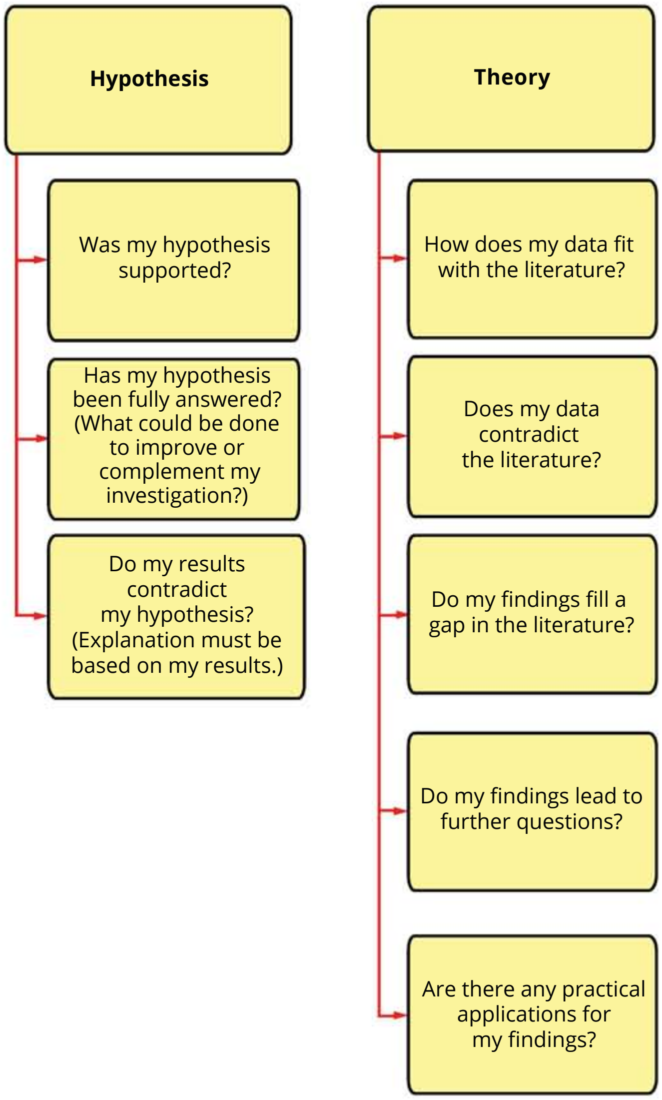


FIGURE 21.3.5 Use these questions to help relate your data to your hypothesis.

DRAWING EVIDENCE-BASED CONCLUSIONS

A conclusion is usually a paragraph that links the collected evidence to your hypothesis and provides a justified and relevant response to your research question.

Read the examples of poor and better conclusions in Tables 21.3.2 and 21.3.3 for the hypothesis and research question shown.

TABLE 21.3.2 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 21.3.3 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.

REFERENCES AND ACKNOWLEDGEMENTS

All the quotations, documents, publications and ideas used in your investigation need to be listed in the references and acknowledgments. In order to avoid plagiarism and to ensure creators are properly credited for their work, this must be completed accurately.

References and acknowledgements also give credibility to your study and allow the audience to locate information sources should they wish to study it further. For example: 'Melbourne Water reported similar turbidity levels in Yarra River water (Melbourne Water, 2015).'

In Chapter 11 on page 270 you will find a guide on how to write citations and references of different types of sources. The standard referencing style used is the American Psychological Society (APA) academic referencing style.

21.3 Review

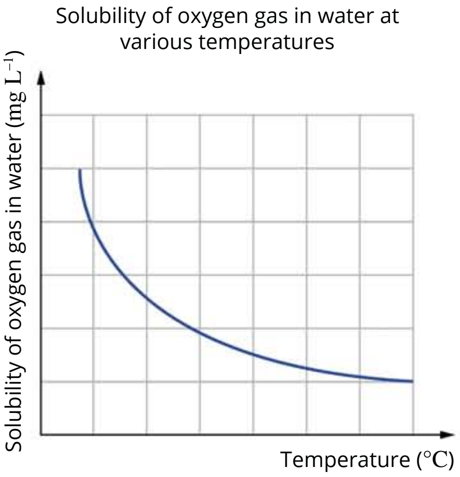
SUMMARY

- A discussion should:
  - analyse and evaluate data
  - identify patterns and limitations
  - identify issues that may have affected validity, accuracy and precision, reliability
  - make recommendations for improving the investigation method
  - explain the link between investigation findings and relevant chemical concepts
  - define concepts and investigation variables
  - discuss the investigation results in relation to the hypothesis
  - link the investigation's findings to existing knowledge and literature
  - discuss the implications and possible applications of the investigation's findings
  - suggest further investigations related to this question.
- A conclusion should:
  - link the evidence collected to the hypothesis and research question
  - indicate whether the hypothesis was supported or refuted.
- References and acknowledgements should be presented in the appropriate format.

KEY QUESTIONS

1 If you hypothesise that the solubility of potassium nitrate in water increases non-linearly with increasing temperature, what would you expect a graph of the data to look like?

2 Describe the trend in the following graph.



3 A scientist designed and completed an experiment to test the following hypothesis:
'Increasing the temperature of water would result in an increase in the measured electrical conductivity of water.'

The discussion section of the scientist's report included comments on the reliability, validity, accuracy and precision of the investigation.

Determine which of the following sentences comment on the reliability, validity, accuracy or precision.

a Three water samples from the same source were examined at each temperature. Each water sample was analysed and the measurements were recorded.

b The temperature and the electrical conductivity of the water samples were recorded using data-logging equipment. The temperature of some of the water samples was measured using a glass thermometer.

c The data logging equipment was calibrated for electrical conductivity against a known standard. The equipment was calibrated before measurements were taken.

d The temperature probe (data logger) measured temperature to the nearest 0.1°C. The glass thermometer measured temperature to the nearest 1°C.

4 The scientist testing the hypothesis from Question 3 concluded that there was no relationship between pH and electrical conductivity. Why is this conclusion invalid?

Chapter review

21

KEY TERMS

accurate
aim
aliquot
bias
biological oxygen demand (BOD)
calibrated
calibration curve
chemical code
concordant titre
conductivity
control
controlled variable
data-logging equipment
dependent variable
deviation
discrete
dissolved oxygen (DO)
hypothesis
independent variable
mean
median
mistake
mode
outlier
parallax error
pH
precise
qualitative
quantitative
random error
range
raw data
reliability
research question
risk assessment
Safety Data Sheet (SDS)
Secchi disk
systematic error
titration
trend
validity
variable

Designing and planning investigations

1 Consider the following research question:
'Is the concentration of lead in water sampled from along the Yarra River within acceptable limits?'
Which of the following is the independent, dependent and controlled variables?
- **A** Concentration of lead
- **B** Analytical technique, temperature of water sample, type of sampling container
- **C** Source and location of water

2 Consider the following hypothesis:
'The phosphate concentration of laundry-waste water will be greater than that of drinking water.'
Name the independent, dependent and controlled variables for an experiment with this hypothesis.

3 Explain the terms 'accuracy' and 'validity.'

4 What are the meanings of the following chemical codes?

a

b

c

Conducting investigations and recording and presenting data

5 Identify whether the following are mistakes, systematic errors or random errors.
- **a** A student spills some solution during a titration.
- **b** The reported measurements are above and below the true value.
- **c** A weighing balance has not been calibrated.

6 Which graph from the following list would be best to use with each set of data listed here?
Graph types: pie diagram, scatter graph (with line of best fit), bar graph, line graph
- **a** The levels of a pesticide detected in drinking water at various locations
- **b** The temperature of water sampled at the same time of day over a period of a month
- **c** A calibration curve showing absorbance of standard solutions of phosphate measured using UV–visible spectroscopy
- **d** The proportion of specific contaminants detected in water

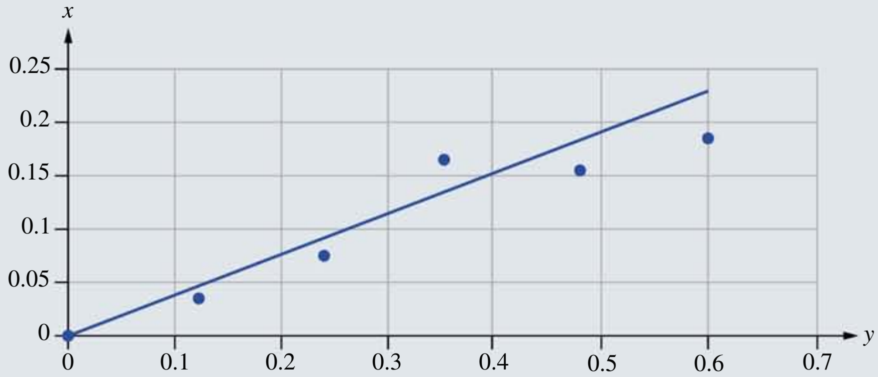
7 **a** Use the following values to plot a calibration curve to determine the concentration of phosphate in samples of water. The absorbance values were obtained during an experiment at 450 nm.

Standard phosphate concentration (mg L^{-1})	**Absorbance**
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'.

8 Biological oxygen demand (BOD) is a measure of the amount of decomposing organic material in a water sample. It can be determined by taking two water samples at a particular location and measuring the dissolved oxygen (DO) content in mg L^{-1} at the time of sampling and then 5 days later. What other measurements should be taken at the time of water sampling?

9 The following calibration curve was obtained by UV–visible spectroscopy at 450 nm. The curve plots the absorbance of phosphate solutions against their concentration.
Describe four changes that should be made to improve the calibration curve.



Discussing investigations and drawing evidence-based conclusions

10 What factors can you look at to ensure you discuss the limitations of your method?

11 Explain the meaning of the term ‘trend’ in a scientific investigation and describe the types of trends that might exist.

12 What is the purpose of referencing and acknowledging documents, ideas and quotations in your investigation?

Connecting the main ideas

13 A scientist designed and completed an experiment to test the following hypothesis:
‘Increasing the temperature of water would result in an increase in the measured electrical conductivity of water.’

- **a** Write a possible aim for this scientist’s experiment.
- **b** What would be the independent, dependent and controlled variables in this investigation?
- **c** What kind of data would be collected? Would it be qualitative or quantitative?
- **d** List the equipment that could be used and the type of precision expected for each item.
- **e** Explain the difference between raw data and processed data, using this as an example. What would you expect the graph of the results to look like if the scientist’s hypothesis was correct?

APPENDIX 1 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				
Length	l	metre		fundamental unit
Area	A	square metre	m^2	
Volume	V	cubic metre	m^3	
Mass	m	kilogram	kg	fundamental unit
Density	d		kg m^{-3}	
Time	t	second	s	fundamental unit
Force	F	newton	N	kg m s^{-2}
Pressure	P	pascal	Pa	N m^{-2}
Energy	E	joule	J	N m
Electricity				
Electric current	I	ampere	A	fundamental unit
Electric charge	Q	coulomb	C	A s
Electric potential difference	V	volt	V	J A^{-1} s^{-1}
Nuclear and chemical quantities				
Atomic number	Z	—	—	—
Neutron number	N	—	—	—
Mass number	A	—	—	$Z + N$
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	Valuev
Avogadro's constant	N_A	6.02×10^{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} mol^2 L^{-2} at 298 K
Molar volume of an ideal gas	V_m	
at 273 K, 100 kPa		22.7 L mol^{-1}
at 298 K, 100 kPa		24.8 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 2 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
- the time '20 minutes' has two significant figures (the zero follows the integer 2)
- the 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?

$$\textit{Average time} = \frac{3.5 \text{ minutes}}{4} = 0.875 = 0.88 \text{ minutes}$$

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 3 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	-	Germanium	Ge	32	72.63	Potassium	K	19	39.098
Aluminium	Al	13	26.9815	Gold	Au	79	196.9666	Praseodymium	Pr	59	140.9077
Americium	Am	95	-	Hafnium	Hf	72	178.49	Promethium	Pm	61	-
Antimony	Sb	51	121.76	Hassium	Hs	108	-	Protactinium	Pa	91	231.0359
Argon	Ar	18	39.948	Helium	He	2	4.00260	Radium	Ra	88	-
Arsenic	As	33	74.9216	Holmium	Ho	67	164.9303	Radon	Rn	86	-
Astatine	At	85	-	Hydrogen	H	1	1.0080	Rhenium	Re	75	186.21
Barium	Ba	56	137.33	Indium	In	49	114.82	Rhodium	Rh	45	102.9055
Berkelium	Bk	97	-	Iodine	I	53	126.9045	Roentgenium	Rg	111	-
Beryllium	Be	4	9.01218	Iridium	Ir	77	192.22	Rubidium	Rb	37	85.468
Bismuth	Bi	83	208.9804	Iron	Fe	26	55.845	Ruthenium	Ru	44	101.07
Bohrium	Bh	107	-	Krypton	Kr	36	83.80	Rutherfordium	Rf	104	-
Boron	B	5	10.81	Lanthanum	La	57	138.9055	Samarium	Sm	62	150.4
Bromine	Br	35	79.904	Lawrencium	Lr	103	-	Scandium	Sc	21	44.9559
Cadmium	Cd	48	112.41	Lead	Pb	82	207.2	Seaborgium	Sg	106	-
Caesium	Cs	55	132.9055	Lithium	Li	3	6.94	Selenium	Se	34	78.97
Calcium	Ca	20	40.08	Livermorium	Lv	116	-	Silicon	Si	14	28.086
Californium	Cf	98	-	Lutetium	Lu	71	174.967	Silver	Ag	47	107.868
Carbon	C	6	12.011	Magnesium	Mg	12	24.305	Sodium	Na	11	22.9898
Cerium	Ce	58	140.12	Manganese	Mn	25	54.9380	Strontium	Sr	38	87.62
Chlorine	Cl	17	35.453	Meitnerium	Mt	109	-	Sulfur	S	16	32.06
Chromium	Cr	24	51.996	Mendelevium	Md	101	-	Tantalum	Ta	73	180.9479
Cobalt	Co	27	58.9332	Mercury	Hg	80	200.59	Technetium	Tc	43	-
Copernicium	Cn	112	-	Molybdenum	Mo	42	95.95	Tellurium	Te	52	127.60
Copper	Cu	29	63.55	Neodymium	Nd	60	144.24	Terbium	Tb	65	158.9254
Curium	Cm	96	-	Neon	Ne	10	20.180	Thallium	Tl	81	204.384
Darmstadtium	Ds	110	-	Neptunium	Np	93	-	Thorium	Th	90	232.038
Dubnium	Db	105	-	Nickel	Ni	28	58.693	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	Osmium	Os	76	190.2	Uranium	U	92	238.0289
Fermium	Fm	100	-	Oxygen	O	8	15.9994	Vanadium	V	23	50.942
Flerovium	Fl	114	-	Palladium	Pd	46	106.4	Xenon	Xe	54	131.29
Fluorine	F	9	18.9984	Phosphorus	P	15	30.9738	Ytterbium	Yb	70	173.05
Francium	Fr	87	-	Platinum	Pt	78	195.08	Yttrium	Y	39	88.9058
Gadolinium	Gd	64	157.25	Plutonium	Pu	94	-	Zinc	Zn	30	65.38
Gallium	Ga	31	69.72	Polonium	Po	84	-	Zirconium	Zr	40	91.22

* 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 4

Atomic radii and boiling temperatures of elements with atomic numbers 1–89

32 **H** 20					Atomic radius ($\times 10^{-12}$ m) **Symbol** Boiling temperature (K)												37 **He** 4
130 **Li** 1615	99 **Be** 2741											84 **B** 4723	75 **C** 5100	71 **N** 77	64 **O** 90	60 **F** 85	62 **Ne** 27
160 **Na** 1156	140 **Mg** 1363											124 **Al** 2792	114 **Si** 3538	109 **P** 554	104 **S** 718	100 **Cl** 239	101 **Ar** 87
200 **K** 1032	174 **Ca** 1757	159 **Sc** 3109	148 **Ti** 3560	144 **V** 3680	130 **Cr** 2944	129 **Mn** 2334	124 **Fe** 3134	118 **Co** 3200	117 **Ni** 3186	122 **Cu** 2833	120 **Zn** 1180	123 **Ga** 2502	120 **Ge** 3106	120 **As** 886	118 **Se** 958	117 **Br** 332	116 **Kr** 120
215 **Rb** 961	190 **Sr** 1650	176 **Y** 3618	164 **Zr** 4679	156 **Nb** 5014	146 **Mo** 4912	138 **Tc** 4535	136 **Ru** 4420	134 **Rh** 3968	130 **Pd** 3236	136 **Ag** 2435	140 **Cd** 1040	142 **In** 2345	140 **Sn** 2875	140 **Sb** 1860	137 **Te** 1261	136 **I** 457	136 **Xe** 165
238 **Cs** 944	206 **Ba** 2118	194 **La** 3737	164 **Hf** 4873	158 **Ta** 5728	150 **W** 5828	141 **Re** 5869	136 **Os** 5281	132 **Ir** 4701	130 **Pt** 4098	130 **Au** 3109	132 **Hg** 630	144 **Tl** 1746	145 **Pb** 2022	150 **Bi** 1837	142 **Po** 1235	148 **At** 640	146 **Rn** 211
242 **Fr** 950	211 **Ra** 1413	201 **Ac** 3473															

APPENDIX 5

TABLE 1 The names and formulas 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	$Cr_2O_7^{2-}$
Hydrogen	H^+	Cobalt(II)	Co^{2+}	Iron(III)	Fe^{3+}	Dihydrogen phosphate	$H_2PO_4^-$	Hydrogen phosphate	HPO_4^{2-}
Lithium	Li^+	Copper(II)	Cu^{2+}			Ethanoate	CH_3COO^-	Oxalate	$C_2O_4^{2-}$
Potassium	K^+	Iron(II)	Fe^{2+}	**+4**		Fluoride	F^-	Oxide	O^{2-}
Rubidium	Rb^+	Lead(II)	Pb^{2+}	Lead(IV)	Pb^{4+}	Hydrogen carbonate	HCO_3^-	Sulfide	S^{2-}
Silver	Ag^+	Magnesium	Mg^{2+}	Tin(IV)	Sn^{4+}	Hydrogen sulfide	HS^-	Sulfite	SO_3^{2-}
Sodium	Na^+	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	$PbCl_2$, $PbBr_2$
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.

Answers

Comprehensive answers and fully worked solutions for all section review questions, Try yourself: Worked examples, chapter review questions and Area of Study review questions are available via Heinemann Chemistry 5th edition ProductLink.

Chapter 1 The atomic nature of matter

1.1 Nanomaterials and nanoparticles

WE 1.1.1 2.43 × 10^{12} nm

1 8.35 × 10^7 nm

2 **a** 1.35 × 10^7 nm **b** 4.2 × 10^6 nm

3 2500 times larger

4 **a**

Shape	Surface area	Volume	$\frac{\text{Surface area}}{\text{Volume}}$
Cube 2 cm × 2 cm × 2 cm	24 cm^2	8 cm^3	3
Sphere of radius 1.38 cm	23.9 cm^2	11 cm^3	2.17
Tube (cylinder) Radius of 1 cm Height of 2 cm	19 cm^2	6.3 cm^3	3

b Sphere

c Sphere

d A large *SA* : *V* ratio is required for rapid cooling. A small *SA* : *V* ratio is required to minimise loss of heat when cold.

5 There are two reasons why their size makes nanoparticles useful for transporting medicine. First, their small size makes it easy for the nanoparticles to get into the body by inhalation, injection or absorption through the skin. Second, their small size gives nanoparticles a large surface area compared to their volume. This means that a large number of molecules can be adsorbed onto the surface of a relatively small volume of nanoparticles.

1.2 The atomic world

1 Noble gases

2 **a** Element **b** Element **c** Compound
d Compound **e** Element **f** Compound
g Element **h** Compound

3 An element is made up of just one type of atom and these atoms are identical. A compound is a molecule that contains at least two different types of atoms in a definite proportion.

4 **a** Iron **b** Potassium **c** Tungsten **d** Lead

1.3 Inside atoms

1 10 000–100 000 larger

2 Protons and neutrons found in the nucleus

3 The electrostatic attraction of the protons; the negative electrons are attracted to the positive protons and pulled towards them.

1.4 Classifying atoms

WE 1.4.1 92 protons, 235 – 92 = 143 neutrons, 92 electrons

1 Mass number

2 Z = 15. Protons = 15, electrons = 15. Neutrons = 31 – 15 = 16

3 Nitrogen

4 Isotopes of the same element have the same atomic number and therefore the same number of protons and electrons. The number of neutrons is different between isotopes of the same element; therefore they have different mass numbers.

5 2 neutrons

1.5 Electronic structure of atoms

1 Each line in an emission spectrum corresponds to a specific amount of energy. This energy is emitted when electrons from higher-energy electron shells transition to a lower-energy shell. Different lines indicate that there are differences in energy between shells. This is evidence that electrons are found in shells with discrete energy levels.

2 Electrons revolve around the nucleus in fixed, circular orbits.
Electrons' orbits correspond to specific energy levels in the atom.
Electrons can only occupy fixed energy levels and cannot exist between two energy levels.
Orbits of larger radii correspond to energy levels of higher energy.

3 Light or electromagnetic radiation

1.6 Electronic configuration and the shell model

WE 1.6.1 2,8,18,6 **WE 1.6.2** 6 electrons

1 **a** 2,3 **b** 2,8,2 **c** 2,8,8,2 **d** 2,8,18,7

2 **a** 2,2 **b** 2,8,6 **c** 2,8,8 **d** 2,8,2 **e** 2,8

4 **a** Helium, He **b** Fluorine, F **c** Aluminium, Al
d Nitrogen, N **e** Chlorine, Cl

5 The electronic configuration is 2,8,18,7. Therefore the number of valence electrons is 7.

1.7 The Schrödinger model of the atom

WE 1.7.1 $1s^22s^22p^63s^23p^63d^34s^2$

1

Element (atomic number)	Electronic configuration using the shell model	Electronic configuration using the subshell model
Boron (5)	2,3	$1s^22s^22p^1$
Lithium (3)	2,1	$1s^22s^1$
Chlorine (17)	2,8,7	$1s^22s^22p^63s^23p^5$
Sodium (11)	2,8,1	$1s^22s^22p^63s^1$
Neon (10)	2,8	$1s^22s^22p^6$
Potassium (19)	2,8,8,1	$1s^22s^22p^63s^23p^64s^1$
Scandium (21)	2,8,9,2	$1s^22s^22p^63s^23p^63d^14s^2$
Iron (26)	2,8,16	$1s^22s^22p^63s^23p^63d^64s^2$
Bromine (35)	2,8,18,7	$1s^22s^22p^63s^23p^63d^{10}4s^24p^5$

2 The subshell model is a refinement of the shell model. The shell model proposed that all electrons in the one shell were of equal energy. Evidence from emission spectra indicated that there were different electronic energy levels (called subshells) within a shell.

Chapter 1 review

2 **a** 5.0 × 10^7 nm **b** 1.2 × 10^7 nm **c** 2.0 × 10^{12} nm

3 Zinc oxide nanoparticles are colourless.

4 Atoms are hard, indivisible structures.

5 Monoatomic = helium, neon, krypton. Molecules = sulfur, oxygen, nitrogen. Large network = copper, gold, diamond, tin

6 The nucleus

7 The protons and neutrons form the nucleus. The electrons are grouped in shells and occupy the space around the nucleus.

8 The mass of a proton is approximately equal to the mass of a neutron and is about 1840 times the mass of an electron. The proton and electron have equal but opposite charges and the neutron has no charge.

9 **a** Atomic number is 24; mass number is 52
b 24 electrons, 24 protons, 52 – 24 = 28 neutrons

10 No. Isotopes have the same number of protons (atomic number) but different numbers of neutrons (and therefore different mass numbers). These atoms have different atomic numbers and different mass numbers.

11 Atoms are electrically neutral. The positive charge on one proton balances the negative charge on one electron. Therefore, for electrical neutrality, there must be an equal number of protons and electrons.

12 Most elements have more than one isotope, so they will have more than one mass number. All bromine atoms have 35 protons in their nuclei. No other type of atom has 35 protons in its nucleus (i.e. no other atom has an atomic number of 35). Isotopes of bromine, however, differ in their mass numbers, so mass number is not fixed for an element. In addition, an isotope of one element may have the same mass number as an isotope of another element.

13 $n = 1$ **14** $n = 3$

15 Magnesium

16
a $1s^2$ **b** $1s^2 2s^2 2p^2$
c $1s^2 2s^2 2p^5$ **d** $1s^2 2s^2 2p^6 3s^2 3p^1$
e $1s^2 2s^2 2p^6 3s^2 3p^6$ **f** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
g $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$

17 A fluorine atom contains nine electrons. The electrons are arranged in energy levels called shells; two electrons are in the first shell and seven electrons are in the second shell, which has higher energy. The electron arrangement in the shells can be written as 2,7.

Shells are regarded as being made up of energy levels called subshells. The first shell contains an s-type subshell, which is labelled ‘1s’. The second shell contains both s- and p-type subshells, labelled ‘2s’ and ‘2p’ respectively.

Within subshells, electrons occupy regions of space known as orbitals. An orbital can hold up to two electrons. Subshells of an s-type contain one orbital, whereas p-type subshells contain three orbitals. The electron arrangement in the subshells of a fluorine atom can be represented as $1s^2 2s^2 2p^5$.

18 $1s^2 2s^2 2p^6 3s^2 3p^4$

19 According to the Schrödinger model, the 4s-subshell is lower in energy than the 3d-subshell. Therefore, the 4s-subshell begins filling after the 3s- and 3p-subshells but before the 3d-subshell.

20 There is very little difference between the energy levels of the 3d- and 4s-subshells. As orbitals fill in sequence, one electron at a time, it is more stable for chromium to have all d-orbitals exactly half-filled than to have one empty d-orbital. Likewise for copper, it is more stable to have all d-orbitals completely filled than to have one half-filled and a full 4s-orbital.

21 Nothing

22
a Until Rutherford’s work, the plum pudding model of the atom was widely accepted. However, his discovery that a beam of alpha particles directed at thin gold foil caused a few particles to deflect through high angles led to the development of a new atomic model.
b Although Rutherford’s atomic model accounted for a number of atomic properties, it was not able to account for the characteristic emission spectrum of each element. The model was also in conflict with the principles of classical physics, which suggested that electrons moving in circular orbits should continuously lose energy and spiral into the nucleus.
c The Bohr model of the atom did not adequately explain why electrons adopted some energy levels but not others. In addition, calculated frequencies for lines in the emission spectra of atoms with more than one electron gave poor agreement with measured values.

Chapter 2 Electron arrangements and the periodic table

2.1 The periodic table

1 Groups 1, 2 and 13–18

2 **a** 1 **b** 15 – 10 = 5 **c** 17 – 10 = 7 **d** 2

3 The element is in period 3 and therefore has three occupied shells. As the element is in group 2, it will have two valence electrons. This gives an electron configuration of 2,8,2.

4
a **i** Group 13 **ii** Group 17 **iii** Group 1
iv Group 18 **v** Group 14 **vi** Group 14
b **i** 4 **ii** 2 **iii** 1 **iv** 1 **v** 7 **vi** 3
c **i** Silicon, Si, 2,8,4 or $1s^2 2s^2 2p^6 3s^2 3p^2$
ii Beryllium, Be, 2,2 or $1s^2 2s^2$
iii Argon, Ar, 2,8,8 or $1s^2 2s^2 2p^6 3s^2 3p^6$

5 Atoms are listed in the periodic table in order of atomic number because the atomic number determines the number of electrons, and this in turn sets the properties that make each element unique. Relative atomic mass does not relate directly to either the atomic number or the electron number.

2.2 Trends in the periodic table—Part 1

WE 2.2.1 Core charge of F = 9 – 2 = +7

1 6 – 2 = +4

2 As core charge increases, electronegativity increases.

3
a **i** F **ii** Fr
b **i** Group 17 **ii** Group 1
c Elements in group 18, the noble gases, have a very stable electronic configuration and so are unreactive.

2.3 Trends in the periodic table—Part 2

1
a Ionisation energy is the least amount of energy needed to remove an electron from an atom or ion in the gas phase.
b Size of the atom, and the charge on the nucleus

2 A metalloid is an element that exhibits both metallic and non-metallic properties.

3 Across a period, the number of occupied shells in the atoms remains constant but core charge increases. The valence electrons become more strongly attracted to the nucleus, so more energy is required to remove an electron from an atom. Therefore, the first ionisation energy increases across a period.

Chapter 2 review

1
a Period 1, s-block **b** Period 2, p-block
c Period 3, p-block **d** Period 4, d-block
e Period 7, f-block

2
a Period 2, group 2 **b** Period 3, group 14
c Period 4, group 13 **d** Period 1, group 18

3
a Elements in the s-block are filling an s-subshell. As an s-subshell accommodates a maximum of two electrons, there are only two groups of elements in the s-block. They have outer-shell configurations of s^1 and s^2.
b Elements in the p-block are filling a p-subshell. As a p-subshell accommodates a maximum of six electrons, there are six groups of elements in the p-block. They have outer-shell configurations of s^2p^1 to s^2p^6.
c Elements in the d-block are filling a d-subshell. As a d-subshell accommodates a maximum of 10 electrons, there are 10 elements in each transition series.
d The lanthanides and actinides are filling an f-subshell. As an f-subshell accommodates a maximum of 14 electrons, there are 14 elements in each of these series.

4
a Silicon **b** Potassium, caesium
c Bromine **d** Nitrogen, arsenic

5 From left to right across groups 1, 2 and 13–17, the charge on the nucleus increases. Each time the atomic number increases by one, the electrons are attracted to an increasingly more positive nucleus. Within a period, the outer electrons are in the same shell—that is, they have the same number of inner-shell electrons shielding them from the nucleus. Therefore, the additional nuclear charge attracts the electrons more strongly, drawing them closer to the nucleus and so decreasing the size of the atom.

6
a Magnesium and phosphorus are both in period 3. Magnesium has a nuclear charge of +12 and a core charge of +2. Phosphorus has a nuclear charge of +15 and a core charge of +5. The stronger attraction of the phosphorus electrons to the core means that more energy is required to remove an electron from a phosphorus atom than from a magnesium atom.

b Both fluorine and iodine are in group 17, so the outer electrons of each atom experience the attraction of the same core charge. Because the outer-shell electrons of a fluorine atom are closer to the nucleus than those of an iodine atom, they are attracted more strongly and so more energy is needed to remove one.

7 **a** $1s^22s^22p^3$ **b** Period 2 and group 15 **c** 5 **d** +5

8 As you move across period 2 from lithium to fluorine:

a the radius of the atoms decreases as the core charge increases

b there is a trend from metals (lithium, beryllium) to non-metals (boron, carbon, nitrogen, oxygen and fluorine)

c electronegativity increases as the core charge increases and size of the atoms decreases.

9 **a** Lithium, sodium, potassium, rubidium

b The reactivity of metals increases down a group. This is because the number of electron shells increases down a group, so the valence electrons are further from the nucleus and more easily lost. Since metals lose electrons in their reactions, those that lose electrons most easily will be most reactive.

10 **a** Fluorine

b Aluminium and magnesium are metals. Fluorine has the highest core charge (it is located furthest right on the periodic table) while also containing the least number of electron shells. This means that fluorine attracts an electron more strongly than other elements and is therefore the most reactive non-metal.

11 **a** Nitrogen **b** Chlorine **c** Chlorine

12 From left to right across the periodic table the reactivity decreases for the metals then increases for the non-metals.

13 Students' own answers.

Chapter 3 Metals

3.1 Properties of metals

WE 3.1.1 +3

1 **a** Li 1+ **b** Mg 2+ **c** Ga 3+ **d** Ba 2+

2 **a** Both have good thermal and electrical conductivity. However, gold has a higher density, and higher melting and boiling temperatures than potassium.

b Sodium

c Silver

d Sodium and potassium are in group 1. Gold and silver are transition metals.

3 **a** Silver, copper, gold, aluminium

b availability, cost, malleability and ductility

4 Sodium belongs to the alkali metals which have relatively low melting and boiling points, relatively low density and are relatively soft. Iron is one of the transition metals, which have relatively high melting and boiling points, relatively high density and are relatively hard.

5 Tensile strength, cost, availability

3.2 Metallic bonding

WE 3.2.1 Its electronic configuration is $1s^22s^22p^63s^2$. Mg atoms will tend to lose the 2 valence (the $3s^2$) electrons to form a cation with a charge of 2+. The outer-shell electrons become delocalised and form the sea of delocalised electrons within the metal lattice. In an electric circuit, these delocalised electrons are able to move through the lattice towards a positively charged electrode.

1 **b** Strong electrostatic forces of attraction between Ca^{2+} ions and the delocalised valence electrons

2 Barium has a high melting temperature because there are strong attractive forces between the positive ions and the delocalised electrons. Barium conducts electricity because the delocalised electrons from the outer shell are free to move.

3 **a** Both graphite and metals are lustrous and conduct heat and electricity.

b Both graphite and metals must contain delocalised electrons.

3.3 Reactivity of metals

1 $2K(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2(g)$

2 **a** Metals react more energetically further down the group.

b Metal atoms further down the group have more electron shells which cause shielding of the valence electrons from the core charge, reducing the electronegativity and allowing more spontaneous reactions.

3 Zn > Fe > Au

4 Calcium is the highest in the series so most reactive.

3.4 Extraction of iron from its ore

1 **a** False **b** False **c** True **d** True **e** False

2 $Fe_3O_4(l) + 4CO(g) \rightarrow 3Fe(l) + 4CO_2(g)$
magnetite + carbon monoxide → iron + carbon dioxide

3 Carbon dioxide carbon + oxygen → carbon dioxide

4 Proximity to a coal mine.
Located away from residential populations, agriculture and conservation areas.
Have suitable accommodation and support for workers.
Access to transport networks such as ports or railways.

3.5 Modifying metals

1 **a** A 20-cent coin contains copper and nickel. High-carbon steel contains iron and carbon.

b The 20-cent coin is a substitutional alloy similar to Figure 3.5.3. High-carbon steel is an interstitial alloy, similar to Figure 3.5.2.

2 The metal in the hooks becomes work hardened and brittle.

3 **a** When aluminium is annealed, the crystal structure is changed to contain more large crystals. Larger crystals are more flexible and easier to shape than smaller crystals and the metal is less likely to break along crystal boundaries during shaping.

b Quenching causes the growth of small crystals. These crystals make the metal stiffer and do not allow the metal to deform as easily.

4 An alloy with properties appropriate to the task is selected. The metal is annealed to allow shaping of the chisel. The chisel is tempered to make the shaft flexible and strong. The tip of the chisel could then be hardened either by work hardening or local quenching.

3.6 Metallic nanomaterials

1 Gold nanoparticles are not large enough to have a 'sea' of delocalised electrons or a consistent surface to reflect light.

2 A is a nanoparticle. B is a nanowire. C is a nanorod. D is not a nanoparticle as all of its dimensions are above 100 nm.

3 iron + oxygen → iron oxide

Chapter 3 review

1 Mg, Ca, Sr

2 **a** Silver

b It is too expensive and tarnishes readily.

c Aluminium, copper (combined with stainless steel)

3 Electrical conductivity

4 **a** Low density

b High electrical conductivity

c High tensile strength

5 20 in Ca, 18 in Ca^{2+}

6 Al: $1s^22s^22p^63s^23p^1$; Al^{3+}: $1s^22s^22p^6$

7 It is able to be drawn into a wire.

8 **a** When a current is applied to the copper wire, the free-moving, delocalised electrons move from one end to the other and so the copper wire conducts electricity.

b The delocalised electrons in the metal spoon obtain energy from the boiling mixture and move more quickly. These electrons move freely throughout the spoon, colliding with other electrons and metal ions, transferring energy so that the spoon becomes warmer and, eventually, too hot to hold.

c A lot of energy is required to overcome the strong forces of attraction between the iron ions and the delocalised electrons in the metal lattice, so that the iron changes from a solid to a liquid.

d Because of the strong forces of attraction between them, the lead ions and the delocalised electrons form a closely packed three-dimensional structure. Also, the lead atom itself has a higher mass-to-volume ratio than the sulfur atom. This means that the density—the mass per volume—is high.

e As the copper is drawn out, the copper ions are forced apart and the delocalised electrons rearrange themselves around these ions and re-establish strong forces of attraction.

9 **a** **i** Valence electrons not restricted to a region between two atoms

ii A regular three-dimensional arrangement of a very large number of positive ions or cations

iii The electrostatic attraction between a lattice of cations and delocalised electrons

b Valence electrons

10 A metal wire contains an extended lattice of metal cations surrounded by a sea of delocalised electrons. The electrons are charged and free to move and so can conduct electricity.

11 The metal cations are in a regular three-dimensional arrangement and are surrounded by a mobile sea of delocalised electrons. This is shown in Figure 3.2.1.

12 **a** Any of the group 2 metals e.g. magnesium

b The transition metals

13 Aluminium

14 The bubbles contain hydrogen gas, which is produced when a reactive metal reacts with water.

15 The reaction on the left is more vigorous and the metal must be more reactive. Iron is a more reactive metal than silver and so iron must be on the left. Silver is less reactive than iron and so silver must be on the right.

16 Metal A is copper. Metal B is sodium. Metal C is aluminium.

17 **a** False **b** True **c** False **d** False **e** True

18 magnesium + oxygen → magnesium oxide

19 Iron reacts with water and oxygen to produce iron oxides found in ores.

20 **a** Rocks and minerals from which iron can be economically extracted

b Naturally occurring solid substances with a definite chemical composition, structure and chemical and physical properties

c The type of iron oxide that is most often found in iron ore. It has the formula Fe_2O_3.

d A compound containing iron and oxygen

21 **a** B, F **b** Coke **c** A mixture. **d** Limestone

22 Iron ore is the source of iron. Limestone is the source of calcium oxide. Coke is used to produce heat and carbon monoxide, which reacts with the iron oxides to form iron metal. Air is pumped in as a source of oxygen for the combustion of the coke.

23 calcium oxide + silica → calcium silicate

24 **a** Copper and nickel; harder, more corrosion resistant and a silver colour

b Tin and lead; lower melting temperature

c Gold, silver and copper; harder

d Iron, nickel and chromium; resists rusting, stronger

e Mercury and zinc (sometimes a little silver is added); harder, non-toxic

25 Needle 2 < needle 3 < needle 1

26 Steel is used instead of iron as this alloy is stronger, more flexible and resistant to corrosion. Heating the horseshoe changes the crystal structure. The final shaping and hammering is an example of work hardening, which aligns the crystals and increases strength.

27 Nanowire

28 8.34×10^{-7} m is 834 nm. No, it is too big.

29 The width of a nanowire is in the range of standard nanomaterials. This changes the properties of the metal atoms as they are not exposed to delocalised electrons in the same way as in bulk metals. The long length of a nanowire is not enough to give it electrons that behave in the same way as electrons in bulk metals.

30 **a** **i** Iron (steel) or aluminium

ii Iron and steel are strong. Aluminium has a low density (light) and can be easily coloured.

iii Iron rusts easily. Aluminium is soft and lacks strength.

b **i** Copper

ii It is a good conductor of electricity and is ductile.

c **i** Gold, silver and platinum

ii They are non-reactive, malleable and ductile, lustrous.

32 **a** Aluminium Al, copper Cu, gold Au, iron Fe, silver Ag

b Aluminium: period 3, group 13, p-block
Copper: period 4, 1st transition series, d-block
Gold: period 6, 3rd transition series, d-block
Iron: period 4, 1st transition series, d-block
Silver: period 5, 2nd transition series, d-block

c Gold and silver

d Copper, gold, iron and silver

e Gold

33 **a** The positive ions are arranged in a regular, three-dimensional lattice.

b Stress corrosion cracking can occur between the crystal grains.

34 **a** Na: group 1, period 3
K: group 1, period 4
Ca: group 2, period 4

b Na: $1s^2,2s^2,2p^6,3s^1$
K: $1s^2,2s^2,2p^6,3s^2,3p^6,4s^1$
Ca: $1s^2,2s^2,2p^6,3s^2,3p^6,4s^2$

c **i** The atoms of Na are smaller than those of K, so the delocalised valence electrons of Na are closer to the positive nuclear charge than those of K. The electrostatic forces of attraction between delocalised electrons and cations are stronger in Na, so Na requires more energy to overcome the metallic bonding to boil the metal.

ii Valence electrons are in the fourth shell in the atoms of both Ca and K. However, there are twice as many valence electrons in the atoms of Ca. Also, the charge on a calcium cation is +2 as opposed to +1 on the potassium cation. So the electrostatic forces of attraction between delocalised electrons and cations are stronger in Ca and so it requires more energy to overcome the metallic bonding to boil the metal.

35 Aluminium is extracted from its ore by electrolysis. There was no source of electricity available for this process until 1886.

Chapter 4 Ionic bonding

4.1 Properties and structures of ionic compounds

1 B

2 **a** The diagram shows that in solid sodium chloride, the sodium and chloride ions are held in fixed positions in the crystal lattice and are not free to move and conduct electricity.

b Molten sodium chloride contains sodium and chloride ions that are free to move and, therefore, it can conduct electricity.

3 Aluminium would lose 3 electrons to have a valence shell with 8 electrons and therefore become a cation (positive ion).

4 The negative ions are slightly further away from each other than they are from the positive ions in the lattice and the attractive force of the oppositely charged ions is greater than the repulsive force of two positively charged or two negatively charged ions near each other.

4.2 Using the ionic bonding model to explain properties

1 The electrostatic forces of attraction between the positive and negative ions holding the lattice together are very strong and a lot of energy is required to break them apart.

2 a When hit with a hammer or hard object, the ions move within the lattice so that like-charged ions line up adjacent to each other.

b When like-charged particles are near each other they repel due to electrostatic repulsion and this causes the ionic compound to shatter.

3 In solid form the ionic compound forms a crystal lattice. This is a very strong structure as the strong electrostatic forces of attraction between the positively charged cations and negatively charged anions means that the ions are not free to move. When heated so the ionic compound is now molten, the charged particles are free to move and so are able to conduct electricity.

4 Salad; salami; saline; expressions such as 'salt of the Earth', 'take with a pinch of salt', 'worth one's salt'; and superstitions, such as throwing salt over one's shoulder to keep away evil spirits.

4.3 Formation of ionic compounds

WE 4.3.1 $3Ca\ (2,8,8,2) + 2P\ (2,8,5) \rightarrow 3Ca^{2+}\ (2,8,8) + 2P^{3-}\ (2,8,8)$

1 Cations: calcium, aluminium. Anions: nitrogen, fluorine and phosphorus. Metals form cations and non-metals form anions. Metals have low electronegativities and so it is easier for metals to lose electrons than it is for non-metals.

3 Group 2 metals have two electrons in their valence shell. They lose these two electrons and therefore become positively charged, as they still have the original number of protons. Cations are ions with a positive charge.

4 Because an atom of K has one more electron than an atom of a noble gas and an atom of Cl has one less, in a reaction one K atom can donate one electron to one Cl atom to give K^+ and Cl^-, both of which have the electronic configuration of the noble gas argon. The formula of this compound is, therefore, KCl.
A Ca atom will lose two electrons to gain a noble gas configuration. Because each Cl atom will gain only one electron, there will be two chlorine atoms for each Ca atom. This reaction will therefore produce Ca^{2+} ions and Cl^- ions. The formula of the compound is, therefore, $CaCl_2$.

5 a $Na\ (2,8,1) + Cl\ (2,8,7) \rightarrow Na^+\ (2,8) + Cl^-\ (2,8,8)$

b $Mg\ (2,8,2) + O\ (2,6) \rightarrow Mg^{2+}\ (2,8) + O^{2-}\ (2,8)$

c $2Al\ (2,8,3) + 3S\ (2,8,6) \rightarrow 2Al^{3+}\ (2,8) + 3S^{2-}\ (2,8,8)$

4.4 Chemical formulas of simple ionic compounds

WE 4.4.1 BaF_2

1 B

2 a 2:1 **b** 1:3 **c** 3:2 **d** 1:1 **e** 1:2

3 a NaCl **b** KBr **c** $ZnCl_2$ **d** K_2O **e** $BaBr_2$
f Al_2I_3 **g** AgBr **h** ZnO **i** BaO **j** Al_2S_3

4 a Potassium chloride **b** Calcium oxide
c Magnesium sulfide **d** Potassium oxide
e Sodium fluoride

4.5 Writing formulas of more complex ionic compounds

1 a Na_2CO_3 **b** $Ba(NO_3)_2$ **c** $Al(NO_3)_3$ **d** $Ca(OH)_2$
e $ZnSO_4$ **f** KOH **g** KNO_3 **h** $ZnCO_3$ **i** K_2SO_4
j $Ba(OH)_2$

2 a CuCl **b** Fe_2O_3 **c** CuO **d** $Cr_2(SO_4)_3$
e FeO **f** $Pb(NO_3)_2$ **g** PbO_2 **h** $Sn(NO_3)_2$

3 a Magnesium hydroxide **b** Sodium carbonate
c Iron(II) sulfate **d** Copper(II) sulfate
e Barium nitrate **f** Copper(I) sulfate
g Iron(III) sulfate **h** Ammonium nitrate
i Disodium hydrogen phosphate

Chapter 4 review

1 a Assemble equipment to test conductivity. Add a globe to the circuit. When the electrodes are touching the solid magnesium chloride, the globe will not light up.

b Using the same equipment with molten sodium chloride, the globe will glow. Care is needed, as sodium chloride melts at 801°C.

c If a crystal of sodium chloride was hit firmly with a hammer, it would shatter. Again, care is needed—safety glasses must be worn.

2 a Both **b** Both **c** Both
d Ionic lattices only **e** Both

3 Top left: Non-metals; gain
Top right: Metals; lose
Bottom left: ionic compound
Bottom right: ionic bonding

4 a The electrostatic forces of attraction between the positive and negative ions are strong and will be overcome only at high temperatures.

b The strong electrostatic forces of attraction between the ions mean that a strong force is needed to break up the lattice, giving the ionic crystals the property of hardness. However, the crystal lattice will shatter when a strong force is applied, suddenly causing ions of like charge to become adjacent to each other and be repelled.

c In the solid state, the ions are not free to move. However, when the solid melts or dissolves in water, the ions are free to move and conduct electricity.

5 a Na^+, Cl^-; Mg^{2+}, O^{2-} **b** MgO

c The strength of electrostatic attraction between ions will depend on the size of the ions and on their charge. The Mg^{2+} ion is slightly smaller than the Na^+ ion, and the O^{2-} ion is much smaller than the Cl^- ion. More importantly, the Mg^{2+} ion and the O^{2-} ions each have twice the charge of the Na^+ ion and the Cl^- ion. The attraction between the ions in MgO is therefore much stronger than in NaCl. Magnesium oxide therefore has a much higher melting temperature.

6 The strength of the forces remains unchanged, but the kinetic energy of the ions increases until the forces can no longer hold the ions in the solid lattice, and the lattice breaks up as the solid melts.

7 a Solid ionic compounds do not conduct electricity.

b Ionic compounds are hard.

c In solution ionic compounds conduct electricity.

9 a 2,8 **b** 2,8 **c** 2,8 **d** 2,8

10 b CD_3 **c** EF **d** G_3H **e** KL

11 a $MgCl_2$ or MgF_2 **b** NaCl or CaS **c** Na_2O or K_2S
d Na_3N or Li_3N **e** $AlCl_3$ or AF_3 **f** Mg_3N_2

12 They have seven electrons in their outer shell so only need to gain one electron to satisfy the octet rule. This means they become more negative by gaining one electron.

13 a $Mg\ (2,8,2) + 2Cl\ (2,8,7) \rightarrow Mg^{2+}\ (2,8) + 2Cl^-\ (2,8,8)$

b $2Al\ (2,8,3) + 3O\ (2,6) \rightarrow 2Al^{3+}\ (2,8) + 3O^{2-}\ (2,8)$

14 a KBr **b** MgI_2 **c** CaO **d** AlF_3 **e** Ca_3N_2

15 a CuCl **b** Ag_2O **c** Li_3N **d** KI

16 They represent the ratio of metal to non-metal ions in the ionic compound.

17 a i −3 **ii** +1 **iii** −2
b i Y_2SO_4 **ii** K_2Z **iii** Y_3X **iv** Y_2Z

18 a $CuNO_3$ **b** CrF_2 **c** K_2CO_3 **d** $Mg(HCO_3)_2$ **e** $Ni_3(PO_4)_2$

19 a Ammonium carbonate **b** Copper(II) nitrate
c Chromium(III) bromide

20 a Agree. In a metallic lattice, the positive ions are surrounded by delocalised electrons; in an ionic lattice, negative ions alternate with the positive ions.

b Agree. In a metallic lattice, each positive ion attracts the delocalised electrons in its region, and each delocalised electron is attracted to all neighbouring positive ions. In an ionic lattice, each positive ion is attracted to the negative ions that surround it, and vice versa.

c Agree. In a metallic solid, there will be repulsion between the positive ions, and between the delocalised electrons. The particles are arranged to minimise these repulsions.
In an ionic lattice, the arrangement of alternating positive and negative ions also minimises repulsion between like charges.

d Agree. The energy required to remove the outer electron(s) is known as the ionisation energy, with each electron removed having a specific ionisation energy.

e Disagree. In a metal, delocalised electrons are free to move so it conducts electricity; in an ionic solid, the ions are not free to move so it does not conduct electricity.

Chapter 5 Quantifying atoms and molecules

5.1 Masses of particles

WE 5.1.1 $A_r(B) = 10.81$ **WE 5.1.2** 28%, 22%, 50%

WE 5.1.3 70.5%, 29.5% **WE 5.1.4** $M_r = 63.0$

WE 5.1.5 Relative formula mass = 187.5

1 B

2 **a** $A_r(O) = 15.999$ **b** $A_r(Ag) = 107.9$ **c** $A_r(H) = 1.008$

3 8%

4 **a** 51%; 11%; 17%; 17%; 4% **b** 91

5 **a** $M_r = 98.1$ **b** $M_r = 17.0$ **c** $M_r = 30.0$

6 **a** $M_r = 74.6$ **b** $M_r = 106.0$ **c** $M_r = 342.3$

5.2 Introducing the mole

WE 5.2.1 9.6×10^{23} molecules **WE 5.2.2** 8.4×10^{23} atoms

WE 5.2.3 0.0013 mol **WE 5.2.4** 1.5 mol

1 Number of particles = amount (mol) × N_A

a $N(Na) = 1.2 \times 10^{24}$ atoms

b $N(N_2) = 6.02 \times 10^{22}$ molecules

c $N(C) = 1.20 \times 10^{25}$ atoms

d $N(H_2O) = 2.5 \times 10^{24}$ molecules

e $N(Fe) = 6.02 \times 10^{21}$ atoms

f $N(CO_2) = 2.78 \times 10^{19}$ molecules

2 **a** 0.5 mol **b** 0.25 mol **c** 70 mol **d** 70 mol

3 **a** 1.7×10^{-4} mol **b** 1.7×10^{-4} mol **c** 1.7×10^{-4} mol

4 **a** 0.8 mol **b** 4.8 mol **c** 0.72 mol **d** 6.0 mol

5.3 Molar mass

WE 5.3.1 496 g **WE 5.3.2** 7.4×10^{21} molecules

1 **a** 28.0 **b** 17.0 **c** 98.1 **d** 241.8

e 60.0 **f** 32.1 **g** 176.0 **h** 249.6

2 **a** 23.0 g **b** 64.0 g **c** 1.60 g **d** 25.5 g

3 **a** 5 mol **b** 2.5 mol **c** 0.10 mol **d** 0.025 mol

e 0.0031 mol **f** 0.0063 mol

g 9.7×10^{-6} mol **h** 3.9×10^{-5} mol

4 **a** 6.0×10^{23} atoms **b** 6.0×10^{22} atoms

c 6.0×10^{21} atoms **d** 3.1×10^{22} atoms

5 **a** **i** 3.0×10^{23} molecules **ii** 6.0×10^{22} molecules

b 6.0×10^{22} atoms **c** 4.07×10^{25} atoms

5.4 Percentage composition and empirical formulas

WE 5.4.1 35.0% **WE 5.4.2** $MgCl_2$ **WE 5.4.3** C_4H_{10}

1 **a** 69.9% **b** 84.8% **c** 26.2% **d** 51.2%

2 **a** HCl **b** CO **c** MgO **d** CH_4

3 **a** C_6H_6 **b** H_2O_2 **c** $C_3H_6O_3$ **d** NO_2 **e** $C_{11}H_{22}$

4 **a** CH_2 **b** C_5H_{10}

5 **a** CH_2O **b** $C_6H_{12}O_6$

Chapter 5 review

1 The relative atomic mass of carbon is the weighted average of the isotopic masses of all carbon isotopes (i.e. ^{12}C, ^{13}C and ^{14}C). Small amounts of ^{13}C and ^{14}C make this average slightly greater than 12, the relative isotopic mass of the ^{12}C isotope.

2 106.4

3 **a** $A_r(Ar) = 39.96$; $A_r(K) = 39.11$

b Although potassium atoms have one more proton than argon atoms, the most abundant isotope of argon has 22 neutrons, giving it a relative atomic mass close to 40. The most abundant isotope of potassium has only 20 neutrons, giving it a relative atomic mass close to 39.

4 **a** 2.2%, 88.9%, 7.4%, 1.5% **b** 52

5 48.0%, 52.0%.

6 **a** 61.5% **b** 20.2%

7 **a** $M_r(H_2O) = 18$ **b** $M_r(P_4) = 124$ **c** $M_r(CO) = 28$

8 **a** 225.2 **b** 171.3 **c** 297.6

9 It is useful to remember the formula $n = \frac{m}{M}$, where m is the mass in grams, n the amount of substance in mol, and M the molar mass. Remember also that the number of particles in 1 mol, Avogadro's number, $N_A = 6.02 \times 10^{23}$.
Use the formula: $n = \frac{\text{number of particles}}{N_A}$. Use a periodic table to work out the molar masses.

a 0.75 mol **b** 15.0 mol

c 3.8×10^4 mol **d** 1.7×10^{-24} mol

10 **a** **i** 8.73×10^{23} molecules **ii** 3.49×10^{24} atoms

b **i** 3.47×10^{23} molecules **ii** 1.04×10^{24} atoms

c **i** 9.21×10^{21} molecules **ii** 4.61×10^{22} atoms

d **i** 1.5×10^{24} molecules **ii** 6.8×10^{25} atoms

11 The molar mass, M, has the same numerical value as the relative molecular mass, M_r, but, M, is the actual mass of one mole and so has the unit g mol^{-1}.

12 **a** 55.8 g mol^{-1} **b** 98 g mol^{-1}

c 62 g mol^{-1} **d** 189.4 g mol^{-1}

e 75.0 g mol^{-1} **f** 342 g mol^{-1}

g 270 g mol^{-1}

13 It is useful to remember the formula $m = nM$, where m is the mass in grams, n the amount of substance in mol, and M the molar mass.

a 1.8 g **b** 58 g **c** 0.41 g **d** 389 g

14 **a** 0.10 mol **b** 0.0389 mol

c 1.25 mol **d** 0.00167 mol

e 3.4×10^4 mol

15 **a** Mass of one atom = $\frac{\text{mass of 1 mole}}{\text{number of particles in a mole}} = \frac{\text{molar mass}}{N_A}$

Mass of one calcium atom = $\frac{40.1}{6.0 \times 10^{23}} = 6.67 \times 10^{-23}$ g

b Mass of one water molecule = $\frac{18}{6.0 \times 10^{23}} = 3.0 \times 10^{-23}$ g

c Mass of one CO_2 molecule = $\frac{44}{6.0 \times 10^{23}} = 7.3 \times 10^{-23}$ g

16 **a** **i** 0.034 mol

ii 2.04×10^{22} molecules

iii 8.2×10^{22} atoms

b **i** 0.292 mol

ii 1.75×10^{23} molecules

iii 1.41×10^{24} atoms

c **i** 0.0088 mol

ii 5.3×10^{21} molecules

iii 1.1×10^{22} atoms

d **i** 1.22×10^{-4} mol

ii 7.3×10^{19} molecules

iii 1.8×10^{21} atoms

17 62.0 g

18 It is useful to remember the formula $n = \frac{m}{M}$, where m is the mass in grams, n the amount of substance in mol, and M the molar mass in g mol^{-1}. Use the periodic table to work out the molar masses.

a **i** $n(NaCl) = 0.100$ mol

ii $n(Na^+) = 0.100$ mol

$n(Cl^-) = 0.100$ mol

b **i** $n(CaCl_2) = 0.405$ mol

ii $n(Ca^{2+}) = 0.405$ mol

$n(Cl^-) = 0.81$ mol

c $n(Fe_2(SO_4)_3) = 0.00420$ mol

$n(Fe^{3+}) = 0.00840$ mol

$n(SO_4^{\;2-}) = 0.0126$ mol

19 **a** 144 g mol^{-1} **b** 100 g mol^{-1}

20 **a** 40 g mol^{-1} **b** 98 g mol^{-1} **c** 44 g mol^{-1} **d** 106 g mol^{-1}

21 B Iron

22 **a** 1.25×10^4 g mol^{-1} **b** 1.6×10^{-7} mol
c 9.6×10^{16} molecules

23 $$\text{Percentage by mass of an element} = \frac{\text{mass of 1 element in mol of compound}}{\text{mass of 1 mol of the compound}} \times 100$$

Use a periodic table to work out the molar masses. A useful check of these answers is provided by seeing that they add up to 100%, or somewhere close to that value.

a $M(\text{Al}) = 27$ g mol^{-1}, $M(\text{O}) = 16$ g mol^{-1}, $M(Al_2O_3) = 102$ g mol^{-1}
%(Al) = 52.9%; %(O) = 47.1%

b Cu 65.1%; O 32.8 %; H 2.1 %

c %(Mg)= 12.0% %(Cl) = 34.9%; %(H) = 5.9%; %(O) = 47.2%

d Fe 27.9%; S 24;1%; O 48.0%

e H 1.0%; Cl 35.3%; O 63.7%

24 **a** 93.8% **b** 40% **c** 19.9% **d** 60.0%

25 The empirical formula provides the simplest whole-number ratio of atoms in a compound. The number of moles of each atom is found by using $n = \frac{m}{M}$, where *m* is the mass in grams and *M* is the molar mass.

a CO **b** CO_2 **c** C_2H_4O **d** $Fe_2(SO_4)_3$ **e** C_6H_5Cl **f** C_7H_{16}

26 $C_2H_5NO_2$ **27** WS_2

28 **a** C_2H_6O **b** C_2H_6O **29** P_2O_5

30 C_3H_4 **31** 58.9 g mol^{-1}

32 184.2 g mol^{-1} **33** 31.0 g mol^{-1}

34 **a** C_2H_5; C_4H_{10} **b** P_4O_{10} **c** $C_6H_{12}O_6$ **d** $H_2S_2O_7$

35 **a** The relative isotopic mass of an isotope is the mass of an atom of that isotope relative to the mass of an atom of ^{12}C, taken as 12 units exactly.

b The relative atomic mass of an element is the weighted average of the relative masses of the isotopes of the element on the ^{12}C scale.

c The relative molecular mass (M_r) of a compound is the mass of one molecule of that substance relative to the mass of a ^{12}C atom, which is 12 exactly. For example, the relative molecular mass of carbon dioxide is 44.0.

d Relative formula mass is calculated by taking the sum of the relative atomic masses of the elements in the formula.

e The molar mass of an element is the mass of one mole of the element. It is equal to the relative atomic mass of the element expressed in grams.

36 **a** $C_4H_5N_2O$ **b** 194 g mol^{-1} **c** $C_8H_{10}N_4O_2$
d 5.15×10^{-3} mol **e** 3.10×10^{21} molecules
f 7.44×10^{24} atoms

37 **a** D, F, E, A, C, B

b

	Metal	Oxygen
Mass (g)	0.542	0.216
Relative atomic mass	40.1	16.0
Moles	0.0135 mol	0.0135 mol
Ratio	1	1

c Calcium

Unit 1 Area of Study 1 How can knowledge of elements explain the properties of matter?

Multiple-choice questions

1 D **2** C **3** B **4** C **5** D **6** D **7** D
8 C **9** C **10** B **11** B **12** B **13** A **14** A
15 C **16** B **17** A **18** A **19** A **20** B

Short-answer questions

21 **a** K_3PO_4 **b** Al_2O_3 **c** $NaNO_3$ **d** Fe_2S_3

22 **a** Calcium nitrate **b** Copper(II) carbonate
c Magnesium hydroxide **d** Chromium(III) oxide

23 **a** E.g. NaCl preserving food, $NaHCO_3$ as baking soda, NaF in toothpaste to harden tooth enamel

b **i** Charged but fixed particles present, so cannot move to carry a current.

ii If a strong force is applied to a crystal of the compound, the layers of ions will move relative to one another, causing ions of like charge to be adjacent and hence repel. The crystal thus shatters.

iii A large amount of energy is needed to overcome the electrostatic attraction between oppositely charged ions.

24 **a** Mass spectrometer **b** 192.2

25 **a** E.g.: aluminium is extracted by electrolysis of molten alumina; uge amounts of electricity are required.

b **i** Harder and more brittle
ii Harder
iii Softer and more ductile

c Quenching is heating the metal to a moderate temperature and then cooling very quickly. Tempering involves first quenching a metal and then heating it again to a lower temperature.

d In annealing, larger crystals forms and in quenching tiny crystals form.

26 **a** $1s^22s^22p^63s^2$

b **i** 0.160 nm

ii Larger radius as there are fewer protons in the nucleus and so the attraction for the outer-shell electrons would be weaker, pulling them less strongly toward the nucleus.

c **i** Lattice of positively charged magnesium ions surrounded by a ‘sea’ of valence electrons. Lattice is held together by the electrostatic attraction between electrons and cations.

ii The electrons are not localised/are free to move and so can conduct an electric current.

iii The model cannot explain the differences in melting points/densities/electrical conductivities/magnetism between metals (for any one answer).

d **i** Observations: bubbles of gas evolved or increase in temperature.
$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$
or $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$

ii Any suitable example such as K, Na, Ca.

e They have an incomplete d-subshell of electrons.

f A substance formed when other materials, usually carbon or other metals, are mixed with a metal. Alloying increases the hardness of a metal.

27 **a** Bohr proposed that electrons can only move in fixed orbits or shells of particular energy and could only jump from one orbit to another without stopping in between; thus, only certain energies can be emitted or absorbed.

b It does not explain why electrons move in circular orbits or why shells have particular energies. Mathematical model does not hold well for larger atoms.

c Electrons behave as waves around the nucleus. There are no definite orbits, instead electrons are thought to move in regions of space called orbitals. Electron shells can be further divided into subshells.

28 **b** An excited atom because the 3d subshell is a higher energy subshell than 4s, which should be filled first.

29 **a** **i** Ca **ii** Ar **iii** C **iv** Na or Mg
v Li **vi** N **vii** F

b Chemical reactivity increases because the outer-shell electrons are further from the nucleus and so are more readily released in a reaction.

30 **a** The total number of protons and neutrons in an atom

b The total number of protons in an atom

c The mass of an atom of the isotope relative to the mass of an atom of ^{12}C taken as 12 units exactly

d 6.02×10^{23}, which is the number of particles in a mole

e An atom, or a group of atoms, that has either gained or lost one or more electrons and so carries a charge

31 **a** Chlorine is further to the right on the periodic table than sodium. Atomic radius decreases across a period because increasing core charge pulls outer-shell electrons more tightly to the nucleus causing volume of atom to decrease.

b Fluorine is further to the right on the periodic table than lithium and core charge increases from left to right across the periodic table. As core charge increases, the electrons are held more tightly to the nucleus and more energy is required to remove the first one.

c Ba and Be are in the same group with Be higher than Ba. Going down a group the atom size is increasing, so outer electron of Be is held more tightly and is less readily released.

d The s-block elements have an s-subshell as their outer occupied electron subshell. It can take 1 or 2 electrons, so block is only 2 groups wide.

32 **a** 0.143 mol **b** 0.430 mol
c 1.12×10^{24} atoms **d** 67.6%

33 **a** CuO
b Ratio of Cu to O would be greater, so the mass of Cu extracted would be greater.

34 **a** 39.1 g mol^{-1} **b** Potassium

35 42.5 g

Chapter 6 Materials made of molecules

6.1 Properties of non-metallic substances

1 Non-metallic elements: H_2 and Br_2 as they consist of only one type of atom. Non-metallic compounds: NO_2 as it consists of more than one type of atom (nitrogen and oxygen).

2 A molecule is a discrete group of atoms of known formula, bonded together.

3 **a** They do not do not contain free-moving charged particles.
b They have weak intermolecular bonds between molecules.

4 **a** True **b** False **c** True **d** False

5 When sugar turns to a liquid, it is melting; the intermolecular bonds are broken. When the liquid turns black and a gas is produced, the intramolecular bonds are broken, allowing new substances to be produced.

6.2 Covalent bonding

1 **a** 1 **b** 3 **c** 2 **d** 1

3 **a** 1 **b** 2 **c** 3 **d** 4 **e** 1 **f** 0

4 Two outer-shell electrons form two single or double bond with suitable non-metal atoms. As the outer shell is now complete, the remaining four electrons are arranged as two lone pairs around the oxygen atom.

5 **a** CCl_4 **b** NBr_3 **c** SiO_2 **d** HF **e** PF_3

6 **a** Ball-and-stick model **b** Electron dot diagram
c Space-filling model

Chapter 6 review

1 The intermolecular bonds must be relatively weak.

2 They do not conduct electricity.

3 Intramolecular bonds hold the atoms within a molecule together. Intermolecular bonds are the forces between molecules. These bonds that are broken when carbon dioxide sublimes.

4 **a** Space-filling model **b** Valence structure
c Ball-and-stick model **d** Electron dot diagram

5 D

6 **a** 6 **b** 3 **c** 4

7 B **8** XY_2

9 Neon will not form bonds to other atoms as it has a stable outer shell.

10 **a** 0 **b** 1 **c** 3 **d** 4

11 **a** 2 bonding electrons, 6 non-bonding electrons
b 4 bonding electrons, 4 non-bonding electrons
c 8 bonding electrons, 24 non-bonding electrons
d 14 bonding electrons, 0 non-bonding electrons.
e 6 bonding electrons, 20 non-bonding electrons
f 4 bonding electrons, 16 non-bonding electrons
g 8 bonding electrons
h 4 bonding electrons, 4 non-bonding electrons

12 **a** All involve the sharing of electron pairs between two atoms.
b They differ in the number of electron pairs shared: one pair (fluorine), two pairs (oxygen) and three pairs (nitrogen).

13 **b** In single bonds there are two electrons are shared between the atoms. In double bonds there are four electrons, so net attraction is stronger and more energy is needed to break the double bond.
c Oxygen needs only two electrons to complete its outer shell and so forms two single covalent bonds or a double bond with another non-metal.

14 Metallic: Ag, Cu; ionic: $CuCl_2$, CaS; molecular: NH_3, HCL, H_2O

15 **a** True **b** True **c** False
d True **e** False **f** True

Chapter 7 Intermolecular forces

7.1 Shapes of molecules

WE 7.1.1 V-shaped

1 The VSEPR theory is based on the principle that negatively charged electron pairs in the outer shell of an atom repel each other and so are arranged as far away from each other as possible.

2 4 pairs

4 **a** V-shaped **b** Linear **c** Tetrahedral
d Pyramidal **e** Linear

5 **a** Tetrahedral **b** Pyramidal **c** V-shaped

7.2 Properties of covalent molecular substances

WE 7.2.1 HCl is more polar than NO.

1 **a** O **b** C **c** N
d N **e** F **f** F

2 **a** P–F **b** C–H

3 H–N, C–N, S–N, O–N, N–N

5 **a** Polar **b** Polar **c** Polar
d Polar **e** Non-polar

7.3 Types of intermolecular forces

1 HCl, CH_3Cl **2** C

3 Dipole–dipole forces: a to h; hydrogen bonds: a, g, h

6 **a** Dispersion forces
b Dispersion forces and hydrogen bonding
c Dispersion and dipole-dipole forces
d Dispersion forces and hydrogen bonding
e Dispersion forces

Chapter 7 review

1 PCl_3 – pyramidal, HOCl – V-shaped, $CHCl_3$ – tetrahedral, HF – linear

2 V-shaped **3** 4 bonding electrons

4 **a** Tetrahedral **b** Pyramidal **c** Tetrahedral
d V-shaped **e** Pyramidal

5 **a** Non-polar **b** Polar **c** Non-polar
d Polar **e** Non-polar **f** Non-polar

6 The O–H bond in water is the most polar bond.

7 **a** Non-polar **b** Polar **c** Non-polar
d Polar **e** Polar

8 Si–O, H–Br, N–O, O–Cl, F–F

9 **a** SO_3 **i** non-polar **ii** dispersion forces
b $SiCl_4$ **i** non-polar **ii** dispersion forces
c CF_4 **i** non-polar **ii** dispersion forces
d NF_3 **i** polar **ii** dipole–dipole attraction
e CH_3NH_2 **i** polar **ii** hydrogen bonding

10 A and C

11 Melting temperatures increase as the molecules increase in mass, size and number of electrons, and strength of the dispersion forces increases.

12 Higher boiling temperature indicates that forces between molecules are stronger in CF_4.

13 Neon: single atoms with very few electrons, weak dispersion forces
Hydrogen fluoride: polar molecules held together by electrostatic attraction between permanent dipoles and hydrogen bonds, which are strong intermolecular bonds and so HF has a much higher boiling temperature than Ne.

14 **a** CCl_4
b Both are non-polar and held together only by dispersion forces. CCl_4 is larger and has more electrons, and so has stronger dispersion forces. Hence it takes more energy to vaporise CCl_4.

15 Dispersion forces are much stronger in iodine than in fluorine.

16 A permanent dipole is formed if there is a difference in electronegativity between the two atoms that form a bond.
A temporary dipole is caused by random fluctuations in the electron distributions around the molecule.

17 **a** **i** N_2 **ii** O_2 **iii** CO_2
b **i** NH_3, HCl, H_2O, $CHCl_3$ **ii** N_2, Cl_2, O_2, CH_4, CO_2, CCl_4
iii NH_3, H_2O

18 If water was a linear molecule, the polarity of the two O–H bonds would cancel each other out and make the molecule non-polar. As water is polar, it cannot be a linear molecule.

19 Intermolecular bonds in covalent molecular substances are much weaker (100 times) than the chemical bonds holding the atoms together in ionic and metallic substances, and so require much less heat energy to break.

Chapter 8 Carbon lattices and carbon nanomaterials

8.1 Carbon lattices

1 Carbon atoms can form four covalent bonds—single, double or triple bonds—and can bond to each other.

2 **a** To turn from a solid directly into a gas.
b They contain extended networks of strong covalent bonds that must be overcome to allow the material to sublime.

3 **a** Diamond is hard because it has strong covalent bonds throughout the lattice.
Graphite is soft because there are weak dispersion forces between the layers, which can slide over each other easily.
b Diamond is a non-conductor of electricity because its electrons are localised in covalent bonds and are not free to move. Graphite conducts electricity because it has delocalised electrons between its layers of carbon atoms.

4 **a** Weak dispersion forces between its layers means the layers slide over each other easily and so reduce friction between moving parts.
b Strong covalent bonding throughout the lattice means the carbon atoms are fixed in place, making diamond very hard.

8.2 Carbon nanomaterials

1 Similar: are allotropes of carbon in which each carbon atom has bonds to 3 other carbon atoms; conduct electricity and heat. Different: are nanomaterials and so have different physical properties.

2 Each carbon atom is covalently bonded to 3 other carbon atom and has one free electron that is shared between the other carbon atoms in the sphere. The structure consists of hexagonal and pentagonal rings of atoms.

3 Each carbon atom is covalently bonded to 3 other carbon atoms and has one free electron that is shared with the other carbon atoms in the sheet. The structure consists of hexagonal rings of atoms. The sheet is one atom thick but may be of any length and width.

4 A space elevator would require an extremely strong, long and uniform cable. Nanotubes are immensely strong for their mass and can be produced in any length.

Chapter 8 review

1 Carbon exists in different forms with different arrangements of atoms.

2 Refer to Figure 8.1.8.

3 Coloured contaminants may form dispersion forces with the surface of charcoal and are trapped in its internal pores.

4 Its extended three-dimensional network of strong covalent bonds must be overcome for sublimation to occur.

5 **a** Methane: strong, covalent intramolecular bonds, very weak intermolecular bonds. Diamond: strong covalent bonds throughout its lattice structure.
b Methane: weak intermolecular forces and so low boiling and melting points. Diamond: extremely hard, does not exist as a liquid and has a very high sublimation point.

6 Diamond: tetrahedral bond geometry. Graphene: trigonal planar bond geometry.

7 Strong covalent bonding between atoms in each layer

8 A cylinder of graphene with half a buckyball on each end

9

Allotrope name	Diamond	Graphite	Carbon nanotube	Graphene
Bonding feature	Each carbon is bonded to 4 others in a network lattice structure	Each carbon is bonded to 3 others in a layered structure	Each carbon is bonded to 3 others in a cylindrical shape	Each carbon is bonded to 3 others in a layer one atom thick
Properties	Hard, brittle	Conducts electricity, soft	Very strong, conducts electricity	Very strong, conducts electricity

10 The common structural feature of graphene and graphite is their layered structure. Both contain layers of carbon atoms with each carbon bonded to three neighbouring atoms, with three covalent bonds. Each carbon atom still has another valence electron that is delocalised in the layer, explaining the electrical conductivity of both allotropes. The bonding between the atoms in the layer is strong. Graphene is just a single layer but graphite contains layer upon layer.
This gives rise to the different properties of graphite and graphene. Graphene is very strong. There are dispersion forces between layers in graphite, allowing the layers to slide past each other. Graphite can therefore act as a lubricant. Both allotropes have a high sublimation point.

11 **a** Conductor must contain charged particles that are free to move.
b Conductive: graphite, graphene and nanotubes. Non-conductive: diamond.

Chapter 9 Organic compounds

9.1 Crude oil as a source of new materials

WE 9.1.1 3-Methylpentane

1 A, D

2 **a** CH_4
b It is a compound of carbon and hydrogen.
c Carbon atoms need four electrons and hydrogen atoms one electron to complete their outer shells. Four hydrogen atoms provide the four electrons required by each carbon atom.
d A tetrahedral arrangement of four hydrogen atoms around the central carbon atom gives minimum electrostatic repulsion between the four pairs of bonding electrons.

3 **a** Propane
b $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$
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

9.2 Unsaturated hydrocarbons

WE 9.2.1 2,3-Dimethylbut-1-ene

1 Ethene (C_2H_4), propene (C_3H_6), methylpropene (C_4H_8), pentene (C_5H_{10}), octene (C_8H_{16})

2 **a** 4 **b** 8 **c** Butene (C_4H_8)
3 B
4 **a** 5 **b** 8 **c** Pentyne
5 **a** Hept-3-ene **b** Hex-3-yne
c 2,3-Dimethylbut-2-ene.

9.3 Alcohols

WE 9.3.1 Propan-2-ol
WE 9.3.2 2,4-Dimethylpent-3-ol
1 C **2** C
3 CH_3OH, C_4H_9OH, $C_5H_{11}OH$
4 **a** Butan-2-ol **b** 3-Methylheptan-2-ol
c 2,3-Dimethylhexan-1-ol
6 **a** Butan-1-ol **b** 2-Methylheptan-3-ol
c 2,3-Dimethylbutan-2-ol

9.4 Carboxylic acids

WE 9.4.1 5-Methylhexanoic acid
1 D **2** A
3 **a** $CH_3CH_2CH_2COOH$
b $(CH_3)_2CHCOOH$
c $CH_3CH_2CH(CH_3)CH(CH_3)COOH$
d $(CH_3)_3CHCH_2COOH$
4 **a** Propanoic acid **b** 2-Methylbutanoic acid
c 2-Ethylhexanoic acid **d** 3,4-Dimethylpentanoic acid

9.5 Esters

WE 9.5.1 Methyl butanoate
1 C **2** C
3 **a** 2 **b** 5 **c** 4 **d** 9 **e** 7
4 **a** CH_3COOCH_3 **b** $CH_3CH_2COOCH_2CH_3$
c $CH_3COOCH_2CH_3$ **d** $CH_3CH_2CH_2COOCH_2CH_2CH_3$
5 **a** Methylpropanoate **b** Ethylpropanoate
c Butylethanoate **d** Butylbutanoate

9.6 Determining the formulas of organic compounds

WE 9.6.1 C = 64.9%, H = 13.5%, O = 21.6%
WE 9.6.2 CH_2O **WE 9.6.3** C_6H_6
1 D
2 C = 76.6%, H = 6.4%, O = 17%
3 **a** Carbon = 60.0 g; oxygen = 26.7 g;
hydrogen = 100.0 – 60.0 – 26.7 = 13.3 g
b C = 5.00 mol, H = 1.67 mol, O = 13.3 mol
c C = 2.99, H = 7.96, O = 1.00
d C : O : H = 3 : 1 : 8 **e** C_3H_8O
4 $C_6H_{14}O_6$

Chapter 9 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. There can also be double and triple bonds between carbon atoms as well as ring structures.
2 A
3 **a** Alkanes **b** $C_{17}H_{36}$ **c** $C_{15}H_{32}$ **d** 234 g
4 **a** $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
b $2C_6H_{14}(l) + 19O_2(g) \rightarrow 12CO_2(g) + 14H_2O(g)$
c $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$
d $C_{31}H_{64}(s) + 47O_2(g) \rightarrow 31CO_2(g) + 32H_2O(g)$
5 **a** Ethane **b** Methylpropane
c 3-methylpentane **d** Pentane
6 **a** Alkane **b** Alkene **c** Alkane **d** Alkyne
e Alkene **f** Alkane **g** Alkyne
7 But-1-ene
But-2-ene
Methylpropene
8 **a** Hex-2-ene
b 3,4-Dimethylpent-1-yne
c 4-Methylhex-2-yne
9 **a** $2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l)$
b $C_3H_6(g) + Br_2(org) \rightarrow C_3H_6Br_2(org)$
c $C_4H_8(g) + H_2O(l) \rightarrow C_4H_9OH(l)$
d $C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(l)$
10 hydroxyl; polar; hydrogen; intermolecular; small
11 **a** True **b** True **c** False
12 Alcohols contain a hydroxyl group and so can form intermolecular hydrogen bonds, which are stronger than the dispersion forces between alkane molecules.
13 **a** Butan-1-ol is a larger molecule, so has stronger dispersion forces between its molecules.
b In butanol, the hydroxyl group could be placed at either carbon number 1 or 2 but methanol only one carbon atom.
14 D **15** A
16 The proportion of the carboxylic acid molecule that is non-polar increases, decreasing its solubility in water.
17 **a** Pentanoic acid **b** 3-Methylbutanoic acid
c 4-Methylhexanoic acid **d** 3-Ethylpentanoic acid
18 **a** Methylethanoate
b Ethylethanoate
c Ethylpropanoate
19 **a** $CH_3COOH(l) + CH_3CH_2CH_2OH(l) \rightarrow CH_3COOCH_2CH_2CH_3(l) + H_2O(l)$
b Esterification reaction
c It acts as a catalyst.
21 m(H) = 0.10 g
22 C_6H_6 C_2H_6 $C_3H_6O_3$ $C_6H_{12}O_2$ C_7H_{14}
23 **a** CH_2 **b** C_3H_6 **c** Alkene
24 **a** CH_2O **b** $C_2H_4O_2$
25 **a** Single covalent bond **b** Hydroxyl group
c Methyl group **d** Carboxyl group
26 Student poster
27 **a** Alkenes contain one double carbon–carbon bond, which requires two carbon atoms.
b Carbon atoms have four electrons in the outer shell, which are available for sharing with other atoms to produce four covalent bonds.
28 **a** Polyunsaturated: contains many double bonds; mono-unsaturated: contains one double bond; saturated: contains only single bonds between carbon atoms.
b Individual students' response required.

Chapter 10 Polymers

10.1 Types of polymers

1 **a** CH_2 **b** CH_2 **c** CH **d** C_2H_3Cl
2 **a** Monomer: C_3H_6, polymer: C_9H_{18}
b Monomer: C_2H_3Cl, polymer: $C_{12}H_{18}Cl_6$
c Monomer: C_2H_4, polymer: $C_{130}H_{260}$
3 4
4 Polymers usually consist of thousands to millions of monomer repeating units.
5 **a** HDPE is made of relatively unbranched chains of polyethene, which can pack more closely together than the branched chains of LDPE. HDPE is therefore stronger and slightly less flexible than LDPE.
b **i** LDPE **ii** HDPE **iii** LDPE

10.2 Designing polymers for a purpose

1 **a** Weak dispersion forces **b** Dipole-dipole attractions
c Weak dispersion forces **d** Weak dispersion forces
e Dipole-dipole attractions
2 Monomers from left to right: ethene, 1,1,2,2-tetrafluoroethene, ethene, 1,1,2,2-tetrafluoroethene
3 –H, –F, –Cl, $–C_6H_5$, $–NC_{12}H_8$
4 **a** Increase **b** Increase **c** Decrease
5 **a** Isotactic **c** 3
d Crystalline. Small side groups and isotactic arrangement allow for close packing and strong interchain bonding.

6 **a** Increase flexibility
b Improved heat insulating or mechanical properties
c Increased crystallinity resulting in a harder, more brittle polymer

Chapter 10 review

1 **b** 6 **c** Dipole–dipole bonds
2 **a** Monomers are small molecules that are able to react to form long chains of repeating units, called polymers. Often contains a carbon–carbon double bond.
b Heating breaks the bonds between molecules they become free to move.
c When the material is heated it does not melt, but at high temperatures covalent bonds are broken and the material decomposes or burns. It cannot be moulded into a different shape.
d One or more covalent bonds that connect neighbouring polymer chains.
e A chemical added to plastics to make them more flexible.
3 **a** False **b** False **c** False **d** True
4 A, C, D
5 **a** It has a carbon-to-carbon double bond.
c No, it cannot undergo addition polymerisation because it is a saturated compound.
6 **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 It is the simplest whole-number ratio of elements in a compound. The empirical formula of ethene is CH_2.
9 Occasional crosslinking 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 10.1.15.
10 They are much stronger in thermosetting polymers.
11 The inter-chain bonds are about the same strength as the covalent bonds within chains. When heated strongly both the inter-chain and within chain bonds break.
13 Distinguishing between thermoplastic and thermosetting polymers is important. The former get soft when heated, whereas the latter remain rigid and will char if heating continues.
a Thermosetting **b** Thermoplastic
c Thermosetting **d** Thermoplastic
e Thermoplastic
14 Plasticisers hold the polymer chains further apart and makes it easier for the polymer chains to slide over each other. So these materials have a lower softening temperature, and are more malleable and soft.
15 No extensive branching and regular chain structures
16 **a** PVC is flexible, non-conducting, strong, has a high melting point and low flammability.
b No free charged particles to conduct electricity, strong inter-chain bonding, strong bonds that do not burn easily, produces chemicals that extinguish flames when burned, plasticised to make it flexible.
17 It has very long polymer chains that result in stronger inter-chain forces than for HDPE.
18 Left: C_8H_8; middle: C_3H_3N; right: C_4H_6
19 **a** Thermoplastic with high melting temperature
b Lower density/more transparent polymer
20 Thermoplastic
21 **a** The polymer used in saucepan handles
b Saucepan handles need to be harder and more heat-resistant 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.
22 Relative molecular mass increased, melting point increased, strength of inter-chain forces increased, electrical conductivity unchanged.

Unit 1 Area of Study 2 How can the versatility of non-metals be explained?

Multiple-choice questions

1	D	**2**	C	**3**	C	**4**	D	**5**	B	**6**	C	**7**	D
8	A	**9**	C	**10**	B	**11**	C	**12**	A	**13**	D	**14**	A
15	A	**16**	A	**17**	D	**18**	B	**19**	B	**20**	B		

Short-answer questions

21 **a** V-shaped/bent and polar
b Triangular pyramid and polar
c Tetrahedral and non-polar
d Linear and non-polar
e Tetrahedral and non-polar
22 **a** Crude oil is fossilised organic material, mostly of plant and microbial origin.
b **i** It is a mixture of hydrocarbons, mostly alkanes from C1 to about C70.
ii Any correct formulas of two hydrocarbons; e.g. C_5H_{12}, C_6H_{14}.
23 **a** But-2-yne **b** Heptane
c 2,2,3-trimethylpentane **d** Butanoic acid
e 2-methylpropan-1-ol
25 **a** $CH_3(CH_2)_4COOH$ or $CH_3CH_2CH_2CH_2CH_2COOH$
b $CH_3C(CH_3)_2CH_2CH(C_2H_5)\ CH_2CH_2CH_3$ or $(CH_3)_3CCH_2CH(C_2H_5)CH_2CH_2CH_3$
c $CH_3CH(OH)CH_2CH_3$
d $CHCCH_3$
e $CH_2C(CH_3)CH_2C(CH_3)CH_2CH_3$
26 **a** Covalent bonds between atoms in the water molecules are much stronger than hydrogen bonds between the molecules of ice, so require much more energy, and thus a higher temperature, to break.
b Each water molecule forms hydrogen bonds with four other water molecules. This arrangement is very open, so ice has a lower density than liquid water.
27 **b** The four electron pairs form a tetrahedral arrangement around the atom due to the repulsion. The result is a pyramidal-shaped molecule.
d **i** N_2: polar bonds, so the intermolecular bonds are weak dispersion forces. CO_2: polar bonds, but molecule overall is symmetrical so dipoles cancel and molecule is non-polar. So the only intermolecular forces are dispersion forces.
ii Nitrogen is a highly electronegative element and consequently the bonds between the atoms of nitrogen and hydrogen are highly polarised. The ammonia molecule is a dipole because its shape is not symmetrical. Electrostatic attractions between dipoles are known as hydrogen bonds.
28 **b** Oxygen, because they are double covalent bonds as opposed to the single covalent bonds in hydrogen peroxide.
c **i** Dispersion forces
ii Hydrogen bonds, which are significantly stronger than the dispersion forces between oxygen molecules, and dispersion forces, which are also stronger than those between oxygen molecules because hydrogen peroxide molecule is larger.
d Oxygen has six valence electrons so achieves stability when it forms two covalent bonds. Nitrogen only has five valence electrons so forms three covalent bonds to achieve stability.
29 **a** HCl, HF, H_2O, H_2S **b** HCl, H_2S
c HCl, HF, F_2, H_2, O_2 **d** H_2O, HF
e O_2
f H_2; it is the smallest non-polar molecule in the list.
30 **a** Allotropes are different physical forms of the same element.
b Both consist of carbon atoms covalently bonded to other carbon atoms.
d The delocalised electrons in graphite are free to move and conduct electricity. In diamond there are no free electrons.

e Weak bonding between the layers of graphite, so layers can slide over one another and onto a page.

31 **b** **i** The plastic will char and blacken.

ii There are strong cross-links between polymer chains so the layers cannot slide past each other and melt.

32 **a** Monomer is a small molecule that is able to bond with other monomers to form a long-chain molecule called a polymer.

b Thermoplastic polymer softens on heating but hardens again when cooled, e.g. polyethene. Thermosetting polymer doesn't soften on gentle heating but if heated sufficiently it will char, e.g. melamine.

c A branched polymer is a linear polymer with some atoms forming branches attached to the polymer backbone, e.g. low density polyethene. Relatively weak intermolecular forces exist between chains.

A cross-linked polymer has covalent bonds linking polymer chains, resulting in a rigid polymer that does not soften on heating, e.g. melamine.

d Crystalline regions: atoms in chains are arranged in a regular pattern thus strengthening the polymer. Non-crystalline regions: atoms in chain are randomly arranged.

33 35.5 g mol^{-1}, Cl

34 **a** C_2H_4O **b** 88 g mol^{-1} **c** $C_4H_8O_2$

35 **a** $CHCl_3$ **b** $CHCl_3$

d Three polar C–Cl bonds in a non-symmetrical molecule, so it is polar overall. Interactions between the molecules are dipole–dipole interactions (as well as dispersion forces).

e 48 g

Chapter 11 Research investigation

11.1 Planning a research investigation

1 **a** Evaluate **b** Compare **c** Contrast **d** Justify

2 D

3 **a** Secondary **b** Primary

c Primary **d** Secondary

4 A, C **5** B **6** A

11.2 Communicating scientific ideas

1 C

2

Model	Advantages	Limitations
a Space-filling models	Useful for representing the sharing of space between 2 atoms where a pair of shared electron orbitals overlap. Useful for representing the overall 3D structure of molecules.	Sizes of atoms may not be accurate.
b Ball-and-stick models	Useful for representing the three-dimensional structure of molecules. Show each covalent bond.	Covalent bonds between atoms are often shown as 'lines' that do not represent actual bond length.
c Structural formula	Easy to draw.	Molecules are actually three-dimensional.

3 A

4 **a** Economic **b** Social

c Social **d** Environmental

5 B

11.3 Writing a scientific report

1 B **2** D

3 Thirty repeats of the procedure were conducted.

4 B

Chapter 11 review

1 C

2 **a** Reflect **b** Create

c Analyse **d** Investigate

e Apply **f** Identify

g Describe

3 C **4** C **5** C **6** C

7 **a** Accuracy **b** Critical thinking

c Precision **d** Validity of data

e Reliability of data **f** Authority of data

8 **a** B

b What's in it for you? It tastes better, naturally. Dairy Good. Good food. Good taste.

9 **a** **i** social **ii** bombarding

b 'Through an electron microscope, Stevens' material looks like a bed of nails, each nail one thousandth the width of a human hair and one thousandth the length of a grain of rice.'

c Possible answers:

1 This article is written in a scientific way because:

- Evidence is provided to support arguments; e.g. 'After one week there was a six-fold increase …'
- Credible sources are cited, e.g. 'Molly Stevens and her team from Imperial College, London.'

2 This article is written in a non-scientific way because:

- Colloquial language is occasionally used such as 'But placing DNA inside cells is tricky.'

d B

Chapter 12 Properties of water

12.1 Essential water

1 **a** Relatively high melting and boiling temperatures, high heat capacity and high latent heat of fusion and evaporation for a substance of its molecular size; decrease in density on freezing.

b H–O bond is highly polar, so hydrogen bonds exist between water molecules. Hydrogen bonds are stronger and require more energy to break than other intermolecular bonds. Thus, water has a relatively high melting and boiling temperatures. Hydrogen bonding between water molecules in ice results in a very open arrangement of molecules, so ice is less dense than liquid water.

3 Each water molecule has two hydrogen atoms and one oxygen atom that has two pairs of non-bonding electrons, each of which can form one hydrogen bond. So one water molecule can form 4 hydrogen bonds: 2 involving the two hydrogen atoms, 2 involving the two pairs of non-bonding electrons on the oxygen atom.

4 **a** H_2S, H_2Se, H_2Te, H_2Po, H_2O

b With the exception of water, the boiling points increase down the group due to increase in strength of dispersion forces with increase in mass. Water has a significantly higher boiling point than the other compounds due to the hydrogen bonds between its molecules.

5 **a** The distribution of hydrogen bonds in ice is almost tetrahedral in shape so molecules occupy more volume than in liquid water.

c Each water molecule in ice forms hydrogen bonds to four others in a very open arrangement in which the molecules are more widely spaced than in liquid water. Therefore, ice is less dense and floats on liquid water.

12.2 Heat capacity

WE 12.2.1 70.5 kJ

1 D

2 Copper, iron, chlorofluorocarbon, concrete, glass, aluminium, wood, ethanediol, water

3 29 J **4** 94 kJ

5 **a** 198 kJ **b** 6.2 kJ

6 32°C

7 $C = 0.39$ J g^{-1} °C^{-1}, therefore the unknown is copper.

12.3 Latent heat

WE 12.3.1 183 kJ

1 Flat regions of graph represent the substance changing state: the first from a solid to a liquid then from liquid to a gas.

2 Hydrogen bonding

3 Latent heat of fusion is the energy required to change the state of water from a solid to a liquid. This only requires the breaking of some hydrogen bonds between water molecules. The latent heat of vaporisation is much higher as the phase change from liquid to gas requires all the breaking of all hydrogen bonds between water molecules.
4 110 kJ 5 245 kJ 6 100 kJ

Chapter 12 review

1 polar, covalent bonds, hydrogen bonds, high, high, 100°C, high, 6.0 kJ mol^{-1}, 44.0 kJ mol^{-1}, high, 4.18 J g^{-1} $°C^{-1}$.
2 a Water molecule
  b Hydrogen atom
  c Hydrogen bond (and dispersion forces)
  d Covalent bond
3 a Intermolecular forces are those between molecules. For water, these are hydrogen bonds. Intramolecular forces are between the atoms in a molecule. For water, these are covalent bonds.
  b Covalent bonds. A higher temperature is required to break the covalent bonds between the oxygen and hydrogen atoms to decompose it into its constituent gases than to change liquid water into gaseous water by breaking the weaker hydrogen bonds.
4 Hydrogen bonds form between water molecules but not hydrogen sulfide molecules and energy is needed to break the bonds.
5 It is the high polarity of the water molecule that allows relatively strong hydrogen bonding to occur between molecules. As a consequence, a relatively large quantity of energy is required to break the hydrogen bonds between water molecules when water changes from a liquid to a gas. This gives water a high boiling point.
6 High latent heat of vaporisation. Water absorbs a relatively large amount of energy when it evaporates.
7 D 8 85.7 kJ 9 420 kJ 10 9.6 kJ
11 67.7°C (68°C) 12 0.42 J g^{-1} $°C^{-1}$
13 a Boiling point b Latent heat of fusion
  c Specific heat capacity d Latent heat of vaporisation
14 B
15 a Solid ice is being converted to liquid water.
  b The added energy is taken up in overcoming the hydrogen bonds between molecules, separating the molecules to form a gas.
16 611 kJ 17 409 g 18 1056 kJ
19 Water's high latent heat of vaporisation means that living organisms need only release small amounts of water onto their skin to efficiently cool themselves. If the value were lower, the water would evaporate more easily, so more sweat would need to be produced to cool the body down. Living organisms would be at a greater risk of dehydration or overheating.
20 a The change in temperature of ethanol will be almost twice that of water.
  b Water has a higher specific heat capacity than ethanol due to the greater strength of its hydrogen bonds. It also has more molecules, and hence more hydrogen bonds per gram than ethanol. Heating ethanol will require less energy than heating water over the same temperature range.
21 0.80 J g^{-1} $°C^{-1}$

Chapter 13 Water, the universal solvent

13.1 Water as a solvent

1 a Water – solvent b Wine – solution
  c Ethanol – solute d Sugar – solute
2 All have water as the solvent.
3 a Ammonia (NH_3^-) – soluble
  b Oxygen gas (O_2) – likely to be insoluble
  c Hydrogen chloride (HCl) – soluble
  d Methanol (CH_3OH) – soluble
  e Methane (CH_4) – likely to be insoluble
  f Hydrogen fluoride (HF) – soluble
  g Carbon dioxide (CO_2) – likely to be insoluble
4 Solute–solvent forces are stronger than solute–solute and solvent–solvent forces.
5 a Soluble b Insoluble c Solute
  d Dissolution e Solution f Solvent
6 CH_4 (methane). Methane is a non-polar molecule and will not dissolve in a polar solvent such as water.
7 Solute–solute bonds between sugar molecules are broken. Solvent–solvent bonds between water molecules are broken. Solute–solvent bonds form.

13.2 Water as a solvent of molecular substances

1 B, E
2 $CH_3OH(l) \xrightarrow{H_2O(l)} CH_3OH(aq)$
  $C_6H_{12}O_6(s) \xrightarrow{H_2O(l)} C_6H_{12}O_6(aq)$
3 Hydrogen bonds between water molecules and between ethanol molecules are broken. New hydrogen bonds form between ethanol and water molecules.
4 $HI(s) + H_2O(l) \rightarrow H_3O^+(aq) + I^-(aq)$
5 Covalent bonds, Hydrogen bonds, ionises, Covalent bonds, H^+, hydronium, Ion–dipole bonds

13.3 Water as a solvent of ionic compounds

WE13.3.1 Soluble
1 $NaNO_3(s) \xrightarrow{H_2O(l)} Na^+(aq) + NO_3^-(aq)$
  $Ca(OH)_2(s) \xrightarrow{H_2O(l)} Ca^{2+}(aq) + 2OH^-(aq)$
  The positive sodium ion attracts the partial negative charges on the oxygen atoms in the water molecule. The negative chloride ion attracts the partial positive charges on the hydrogen atoms in the water molecule.
3 A, B, D, E, H 4 A, C, D, E, F, H
5 a Na^+, CO_3^{2-} b Ca^{2+}, NO^{3-} c K^+, Br^-
  d Fe^{3+}, SO_4^{2-} e Cu^{2+}, Cl^-
6 a Nitrates are highly soluble in water so are found only in areas of low rainfall.
  b All sodium salts, most chlorides and most sulfates are soluble. They dissolve and flow into the world's oceans.

13.4 Precipitation reactions

WE 13.4.1 Copper(II) sulfide
WE 13.4.2 $CuSO_4(aq) + NaOH(aq) \rightarrow Cu(OH)_2(s) + Na_2SO_4(aq)$; Spectator ions: Na^+, SO_3^{2-}
1 a Silver carbonate b Lead(II) hydroxide
  c Magnesium sulfide d No precipitate
2 a i Magnesium sulfide ii Silver chloride
    iii Aluminium hydroxide iv Magnesium hydroxide
  b i $K_2S(aq) + MgCl_2(aq) \rightarrow MgS(s) + 2KCl(aq)$
    ii $CuCl_2(aq) + 2AgNO_3(aq) \rightarrow 2AgCl(s) + Cu(NO_3)_2(aq)$
    iii $AlCl_3(aq) + 3KOH(aq) \rightarrow Al(OH)_3(s) + 3KCl(aq)$
    iv $MgSO_4(aq) + 2NaOH(aq) \rightarrow Mg(OH)_2(s) + Na_2SO_4(aq)$
3 a i $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
    ii $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
  b i $CuSO_4(aq) + Na_2CO_3(aq) \rightarrow CuCO_3(s) + Na_2SO_4(aq)$
    ii $Cu^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CuCO_3(s)$
  c i $(NH_4)_2SO_4(aq) + BaCl_2(aq) \rightarrow BaSO_4(aq) + 2NH_4Cl(aq)$
    ii $SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(aq)$
  d i $K_2S(aq) + Pb(NO_3)_2(aq) \rightarrow PbS(s) + 2KNO_3(aq)$
    ii $S^{2-}(aq) + Pb^{2+}(aq) \rightarrow PbS(s)$
  e i $3CaCl_2(aq) + 2Na_3PO_4(aq) \rightarrow 6NaCl(aq) + Ca_3(PO_4)_2(s)$
    ii $3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s)$
  f i $2NaOH(aq) + Pb(NO_3)\ {}_2(aq) \rightarrow 2NaNO_3(aq) + Pb(OH)_2(s)$
    ii $2OH^-(aq) + Pb^{2+}(aq) \rightarrow Pb(OH)_2(s)$

4 **a** Na^+, NO_3^- **b** Na^+, SO_4^{2-} **c** NH_4^+, Cl^-
d K^+, NO_3^- **e** Na^+, Cl^- **f** Na^+, NO_3^-

Chapter 13 review

1 Dispersion forces, hydrogen bonds, covalent bonds.

2 A solution is most likely to form when the polarity of bonding of the solute is similar to that of the solvent. Water is polar and therefore a good solvent for ionic and polar substances.

3 Using the 'like dissolves like' rule, only polar substances will dissolve in water, so ethanol, a small polar molecule, can be expected to dissolve in water. Nitrogen and ethene are non-polar and would not be expected to dissolve in water.

4 Each C–H bond is slightly polar, however, the resulting partial charges are distributed symmetrically across the octane molecule, making the molecule non-polar overall. The energy released in the formation of solute–solvent bonds is not enough to overcome the intermolecular bonds between solute molecules and the intermolecular bonds between solvent molecules, so octane will not dissolve in water.

5 **a** Water dissolves wastes in the body so they can be safely removed from cells and the body. It dissolves glucose and other nutrients so they can be transported for use in energy production.
b Aqueous solutions are the basis for many drinks including tea, coffee, cordial, wine and soft drinks. Most paints and cleaning products used for residential purposes contain solutes dissolved in water.
c Farmers add water-soluble fertilisers to increase crop growth. Many medicines are water-soluble. Water is used as a solvent in the production of paints, foods, paper and other products.

6 $C_6H_{12}O_6$ and C_3H_7OH are polar molecules. They contain the polar –OH group and so are able to form hydrogen bonds with water. HI and HNO_3 contain polar molecules but they are unable to form hydrogen bonds with water. They dissolve by ionising. I_2, CH_4 and C_2H_4 are non-polar covalent molecules. They do not dissolve well in polar water.

7 Y, Z, X

8 DDT is most likely non-polar because it is soluble in fats, which are non-polar, and insoluble in polar water.

9 **a** Dissociation
b **i** $Cu^{2+}(aq)$, $NO_3^-(aq)$
ii $Zn^{2+}(aq)$, $SO_4^{2-}(aq)$
iii $NH_4^+(aq)$, $PO_4^{3-}(aq)$

10 **a** K^+, CO_3^{2-} **b** Pb^{2+}, NO_3^- **c** Na^+, OH^- **d** Na^+, SO_4^{2-}
e Mg^{2+}, Cl^- **f** Zn^{2+}, NO_3^- **g** K^+, S^{2-} **h** Fe^{3+}, NO_3^-

11 **a** $MgSO_4(s) \xrightarrow{H_2O(l)} Mg^{2+}(aq) + SO_4^{2-}(aq)$
b $Na_2S(s) \xrightarrow{H_2O(l)} 2Na^+(aq) + S^{2-}(aq)$
c $KOH(s) \xrightarrow{H_2O(l)} K^+(aq) + OH^-(aq)$
d $(CH_3COO)_2Cu(s) \xrightarrow{H_2O(l)} 2CH_3COO^-(aq) + Cu^{2+}(aq)$
e $Li_2SO_4(s) \xrightarrow{H_2O(l)} 2Li^+(aq) + SO_4^{2-}(aq)$

12 Hydrated hydronium ions and chloride ions, water molecules and a very few HCl molecules.

13 Magnesium ions are cations; they have a positive charge. The water molecules arrange around the magnesium ion with their negatively charged non-bonding electron pairs on the oxygen atoms closest to it.
Chloride ions are anions; they have a negative charge. The water molecules arrange around the chloride ion with their hydrogen atoms, which have a partial positive charge, closest to it.

14 Examples:
a Na_2CO_3, Li_2CO_3 and K_2CO_3 **b** $CaCO_3$, $MgCO_3$ and Ag_2CO_3

15 Examples:
a Na_2SO_4, K_2SO_4 and $(NH_4)_2SO_4$
b $CaSO_4$, $BaSO_4$ and $PbSO_4$

16 When potassium bromide is added to water, the hydrogen atoms of the water molecules are attracted to the negative bromide ions, and the oxygen atoms of the water molecules are attracted to the positive potassium ions. Ion–dipole bonds form between the ions and water molecules and the surface ions are pulled into solution. Gradually the ionic lattice dissociates and a solution is formed.

17 **a** True **b** True **c** False **d** False **e** True **f** False

18

	NaOH	KBr	NaI	$MgSO_4$	$BaCl_2$
$Pb(NO_3)_2$	$Pb(OH)_2$	$PbBr_2$	PbI_2	$PbSO_4$	$PbCl_2$
KI					BaI_2
$CaCl_2$	$Ca(OH)_2$			$CaSO_4$	
Na_2CO_3				$MgCO_3$	$BaCO_3$
Na_2S				MgS	BaS

19 PO_4^{3-} and S^{2-} to produce $Fe_3(PO_4)_2$ and FeS

20 **a** Barium sulfate **b** None
c Lead(II) sulfate **d** None

21 **a** $NH_4Cl(aq) + AgNO_3(aq) \rightarrow NH_4NO_3(aq) + AgCl(s)$
$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
b $Fe\,Cl_2(aq) + Na_2S(aq) \rightarrow FeS(s) + 2NaCl(aq)$
$Fe^{2+}(aq) + S^{2-}(aq) \rightarrow FeS(s)$
c $Fe(NO_3)_3(aq) + 3KOH(aq) \rightarrow 3KNO_3(aq) + Fe(OH)_3(s)$
$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$
d $CuSO_4(aq) + 2NaOH(aq) \rightarrow Cu(OH)_2(s) + Na_2SO_4(aq)$
$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$
e $Ba(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$
$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

22 **a** $CuSO_4(aq) + Na_2CO_3(aq) \rightarrow CuCO_3(s) + Na_2SO_4(aq)$
$Cu^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CuCO_3(s)$
Spectator ions: Na^+, SO_4^{2-}
b $AgNO_3(aq) + KCl(aq) \rightarrow AgCl(s) + KNO_3(aq)$
$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
Spectator ions: K^+, NO_3^-
c $Na_2S(aq) + Pb(NO_3)_2(aq) \rightarrow PbS(s) + 2NaNO_3(aq)$ $Pb^{2+}(aq) + S^{2-}(aq) \rightarrow PbS(s)$
Spectator ions: Na^+, NO_3^-
d $FeCl_3(aq) + 3NaOH(aq) \rightarrow Fe(OH)_3(s) + 3NaCl(aq)$
$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$
Spectator ions: Na^+, Cl^-
e $Fe_2(SO_4)_3(aq) + 6KOH(aq) \rightarrow 2Fe(OH)_3(s) + 3K_2SO_4(aq)$
$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$
Spectator ions: K^+, SO_4^{2-}

23 **i** e **ii** d **iii** d **iv** c **v** a

24 **a** Ammonia is a highly polar molecule and forms hydrogen bonds with water. It is therefore very soluble in water. Methane, however, is non-polar and does not dissolve in water.
b Glucose dissolves in water because it has very polar –OH groups that can form hydrogen bonds with water molecules. Sodium chloride is ionic; hence, there is ion–dipole attraction between the ions and water. This is strong enough to overcome the attraction between the sodium ions and chloride ions in the solid NaCl lattice.

25 Adding aqueous silver nitrate to a sample of NaCl would form a white precipitate of AgCl(s); the glucose solution would not form a precipitate. Electrical conductivity could also be used, as the solution of dissociated ions (NaCl) would conduct an electrical current; glucose solution would not.

Chapter 14 Aqueous solutions

14.1 Solubility

WE 14.1.1 140 g **WE 14.1.2** 210 g added

1 **a** Saturated **b** Unsaturated
c Supersaturated

2 C

3 Saturated: orange dot, unsaturated: blue dot, supersaturated: green dot

4 **a** 40 g **b** 160 g **c** 20 g

5 **a** 48 g **b** 200 g **c** 70 g
6 **a** Supersaturated **b** Unsaturated **c** Unsaturated

14.2 Crystallisation

WE 14.2.1 10 g
1 D **2** A **3** B **4** 20 g **5** 55 g
6 Granite cools slowly; forms large crystals. Basalt cools faster, with smaller crystals.

14.3 Concentration of solutions

WE 14.3.1 20.0 g L^{-1} **WE 14.3.2** 215 ppm
1 D
2 **a** 5.0 ppm **b** 625 ppm **c** 27 ppm
3 Sugar = 14.0%(m/v); fat = 3.0%(m/v)
4 214 ppb

14.4 Molar concentration

WE 14.4.1 0.48 mol L^{-1} or 0.48 M
WE 14.4.2 0.667 mol L^{-1} or 0.667 M
WE 14.4.3 2.5×10^{-3} mol
1 B
2 **a** 0.08 M **b** 0.3 M **c** 0.19 M
3 **a** 0.25 M **b** 0.50 M **c** 0.438 M
4 0.120 M **5** 7.10×10^{-3} M
6 **a** 2.2×10^{-2} mol **b** 6.4×10^{-3} mol
c 2.34×10^{-4} mol **d** 0.78 mol

14.5 Dilution

WE 14.5.1 2.5×10^{-2} mol **WE 14.5.2** 400 ppm
1 **a** 0.4 M **b** 0.075 M **c** 0.025 M
2 D **3** 8.0×10^{-2} M **4** 4.25 mol L^{-1}

Chapter 14 review

1 **a** 50 g **b** 10.5 g **c** 25 g
2 **a** 1000 g **b** 20 g
3 10°C **4** 60 g
5 Solubility of most gases in water decreases as temperature increases, so less gases available.
6 CO
7 142 g
8 **a** 2 ppm **b** %(m/m) = 2×10^{-4}
9 %(m/m) = 5
10 %(m/v) = 4.0×10^{-2}
11 2.38 M **12** 0.38 M **13** 0.300 M
14 **a** 2.6×10^{-3} mol
b 3.75×10^{-3} mol
c 2.3×10^{-2} mol
15 **a** 2.04 g **b** 1.7 g
16 1.00 M **17** 37.5 mL **18** 0.533 ppm
19 **a** $\div M$ **b** ÷ 6.022 × 1023
c $\times M$ **d** $\div V$
e $\times V$
20 **a** 700 g **b** 45 g
c 66 g **d** 6.7 M
21 **a** 180 g **b** 30 g
c 1.4 M **d** 8.0 g L^{-1}
22 0.80 M

Chapter 15 Acid–base reactions in water

15.1 Introducing acids and bases

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 involve exchange of a proton (H^+ ion): HCl loses a proton to the base.
$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
6 Acting as an acid: 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: 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 $H_2O + H_2O(l) \rightarrow H_3O^+(aq) + OH^-(aq)$

15.2 Strengths of acids and bases

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 (1) $H_3AsO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + H_2AsO_4^-(aq)$
(2) $H_2AsO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HAsO_4^{2-}(aq)$
(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, making it a better conductor of electricity.

15.3 Acidity of solutions

WE 15.3.1 $[H_3O^+] = 5.6 \times 10^{-6}$ M, $[OH^-] = 1.8 \times 10^{-9}$ M
WE 15.3.2 pH = 8.2 **WE 15.3.3** pH = 12.3
WE 15.3.4 pH = 12.25 **WE 15.3.5** 4×10^{-11} M
1 $[OH^-] = 1.00 \times 10^{-11}$ **2** $[OH^-] = 1.75 \times 10^{-6}$
3 $[H_3O^+] = 1.00 \times 10^{-9}$ **4** pH = 2
5 pH = 3 **6** $[H_3O^+] = 1.0 \times 10^{-6}$ (or 0.000001) M
7 pH = 1.3

15.4 Dilution of acids and bases

WE 15.4.1 1.00 M **WE 15.4.2** 60.0 mL
WE 15.4.3 pH = 1.5 **WE 15.4.4** pH = 11.7
1 0.075 M **2** 30 mL **3** 100 mL
4 Increases the pH by one unit.
5 pH = 12.6
6 **a** **i** $[H_3O^+] = 0.0010$ M = 10^{-3} M
ii $[OH^-] = 1.0 \times 10^{-11}$ M
iii pH = 3
b **i** $[H_3O^+] = 0.030$ M
ii $[OH^-] = 3.33 \times 10^{-13}$ M
iii pH = 1.52
c **i** $[H_3O^+] = 1.0 \times 10^{-12}$ M
ii $[OH^-] = 0.010$ M
iii pH = 12
d **i** $[H_3O^+] = 3.16 \times 10^{-5}$ M
ii $[OH^-] = 3.16 \times 10^{-10}$ M
iii pH = 4.5
e **i** $[H_3O^+] = 1.0 \times 10^{-12}$ M
ii $[OH^-] = 0.010$ M
iii pH = 12

15.5 Reactions of acids and bases

WE 15.5.1 $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
WE 15.5.2 $H^+(aq) + HCO_3^-(aq) \rightarrow H_2O(l) + CO_2(g)$
WE 15.5.3 $6H^+(aq) + 2Al(s) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$
1 **a** $Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$
$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$
b $Ca(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2(g)$
$Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$
c $Zn(s) + 2CH_3COOH(aq) \rightarrow Zn(CH_3COO)_2 + H_2(g)$
$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
d $2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$
$2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$
2 **a** Magnesium sulfate **b** Calcium chloride
c Zinc acetate **d** Aluminium chloride
3 **a** **i** $ZnO(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2O(l)$
ii $ZnO(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2O(l)$

b **i** $Ca(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2(g)$
ii $Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$
c **i** $Cu(OH)_2(s) + 2HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2H_2O(l)$
ii $Cu(OH)_2(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + 2H_2O(l)$
d **i** $Mg(HCO_3)_2(s) + 2HCl(aq) \rightarrow MgCl_2(s) + 2H_2O(l) + 2CO_2(g)$
ii $Mg(HCO_3)_2(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2O(l)$
e **i** $SnCO_3(s) + H_2SO_4(aq) \rightarrow SnSO_4(s) + H_2O(l) + CO_2(g)$
ii $SnCO_3(s) + 2H^+(aq) \rightarrow Sn^{2+}(s) + H_2O(l) + CO_2(g)$

4 **a** $2KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$
$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$
b $NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$
$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$
c $Mg(OH)_2(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l)$
$Mg(OH)_2(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + 2H_2O(l)$
d $CuCO_3(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l) + CO_2(g)$
$CuCO_3(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + H_2O(l) + CO_2(g)$
e $KHCO_3(aq) + HF(aq) \rightarrow KF(aq) + H_2O(l) + CO_2(g)$
$HCO_3^-(aq) + H^+(aq) \rightarrow H_2O(l) + CO_2(g)$
f $Zn(s) + 2HNO_3(aq) \rightarrow Zn(NO_3)_2(aq) + H_2(g)$
$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
g $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$
$CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)$
h $NaHCO_3(s) + CH_3COOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l) + CO_2(g)$
$NaHCO_3(s) + H^+(aq) \rightarrow Na^+(aq) + H_2O(l) + CO_2(g)$

15.6 Ocean acidity

1 D
2 $H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$
$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$
3 Calcium carbonate; calcification
4 $CO_3^{2-}(aq) + H_3O^+(aq) \rightarrow HCO_3^-(aq) + H_2O(l)$

Chapter 15 review

1 **a** NH_4^+ **b** HCl **c** HCO_3^- **d** H_3O^+
e $CH_3COOH(aq)$
2 **a** $PO_4^{3-}(aq) + H_2O(l) \rightarrow HPO_4^{2-}(aq) + OH^-(aq)$
b $H_2PO_4^-(aq) + H_2O(l) \rightarrow HPO_4^{2-}(aq) + H_3O^+(aq)$
c $H_2S(aq) + H_2O(l) \rightarrow HS^-(aq) + H_3O^+(aq)$
3 **a** Cl^- **b** H_3O^+ **c** OH^- **d** SO_4^{2-}
4 **a** Diprotic: can donate two protons to a base (e.g. H_2SO_4)
Amphiprotic: can act as either an acid or a base (e.g. HSO_4^- ion)
b A strong acid ionises completely in solution (e.g. HCl).
A concentrated acid has a large amount of acid dissolved in a given volume of solution (e.g. 5 M HCl, 5 M CH_3COOH)
6 **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-}.
7 $HClO_4(aq) + H_2O \rightarrow H_3O^+(aq) + ClO_4^-(aq)$
8 $HClO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO_3^-(aq)$
9 $NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$
10 $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3PO_4(aq) + OH^-(aq)$
11 **a** 10^{-11} M **b** 10^{-9} M
c 1.8×10^{-6} M **d** 2.9×10^{-3} M
e 1.5×10^{-13} M **f** 4.5×10^{-2} M
12 **a** **i** 0.1 M **ii** 1.0×10^{-13} M
b **i** 10^{-3} M **ii** 10^{-11} M
c **i** 10^{-7} M **ii** 10^{-7} M
d **i** 2×10^{-12} M **ii** 5×10^{-3} M
13 Basic. That at ~38°C, the ionisation of water is same as at 25°C.
14 100 times
15 **a** $[H^+] = 0.001$ M, $[OH^-] = 1.0 \times 10^{-11}$ M
b $[H^+] = 1.0 \times 10^{-10}$ M, $[OH^-] = 1.0 \times 10^{-4}$
c $[H^+] = 3.16 \times 10^{-9}$ M, $[OH^-] = 3.16 \times 10^{-6}$ M
d $[H^+] = 1.58 \times 10^{-6}$ M, $[OH^-] = 6.3 \times 10^{-9}$ M
e $[H^+] = 2.5 \times 10^{-10}$ M, $[OH^-] = 4.0 \times 10^{-5}$ M
f $[H^+] = 3.16 \times 10^{-14}$ M, $[OH^-] = 0.316$ M
16 $[OH^-] = 2.0 \times 10^{-9}$ M
17 **a** 0.01 M **b** 0.005 mol
18 **a** pH = 2.3 **b** pH = 10.3 **c** pH = 3
19 111 mL **20** 990 mL **21** Increase
22 **a** $HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + H_2O(l)$
b $H_2SO_4(aq) + K_2CO_3(aq) \rightarrow K_2SO_4(aq) + H_2O(l) + CO_2(g)$
c $2H_3PO_4(aq) + 3Ca(HCO_3)_2(s) \rightarrow Ca_3(PO_4)_2(s) + 6H_2O(l) + 6CO_2(g)$
d $2HF(aq) + Zn(OH)_2(s) \rightarrow ZnF_2(aq) + 2H_2O(l)$
23 E
24 $2H^+(aq) + CO_3^{2-}(aq) \rightarrow H_2O(l) + CO_2(g)$
25 A carbonate
26 **a** $2Al(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$
b $2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$
27 $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$
28 Photosynthesis
29 $H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$
$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$
30 **a** Krill eggs will not hatch at lower pH.
b Krill are a food source for many marine animals, so decrease will also lead to decrease in the numbers of larger species.
31 A: ammonia, B: glucose, C: sodium hydroxide, D: hydrochloric acid, E: ethanoic acid
32 **a** **i** It is a proton donor.
ii A substance that ionises completely in water.
iii A measure of concentration of a solution expressed in mol L^{-1}.
iv Contains one more hydrogen ion (proton) than the base.
b Amphiprotic substance can act as an acid (proton donor) or a base (proton acceptor).
33 Student answer.

Chapter 16 Redox reactions in water

16.1 Introducing redox reactions

WE 16.1.1 $Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$
WE 16.1.2 Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$; Cu(s) is being oxidised.
Reduction: $Ag^+(aq) + e^- \rightarrow Ag(s)$; $Ag^+(aq)$ is being reduced
WE 16.1.3 $O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$; $4K(s) \rightarrow 4\ K^+(s) + 4e^-$;
Overall equation: $4K(s) + O_2(g) \rightarrow 2K_2O(s)$
WE 16.1.4 **a** $2I^-(aq) \rightarrow I_2(aq) + 2e^-$
b $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
c $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(aq)$
1 **a** Oxidation **b** Reduction
c Reduction **d** Oxidation
2 **a** $Fe(s) \rightarrow Fe^{3+}(aq) + 3e^-$ – oxidation
b $K(s) \rightarrow K^+(aq) + e^-$ – oxidation
c $F_2(g) + 2e^- \rightarrow 2F^-(aq)$ – reduction
d $O_2(g) + 4e^- \rightarrow 2O^{2-}(aq)$ – reduction
3 **a** Fe(s), $Fe^{2+}(aq)$ **b** $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
c $H^+(aq)$ **d** $H^+(aq)$, H_2
e $2H^+(aq) + 2e^- \rightarrow H_2(g)$ **f** Fe(s)
g $Fe^{2+}(aq)/Fe(s)$ and $H^+(aq)/H_2(g)$
4 **a** Magnesium is oxidised, copper ions are reduced.
b $Mg(s) \rightarrow Mg^{2+}(aq) + e^-$
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 Due to the loss of $Cu^{2+}(aq)$, which reacts to form Cu(s).
5 **a** Cu^{2+} **b** Cu
6 **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

16.1 Extension answers

1 **a** $SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow SO_2(g) + 2H_2O(l)$
b $H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^-$
c $H_2S(g) \rightarrow S(s) + 2H^+(aq) + 2e^-$
d $MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l)$
e $Ta_2O_5(s) + 10H^+(aq) + 10e^- \rightarrow 2Ta(s) + 5H_2O(l)$
f $SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^-(aq) + 2H^+(aq) + 2e^-$
g $IO_3^-(aq) + 6H^+(aq) + 6e^- \rightarrow I^-(aq) + 3H_2O(l)$
2 **a** $4H_2O_2(aq) + PbS(s) \rightarrow PbSO_4(s) + 4H_2O(l)$
b $I_2(aq) + H_2S(g) \rightarrow 2I^-(aq) + S(s) + 2H^+(aq)$
c $5SO_3^{2-}(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 5SO_4^{2-}(aq) + 2Mn^{2+}(aq) + 3H_2O(l)$
d $2NO(g) + Cr_2O_7^{2-}(aq) + 6H^+(aq) \rightarrow 2NO_3^-(aq) + 2Cr^{3+}(aq) + 3H_2O(l)$

16.2 The reactivity series of metals

WE 16.2.1 Yes, $2Au^{3+}(aq) + 3Cu(s) \rightarrow 2Au(s) + 3Cu^{2+}(aq)$
1 **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, lead

16.3 Corrosion

1 $2Fe(s) + O_2(aq) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4OH^-(aq)$
$4Fe(OH)_2(s) + O_2(aq) + 2H_2O(l) \rightarrow 4Fe(OH)_3(s)$
2 Salts in air are good electrolytes and accelerate the rusting process.
3 **a** Magnesium, zinc
b Metals must be more reactive than iron.
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. The anodic region, then, 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 Prevents oxidation of the steel as zinc is more readily oxidised than steel (sacrificial protection). Copper and tin are less readily oxidised.

Chapter 16 review

1 D **2** A **3** B **4** C
5 **a** Oxidation is the gain of oxygen atoms; reduction is the loss of oxygen atoms.
b Oxidation is the loss of electrons; reduction is the gain of electrons.
6 $Zn^{2+}(aq)/Zn(s)$ and $Co^{2+}(aq)/Co(s)$
7 **a** Oxidation **b** Oxidation
c Reduction **d** Reduction
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 **a** $Mg(s)$ oxidised, $Cu^{2+}(aq)$ reduced
b $Zn(s)$ oxidised, $Ag^+(aq)$ reduced
c $CO(g)$ oxidised, $PbO(s)$ reduced
d $Ca(s)$ oxidised, $H^+(aq)$ reduced
e $Fe(s)$ oxidised, $Pb^{2+}(aq)$ reduced
10 **a** Zinc **b** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
c $H^+(aq)$ **d** $2H^+(aq) + 2e^- \rightarrow H_2(g)$
e $H^+(aq)$ **f** $Zn(s)$
g $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$
11 Ag, Cu, Sn, Ni, Mg, Li
12 **a** $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$
b, c No reaction
d $Mg(s) + Pb^{2+}(aq) \rightarrow Mg^{2+}(aq) + Pb(s)$
e–g No reaction
h $Pb(s) + 2Ag^{2+}(aq) \rightarrow Pb^{2+}(aq) + 2Ag(s)$
13 **a** No
b $Zn(s) + 2AgNO_3(aq) \rightarrow Zn(NO_3)_2(aq) + 2Ag(s)$
c $Zn(s) + SnCl_2(aq) \rightarrow ZnCl_2(aq) + Sn(s)$
d $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$
15 Zinc
16 $CuSO_4$ and $Pb(NO_3)_2$. Contain oxidants strong enough to react with iron metal.
17 D **18** C
19 $Fe^{2+}(aq) + OH^-(aq)$, $Fe(OH)_2(s)$, $Fe(OH)_3(s)$, $Fe_2O_3.xH_2O$
20 Protection of a metal, usually iron, by making it the cathode of a cell by joining to a more reactive metal, or connecting it to the negative terminal of a DC power source.
21 Copper is not a very reactive metal and so is not easily oxidised.
22 Tin is less readily oxidised than iron, so not protective.
23 Salts in air are good electrolytes and accelerate the rusting process.
24 Individual student responses required.
25 **a** $Ag^+(aq)$; $Mg^{2+}(aq)$ **b** $Mg(s)$; $Ag(s)$
c Silver nitrate **d** Zinc and magnesium
26 S < R < T
27 Group A: oxidised. Group B: reduced.
28 **a** Tin is not very reactive and so does not corrode readily. It protects the steel layer under it from corroding by preventing its contact with water and oxygen.
b Zinc is too reactive; oxidised easily by the contents and so contaminate the food.
c Tin layer may be cracked, allowing steel to corrode and contaminate the food.

Unit 2 Area of Study 1 How do substances interact with water?

Multiple-choice questions

1 D **2** C **3** D **4** B **5** C **6** A **7** B
8 A **9** B **10** D **11** D **12** C **13** A **14** C
15 D **16** A **17** C **18** B **19** B **20** A

Short-answer questions

21 **a** Water molecules are highly polar, so there are hydrogen bonds as well as weak dispersion forces.
H_2S molecules are much less polar, so there are dipole–dipole interactions and weak dispersion forces. H_2S molecules are larger than water molecules, so dispersion forces between H_2S molecules are greater than those between water molecules. However, hydrogen bonds are much stronger than dipole–dipole interactions, so, overall, the intermolecular bonds between H_2S molecules are weaker than those between water molecules and the boiling point of H_2S is consequently lower.
b The polarity of H_2Se is about the same as that of H_2S. However, H_2Se consists of much larger molecules, so the dispersion forces between them are more significant. Therefore, intermolecular forces between H_2S molecules are weaker than those between H_2Se molecules and the boiling point of H_2S is consequently lower.
22 **a** 8.6×10^4 J **b** 8.0×10^3 J **c** 13°C
d The high heat capacity is due to the relatively strong hydrogen bonds between water molecules.
e E.g. as a coolant in factories
23 **a** A measure of the energy required to raise the temperature of a certain amount of the substance (usually 1 g) by 1°C.
b The bonds between water molecules are relatively strong hydrogen bonds whereas those between hexane molecules are weaker dispersion forces.
Water has a higher specific heat capacity than ethanol because of the greater strength of its hydrogen bonds.
c 41.9°C
24 **a** The water molecule is very polar. It forms ion–dipole interactions with ionic compounds and hydrogen bonds with polar covalent compounds, thus allowing them to dissolve in water. Some polar covalent compounds dissolve by ionising in water.

b Necessary substances for metabolic processes include ionic compounds such as NaCl and molecular compounds such as glucose. These readily dissolve in water and are carried to the various parts of the body dissolved in the blood stream. Waste products such as urea are also water soluble and can be excreted as a solution.

c Water is an excellent solvent, so water in nature contains dissolved mineral salts, some soluble organic matter and dissolved gases.

25 **a** **i** $MgCl_2(s) \xrightarrow{H_2O(l)} Mg^{2+}(aq) + 2Cl^-(aq)$
ii Ionic bonds
iii Ion–dipole interactions
b **i** $C_2H_5OH(l) \xrightarrow{H_2O(l)} C_2H_5OH(aq)$
ii Hydrogen bonds
iii Hydrogen bonds
c The magnesium chloride solution, as $Mg^{2+}(aq)$ and $Cl^-(aq)$ ions are present in the solution after the $MgCl_2$ has dissolved; dissolved ethanol does not contain charged particles.

26 **a** $2HCl(aq) + Zn(s) \rightarrow ZnCl_2(aq) + H_2(g)$
b $2HNO_3(aq) + Ca(OH)_2(aq) \rightarrow Ca(NO_3)_2 + 2H_2O(l)$
c $H_2SO_4(aq) + Na_2CO_3(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l)$
d $Cu(s) + 2AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2Ag(s)$

27 **a** $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$
b $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
c $2H^+(aq) + CO_3^{2-}(aq) \rightarrow CO_2(g) + H_2O(l)$
d $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

28 **a** An acid that readily donates protons, or one that completely ionises in water.
b H_2CO_3 or H_2SO_4 or H_3PO_4 (or other correct polyprotic acid)
c **i** $HCO_3^-(aq) + H_2O(l) \rightarrow H_2CO_3(aq) + OH^-(aq)$
ii $HCO_3^-(aq) + H_2O(l) \rightarrow CO_3^{2-}(aq) + H_3O^+(aq)$
d H_3O^+

29 **a** **i** pH = 13.00 **ii** pH = 1.000 **iii** pH = –0.014
b 16.8 g

30 **a** C. It is the only solution with a pH above 7.00 and sodium hydroxide is a base.
b B. A and B must both be acids (pH less than 7 or turns litmus red). B has the higher conductivity and, as they all have the same concentration, B must ionise the most and so must be the stronger acid.
c The pH of A must be greater than 1.5 but less than 7. It will have a higher pH than solution B because it has a lower conductivity.
d **i** $[H_3O^+] = 10^{-pH} = 10^{-1.5} = 0.03$ M
ii $[H_3O^+] = 10^{-pH} = 10^{-10.5} = 3 \times 10^{-11}$ M

31 **a** Propanoic acid is a weak acid so it is partially ionised. The concentration of $H^+(aq)$ ions in a propanoic acid solution will therefore be lower than in solutions of nitric or sulfuric acid and hence will have the highest pH.
b Sulfuric acid is diprotic. It donates one hydrogen ion completely to water and there is partial ionisation of the $HSO_4^-(aq)$ ion to release a second hydrogen ion. So the overall concentration of $H^+(aq)$ ions is highest and its pH will be lowest.

32 **a** $Pb(NO_3)_2(aq) + 2KCl(aq) \rightarrow PbCl_2(s) + 2KNO_3(aq)$
b $Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$
c **i** Lead(II) chloride
ii Potassium ions and nitrate ions
d **i** 0.00951 mol
ii 2.65 g

33 **a** $O_2(g) + 2H_2O(l) + 2Fe(s) \rightarrow 4OH^-(aq) + 2Fe^{2+}(aq)$
b Oxidising agent is oxygen; Fe is the reducing agent.
c **i** Zn(s) is more reactive than iron and so will lose electrons in preference to Fe. So when there is some Zn attached to the Fe, the Zn is oxidised and the Fe is protected.
ii Sn is less reactive than Fe so if Fe were to be in contact with oxygen, it is the Fe that will preferentially corrode. If the Sn completely covers the Fe, the oxygen is prevented from reaching the Fe and the Fe is thus protected.

34 **a** **i** $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$
ii $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$
b $H_2O_2(aq) + 2H^+(aq) + 2Ag(s) \rightarrow 2H_2O(l) + 2Ag^+(aq)$

35 **a** **i** V and VII
ii In V, there is proton donation from HCOOH to $H_2O(l)$. In VII, there is proton donation from HCl to NH_3.
iii Any of $HCOOH/HCOO^-$, H_3O^+/H_2O, NH_4^+/NH_3, HCl/Cl^-
b **i** Any two of II, III and VI
ii In II, electrons are transferred from Ca to H^+.
In III, electrons are transferred from Mg to O_2.
In VI, electrons are transferred from Cl^- to Br_2.
iii Any one of Ca^{2+}/Ca, H^+/H_2, MgO/Mg, O_2/MgO, Cl_2/Cl^-, Br_2/Br^-
c **i** I and IV
ii In I, a precipitate of $PbCl_2(s)$ forms when two soluble compounds react
In IV, a precipitate of $Fe(OH)_3(s)$ when two soluble compounds react.
iii In IV, Na^+ ions and NO_3^- ions are spectator ions.

Chapter 17 Water sample analysis

17.1 The availability of drinking water

1 Surface water
2 Reservoirs
3 Most freshwater is locked in ice caps, glaciers or the soil.
4 Australia is the driest inhabited continent with variable rainfall.

17.2 Water quality

1 A
2 Take sample upstream from where the person taking the sample stands.
3 To determine if the water is mixed and so from what depth to take the samples.

Chapter 17 review

1 oceans reservoirs rivers quality
2 A **3** Bore water **4** Reservoirs
5 Oceans, ice caps and glaciers, groundwater, ground ice and permafrost, lakes, soil moisture, atmosphere as water vapour, rivers
6 Considerations include:
- which chemical is to be analysed
- why the testing is to take place
- what are the health risks associated with the sampling
- which equipment is required
- what is the sample size required for the selected test
- what method is to be used to record the measurements
- where and at what depths should the samples should be taken
- how to obtain a representative sample
- what are the labelling, storage and transport requirements for the sample

7 D
8 Above: lead, mercury. Below: arsenic, cadmium, copper
9 **a** Unsafe position
b Sample taken from surface of groundwater
c Container not sterile
d Container not protected from light
e Water sample not secured safely
10 To ensure they are collected in a consistent manner with the correct equipment.
11 Water can be used as a coolant in energy production, such as in power plants. It is used to remove wastes or as a cleaning agent in industries ranging from food production to car manufacture. Farming activities use large volumes of water for irrigation.

Chapter 18 Analysis for salts in water

18.1 The source of salts in water

1 One with relatively high density (e.g. lead, mercury, copper, cadmium, chromium and the metalloid arsenic)

2 Combustion of fuels and wastes (indirect), improper disposal of batteries, natural deposits in the Earth, and leaching from landfill

3 A

4 **a** Calcium ions, iron ions, magnesium ions

b $2C_{17}H_{35}COO^{-}(aq) + Ca^{2+}(aq) \rightarrow Ca(C_{17}H_{35}COO)_2(s)$

5 Precipitates calcium and magnesium ions from solution.
Ionic equation: $CO_3^{2-}(aq) + Ca^{2+}(aq) \rightarrow CaCO_3(s)$ or
$CO_3^{2-}(aq) + Mg^{2+}(aq) \rightarrow MgCO_3(s)$

6 Total dissolved solids

7

Electrical conductivity, EC (μS cm^{-1})	a TDS (mg L^{-1})	b Fit or unfit to drink
240	144	Fit
3200	1920	Fit
12 000	7200	Unfit

8 Relatively safe: Na^+, Mg^{2+}, Li^{2+}, K^+. Very toxic: Cu^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+}.

18.2 Gravimetric analysis

WE 18.2.1 0.60 mol **WE 18.2.2** 1.486 g **WE 18.2.3** 1.72%

1 C

2 **a** False **b** True **c** True **d** True **e** True

3

Poor practice initially displayed	Impact
Precipitate is not dried to constant mass.	Mass of the precipitate is high due to the presence of water.
Precipitate is not washed with deionised water.	Mass of the precipitate is high due to the presence of impurities.
Precipitate is left on the sides of the flask.	Precipitate is pure but its measured mass is lower than it should be.
Precipitate decomposes when heated.	The composition of the precipitate is not consistent.

4 $m(Ca(NO_3)_2) = 8.95$ g

5 **a** Silver nitrate. All nitrate salts are highly soluble but AgCl is insoluble.

b $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
The mass of the precipitate will be used to initially calculate the number of moles of silver chloride.

c Mole ratio = 1:1

6 **a** 0.020 mol **b** Mole ratio = 2:1 **c** 8.52 g

7 $m(Hg(CH_3COO)_2) = 3.38$ g

8 50.00 mL sample of hard water measured.
Excess of sodium carbonate is added.
Reaction mixture is filtered.
Precipitate is dried.
Precipitate is weighed.
Number of mole of precipitate is calculated.
Number of mole of calcium is calculated.
Mass of calcium ions is calculated.

18.3 Calculations involving excess reactants

WE 18.3.1 a $Pb(NO_3)_2$ **b** 0.835 g

1 B, D, A, E, C

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** $Pb(NO_3)_2$, 0.50 mol **b** $Pb(NO_3)_2$, 1.75 mol

c KI, 1.39 g **d** $Pb(NO_3)_2$, 8.64 g

18.4 Determining salt concentration by colorimetry and UV-visible spectroscopy

WE 18.4.1 8.8 mg L^{-1}

1 **a** 0.080 M solution **b** 0.30 M solution

2 Copper sulfate is blue because it absorbs light of all frequencies other than blue. Colorimeter measures the amount of light absorbed by a sample, so light of a colour other than blue must be used.

3 Blue

4 **a** 0.15 M Fe^{2+} **b** 0.15 × 4 = 0.6 M

c Fe^{2+} ions are oxidised to Fe^{3+} with acidified permanganate (MnO_4^-/H^+) before the addition of KSCN. Reaction of KSCN with Fe^{3+} forms the highly coloured, red metal complex $FeSCN^{2+}$.

5

Solution colour	Complementary colour
Green	Purple
Purple	Green
Orange	Blue
Green–yellow	Violet
Blue-green	Red
Green	Purple

6 **b** 175 mg L^{-1}

7 Blue is the complementary colour of orange. If potassium dichromate solutions are analysed in a colorimeter, a blue filter should be used. The sample will be placed in a glass or plastic cell and light directed at it. The higher the concentration of the solution, the more light is absorbed and the lower the intensity of the light arriving at the detector.

8 **a** 420 nm and 660 nm

b 660 nm or 420 nm; chlorophyll absorbs strongly at both.

18.5 Determining concentration by atomic absorption spectroscopy

WE 18.5.1 52 mg L^{-1}

1 electrons, higher, emit, lower

2 The spectrum of the light emitted by an element when it is heated.

3

Component	Description
Flame	Where the sample is sprayed and light is absorbed
Hollow source cathode lamp	Produces light with wavelengths that are absorbed by the metal being analysed
Computer	Converts the amount of light detected into the amount of light absorbed by the sample
Monochromator	Selects a specific wavelength of light
Detector	Measures the amount of light

4 C

5 **b** 4.8 mg L^{-1}

Chapter 18 review

1 **a** Any three of the following human activities lead to an increase in salts in our waterways: mining and industry lead to an increase of mercury and other heavy metals in the water system, the burning of fuels containing trace amounts of mercury, leaching from landfill, incorrect disposal of batteries and fluorescent light bulbs.
Run off from agriculture increases ammonium and phosphate levels due to fertilisers. Sewage treatment and domestic grey water increase levels of phosphate.

b By precipitation reactions

2 ions, higher, 25°C, cannot

3 B

4 E.g. methylmercury; substances with at least one carbon–metal bond.

5

$Ca(NO_3)_2$	Na_3PO_4	$Ca_3(PO_4)_2$	$NaNO_3$
27 mol	18	9.0	54
0.72	0.48 mol	0.24	0.44
0.54	0.36	0.18 mol	1.08
1.2	0.8	0.4	2.4 mol

6 **a** Lead(II) chloride, lead(II) hydroxide, copper(II) hydroxide

b $Pb(NO_3)_2(aq) + CuCl_2(aq) \rightarrow PbCl_2(s) + Cu(NO_3)_2(aq)$
$Pb^{2+}(aq) + 2Cl^{-}(aq) \rightarrow PbCl_2(s)$
$Pb(NO_3)_2(aq) + Ba(OH)_2(aq) \rightarrow Pb(OH)_2(s) + Ba(NO_3)_2(aq)$
$Pb^{2+}(aq) + 2OH^{-}(aq) \rightarrow Pb(OH)_2(s)$
$CuCl_2(aq) + Ba(OH)_2(aq) \rightarrow Cu(OH)_2(s) + BaCl_2(aq)$
$Cu^{2+}(aq) + 2OH^{-}(aq) \rightarrow Cu(OH)_2(s)$

7 $\frac{1}{2}, \frac{2}{1}, \frac{1}{1}$

8 %(Ag) = 18.3%

9 3.07%

10 **a** 1.2%

b You would need to consider the fact that the percentage of phosphate in the washing powder is greater than the percentage of the phosphorus.

11 Precipitate was not washed or not dried completely; presence in the solution of other metal ions that form precipitates.

12

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

13 **a** Oxygen **b** $n(Na_2O) = 1.5$ mol

14 **a** $m(S) = 22.6$ g **b** $m(SO_2) = 4.93$ g

15 **a** P_4O_6, 2.77 g **b** 3.37 g **c** 1.26 g

d 4.63 g; 4.63 g of products formed plus 2.78 g unreacted P_4O_6 = 7.40 g, which is total mass of reactants

16 Left to right: light source, monochromator, sample solution, detector, recorder

17 **a** 800 nm **b** Red **c** Blue

18

Component	Function
Detector	Measures the intensity of light
Filter	Selects a range of wavelengths of light
Light source	Provides ultraviolet and visible light of all wavelengths
Monochromator	Allows selection of light of a particular wavelength
Glass cell	Transparent container that holds the sample
Recorder	Displays the absorbance measurement

19 **a** 39 mg L^{-1} **b** 3.2%

c It is strongly absorbed by a blue solution.

20 False False True False

21 **a** Green

b To vaporise traces of other substances that could lead to a false result.

c Copper wire would give the flame a green colour, and interfere with the test.

d Relatively few elements can be analysed, presence of one element may mask presence of another, colours emitted can be difficult to distinguish, relatively large amount of sample is needed.

22 Electrons can return to the ground state from excited states by undergoing a number of transitions of different energy. (This is shown in the diagram.) Each transition results in a line of specific energy in the emission spectrum.

23 In the flame.

24 **a** Both involve the absorption of electromagnetic radiation of particular wavelengths characteristic of the substance under investigation. The amount of radiation absorbed is measured by a detector. The amount of light absorbed is proportional to the amount of the light-absorbing substance in the sample.

b In AAS, the sample is sprayed into a flame and light of a particular wavelength is passed through the flame. Atoms of the element being analysed absorb some of the radiation and the amount of light absorbed indicates the amount of the element present in the sample. AAS can be used to detect most metals.
In UV-visible spectroscopy, two lights are used to produce radiation covering the visible and UV spectrum. The 'light' is passed through a prism to produce the desired wavelength; for UV analysis a silica sample holder is used. UV spectroscopy can be used to analyse many colourless compounds as well as coloured ones. It can give information about the structure of the substance. UV-visible spectroscopy can be used to determine the concentration of atom ion and molecules include complex organic substances.

25 **b** 26 mg L^{-1}

26

Technique	Feature
Electrical conductivity	Ions flow between electrodes in a solution.
Atomic emission spectroscopy	A sample is injected into a flame.
Colorimetry	A filter is used to select a range of wavelengths of visible light.
UV-visible spectrophotometry	A monochromator allows complementary light of an exact wavelength to be used.
Gravimetric analysis	The mass of a precipitate is used to determine the concentration of a salt.

27 **a** $Al_2(SO_4)_2(aq) + 3Ba(NO_3)_2(aq) \rightarrow 3BaSO_4(s) + 2Al(NO_3)_2(aq)$
$Na_2SO_4(aq) + Ba(NO_3)_2(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$

b 0.0161 mol

c $n(Al_2(SO_4) = 0.00403$ mol, $n(Na_2SO_4) = 0.00403$ mol

28 **a** Fe_2O_3 **b** 4.8 mol

c No. All sodium ions are soluble in water.

29 **a** Green **b** Mole ratio = 1: 1

c Absorbance of sample is determined on a calibration curve constructed from a series of standard solutions of the $FeSCN^{2+}$ complex.

d Hollow cathode lamp with an iron (Fe) filament

Chapter 19 Analysis for organic compounds in water

19.1 Organic contaminants in water

1 A, B **2** A, D, E **3** B **4** D **5** B

6 burning, chlorine, water supplies, insoluble, fat, adverse

7 C, D, F

19.2 Principles of chromatography

WE 19.2.1 $R_f = 0.3$

1 B

2

Term	Description
Adsorption	The attraction of one substance to the surface of another
Desorption	The breaking of the attraction between a substance and the surface to which the substance is adsorbed
Components	The different compounds in the mixture, which can be separated by chromatography
Polar molecule	A molecule that acts as a dipole; it has one or more polar covalent bonds, with the charge being distributed asymmetrically
Mobile phase	The solvent that moves over the stationary phase in chromatography
Stationary phase	The components of a mixture undergo adsorption to this phase

3

Band	**a** Distance from origin (mm)	**b** R_f	**c** Compound
Light green	20	0.33	Chlorophyll b
Dark green	27	0.45	Chlorophyll a
Orange	40	0.67	Xanthophyll
Yellow	50	0.83	β-Carotene
Solvent front	60	–	–

d No. Separation of components depends on their solubility in the mobile phase so polarity of the solvent used affects R_f of components.

4 **Step 1:** Dissolve a sample of pure phenacetin in a volume of chloroform. This is the standard solution.
Step 2: Dissolve a tablet of the analgesic in chloroform. This is the sample solution.
Step 3: Place a small spot of the sample solution near the bottom of a thin-layer plate. Place a spot of the standard solution next to it, at the same distance from the bottom of the plate.
Step 4: When the spots are dry, place the plate in a container with a small volume of solvent, such as chloroform. The lower edge of the plate, but not the spots, should be immersed.
Step 5: Allow the solvent to rise until it almost reaches the top of the plate and then remove the plate from the container.
Step 6: Let the plate dry and examine it under ultraviolet light. If a spot from the sample appears at the same distance from the origin as the spot from the standard solution, the tablet is likely to contain phenacetin.

19.3 High performance liquid chromatography

WE 19.3.1 0.75 mg kg^{-1}

1 A **2** A
3 adsorb, desorb, stationary, mobile, longest
4 B, A, C **5** **b** 0.7%

Chapter 19 review

1 A **2** B
3 H, D, G, B, E, A, C, F
4 **a** True **b** False **c** True **b** True **e** False
5 Whale, large fish, small fish, zooplankton, aquatic plants
6 B
7 fungicide, half-life, insoluble, fat
8 Beneficial: b, c Adverse: a, d
9 stationary, origin, components, above, mobile, stationary, components
10 **a** **i** *absorbed* **ii** *adsorbed*
b Absorb: Atoms or molecules are taken *into* the material.
Adsorb: Atoms or molecules accumulate and bond weakly to the *surface* of a solid or liquid.
11 R_f(blue) = 0.8, R_f(purple) = 0.6, R_f(yellow) = 0.2
12 R_f(blue) = 0.83, R_f(red) = 0.58
13 **a** If the solvent were above the level of the origin, the compounds under test would dissolve and disperse throughout the solvent.
b Components cannot move faster than the solvent and R_f = distance dye has moved divide by distance solvent front has moved.
c 3
d B: blue; C: green. By colour and R_f values.
e Blue
f 0.63; 0.13
14 **a** 3.2 cm **b** 15 cm
15 **a** Taurine, glycine
b samples can be visualised using stains.
c $R_f(\text{taurine}) = \frac{0.6}{5.0} = 0.12$
d Leucine
16 A, increased the column length, smaller, high
17 A **18** A **19** B, D, A, C, E
20 **a** Number and the absorption, and hence, concentration, of components.
b 4
c Solid samples are dissolved in a suitable solvent. The liquid sample is injected into the top of an HPLC column. The stationary and mobile phases are chosen to achieve a good separation of the components in the sample. The sample components alternately adsorb onto the stationary phase and then desorb into the solvent as they are swept forward. The time taken to exit the column increases if the component strongly absorbs onto the stationary phase and has a low solubility in the mobile phase.
21 B
22 **a** 3.0×10^{-11} mg **b** 1.8×10^{-8} mg
c 22.5 mg

23

Technique	Problem
Paper or thin-layer chromatography	B, D
High performance chromatography (HPLC)	A, C, D

24 Most components of crude oil are insoluble in water and have a lower density than water. They form a slick on top of the water that spreads.
Booms are used to contain the slick. Some of the more volatile components will evaporate. Other components can be ‘skimmed’ from the surface.
Dispersants are used on larger spills to break up the slick. Oil reaching the coast often has to be collected manually.

25 **a**

Standard	Peak height (cm)
Standard 0 ppm parathion	0.2
Standard 10 ppm parathion	1.5
Standard 20 ppm parathion	3.1
Standard 30 ppm parathion	4.4
Reservoir water	2.0

c 13 ppm
d No, over 1000 times allowable concentration.
e LD_{50} of 8 mg kg^{-1} = 8 mg per 1000 g × 150 g = 1.2 mg. A mouse of 150 g has a 50% chance of being killed by a 1.2 mg dose of parathion.

Chapter 20 Volumetric analysis

20.1 Sources of acids and bases in water

1 Calcium carbonate
2 Produced by reaction of nitrogen and oxygen in internal combustion engines; lower the pH.
3 $4FeS_2(s) + O_2(g) + 15H_2O(l) \rightarrow Fe(OH)_3(s) + 8H_2SO_4(aq)$
4 $CaCO_3(s) + H^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(l)$

20.2 Standard solutions

WE 20.2.1 4.00 M

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 to dissolve the solid. Fill the flask with deionised water to just below the calibration mark. Add deionised water drop by drop until the bottom of the meniscus touches the calibration line. Stopper and shake the solution.
2 0.2000 M **3** 13.3 g

20.3 Calculations involving acids and bases

WE 20.3.1 10 mL
WE 20.3.2 a H_2SO_4 **b** 0.523 g
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 M

3 **a** 0.00200 mol **b** 0.00160 mol
c Na_2CO_3 is the limiting reactant and H_2SO_4 is in excess.
d 0.00040 mol H_2SO_4 in excess

4 **a** $HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + H_2O(l)$
b 0.001985 mol
c $n(HNO_3) = n(KOH) = 0.001985$ mol
d 0.1087 M

20.4 Volumetric analysis

1 A

2

Indicator	Colour after adding indicator
Alizarin yellow	Yellow
Bromothymol blue	Yellow
Methyl red	Orange
Methyl orange	Yellow
Phenolphthalein	Colourless

3 Average titre = 25.42 mL

20.5 Calculations in volumetric analysis

WE 20.5.1 0.108 M **WE 20.5.2** 12.88 M

1 0.770 M

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 M

3 9.032 M

Chapter 20 review

1 B

2 Iron(III) hydroxide, sulfuric acid and heavy metal ions

3 SO_2, NO and NO_2. Pollutant gases generated by smelters, internal combustion engines and the burning of fossil fuels.

4 D. Both reactions occur in river water. Carbon dioxide is absorbed from the atmosphere and is also produced by decaying plants. A small amount of calcium carbonate reacts with water when a river flows through limestone. Because the pH > 7, there must be an excess of OH^- ions, so the second equation is occurring to a greater extent.

5 C **6** 0.8003 M **7** 21.2 g **8** 15.0 mL

9 **a** 0.0200 mol **b** 0.0160 mol
c K_2CO_3 **d** 0.0060 mol

10 40 mL

11 **a** HNO_3 **b** 0.690 g

12 **a** Delivers a precise variable volume of solution.
b Delivers a precise known volume of solution.
c Used to prepare a solution of known concentration.

13 Equivalence point: point in the reaction at which equivalent amounts of acid and base have been mixed. End point: point in the titration at which the indicator changes colour.

14 Selecting the indicator based on the expected equivalence point enables for a sharp end point (indicator changes colour with just one additional drop) to be seen.

15 **a** $H_2SO_4(aq) + K_2CO_3(aq) \rightarrow K_2SO_4(aq) + H_2O(l) + CO_2(g)$
b 0.03557 M **c** 0.0315 M

16 **a** $2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$
b 0.05125 M
c 0.1013 M
d Sulfuric acid is a diprotic acid so only half as much acid, so half the volume of sulfuric acid is required.

17 **a** 0.04166 M **b** 0.07100 M

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.
c Rinse the burette with the acid solution, the pipette with the base, the conical flask with the deionised water.
d 13.56 M **e** No

Unit 2 Area of Study 2 How are substances in water measured and analysed?

Multiple-choice questions

1	C	**2**	A	**3**	C	**4**	B	**5**	C	**6**	A	**7**	A
8	A	**9**	C	**10**	B	**11**	D	**12**	B	**13**	D	**14**	A
15	C	**16**	D	**17**	B	**18**	C	**19**	B	**20**	D		

Short-answer questions

21 **a** An element or compound that may be harmful if consumed. It can occur in nature or be synthetic (i.e. manufactured).
b Examples: lead or cadmium from mining, fungicides or herbicides from agricultural runoff

22 **a** The solubility of gases increases as temperature decreases. More carbon dioxide is therefore dissolved in cold lemonade than in lemonade at room temperature.
b When the water temperature is increased, gases come out of solution because their solubility has decreased. The decrease in oxygen concentration, in particular, may make the waterways unsuitable for some forms of aquatic life.
c Dissolved ionic compounds are the cause of salinity. The greater the salinity, the more dissociated ions there are in solution and hence the greater the conductivity.

23 **a** **i** 110 g
ii Crystals of $NaNO_3$ would precipitate out of the solution.
iii 138 g
b At 20°C, the solubility of sucrose is 200 g in 100 g water, so in 200 g water, 400 g sucrose can dissolve.
c **i** A solution containing 30 g KNO_3 in 100 g water is unsaturated because up to 80 g can dissolve in that quantity of water at 50°C. The solution containing 80 g of KNO_3 is saturated; it contains the maximum amount of KNO_3 that can dissolve at that temperature. The one containing 87 g of KNO_3 is supersaturated; it contains more than the maximum amount of KNO_3 that can dissolve at that temperature.
ii A small amount of solute added to an unsaturated solution will dissolve. A small amount of solute added to a saturated solution will not dissolve. A small amount of solute added to a supersaturated solution or even knocking the solution will cause the excess solute to crystallise out of the solution.
iii On cooling the solutions to 30°C, crystals will precipitate out of the saturated and supersaturated solutions but not from the unsaturated one, because even at 30°C the solution can hold more than 30 g KNO_3 in 100 g water.
d 175 g

24 **a** 16 g
b **i** 6 g **ii** 9 g
c None will dissolve. **d** 0.688 mol L^{-1}
e **i** Add the mixture to 50 g water and heat to 80°C. Both salts are soluble at this temperature but graphite is insoluble and can be filtered out.
Allow the filtrate to cool to 20°C. Some of the K_2SO_4 will precipitate and can be filtered. The filtrate should be dried in an oven to obtain a pure sample of potassium sulfate.
ii 3.0 g
f Sodium chloride is highly soluble at both 20°C. and 80°C and the solutions are unsaturated at both temperatures, so NaCl will not precipitate out of solution. The solution contains both sodium chloride and potassium sulfate, so a pure sample could not be obtained even if the mixture was evaporated to dryness.

25 **a** **i** A colourless, odourless gas is produced.
ii No change
iii A white precipitate is formed.
iv A green precipitate is produced.

v No change **vi** No change **vii** No change
viii No change **ix** No change **x** No change
b **i** $CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$
iii Mg2+(aq) + CO32–(aq) → MgCO3(s)
iv $Cu^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CuCO_3(s)$
26 **a** 10^{-10} mol L^{-1} **b** pH = 11.00
27 **a** 0.592 M **b** 0.370 M
c **i** $Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$ **ii** 7.49 g
28 **a** $Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$
b $2Fe(OH)_3(s) \rightarrow Fe_2O_3(s) + 3H_2O(g)$
c **i** 0.766 g **ii** 0.589 M
29 **a** A sample of a solution containing Ni2+ ions is scanned in a UV-visible spectrophotometer to determine its absorbance across a range of wavelengths. The wavelength that gives the highest absorbance is then chosen.
b Prepare a series of standard solutions containing nickel ions. Measure their absorbance at an appropriate wavelength and plot a calibration curve. Measure the absorbance of the unknown solution and determine its concentration from the calibration curve.
30 **a** 0.840 g
b **i** $NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$
ii 0.0285 M
31 **a** $NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$ or $NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$
b 0.827 mol L^{-1} **c** 10.5 g
d Yellow at the start, orange at equivalence point and pink when excess acid is present
e **i** Same; the amount, in mole, of ammonia in the flask is unchanged by the addition of water.
ii Lower; phenolphthalein indicator would change colour before equivalence point is reached, so the titre of HCl, and hence the calculated concentration of ammonia, would be lower than the actual one.
iii Higher; the flask would contain some drops of diluted cleaner as well as the 20.00 mL of it measured out, so the calculated concentration of ammonia would be higher than the actual one.
32 **a** 0.00924 mol
b **i** 0.462 M **ii** 54.6 g L^{-1} **iii** 5.46 %(m/v)
c Solution was not saturated, or the solution cooled during handling and so the solubility decreased.
33 **a** **i** 2.23×10^{-4} mol L^{-1} **ii** 7.13 ppm
b 78%
c It would be less than 9.2 as gases become less soluble as the temperature rises.
d **i** To obtain a reliable estimate of the overall oxygen level, as the concentration of oxygen may vary at different locations and depths.
ii To prevent dissolved oxygen from escaping into the atmosphere.
34 **a** **i** 0.067% **b** 6.7 × 102 ppm
35 **a** Insecticides, pesticides, oil, dioxins
b **i** X; it had the smallest retention time.
ii Y; it has the highest peak area.
c **i** To relate the concentration of a substance to the area of the peak.
ii A solution of X of precise concentration is made up and a set of standard diluted solutions prepares. Analyse these diluted solutions by the HPLC under the same conditions as the analysis of the pond water.
Plot the area under the peak against the concentration of each standard.

Chapter 21 Practical investigation

21.1 Designing and planning investigations

1 **a** Electrical conductivity **b** Concentration of lead
c Electrical conductivity **d** pH
2 A hypothesis is a suggested outcome, based on evidence and prior knowledge, to answer the research question.
3 **a** pH of the water **b** Mussel shells dissolving
c Difference in mass of the mussel shells before and after the experiment
d Temperature of the water, the mass of mussel shells, the length of time the mussel shells are left in the water

21.2 Conducting investigations and recording and presenting data

1 17.34 mL, 17.38 mL, 17.44 mL
2 B
3 **a** Systematic error **b** Mistake **c** Random error
4 C
5 The mean

21.3 Discussing investigations and drawing evidence-based conclusions

2 Inverse, non-linear relationship
3 **a** Reliability **b** Validity
c Accuracy **d** Precision
4 It is not directly related to the hypothesis—it should have referred to the temperature of the water and its electrical conductivity.

Chapter 21 review

1 Independent variable: C; dependent variable: A; controlled variable: B
2 Independent variable = source of the water, dependent variable = phosphate concentration, controlled variables = temperature, time of testing, method of testing
3 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
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 on fire.
5 **a** Mistake **b** Random error **c** Systematic error
6 **a** Bar graph **b** Line graph
c Scatter graph (with line of best fit) **d** Pie chart
7 **b** Data point 4
c An outlier is a point in the data that does not fit the trend.
8 Temperature
9 Add a title, label the *x*- and *y*-axes, add units to the *x*-axis variable, exclude the obvious outliers from line of best fit.
10 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
11 A pattern or relationship between the dependent and independent variables; may be linear, positive non-linear, linear or non-linear inverse
12 To avoid plagiarism and ensure creators and sources are properly credited for their work.
13 **a** Aim: To determine the effect of increasing water temperature on the electrical conductivity of water.
b Independent variable: water temperature; dependent variable: electrical conductivity of water; controlled variables: pH, water source, sampling container
c Conductivity, using a probe; quantitative.
d 10 mL measuring cylinder ±0.1 mL, pH probe ±0.02, alcohol-filled glass thermometer ±0.1°C, electrical conductivity probe ±2
e Raw data is data collected in the field and recorded as measurements are taken. Processed data is data that has been manipulated in some way (e.g. calculated, tabulated).

Glossary

A

absorbance A measure of the capacity of a substance to absorb light of a specified wavelength.

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).

acid mine drainage Acidic water that forms by production of sulfuric acid from minerals.

acid rain Rainwater that has reacted with acidic emissions from industry and has a pH less than 5.5.

acid–base reaction A reaction in which one substance, an acid, donates a hydrogen ion (proton) to another substance, a base.

acidic proton A proton bonded to an electronegative element (oxygen, nitrogen of fluorine) that is donated to a base during an acid–base reaction.

acidic solution An aqueous solution in which the concentration of hydronium ions (H_3O^+) is greater than the concentration of hydroxide ions (OH^-). At 25°C, pH < 7.

acidity The concentration of H_3O^+ ions in an aqueous solution. Acidity is measured using the pH scale.

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 by which a polymer is formed by an addition reaction, where many unsaturated 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 binds to an unsaturated hydrocarbon, forming a single carbon–carbon bond. In this process two reactant molecules form one product.

adsorption The attraction of one substance to the surface of another.

affiliation Connecting or associating with a person or organisation.

agenda Motivation, often unstated, to produce a particular outcome.

alcohol An organic compound containing the hydroxyl (–OH) functional group; its name ends in '-ol'.

aliquot A volume of liquid measured by a pipette.

alkali A soluble base or a solution of a soluble base.

alkali metal A group 1 metal—Li, Na, K, Rb, Cs and Fr.

alkane A saturated hydrocarbon; general formula C_nH_{2n+2}.

alkene An unsaturated hydrocarbon containing one carbon–carbon double bond; general formula C_nH_{2n}.

alkyl group A group obtained by removing a hydrogen atom from an alkane; general formula C_nH_{2n+1}, e.g. methyl ($-CH_3$).

alkyne An unsaturated hydrocarbon containing one carbon–carbon triple bond; general formula C_nH_{2n-2}.

allotrope Different forms of the same element in which the atoms combine in different ways.

alloy A substance formed when other materials (e.g. carbon, other metals) are mixed with a metal.

alpha particle A positively charged particle formed from ionising radiation.

amorphous A structure that has no consistent arrangement of particles.

amorphous region A region in a polymer in which molecules are tangled in a random arrangement.

amount A measure used by chemists for counting particles; the unit is the mole

amphiprotic The ability to act as an acid (proton donor) and also as a base (proton acceptor).

analyte The chemical substance that is of interest in a chemical analysis.

anhydrous Containing no water.

anion A negatively charged ion, e.g. a chloride ion, Cl^-.

annealing Heating a metal to a moderate temperature and then allowing it to cool slowly to make it softer and more ductile.

anode An electrode at which an oxidation reaction occurs.

aqueous When a chemical species has been dissolved in water, the resulting solution is said to be aqueous. This can be shown by writing '(aq)' after the name or symbol of the chemical.

aquifer A rock formation that is permeable and allows groundwater to flow through it.

artesian basin An underground area of porous rock surrounded by rock that is not permeable to water. Rain seeps into the rock and is stored underground.

asymmetrical molecule A molecule in which the polar bonds are unevenly (or asymmetrically) distributed. The bond dipoles do not cancel and an overall molecular dipole is created.

atactic Random orientation of side groups along a polymer chain.

atom The basic building block of matter. It is made up of subatomic particles—protons, neutrons and electrons.

atomic absorption spectroscopy (AAS) An analytical technique that uses light absorption to measure the concentration of a metal in a sample.

atomic number The number of protons in the nucleus of an atom; identical to the charge number of the nucleus; symbol Z.

atomic radius A measurement used for the size of atoms; the distance from the nucleus to the outermost electrons.

atomic theory of matter A theory proposed by John Dalton in 1802 that states that all matter is made up of atoms. He said that atoms are indivisible, atoms of the same element are identical and compounds are made up of different types of atoms in fixed ratios.

average titre The average of concordant titres.

Avogadro's number The number of particles in a mole; symbol $N_A = 6.02 \times 10^{23}$ mol^{-1}.

B

ball-and-stick model A model that displays both the three-dimensional position of the atoms and the bonds between them. The atoms are represented by coloured spheres that are connected by rods to represent the bonds.

base A substance capable of accepting a hydrogen ion (proton).

basic solution An aqueous solution in which $[H_3O^+] < [OH^-]$. For a basic solution at 25°C, pH > 7.

bias Measured values consistently in one direction from the actual value; they may be too high or too low.

bibliography A list of resources referred to in your research.

bioaccumulation The build-up of heavy metals or other toxins in higher-order predators in a food chain.

biochar Charcoal produced from plant matter and stored in the soil.

biodegradable Capable of being decomposed by bacteria or other living organisms.

biological half-life The time it takes for half of the total amount of a particular substance to be degraded by biological processes.

biological oxygen demand (BOD) The amount of oxygen in water available to marine life.

blast furnace A type of furnace used for the extraction of metals from their ores, including iron from iron oxides.

block (periodic table) One of four main parts of the periodic table where elements have the same highest energy subshell filled, i.e. s, p, d or f subshell.

Bohr model A theory of the atom proposed by Niels Bohr that states that electrons in an atom occupy fixed, circular orbits that correspond to specific energy levels.

bore water Water collected in aquifers (underground water-bearing rock) below the Earth's surface. Bore water may be accessed by drilling and sinking a bore pipe into the aquifer.

brittle Shatters when given a sharp tap.

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.

buckyball A ball-like polyhedral molecule consisting of carbon atoms of the type found in fullerenes.

burette A graduated glass tube with a tap at one end that delivers known volumes of liquid.

C

calcification The building of a deposit of insoluble calcium salts, mainly calcium carbonate. It occurs in the formation of bone and in the development of shells in marine organisms.

calibrate To determine, check or rectify the graduation of any instrument giving quantitative measurements.

calibration curve A plot of data involving two variables that is used to determine the values for one of the variables.

carbon-12 The isotope of carbon that has a mass number of 12. The isotope contains 6 protons and 6 neutrons. One atom of carbon-12 is taken as having a mass of exactly 12 units. This is the standard from which all other relative masses are calculated.

carbonyl group A functional group composed of a carbon atom that has a double bond to an oxygen atom, e.g. $C{=}O$.

carboxyl group A functional group made up of a carbon atom, two oxygen atoms and a hydrogen atom. One oxygen atom forms a double bond to the carbon atom and the other oxygen atom forms single bonds to both the carbon and the hydrogen atoms. Written as $-COOH$ in condensed structural formulas.

carboxylic acid An organic compound containing the carboxyl ($-COOH$) functional group; its name ends in '-oic acid'.

catalyst A substance that increases the rate of a reaction but is not consumed in the reaction. The catalyst provides a new 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.

ceramic Material that is produced by the firing (heating followed by cooling) of clay.

chemical code Classification of chemicals into hazardous categories.

chemical contaminant An element or a compound that may be harmful if consumed in drinking water. It can be naturally occurring or synthetic.

chemical formula A representation of a substance using symbols for its constituent elements. It shows the ratio of atoms present in the substance.

chemical symbol A symbolic representation of an element, usually one or two letters, where the first letter is capitalised and the second letter is lower case, e.g. carbon's symbol is C and sodium's symbol is Na.

chromatogram The output of a chromatography procedure. In TLC and paper chromatography, it is the pattern of bands or spots formed on a plate or on the paper. In HPLC, it is the graph produced.

chromatography A technique for separating the components of a mixture. The components are carried by a mobile phase over the adsorbent surface of the stationary phase.

coke A solid that contains 80–90% carbon. It is produced by strongly heating coal in the absence of air.

colloid A mixture in which very small particles are spread throughout a liquid, solid or gas. The particles are bigger than single molecules, but so small that they do not settle on standing.

colorimeter An instrument that measures the absorbance of a selected colour of light by a sample solution.

column chromatography A chromatographic technique in which the stationary phase is in a column, e.g. high performance liquid chromatography (HPLC).

combustion A rapid reaction with oxygen accompanied by the release of large amounts of heat; also called burning.

complementary colours Pairs of colours that are often described as 'opposites'. When combined with each other, these colours 'cancel' each other out to form a greyscale colour such as white or black.

complete combustion A hydrocarbon undergoes complete combustion with oxygen at high temperatures when the only products are carbon dioxide and water.

components The chemicals in a mixture. The components can be separated by chromatography.

compound A pure substance made up of different types of atoms combined in a fixed ratio.

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.

concordant titre A set of titres that vary within a narrow range, e.g. within 0.10 mL from smallest to largest titre.

condensation polymer A polymer formed by a condensation reaction, involving the elimination of a small molecule (often water) when monomers bond together. The monomers have functional groups at both ends of the molecule.

condensation reaction A reaction in which two molecules link together, eliminating a small molecule such as water.

condensed structural 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. $CH_3CH_2CH_3$.

conductive polymer A polymer that is able to conduct electricity.

conductivity Permitting the flow of electric charges.

conductor An object or type of material that permits the flow of electric charges, e.g. a wire is an electrical conductor that can carry electricity along its length.

conflict of interest A personal benefit can derive from actions or decisions made in a professional situation.

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 its corresponding reduced form, e.g. Cu^{2+}/Cu.

control 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.

core charge The effective nuclear charge experienced by the outer-shell electrons in an atom. It indicates the attractive force felt by the valence electrons towards the nucleus.

covalent bond The force of attraction formed when one or more pairs of electrons are shared between two nuclei.

covalent layer lattice An arrangement of atoms in a lattice in which there are strong covalent bonds between the atoms that have formed in a layer.

covalent network lattice An arrangement of atoms in a lattice in which there are strong covalent bonds between the atoms in all three dimensions.

cracking A chemical process during which carbon–carbon bonds in alkanes are broken to form smaller molecules and some unsaturated molecules.

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.

crystal A solid made up of atoms or molecules arranged in a repeating three-dimensional pattern.

crystal lattice The symmetrical three-dimensional arrangement of atoms or ions inside a crystal.

crystalline region A region where polymer molecules line up parallel to each other and pack closely together.

crystallisation The process in which solid crystals are deposited when the concentration of a solute in a solution increases past the point of saturation.

crystallise Form solid crystals.

D

datalogging equipment Digital probes that connect to a computer to enable automatic measurements; e.g. temperature, pH.

decalcification The removal or loss of calcium or calcium compounds.

delocalise Spread out.

delocalised electron An electron that is not restricted to the region between two atoms.

density A measure of the amount of mass per unit volume. It has the SI units of $kg\ m^{-3}$, but is commonly quoted in $g\ cm^{-3}$.

dependent variable The variable that is measured or observed to determine the effect of changes in the independent variable.

desalinated seawater Fresh water made by removing the salt from seawater.

desalination The removal of salts from seawater to obtain fresh water.

desorption The breaking of the attraction between a substance and the surface to which the substance is adsorbed.

deviation Difference(s) from expected value.

diamond A form of pure carbon that is the hardest naturally occurring substance.

diatomic molecule A molecule formed from two atoms only, e.g. Cl_2.

dilute solution A solution that has a relatively low ratio of solute to solvent.

dilution factor The ratio of the final volume to the aliquot volume.

dilution The addition of a solvent to a solution to reduce its concentration.

dimer A molecule composed of two identical subunits that may be molecules in their own right, joined by strong intermolecular forces, such as hydrogen bonds.

dioxin A family of extremely toxic organic compounds that contain chlorine atoms and a six-membered ring made up of four carbon atoms and two oxygen atoms.

dipole The separation of positive and negative charges in a molecule.

dipole–dipole forces A form of intermolecular force that occurs between polar molecules where the partially positively charged end of one molecule is attracted to the partially negatively charged end of another molecule.

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 $Mg(s) + O_2(g) \rightarrow 2MgO(s)$.

discrete A separate thing.

dispersant A substance added to a mixture to separate particles from a suspension and to prevent settling or clumping.

dispersion force The 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.

dissociation The separation of positive and negative ions as an ionic lattice melts or dissolves. The process is usually reversible.

dissolution The process of dissolving a solute in a solvent to form a solution.

dissolve To incorporate a solid or gas into a liquid so as to form a solution.

dissolved oxygen (DO) The concentration of oxygen gas dissolved in water, in mg L^{-1}.

double covalent bond A covalent bond in which four electrons (two electron pairs) are shared.

dry corrosion See *direct corrosion.*

ductile Able to be drawn into a wire.

E

economic Relating to the economy (income and wealth).

effluent Liquid waste or sewage discharged into a water system such as a river or the sea.

elastomer A rubbery material composed of long molecules that is capable of recovering its original shape after being stretched.

electric dipole The separation of positive and negative charges in a bond or a molecule.

electrical conductivity The degree to which a specified material or solution conducts electricity.

electrolysis The production of a reaction by the passage of electrical energy from a power supply through a conducting liquid.

electrolyte A solution or molten substance that conducts electricity by means of the movement of ions, e.g. a solution of sodium chloride (table salt).

electromagnetic radiation A form of energy that moves through space. Visible light, radio waves and X-rays are forms of electromagnetic radiation.

electromagnetic spectrum All possible frequencies of electromagnetic radiation shown in order of their wavelengths or frequencies.

electron A negatively charged, subatomic particle that occupies the region around the nucleus of an atom.

electron density The concentration of electrons that usually refer to the regions around an atom or molecule.

electron dot diagram A representation of the electron arrangement in a molecule in which outer-shell electrons are represented by dots or crosses.

electron shell In the shell model of an atom, an electron shell is the fixed energy level that corresponds to a circular orbit of the electrons. In the Schrödinger model, a shell contains subshells and orbitals of equal or similar energy.

electron transfer diagram A diagram that shows how electrons move from a metal atom to a non-metal to form ions.

electronegativity The ability of an atom to attract electrons in a covalent bond towards itself.

electronic configuration In the shell model of an atom, the electronic configuration is a means of representing the number of electrons in each shell.

electroplating The deposition of a layer of one metal on the surface of another material by electrical means. Electroplating can be used to prevent corrosion by coating a relatively reactive metal, such as iron, with a less reactive metal, such as chromium.

electrostatic attraction The force of attraction between a positively charged particle and a negatively charged particle.

electrovalency The charge on an ion.

element A substance made up of atoms with the same atomic number.

elemental analysis A process that determines the mass of each element in a sample of a compound.

eluent The solvent that carries the components and passes through a chromatography column.

emission spectrum A spectrum produced when an element is excited by heat or radiation. It appears as distinct lines characteristic of the element.

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.

energy level One of the different shells of an atom in which an electron can be found.

environmental Relating to the air, water, minerals, organisms etc.

equivalence point The point in a titration at which the reactants have reacted in their correct mole ratios.

ester A molecule that contains the ester functional group (–COO–), which is made up of a carbonyl group, with another oxygen atom bonded to it. This functional group is not found on the end carbon of a molecule.

esterification reaction The chemical reaction between an alcohol and a carboxylic acid to form an ester as the main product.

ethical Relating to morals, and determining right and wrong.

eutrophication A process by which pollution from sources such as chemical fertiliser or sewage cause the over-enrichment of water by nutrients. This causes the overgrowth and decay of plants, de-oxygenation of water and the death of organisms.

excess reactant A reactant that is not completely consumed in a chemical reaction.

excited electron An electron that has absorbed a particular quantity of energy and moved from its ground state to a higher energy level. An atom is said to be excited when an electron is not in the lowest electron energy level possible (i.e. not in the ground state).

excited state A term used to describe an atom in which electrons occupy higher energy levels than the lowest possible energy levels.

expertise Expert knowledge or skills in a field.

F

first ionisation energy The energy required to remove one electron from an atom of an element in the gas phase.

formula A representation of an element or compound using symbols for its constituent elements. It shows the ratio of atoms in a compound or the number of atoms in a molecule.

fossil fuel A fuel formed by the decomposition of plant and animal material over millions of years, including coal, oil and natural gas.

fractional distillation A separation method based on the different boiling points of the components of a mixture, such as crude oil. The fractionating tower contains a series of trays holding condensed liquid, which vapour rising up the tower must bubble through to provide better separation.

full equation A representation of a reaction that uses formulas.

fullerene A molecule composed entirely of carbon, in the form of a hollow sphere or tube. Other shapes are possible. Each carbon atom is bonded to three other carbon atoms.

functional group An atom or group of atoms in an organic molecule that largely determine the molecule's properties and reactions, e.g. –OH, –COOH.

fungicide A chemical used to destroy fungi or inhibit their growth.

G

gas chromatography A very sensitive form of chromatography in which the mobile phase is a gas.

gemstone A precious stone that is usually ionic in structure.

giant molecule A molecule formed by some non-metals, e.g. the large network lattices such as diamond and graphite.

grant Funding given by a government or organisation for a particular project or purpose.

graphene A form of carbon consisting of planar sheets one atom thick in which each carbon atom is bonded to three neighbouring carbon atoms.

graphite A form of carbon in which the carbon atoms are arranged in layers.

gravimetric analysis A technique used for the quantitative determination of the amount of solute in a solution based on the mass of a solid.

Great Artesian Basin A very large reservoir of groundwater in Australia. It is the largest basin of its kind in the world.

greenhouse effect The warming of the Earth's atmosphere due to the absorption of infrared radiation by gases such as carbon dioxide, water and methane.

ground state A term used to describe an atom in which the electrons occupy the lowest possible energy levels.

groundwater Water found below the Earth's surface in porous rock or fractures.

group (periodic table) A vertical column of elements in the periodic table.

H

haematite A mineral containing iron. Composed of iron oxides with the formula Fe_2O_3. Haematite is the main source of iron ore in Australia.

half-equation A balanced chemical equation that shows the loss or gain of electrons by a species during oxidation or reduction, e.g. the oxidation of magnesium is written as the half-equation $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$.

hard water Water that requires a lot of soap to obtain a lather or froth.

hardness Water hardness is a measure of the amount of metal ions (mainly calcium and magnesium) in the water; the more minerals in the water, the harder the water. This 'hardness' means it is hard to get soapsuds from soap or detergents in this particular water. This happens because the metal ions react strongly with the negatively charged ions in soap molecules to form insoluble compounds. This effectively removes soap from the solution, so more soap is needed to achieve a lather.

heat capacity A measure of a substance's capacity to absorb and store heat energy. The heat capacity of 1 g of water is 4.18 J °C^{-1}. This tells you 1 g of water will absorb 4.18 J of heat energy to heat up by 1°C.

heat treatment Heating a metal in different ways to alter its structure and physical properties.

heavy metal A metal with high density; usually used to describe a metal that poses a threat to health.

herbicide A substance that is toxic to plants; it is used to destroy unwanted vegetation.

heterogeneous Diverse, different. A heterogeneous substance or solution possesses two or more different types of phases in the one sample, e.g. a suspension.

high density polyethene (HDPE) A form of the polymer polyethene that is formed from polymer chains with very few, short branches. This means the polymer chains are packed together closely, making the polymer dense. HDPE can have a percentage crystallinity as high as 95% and has excellent mechanical properties. HDPE is used to make pipes, buckets and food containers, such as milk bottles.

high-performance, or high-pressure, liquid chromatography (HPLC) A very sensitive technique used to separate the components in a mixture, to identify each component, and to measure the concentrations of the components. It relies on pumps to pass a pressurised liquid solvent containing the sample mixture through a column filled with a solid adsorbent material.

homogeneous Uniform. The components of a homogeneous substance are uniformly distributed throughout the substance, e.g. a solution is homogeneous because the solute and the solvent cannot be distinguished from each other.

homologous series A series of compounds with similar properties and the same general formula, in which each member contains one CH_2 unit more than the previous member.

hydrated An ion surrounded by water molecules. Hydrated ions can be found in aqueous solutions or crystalline solids.

hydride A compound in which hydrogen is bonded to another element. HF, HCl and HI are hydrides of group 17 elements.

hydrocarbon A compound that contains carbon and hydrogen only, e.g. the alkanes, alkenes and alkynes.

hydrogen bond A type of intermolecular, dipole–dipole force where a hydrogen atom is covalently bonded to a highly electronegative atom such as oxygen, nitrogen or fluorine. Due to the disparity of electronegativity values between the atoms involved, the hydrogen develops a partial positive charge and bonds to lone pairs of electrons on neighbouring atoms of oxygen, nitrogen or fluorine.

hydronium ion The $H_3O^+(aq)$ ion.

hydroxide ion The $OH^-(aq)$ ion.

hydroxyl group A functional group made up of an oxygen atom with a hydrogen atom bonded to it. Written as –OH in condensed structural formulas.

hypothesis A prediction based on previous knowledge; a possible outcome of the experiment.

I

incinerator Apparatus for burning waste material, especially industrial waste, at high temperatures until it is reduced to ash.

independent variable A variable that is changed by the researcher.

indicator A substance that is different colours in its acid and base forms.

inert Not chemically reactive.

ingestion The consumption of a substance by an organism, normally accomplished by taking the substance through the mouth.

inhalation The flow of air into an organism.

insecticide A substance used for killing insects.

instantaneous dipole A net dipole formed in a molecule due to temporary fluctuations in the electron density in the molecule.

intermolecular bond The net forces of attraction that act between neighbouring molecules.

intermolecular force An electrostatic force of attraction between molecules, including dipole–dipole forces, hydrogen bonds and dispersion forces.

interstitial alloy An alloy made by adding smaller atoms to a metal.

intramolecular bond A force that holds the atoms within a molecule together.

ion A positively or negatively charged atom or group of atoms.

ion–dipole attraction The attraction that forms between dissociated ions and polar water molecules when an ionic solid dissolves in water.

ionic bonding A type of chemical bonding that involves the electrostatic attraction between oppositely charged ions.

ionic compound A type of chemical compound that involves the electrostatic attraction between oppositely charged ions.

ionic equation An equation for a reaction that only includes the ions that are involved in the reaction, e.g. $Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$.

ionic product of water See *ionisation constant of water.*

ionisation (i) The removal of one or more electrons from an atom or ion; (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, $K_w = 1.00 \times 10^{-14}$ M^2.

ionisation energy The energy required to remove one electron from an atom of an element in the gas phase.

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

iron oxide A compound containing the elements iron and oxygen, e.g. Fe_2O_3, Fe_3O_4, FeO.

isotactic All the side groups of an isotactic polymer molecule are oriented along the same side of the polymer chain.

isotope Each of two or more forms of the same element that contain equal numbers of protons but different numbers of neutrons in their nuclei, e.g. ^{12}C and ^{13}C are isotopes of carbon.

L

latent heat The heat energy required to change the state of a substance without changing the temperature.

latent heat of fusion The energy required to change a fixed amount of solid to liquid at its melting temperature. The latent heat of fusion of water is 6.0 kJ mol^{-1}, meaning 6.0 kJ of energy is needed to change one mole of water from a solid to a liquid at 0°C.

latent heat of vaporisation The energy required to change a fixed amount of liquid to a gas at its boiling temperature. The latent heat of vaporisation of water is 44.0 kJ mol^{-1}, meaning 44.0 kJ is needed to change one mole of water from a liquid to a gas at 100°C.

lattice A regular arrangement of large numbers of atoms, ions or molecules.

limestone A mineral composed of calcium carbonate ($CaCO_3$).

limewater test A test for carbon dioxide gas. The presence of carbon dioxide is detected by bubbling the gas through a calcium hydroxide solution ($Ca(OH)_2(aq)$). The limewater reacts with the carbon dioxide and turns milky.

limiting reactant A reactant that is completely consumed in a reaction and which determines the amount of products formed.

line spectrum See *emission spectrum*

lone electron pair An outer-shell electron pair that does not form a bond with other atoms.

lone pair See *lone electron pair.*

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. It has therefore weaker intermolecular forces resulting in a lower tensile strength and increased ductility.

M

main group element An element in groups 1, 2 or 13–18 in the periodic table.

malleable Able to be bent or beaten into sheets.

mass number The number of protons and neutrons in the nucleus of an atom.

mass spectrometer An instrument that measures the mass-to-charge ratio of particles.

mass spectrum A plot of the isotopic mass, relative to the mass of carbon-12 taken as 12 units exactly, against the relative abundance of each isotope present in a sample.

matter Anything that has mass and occupies space.

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.

median The middle value of an ordered data set. To calculate the median, arrange the data set in ascending order, then count the number of data values. If the number of values is odd, select the middle value. If the number of values is even, select the two middle values, add them together and divide by 2.

metal complex A central metal atom surrounded by molecules or ions.

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.

metallic bonding The electrostatic attractive forces between delocalised valence electrons and positively charged metal ions.

metallic bonding model A description that explains the properties and behaviour of metals in terms of the particles in metals.

metalloid An element that displays both metallic and non-metallic properties, e.g. germanium, silicon, arsenic, tellurium.

mineral A naturally occurring inorganic substance that is solid and can be represented by a chemical formula, e.g. quartz.

miscible Liquids that can be mixed in any ratio to form a homogeneous solution.

mistake An avoidable error.

mobile phase The phase that moves over the stationary phase in a chromatographic separation.

mode The most frequent value in a data set. Arrange the data set in ascending order, then count the number of each data value.

model A description that scientists use to represent the important features of what they are trying to describe.

molar mass The mass of one mole of a substance measured in g mol^{-1}; symbol M.

molarity The amount of solute, in moles, dissolved in 1 litre of solution (mol L^{-1}).

mole The amount of substance that contains the same number of fundamental particles as there are atoms in 12 g of carbon-12; symbol n; unit mol.

mole ratio The ratio of species involved in a chemical reaction, based on the ratio of their coefficients in the reaction equation.

molecular formula A formula of a compound that gives the actual number and type of atoms present in a molecule. It may be the same as or different from the empirical formula.

molecule A group of two or more atoms covalently bonded together, and representing the smallest fundamental unit of a chemical compound.

molten Materials that are normally found as solids but are liquid, melted, due to elevated temperature.

monatomic Composed of single atoms, e.g. neon gas.

monochromator An instrument that transmits a narrow band of wavelengths of light or other radiation. The name is from the Greek words *mono* ('single') and *chroma* ('colour').

monomer A small molecule that can react to form long chains of repeating units, called polymers.

monoprotic acid An acid molecule that generates only one hydronium ion when ionised in water.

N

nanomaterial A material with nanoscale features.

nanoparticle A particle in the size range 1–100 nm.

nanorod A nanoscale rod in which length and width are in the range 1–100 nm. The length of the rod is 3–5 times its width.

nanoscale The scale used to classify objects 1–100 nm in size.

nanoscience The study of nanoparticles and nanotechnology.

nanotechnology The use of technologies that manipulate and investigate the properties of nanomaterials.

nanotube An allotrope of carbon that consists of layers of carbon atoms formed into a long cylinder.

nanowire A wire that has a diameter measured on the nanoscale. Its length is unrestricted.

neutral solution A solution in which the concentrations of H_3O^+ ions equals the concentration of OH^- ions; is neither acidic nor basic. At 25°C a neutral solution has a pH of 7.

neutralisation reaction An acid reacts with a base in stoichiometric proportions to form a salt plus water.

neutralise To react an acid with a base in stoichiometric proportions to form a solution of a salt and water.

neutron An uncharged subatomic particle found in the nucleus of an atom.

noble gas An unreactive gaseous element in group 18 of the periodic table. With the exception of helium, noble gases have eight electrons in their outer shells.

non-bonding electron An outer-shell electron that is not shared between atoms.

non-polar Bonds or molecules that do not have a permanent dipole. They have an even distribution of charge.

non-polar solvent A liquid or solvent that is a compound of two or more elements whose electronegativities are almost the same, e.g. oil.

nucleon A particle that makes up the nucleus of an atom, i.e. protons and neutrons.

nucleus The positively charged core at the centre of an atom, consisting of protons and neutrons.

O

ocean acidity The reduction in the pH of the ocean caused mainly by absorption of atmospheric carbon dioxide.

octet rule A rule used as part of the explanation for electron configuration and in bonding. The rule is that during a chemical reaction, atoms tend to lose, gain or share their valence electrons so that there are eight electrons in the outer shell.

orbital In the Schrödinger model, an orbital is a component of a subshell. It is a region of space in which electrons move. Each orbital holds two electrons.

ore A mineral or an aggregate of minerals that contains a valuable constituent, such as a metal, which is mined or extracted.

organometallic compound A substance that contains at least one carbon–metal bond.

origin The point at which a small spot of a mixture is placed so that it can be separated by paper or thin-layer chromatography.

osmosis The tendency of a solvent to pass through a semipermeable membrane from an area of low solute concentration to an area of higher solute concentration.

outermost shell See *valence shell.*

outlier A value that lies outside most of the other values in a set of data.

oxidant A reactant that causes another reactant to lose electrons during a redox reaction. This reactant is, itself, reduced and gains electrons, e.g. in the reaction between magnesium and oxygen, the oxygen is the oxidising agent, as it causes magnesium to lose electrons and form Mg^{2+}: $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$.

oxidation The process by which a chemical species such as a metal atom or a non-metal ion loses electrons. An oxidation half-equation will show the electrons as products (on the right-hand side of the arrow).

oxidised The loss of electrons. When a substance is oxidised, the electrons are written on the right-hand side of the arrow.

oxidising agent See *oxidant.*

P

paper chromatography An analytical technique for separating and identifying mixtures which uses paper as the stationary phase.

parallax error The perceived shift in an object's position as it is viewed from different angles.

percentage composition The proportion by mass of the different elements in a compound. % by mass of an element in a compound =

$$\frac{\text{mass of the element present}}{\text{total mass of the compound}} \times 100$$

period (periodic table) A horizontal row of elements in the periodic table. The start of a new period corresponds to the outer electron of that element beginning a new shell.

periodic law The way properties of elements vary periodically with their atomic number.

periodic table A table that organises the elements by grouping them according to their electronic configurations.

periodicity The periodic pattern of properties of the elements.

permafrost A layer of soil that remains solid as it is frozen all year long. Permafrost occurs in the polar regions.

persistent organic pollutant (POPs) A hazardous organic chemical compound that is resistant to biodegradation and remains in he environment for a long period of time.

persuasion Attempting to convince (someone of) or induce an opinion or outcome.

pesticide A substance used for destroying animals or other organisms harmful to cultivated plants or to animals.

pH 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 $\text{pH} = -\log_{10}[H_3O^+]$.

pH curve A graph of pH against volume of titrant.

pH scale See *pH*.

phenomenon Something that occurs and can be observed (or felt, heard etc.) to have occurred.

photoconductive polymer A polymer whose electrical conductivity increases on exposure to light.

photosynthesis A reaction that occurs in the leaves of plants between carbon dioxide and water, in the presence of sunlight and chlorophyll, to form glucose and oxygen. The photosynthesis process can be represented by the equation: $6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$

photovoltaic cell A device constructed from a specialised semiconductor that can produce a flow of electrons from light energy.

pipette A calibrated glass tube used to transfer known volumes of liquid.

plagiarism Using the work of other people without recognising them as the author or creator.

plasma An ionised state of matter, similar to a gas.

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.

polarity The measure of how polar a molecule or bond is. The difference in charge between the positive and negative ends of an electric dipole. The difference in charge between the positive and negative ends of a polar molecule or covalent bond.

polyatomic ion An ion that is made up of more than one element, e.g. the carbonate ion (CO_3^{2-}).

polyatomic molecule A molecule that consists of more than two types of atoms, e.g. H_2O.

polymer A long-chain molecule that is formed by the reaction of large numbers of repeating units (monomers).

polymerisation The process of synthesising a polymer.

polyprotic acid An acid molecule that generates more than one hydronium ion when ionised in water.

potable water Water that is suitable for drinking.

ppb (parts per billion) A unit of concentration which states the number of grams of solute in 1 billion grams of solution. It is equivalent to the number of mg of solute per kg of solution.

ppm (parts per million) A unit of concentration which states the number of grams of solute in 1 million grams of solution. It is equivalent to the number of mg of solute per kg of solution.

precipitate The solid formed during a reaction in which two or more solutions are mixed.

precipitation reaction A reaction between substances in solution in which one of the products is insoluble.

precise When repeated measurements of the same quantity give values that are in close agreement.

primary source A source that is a first-hand account.

primary standard A substance of known high purity which may be dissolved in a known volume of solvent.

protected catchment An area set aside to harvest and store water. There is no public access to protected catchments to ensure the quality of the water is high.

proton A positively charged, subatomic particle bound to neutrons in the nucleus of an atom.

Q

qualitative Relating to quality and not measured values.

qualitative analysis An analysis to determine the identity of the chemical(s) present in a substance.

quantised In specific quantities or chunks.

quantitative Relating to measured values rather than quality.

quantitative analysis An analysis to determine the concentration of the chemicals present in a mixture.

quantum mechanics A branch of science that describes the behaviour of extremely small particles such as electrons.

quenching Heating a metal to a moderate temperature and then cooling it rapidly to make it harder and more brittle.

R

radioactive Spontaneously undergoing nuclear decay to produce radiation such as beta particles, alpha particles and gamma rays.

random error An error that follows no regular pattern. (The effects of random errors can be reduced by taking the average of many observations.)

range The spread of values in the data set. It is taken as the largest data value minus the smallest data value.

raw data The information and results collected and recorded during an experiment.

reactivity The ease with which a chemical can undergo reactions.

reactivity series of metals 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.

recycled water Water recovered by the purification of wastewater.

redox reaction A reaction in which electron transfer occurs from the reducing agent to the oxidising agent. In a redox reaction, both oxidation and reduction occur.

reduced Has gained electrons. When a substance is reduced, the electrons are written on the left-hand side of the arrow (as reactants) in the half-equation.

reducing agent A reactant that causes another reactant to gain electrons during a redox reaction. This reactant is oxidised and loses electrons; e.g. in the reaction between magnesium and oxygen, the magnesium is the reducing agent, as it causes oxygen to gain electrons and form O^{2-} ions: $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$.

reductant See *reducing agent*.

reduction The process by which a chemical species gains electrons. A reduction half-equation will show the electrons on the reactant side (left-hand side) of the equation.

relative atomic mass The weighted average of the relative isotopic masses of an element on the scale where ^{12}C is 12 units exactly; symbol A_r.

relative formula mass The mass of a formula unit relative to the mass of an atom of ^{12}C taken as 12 units exactly. It is numerically equal to the sum of the relative atomic masses of the atoms making up the formula. Substances that contain atoms or ions bonded in lattice structures have a relative formula mass. Such compounds include ionic compounds and covalent network substances.

relative isotopic abundance The percentage abundance of a particular isotope in a sample of an element.

relative isotopic mass The mass of an atom of the isotope relative to the mass of an atom of carbon-12 taken as 12 units exactly.

relative molecular mass The mass of a molecule relative to the mass of an atom of ^{12}C, taken 12 units exactly; symbol M_r.

reliability An experiment can be repeated several times with consistent results.

reputation The belief that someone or something has a particular characteristic.

research question A statement defining what is being investigated.

retardation factor (R_f) The ratio of the distance a component has moved from the origin to the distance the solvent has moved from the origin.

retention time (R_t) The time taken for a component to pass through a chromatography column.

reticulated water A water supply that carries water by a network of pipes, such as a town supply. In Australian capital cities, 99% of households are connected to mains or town supply.

retracted Taken back or withdrawn.

reverse osmosis A process by which pure water can be obtained from salt water. Pressure is applied to the salt water, causing a net flow of water molecules away from the solution through a semipermeable membrane.

rhetoric Speaking or writing with the aim of persuading.

risk assessment A formal way of identifying risks and assessing potential harm from hazards in an experiment.

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.

salinity The presence of salt in water and soil that can damage plants or inhibit their growth.

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.

sample group A selection taken from a larger group.

saturated (i) A hydrocarbon that is composed of molecules with only carbon–carbon single bonds. (ii) Combined with or containing all the solute that can normally be dissolved at a particular temperature.

saturated solution A solution that cannot dissolve any more solute at the given temperature.

scanning tunnelling microscope (STM) A microscope that images atoms by using a sharp metallic tip to sense the atoms on the surface of a crystal.

Schrödinger model A model for the behaviour of electrons in atoms. It describes electrons as having wave-like properties.

Secchi disk Equipment used to measure the turbidity (clarity) of water.

secondary source A source derived from the original data or account.

sediment The solid material that settles to the bottom of a body of water.

seed crystal A small crystal from which a large crystal of the same material can typically be grown.

self-ionisation An ionisation reaction of pure water in which water behaves as both an acid and a base.

semipermeable membrane A membrane that allows solvent but not solute to pass through.

side group A group of atoms attached to a backbone chain of a long molecule.

single covalent bond A covalent bond in which two electrons are shared between two nuclei. It is depicted in a valence structure as a line between the two atoms involved.

slag A mixture of waste materials left over after a desired metal has been removed from its ore.

social Relating to society (human beings in a community).

soft water Water that contains very low concentrations of dissolved salts.

solubility A measure of the amount of solute dissolved in a given amount of solvent at a given temperature.

solubility curve A graph of solubility versus temperature for a particular solute dissolved in a particular solvent.

solubility table A reference table that can be used to predict the solubility of ionic compounds.

solute A substance that dissolves in a solvent, e.g. sugar is the solute when it dissolves in water.

solution A homogeneous mixture of a solute dissolved in a solvent.

solvent A substance, usually a liquid, which is able to dissolve a solute to form a solution. Water is a very good solvent.

space-filling model A three-dimensional model in which the atoms are represented by spheres with radii proportional to the radii of the atoms involved. The distances between spheres are also proportional to the distances between the atomic nuclei.

specific heat capacity The amount of energy required to raise the temperature of an amount of a substance, usually 1 gram, by 1°C. The unit for specific heat capacity is usually J g^{-1} °C^{-1}, e.g. the specific heat capacity of water is 4.18 J g^{-1} °C^{-1}.

spectator ion An ion that remains in solution and is unchanged in the course of a reaction. Spectator ions are not included in ionic equations.

spectroscopy The study of the way that radiation, such as light and radio waves, interacts with matter.

spontaneous redox reaction A redox reaction that occurs naturally.

stakeholder A person with an interest or concern in the matter being discussed.

standard solution A solution that has an accurately known concentration.

stationary phase A solid, or a solid that is coated in a viscous liquid, used in chromatography. The components of a mixture undergo adsorption to this phase as they are carried along by the mobile phase.

steel A generally hard, strong, durable and not malleable alloy of iron and carbon, usually containing 0.2–1.5% carbon, often with other constituents such as manganese, chromium, nickel, molybdenum, copper, tungsten, cobalt or silicon, depending on the desired alloy properties.

stem name The name that corresponds to the prefix for the longest chain of carbons in the molecule.

sterile An environment that is totally clean and free from living microorganisms.

stoichiometric calculation The calculation of relative amounts of reactants and products in a chemical reaction.

stoichiometry The calculation of relative amounts of reactants and products in a chemical reaction. Chemical equations give the ratios of the amounts (moles) of the reactants and products.

strong acid An acid that readily donates a hydrogen ion (proton) to a base.

strong base A base that readily accepts a hydrogen ion (proton) from an acid.

structural formula A formula that represents the three-dimensional arrangement of atoms in a molecule and shows all bonds as well as all atoms.

structural isomer A compound with the same molecular formula, but different structures.

subatomic particle A particle that makes up an atom—protons, neutrons and electrons.

sublimation The process by which a substance goes directly from the solid phase to the gaseous phase, without passing through a liquid phase.

subshell A component of a shell in the Schrödinger model, made up of orbitals. Each subshell can be regarded as an energy level that electrons can occupy.

substitutional alloy An alloy made from elements of similar chemical properties and size.

super acid An acid that has acidity greater than the acidity of 100% sulfuric acid.

supersaturated solution An unstable solution that has more solute dissolved at a given temperature than a saturated solution.

surface tension The resistance of a liquid to increase its surface area.

suspension A heterogeneous mixture containing solid particles that are large enough to sink to the bottom of the mixture if it is left to stand (sedimentation), e.g. sand in a container of water that has just been shaken.

symmetrical molecule A molecule in which the polar bonds are evenly (or symmetrically) distributed. The bond dipoles cancel out and do not create an overall molecular dipole.

syndiotactic The side groups of the polymer molecule are oriented in regular alternating directions along the polymer chain.

systematic error An error that produces a constant bias in measurement. (Systematic errors are eliminated or minimised through calibration of apparatus and the careful design of a procedure.)

T

tempering A process in which a metal that has been quenched is warmed again to a lower temperature to reduce its brittleness but to retain its hardness.

temporary dipole A net dipole formed in a molecule due to temporary fluctuations in the electron density in the molecule.

tensile strength The maximum resistance of a material to a force which is pulling it apart before breaking, measured as the maximum stress the material can withstand without tearing.

tetrahedral shape The shape of a molecule with a central atom surrounded by four other atoms. The bond angle between two outer atoms and the central atom is 109.5°.

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.

thin-layer chromatography An analytical technique for separating and identifying mixtures; it uses a thin layer of fine powder spread on a glass or plastic plate as the stationary phase.

titration The process used to determine the concentration of a reactant where one solution is added from a burette to a known volume of another solution.

titration curve A plot of the pH versus the equivalents of acid or base added during the titration of the other.

titre The volume of liquid, measured by a burette, used in a titration.

total dissolved solids (TDS) The total amount of mobile charged ions, including minerals, salts or metal ions dissolved in a given quantity of water.

transition metal An element in groups 3–12 in the periodic table.

transparency Operating in a way that makes it easy for others to see.

trend An observed pattern of data in a particular direction.

triple covalent bond A covalent bond in which six electrons are shared between two nuclei. It is depicted in a valence structure as three lines between the two atoms involved.

triprotic acid An acid molecule that generates three hydronium ions when ionised in water.

turbidity A measure of the cloudiness of water due to suspended solids.

U

uncertainty An error associated with measurements made during experimental work.

unsaturated A hydrocarbon composed of molecules with one or more carbon–carbon double or triple bonds.

unsaturated solution A solution that contains less solute dissolved at a given temperature than a saturated solution.

UV–visible spectrophotometer An analytical device that measures the absorbance of a solution in the UV–visible region of the spectrum.

V

valence electron An electron found in the valence shell; an outermost electron in an atom or ion.

valence shell The highest energy shell (outer shell) of an atom that contains electrons.

valence shell electron pair repulsion theory (VSEPR) A model used to predict the shape of molecules. The basis of VSEPR is that the valence electron pairs surrounding an atom mutually repel each other, and therefore adopt an arrangement that minimises this repulsion, thus determining the molecular shape.

valence structure A representation of the electron arrangement in a molecule in which covalent bonds are represented by lines.

validity Refers to whether the evidence supports the argument.

Van Dorn sampler A tool used to collect water samples at different depths. It is made up of a polymer with caps at both ends attached to a rope at the surface.

variable Any factor that can be controlled, changed and measured in an experiment.

vested interest A personal gain from being involved in a situation.

volumetric analysis Analysis using measurement of volumes, e.g. titration.

volumetric flask A laboratory flask calibrated to contain a precise volume.

vulcanisation A chemical process for converting natural rubber or related polymers into more durable materials through the addition of sulfur or other cross-linking agents.

W

water cycle The continuous process by which water is circulated throughout the Earth and the atmosphere. Water passes into the atmosphere as water vapour, precipitates to Earth in liquid or solid form, and returns to the atmosphere through evaporation.

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.

work hardening The increase in strength that results from processes such as hammering, rolling and drawing a metal.

Z

Ziegler–Natta catalyst A catalyst for addition polymerisation developed by Karl Ziegler and Giulio Natta. The catalyst contains a mixture of titanium chloride ($TiCl_3$) and triethylaluminium ($Al(CH_2CH_5)_3$).

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Acknowledgements

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TarraWarra Estate: p.350b.

Tentotwo: p.431cr.

University of Idaho Coeur d' Alene: Marie Pengilly, p.438r.

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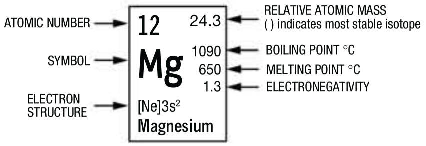
Volvo Car Corporation: Volvo Cars, p.187t.

Notes

Groups



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Periods	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1									1 1.0 **H** -252.9 -259 2.2 $1s^1$ Hydrogen									2 4.0 **He** -268.9 -272 – $1s^2$ Helium
2	3 6.9 **Li** 1347 180 1.0 $1s^22s^1$ Lithium	4 9.0 **Be** 2468 1287 1.6 $1s^22s^2$ Beryllium											5 10.8 **B** 4000 2077 2.0 $1s^22s^22p^1$ Boron	6 12.0 **C** 4827 3500 2.6 $1s^22s^22p^2$ Carbon	7 14.0 **N** -195.8 -210 3.0 $1s^22s^22p^3$ Nitrogen	8 16.0 **O** -183 -219 3.4 $1s^22s^22p^4$ Oxygen	9 19.0 **F** -188.1 -220 4.0 $1s^22s^22p^5$ Fluorine	10 20.2 **Ne** -246 -249 – $1s^22s^22p^6$ Neon
3	11 23.0 **Na** 882.9 97.8 0.9 $[Ne]3s^1$ Sodium	12 24.3 **Mg** 1090 650 1.3 $[Ne]3s^2$ Magnesium											13 27.0 **Al** 2519 660.3 1.6 $[Ne]3s^23p^1$ Aluminium	14 28.1 **Si** 3265 1414 1.9 $[Ne]3s^23p^2$ Silicon	15 31.0 **P** 280.5 44.2 2.2 $[Ne]3s^23p^3$ Phosphorus	16 32.1 **S** 444.6 115.2 2.6 $[Ne]3s^23p^4$ Sulfur	17 35.5 **Cl** -34 -102 3.2 $[Ne]3s^23p^5$ Chlorine	18 39.9 **Ar** -185.8 -189 – $[Ne]3s^23p^6$ Argon
4	19 39.1 **K** 758.8 63.5 0.8 $[Ar]4s^1$ Potassium	20 40.1 **Ca** 1484 842 1.0 $[Ar]4s^2$ Calcium	21 45.0 **Sc** 2836 1541 1.4 $[Ar]3d^14s^2$ Scandium	22 47.9 **Ti** 3287 1670 1.5 $[Ar]3d^24s^2$ Titanium	23 50.9 **V** 3407 1910 1.6 $[Ar]3d^34s^2$ Vanadium	24 52.0 **Cr** 2671 1907 1.7 $[Ar]3d^54s^1$ Chromium	25 54.9 **Mn** 2061 1246 1.6 $[Ar]3d^54s^2$ Manganese	26 55.8 **Fe** 2861 1538 1.8 $[Ar]3d^64s^2$ Iron	27 58.9 **Co** 2927 1495 1.9 $[Ar]3d^74s^2$ Cobalt	28 58.7 **Ni** 2913 1455 1.9 $[Ar]3d^84s^2$ Nickel	29 63.5 **Cu** 2560 1085 1.9 $[Ar]3d^{10}4s^1$ Copper	30 65.4 **Zn** 907 419.5 1.6 $[Ar]3d^{10}4s^2$ Zinc	31 69.7 **Ga** 2229 27.8 1.8 $[Ar]3d^{10}4s^24p^1$ Gallium	32 72.6 **Ge** 2833 938.2 2.0 $[Ar]3d^{10}4s^24p^2$ Germanium	33 74.9 **As** 613 816.8 2.2 $[Ar]3d^{10}4s^24p^3$ Arsenic	34 79.0 **Se** 684.8 220.8 2.6 $[Ar]3d^{10}4s^24p^4$ Selenium	35 79.9 **Br** 58.8 -7.2 3.0 $[Ar]3d^{10}4s^24p^5$ Bromine	36 83.8 **Kr** -153.4 -157 – $[Ar]3d^{10}4s^24p^6$ Krypton
5	37 85.5 **Rb** 687.8 39 0.8 $[Kr]5s^1$ Rubidium	38 87.6 **Sr** 1377 777 1.0 $[Kr]5s^2$ Strontium	39 88.9 **Y** 3345 1522 1.2 $[Kr]4d^15s^2$ Yttrium	40 91.2 **Zr** 4406 1854 1.3 $[Kr]4d^25s^2$ Zirconium	41 92.9 **Nb** 4741 2477 1.6 $[Kr]4d^45s^1$ Niobium	42 96.0 **Mo** 4639 2622 2.2 $[Kr]4d^55s^1$ Molybdenum	43 (98) **Tc** 4262 2157 2.1 $[Kr]4d^55s^2$ Technetium	44 101.1 **Ru** 4147 2333 2.2 $[Kr]4d^75s^1$ Ruthenium	45 102.9 **Rh** 3695 1963 2.3 $[Kr]4d^85s^1$ Rhodium	46 106.4 **Pd** 2963 1555 2.2 $[Kr]4d^{10}5s^0$ Palladium	47 107.9 **Ag** 2162 961.8 1.9 $[Kr]4d^{10}5s^1$ Silver	48 112.4 **Cd** 766.8 321.1 1.7 $[Kr]4d^{10}5s^2$ Cadmium	49 114.8 **In** 2072 156.6 1.8 $[Kr]4d^{10}5s^25p^1$ Indium	50 118.7 **Sn** 2602 231.9 2.0 $[Kr]4d^{10}5s^25p^2$ Tin	51 121.8 **Sb** 1587 630.6 2.0 $[Kr]4d^{10}5s^25p^3$ Antimony	52 127.6 **Te** 987.8 449.5 2.1 $[Kr]4d^{10}5s^25p^4$ Tellurium	53 126.9 **I** 184.4 113.7 2.7 $[Kr]4d^{10}5s^25p^5$ Iodine	54 131.3 **Xe** -108.1 -112 2.6 $[Kr]4d^{10}5s^25p^6$ Xenon
6	55 132.9 **Cs** 670.8 28.5 0.8 $[Xe]6s^1$ Caesium	56 137.3 **Ba** 1845 727 0.9 $[Xe]6s^2$ Barium	57 138.9 **La** 2464 920 1.1 $[Xe]5d^16s^2$ Lanthanum	72 178.5 **Hf** 4600 2233 1.3 $[Xe]4f^{14}5d^26s^2$ Hafnium	73 180.9 **Ta** 5455 3017 1.5 $[Xe]4f^{14}5d^36s^2$ Tantalum	74 183.8 **W** 5555 3414 1.7 $[Xe]4f^{14}5d^46s^2$ Tungsten	75 186.2 **Re** 5596 3454 1.9 $[Xe]4f^{14}5d^56s^2$ Rhenium	76 190.2 **Os** 5008 3033 2.2 $[Xe]4f^{14}5d^66s^2$ Osmium	77 192.2 **Ir** 4428 2446 2.2 $[Xe]4f^{14}5d^76s^2$ Iridium	78 195.1 **Pt** 3825 1768 2.2 $[Xe]4f^{14}5d^96s^1$ Platinum	79 197.0 **Au** 2836 1064 2.2 $[Xe]4f^{14}5d^{10}6s^1$ Gold	80 200.6 **Hg** 356.6 -38.8 1.9 $[Xe]4f^{14}5d^{10}6s^2$ Mercury	81 204.4 **Tl** 1473 303.8 1.8 $[Xe]4f^{14}5d^{10}6s^26p^1$ Thallium	82 207.2 **Pb** 1749 327.5 1.8 $[Xe]4f^{14}5d^{10}6s^26p^2$ Lead	83 209.0 **Bi** 1564 271.4 1.9 $[Xe]4f^{14}5d^{10}6s^26p^3$ Bismuth	84 (210) **Po** 962 253.8 2.0 $[Xe]4f^{14}5d^{10}6s^26p^4$ Polonium	85 (210) **At** 366.8 301.8 2.2 $[Xe]4f^{14}5d^{10}6s^26p^5$ Astatine	86 (222) **Rn** -61.8 -71.2 – $[Xe]4f^{14}5d^{10}6s^26p^6$ Radon
7	87 (223) **Fr** 676.8 27 0.7 $[Rn]7s^1$ Francium	88 (226) **Ra** 1140 699.8 0.9 $[Rn]7s^2$ Radium	89 (227) **Ac** 3200 1050 1.1 $[Rn]6d^17s^2$ Actinium	104 (261) **Rf** – – – $[Rn]5f^{14}6d^27s^2$ Rutherfordium	105 (262) **Db** – – – $[Rn]5f^{14}6d^37s^2$ Dubnium	106 (266) **Sg** – – – $[Rn]5f^{14}6d^47s^2$ Seaborgium	107 (264) **Bh** – – – $[Rn]5f^{14}6d^57s^2$ Bohrium	108 (267) **Hs** – – – $[Rn]5f^{14}6d^67s^2$ Hassium	109 (268) **Mt** – – – $[Rn]5f^{14}6d^77s^2$ Meitnerium	110 (271) **Ds** – – – $[Rn]5f^{14}6d^87s^2$ Darmstadtium	111 (272) **Rg** – – – $[Rn]5f^{14}6d^97s^2$ Roentgenium	112 (285) **Cn** – – – $[Rn]5f^{14}6d^{10}7s^2$ Copernicium	113 (284) **Uut*** – – – $[Rn]5f^{14}6d^{10}7s^17p^1$ Ununtrium	114 (289) **Fl** – – – $[Rn]5f^{14}6d^{10}7s^27p^2$ Flerovium	115 (289) **Uup*** – – – $[Rn]5f^{14}6d^{10}7s^27p^3$ Ununpentium	116 (292) **Lv** – – – $[Rn]5f^{14}6d^{10}7s^27p^4$ Livermorium	117 (294) **Uus*** – – – $[Rn]5f^{14}6d^{10}7s^27p^5$ Ununseptium	118 (294) **Uuo*** – – – $[Rn]5f^{14}6d^{10}7s^27p^6$ Ununoctium

*temporary names

f BLOCK

58 140.1 **Ce** 3443 799 1.1 $[Xe]4f^25d^06s^2$ Cerium	59 140.9 **Pr** 3520 931 1.1 $[Xe]4f^35d^06s^2$ Praseodymium	60 144.2 **Nd** 3074 1016 1.1 $[Xe]4f^45d^06s^2$ Neodymium	61 (145) **Pm** 3000 1042 – $[Xe]4f^55d^06s^2$ Promethium	62 150.4 **Sm** 1794 1072 1.1 $[Xe]4f^65d^06s^2$ Samarium	63 152.0 **Eu** 1794 1072 – $[Xe]4f^75d^06s^2$ Europium	64 157.3 **Gd** 3273 1313 1.2 $[Xe]4f^75d^16s^2$ Gadolinium	65 158.9 **Tb** 3230 1359 – $[Xe]4f^95d^06s^2$ Terbium	66 162.5 **Dy** 2567 1412 1.2 $[Xe]4f^{10}5d^06s^2$ Dysprosium	67 164.9 **Ho** 2700 1472 1.2 $[Xe]4f^{11}5d^06s^2$ Holmium	68 167.3 **Er** 2868 1529 1.2 $[Xe]4f^{14}5d^06s^2$ Erbium	69 168.9 **Tm** 1950 1545 1.2 $[Xe]4f^{12}5d^06s^2$ Thulium	70 173.1 **Yb** 1196 824 – $[Xe]4f^{14}5d^06s^2$ Ytterbium	71 175.0 **Lu** 3402 1663 1.0 $[Xe]4f^{14}5d^16s^2$ Lutetium
90 232.0 **Th** 4875 1750 1.3 $[Rn]5f^06d^27s^2$ Thorium	91 231.0 **Pa** – 1572 1.5 $[Rn]5f^26d^17s^2$ Protactinium	92 238.0 **U** 4131 1135 1.7 $[Rn]5f^36d^17s^2$ Uranium	93 (237) **Np** 3902 644 1.3 $[Rn]5f^46d^17s^2$ Neptunium	94 (244) **Pu** 3228 640 1.3 $[Rn]5f^66d^07s^2$ Plutonium	95 (243) **Am** 2011 1176 – $[Rn]5f^76d^07s^2$ Americium	96 (247) **Cm** – 1345 – $[Rn]5f^76d^17s^2$ Curium	97 (247) **Bk** – 986 – $[Rn]5f^96d^07s^2$ Berkelium	98 (251) **Cf** – 900 – $[Rn]5f^{10}6d^07s^2$ Californium	99 (252) **Es** – 860 – $[Rn]5f^{11}6d^07s^2$ Einsteinium	100 (257) **Fm** – 1527 – $[Rn]5f^{12}6d^07s^2$ Fermium	101 (258) **Md** – 827 – $[Rn]5f^{13}6d^07s^2$ Mendelevium	102 (259) **No** – 827 – $[Rn]5f^{14}6d^07s^2$ Nobelium	103 (262) **Lr** – 1627 – $[Rn]5f^{14}6d^17s^2$ Lawrencium