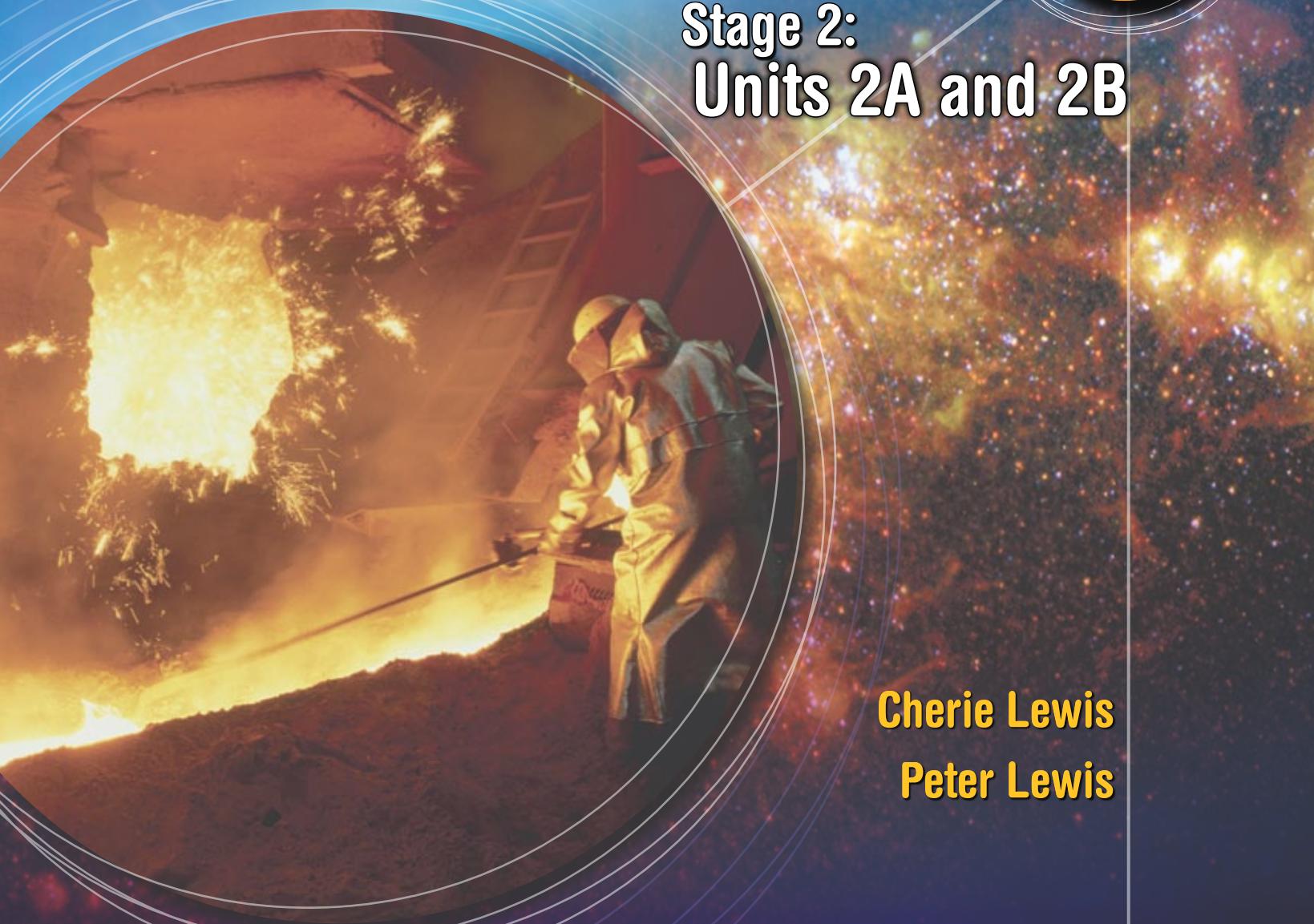


# Chemistry for WA 1

Stage 2:  
Units 2A and 2B



**Cherie Lewis  
Peter Lewis**

## Pearson Heinemann

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### Chapter opening photographs

- 1 An early periodic table of elements.
- 2 Car manufacturing plant.
- 3 Salt pans, Dampier Salt, Port Hedland.
- 4 Molecular graphic of the structure of water vapour.
- 5 The sand spit at Willie Creek, at the north end of Cable Beach, is some thirteen miles north of Broome.
- 6 Mortar and pestle.
- 7 Full view of iceberg.
- 8 Dissolution of a sugar cube in water.
- 9 Precipitation of lead iodine. A yellow precipitate of lead iodide formed by the reaction of lead nitrate solution and potassium iodide solution in water.
- 10 Burning match.
- 11 Mine blasting in Cerro Colorado Copper Mine, Chile.
- 12 A major street in the Miguel Hidalgo area of Mexico City is clogged with traffic and smog during the morning rush hour.
- 13 Trees killed by acid rain and pollution.
- 14 Light micrograph in incident illumination of crystalline silver deposited on a copper wire.
- 15 Electroplating equipment.
- 16 Containers of crude oil and various products obtained from crude oil, on a background of a silhouetted oil refinery.
- 17 Aerial of alumina plant, QLD.

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# Chemistry for WA 1

## The complete chemistry package

*Chemistry for WA* is the most up to date and complete package designed and written for the Chemistry course of study in Western Australia. This two-book series adopts a student-centred approach, maintaining a focus on chemical knowledge, skills and application, while presenting chemistry through varied contexts to engage and stimulate students.

*Chemistry for WA 1* is written to cover Units 2A and 2B. Unit 2A is designed to allow students to develop a thorough working knowledge of basic chemical principles and skills, building a strong foundation that is then applied to various contexts related to chemistry in and around the home. Unit 2B uses the context of chemistry, me and my environment, to explore the relationship of chemistry to students' lives, while ensuring they continue to develop a clear understanding and application of fundamental chemical concepts.

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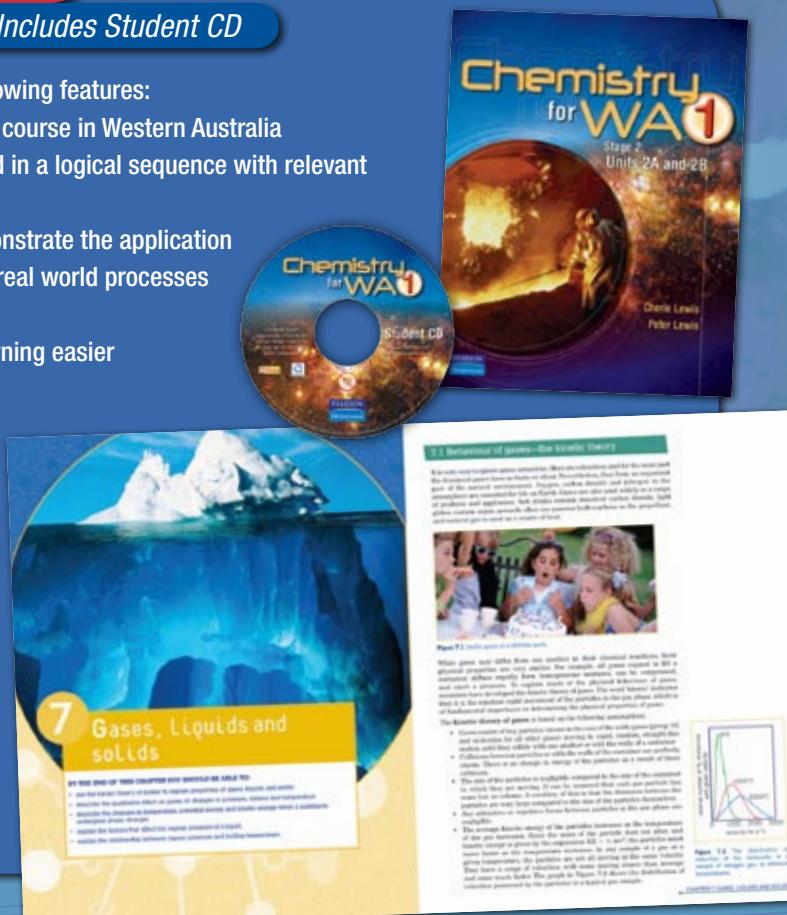
*Includes Student CD*

The *Student Book* consists of chapters with the following features:

- specifically written for Stage 2 of the Chemistry course in Western Australia
- chapters focused on core unit content presented in a logical sequence with relevant contexts to engage and stimulate students
- applied chemistry units within chapters to demonstrate the application of chemical models, principles and concepts to real world processes
- engaging colour photos
- illustrations designed to make teaching and learning easier
- theory broken into manageable chunks
- comprehensive review questions throughout each chapter
- chapter review with main ideas summary and extensive revision questions that focus on content and its contextual application
- unit reviews with exam-style questions that tie together concepts from a group of chapters.

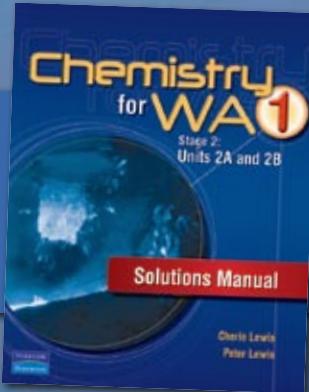
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## Chemistry for WA 1 Solutions Manual

The *Solutions Manual* is available for teacher and student purchase. It contains detailed, fully worked solutions to Student Book questions.



## Chemistry for WA 1 Companion Website



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The Companion Website is available online. It contains a wealth of support material for students and teachers including:

### Student resources:

- **Review questions:** autocorrecting multiple choice questions for exam revision.
- **Interactive animations** or learning objects to engage students in exploring concepts and key ideas.
- **QuickTime videos** to explore chemical concepts in a visually stimulating way.
- **3D molecules gallery** for interactive manipulation and viewing of molecular structures.
- **Web destinations:** a list of reviewed websites that support further investigation and exploration.
- **Answers:** Numerical and short-answer responses for the review exercises, end of chapter questions and unit review questions in the student book.

### Teacher's Resource Centre:

The documents available in the *Teacher's Resource Centre* of the Companion Website are password protected.

All resources are available as:

- PDF format to make printing easy
- editable MS Word format, which allows you to modify and adapt any resources to meet your needs.

The Teacher's Resource provides a wealth of teacher-support material including:

- teaching programs
- curriculum grids
- chapter tests with answers
- worksheets and answers
- teacher demos with support notes and risk assessments.

**For more information on the *Chemistry for WA* series,  
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To help students consolidate knowledge and encourage independent learning, each chapter ends with a comprehensive review including:

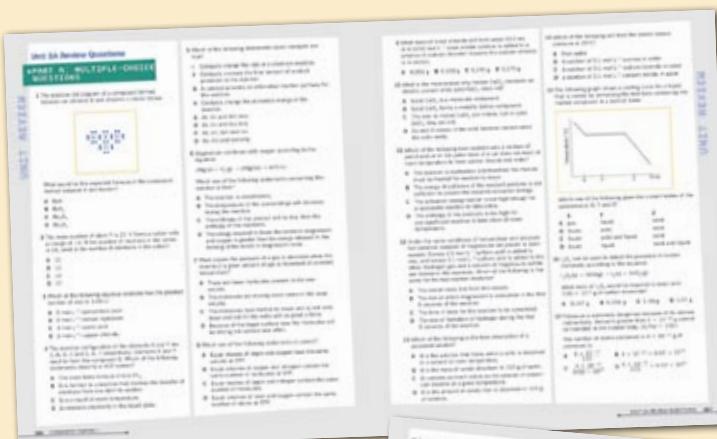
- **Major ideas summary** focusing on the key points of the chapter
- **Questions** that draw on the key ideas throughout the chapter. These questions test students' chemical knowledge and skills, and their ability to apply their knowledge to varied situations and contexts. Chapter review questions involve students using various skills including application, problem solving, investigation, research, data analysis, processing, analysing, assessing, evaluating and interpreting. This will challenge students to think beyond basic chemical knowledge to real world applications.



## Each Student Book includes the Chemistry for WA 1 Student CD

The *Chemistry for WA 1 Student CD* is a comprehensive resource that will allow students to review their work and revise key concepts, as well as providing an opportunity for accelerated learning. The student CD included with this book contains:

- an electronic version of the Student Book
- the Companion Website on CD
- a link to the live Companion Website.



Two unit reviews provide students with practice at exam-style questions. These questions revise key ideas from a series of chapters and allow students to demonstrate their learning in various ways.



## Chemistry for WA 1 package

Don't forget the other *Chemistry for WA 1* components that will help engage students in learning in Chemistry:

- *Chemistry for WA 1 Solutions Manual*
- *Chemistry for WA 1 Companion Website*—containing teacher and student resources



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# CURRICULUM GUIDE

This guide maps the Course content, as described in the Curriculum Council of WA Chemistry document and the relevant chapters in the Chemistry for WA 1 Student Book.

## UNIT 2A

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17

Macroscopic properties of matter																		
Pure substances and mixtures						◆												
Kinetic Theory of Matter								◆										
Pressures and volumes of gases							◆											
Vapour pressure and boiling point						◆												
Saturated, unsaturated and supersaturated solutions								◆										
Predictions of precipitation reactions									◆									
Colligative properties								◆										
Electrolytes							◆											
Atomic structure and bonding																		
Sub-atomic structure of atoms	◆																	
Atomic number, mass number, isotopes	◆																	
Shell model of electron structure of atoms	◆																	
Groups and periods in periodic table	◆	◆	◆	◆	◆													
Ionic compounds			◆															
Metals		◆																
Covalent network and molecular substances				◆	◆													
Electron dot diagrams			◆	◆														
Chemical reactions																		
Equations for simple chemical reactions												◆						
Conservation of mass, atoms and charge												◆						
Calculations involving moles, mass, gas volume							◆					◆						
Concentration calculations										◆			◆					
Percentage composition								◆										
Simple stoichiometric problems												◆						
Endothermic and exothermic reactions													◆					
Rates of reactions														◆				
Collision theory														◆				
Applied chemistry																		
Solutions around the home												◆						
Uses of household substances		◆	◆	◆	◆													
Rates and heats of household reactions													◆	◆				
Biological, environmental and industrial processes	◆	◆	◆	◆	◆							◆	◆	◆	◆	◆		◆

## UNIT 2B

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
<b>Chemical reactions</b>																	
Ionic equations												◆	◆	◆			
Stoichiometric calculations – limiting reagent								◆			◆						
Empirical formula calculations											◆			◆			
<b>Acids and bases in aqueous solutions</b>																	
Arrhenius and Brønsted-Lowry models of acids and bases												◆					
Properties of acids and bases												◆					
Polyprotic acids												◆					
Qualitative application of the pH scale												◆					
Properties of non-metal and metal oxides												◆					
<b>Oxidation and reduction</b>														◆			
Oxidation-reduction processes														◆			
Oxidation numbers													◆				
Metal and halogen displacement reactions												◆					
Simple redox equations												◆					
Operation of electrolysis cells													◆				
Electrolysis of molten salts												◆		◆			
<b>Organic chemistry</b>																	
Bonding capacity of carbon														◆			
Alkanes – structures and reactions														◆			
Alkenes – structures and reactions														◆			
Benzene – structure														◆			
Structural and geometrical isomers														◆			
<b>Applied chemistry</b>																	
Acids in the environment															◆		
Electrowinning and electrorefining														◆			
Sources and uses of hydrocarbons														◆			
Biological, environmental or industrial processes														◆	◆	◆	

PLATE IV. This plate contains the figures or signs chosen to represent the several chemical or ultimate particles.

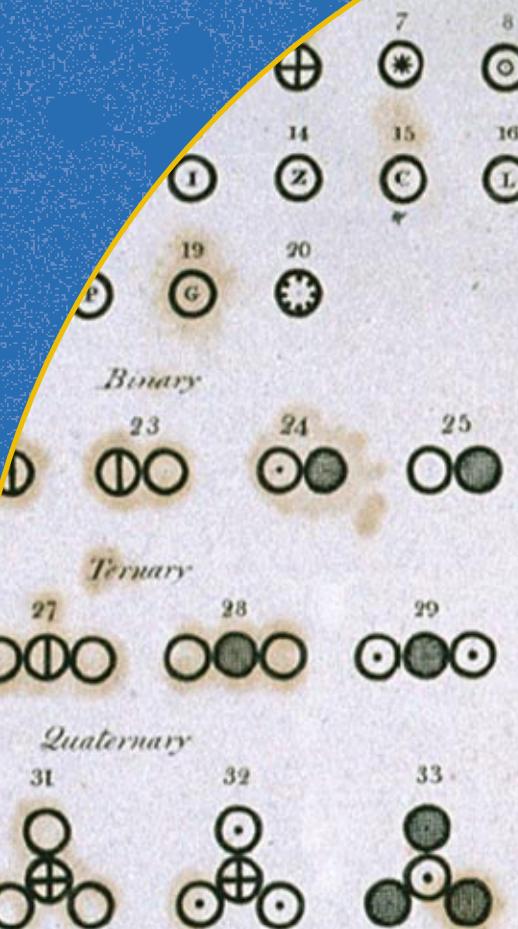


Fig.		Fig.
1	Hydrog. its rel. weight	11 Strontites - - -
2	Azote, - - -	12 Barytes - - -
3	Carbone or charcoal, -	13 Iron - - -
4	Oxygen, - - -	14 Zinc - - -
5	Phosphorus, - - -	15 Copper - - -
6	Sulphur, - - -	16 Lead - - -
7	Magnesia, - - -	17 Silver - - -
8	Lime, - - -	18 Platina - - -
9	Soda, - - -	19 Gold - - -
10	Potash, - - -	20 Mercury - - -

21.	An atom of water or steam, composed of 1 of oxygen and 1 of hydrogen, retained in physical contact by a strong affinity, and supposed to be surrounded by a common atmosphere of heat; its relative weight =	8
22.	An atom of ammonia, composed of 1 of azote and 1 of hydrogen - - -	6
23.	An atom of nitrous gas, composed of 1 of azote and 1 of oxygen - - -	12
24.	An atom of olefiant gas, composed of 1 of carbone and 1 of hydrogen - - -	6
25.	An atom of carbonic oxide composed of 1 of carbone and 1 of oxygen - - -	12
26.	An atom of nitrous oxide, 2 azote + 1 oxygen -	17
27.	An atom of nitric acid, 1 azote + 2 oxygen -	19
28.	An atom of carbonic acid, 1 carbone + 2 oxygen -	19
29.	An atom of carburetted hydrogen, 1 carbone + 2 hydrogen -	7
	azote + 3 oxygen	26
	sulphur + 3 oxygen	34
	gen, 1 sulphur + 3	
	+ 1 hydrogen	16
	ic acid + 1 nitrous	
	- - -	
	one + 2 water	
	, 1 nitric acid -	
	- - -	
	1 carbonic	

# 1

## Atomic theory

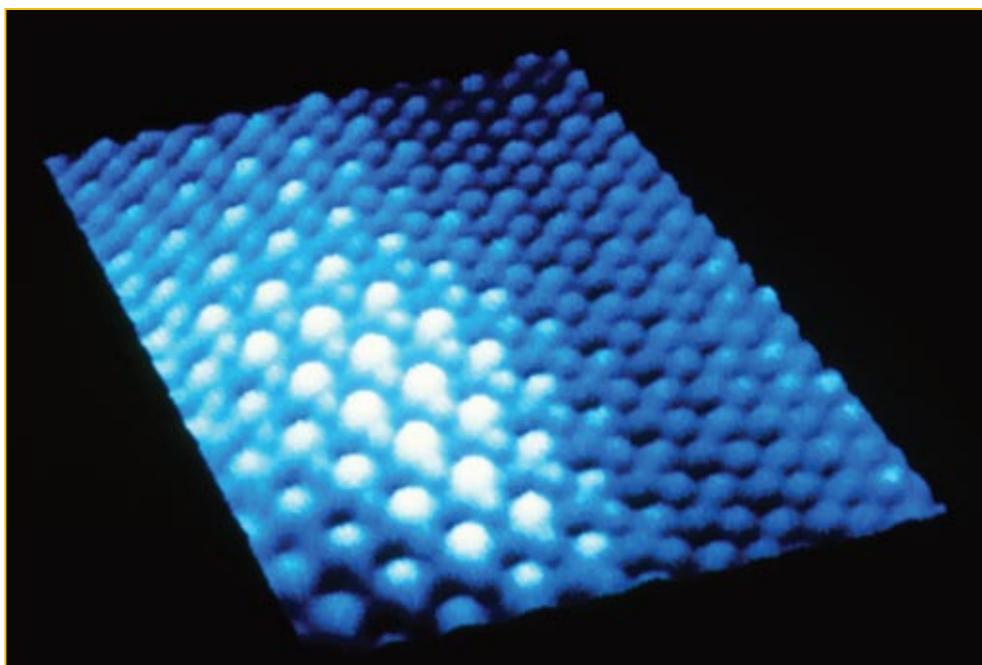
### BY THE END OF THIS CHAPTER YOU SHOULD BE ABLE TO:

- use a simple model to describe the subatomic structure of an atom
- describe the arrangement of electrons in energy levels or shells in atoms and ions
- determine the number of protons, neutrons and electrons in an atom or simple ion using the relationship between atomic number and mass number
- describe an isotope in terms of the number of neutrons in the nucleus
- explain and describe the arrangement of elements in the periodic table
- identify the group and period of the periodic table to which an element belongs, given its atomic number.

## 1.1 Atomic structure

In an attempt to answer questions like ‘What are we made up of?’, ‘Why do substances behave in particular ways?’ and ‘Why do materials have particular properties?’, scientists have developed the atomic theory. This theory is based on the assumption that all materials are made up of atoms. But what are atoms?

Individual atoms have never been seen because they are extremely small. Approximately 100 000 000 ( $1 \times 10^8$ ) atoms would fit across the full stop at the end of this sentence. Despite their small size, images of atoms like the example shown in Figure 1.1, have been obtained using instruments such as the scanning tunnelling microscope (STM).



**Figure 1.1** Obtained with a scanning tunnelling microscope, this computer-enhanced image of palladium on graphite shows the individual atoms.

Experimental evidence gathered over the past 100 years has led scientists to believe that all atoms are composed of the same three subatomic particles called protons, electrons and neutrons. However, because of results from experiments carried out in more recent times, scientists have now come to the conclusion that protons and neutrons are composed of even smaller particles such as quarks. Despite the more recent developments in the atomic theory, in this textbook the properties and uses of materials will be examined at the atomic level in terms of protons, neutrons and electrons.

### Pass it on

*'If, in some cataclysm, all scientific knowledge were to be destroyed, and only one sentence passed on to the next generations of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis that'*

*all things are made of ATOMS—little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another.*

*In that one sentence there is an enormous amount of information about the world, if just a little imagination and thinking are applied.'*

**Richard P. Feynman**

Protons, neutrons and electrons differ in mass and charge as summarised in Table 1.1.

TABLE 1.1 PROPERTIES OF PROTONS, NEUTRONS AND ELECTRONS

Particle	Symbol	Mass (kg)	Relative mass	Charge (coulomb)	Relative charge
Proton	p	$1.673 \times 10^{-27}$	1	$1.60 \times 10^{-19}$	+1
Neutron	n	$1.675 \times 10^{-27}$	1	0	0
Electron	e	$9.110 \times 10^{-31}$	$\sim \frac{1}{2000}$	$-1.60 \times 10^{-19}$	-1

Protons and neutrons have approximately the same mass, about  $1.67 \times 10^{-27}$  kg. Electrons have a much smaller mass, about  $\frac{1}{2000}$ th the mass of protons and neutrons. The mass of an electron is therefore almost negligible for most purposes when compared with the masses of protons and neutrons.

Protons and electrons have equal but opposite charges of  $1.60 \times 10^{-19}$  C. By convention, protons are described as being positively charged, and electrons as being negatively charged. For simplicity, the proton and electron are usually described as having charges of +1 and -1 respectively. Neutrons are uncharged.

According to the atomic theory, an atom is visualised in terms of two main regions. These regions are the nucleus and the surrounding space occupied by the electrons.

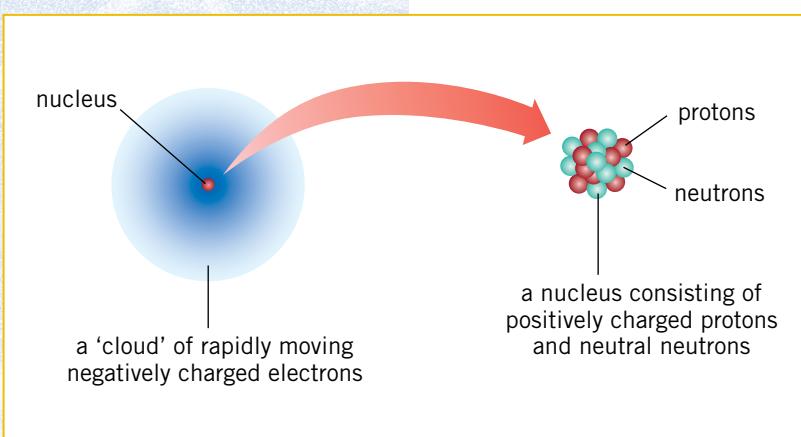


Figure 1.2 A representation of an atom, showing its general features.

#### The nucleus:

- is the central part of the atom and is composed of protons and neutrons
- has a positive charge equal to the number of protons
- is extremely small compared with an atom. The diameter of an average nucleus is  $10^{-15}$  m compared with an average atomic diameter of  $10^{-10}$  m. That is, the diameter of an atom is about 100 000 times larger than the diameter of its nucleus
- contains over 99.9% of the mass of an atom. This is due to the relatively large masses of the proton and neutron compared with the mass of the electron
- is very dense. This is due to its large mass and small volume.

#### The electrons:

- move in a relatively large space, often called an electron cloud, outside the nucleus
- being negatively charged, are kept moving around the nucleus by attractive electrostatic forces between them and the positively charged nucleus.

## \* Review exercise 1.1

- 1 Which of the following are not composed of atoms?

blood	air	white light	the Sun
limestone	gravity	a plant cell	
- 2 Most of the carbon atoms in the human body are made up of 6 protons, 6 neutrons and 6 electrons.
  - a Describe the relative positions of the protons, neutrons and electrons in the carbon atoms.
  - b Apart from position in the atom, list other ways in which these three different types of subatomic particles differ.
  - c If most of the hydrogen atoms found in the human body are made up of 1 proton and 1 electron, compare the mass of one of the carbon atoms described above with the mass of one of these hydrogen atoms.
- 3 In the manufacture of jewellery, gold is normally mixed with other metals, such as nickel, platinum or palladium, to make it less soft. Naturally occurring gold atoms are composed of 79 protons, 118 neutrons and 79 electrons. Use the data given in Table 1.1 to calculate the approximate number of gold atoms in an 18-carat gold ring that is made up of 2 g of gold mixed with 0.7 g of other metals.
- 4
  - a Atoms have a diameter of the order of  $10^{-8}$  cm and the nucleus within the atom has a diameter of approximately  $10^{-13}$  cm. If an atom was scaled up to the size of Subiaco Oval, which has a diameter of approximately 150 m (Figure 1.3), would you expect the scaled-up nucleus in the centre to occupy a region the size of:
    - i a grain of sand (diameter of 0.1 cm)
    - ii a marble (diameter of 1 cm)
    - iii a car (length of 2–3 m)
    - iv a basketball court (length of 30 m)?
  - b What is thought to be between the nucleus and the electrons in atoms?
- 5 Why do you think it took so long for scientists to discover the existence of neutrons in atoms?



**Figure 1.3** If an atom had the same diameter as the Subiaco Oval, what would be the size of the region occupied by the nucleus of the atom?

## 1.2 Different types of atoms

An atom's identity is determined by the number of protons in its nucleus. For example, atoms with only 1 proton in their nuclei are hydrogen atoms, atoms with 6 protons in the nuclei are carbon atoms, and if an atom has 26 protons in its nucleus, it is an iron atom. These different types of atoms have been given unique names and symbols. Table 1.2 shows some common atoms and their symbols. The periodic table, shown inside the front cover of this book, lists all the symbols of the atoms known at the present time.

Usually one or two letters are used for the symbols of atoms. Where a one-letter symbol is used it is written in upper case and where two letters are used the first is written in upper case and the second in lower case. Some symbols, such as H (hydrogen), C (carbon), Ca (calcium) and Cl (chlorine), are clearly an abbreviation of the English name of the atom. Others, such as Fe (iron), Na (sodium) and Hg (mercury), are abbreviations of their Latin names: ferrum, natrium and hydrargyrum respectively.

TABLE 1.2 EXAMPLES OF ATOMS AND THEIR SYMBOLS

Name	Symbol	Name	Symbol
Aluminium	Al	Magnesium	Mg
Argon	Ar	Manganese	Mn
Barium	Ba	Mercury	Hg
Bromine	Br	Neon	Ne
Calcium	Ca	Nickel	Ni
Carbon	C	Nitrogen	N
Chlorine	Cl	Oxygen	O
Chromium	Cr	Phosphorus	P
Copper	Cu	Potassium	K
Fluorine	F	Silicon	Si
Gold	Au	Silver	Ag
Helium	He	Sodium	Na
Hydrogen	H	Sulfur	S
Iodine	I	Tin	Sn
Iron	Fe	Uranium	U
Lead	Pb	Zinc	Zn

### Atomic number

The number of protons in an atom is called the atomic number ( $Z$ ) of the atom. Helium atoms, for example, have 2 protons and so helium has an atomic number of 2. Carbon atoms have 6 protons in their nuclei and so the atomic number of carbon is 6. The atomic number of each different type of atom is usually given in a periodic table.

In an electrically neutral atom the numbers of electrons and protons are equal because the electrical charge of a proton, +1, and the electrical charge of an electron, -1, are exactly equal but opposite. Therefore, if an atom has no net charge the number of electrons as well as the number of protons in the atom can be determined from the atomic number. For instance, because helium has an atomic number of 2, it can be concluded that all neutral helium atoms contain 2 protons and 2 electrons.

### Mass number

The positively charged protons in a nucleus exert a repulsive electrostatic force on one another but the presence of neutrons prevents the nucleus from splitting apart. Attractive forces known as strong forces, or nuclear forces, exist between the nucleons (the protons and neutrons) in the nucleus. Nuclear forces are much stronger than electrostatic forces, but they only act over extremely small distances.

In lighter atoms, the numbers of neutrons and protons in the nucleus are approximately equal, while heavier atoms have a larger number of neutrons than protons. For example, most atoms of oxygen have 8 protons and 8 neutrons, but the uranium atoms responsible for the fission reaction in atomic bombs and nuclear reactors have 92 protons and 143 neutrons.

The total number of protons plus neutrons in the nucleus is called the mass number ( $A$ ) of the atom. The relationship between the mass number, the atomic number and the number of neutrons in a nucleus can be represented in the following way:

$$\text{mass number} = \text{atomic number} + \text{number of neutrons}.$$

For example, the oxygen atom with 8 protons and 8 neutrons will have a mass number of 16, and the uranium atom with 92 protons and 143 neutrons will have a mass number of  $92 + 143 = 235$ .

If the mass number and atomic number of an atom are known, it is possible to work out the number of neutrons in the nucleus of the atom. A fluorine atom with an atomic number of 9 and a mass number of 19 will have 9 protons and  $19 - 9 = 10$  neutrons in its nucleus.

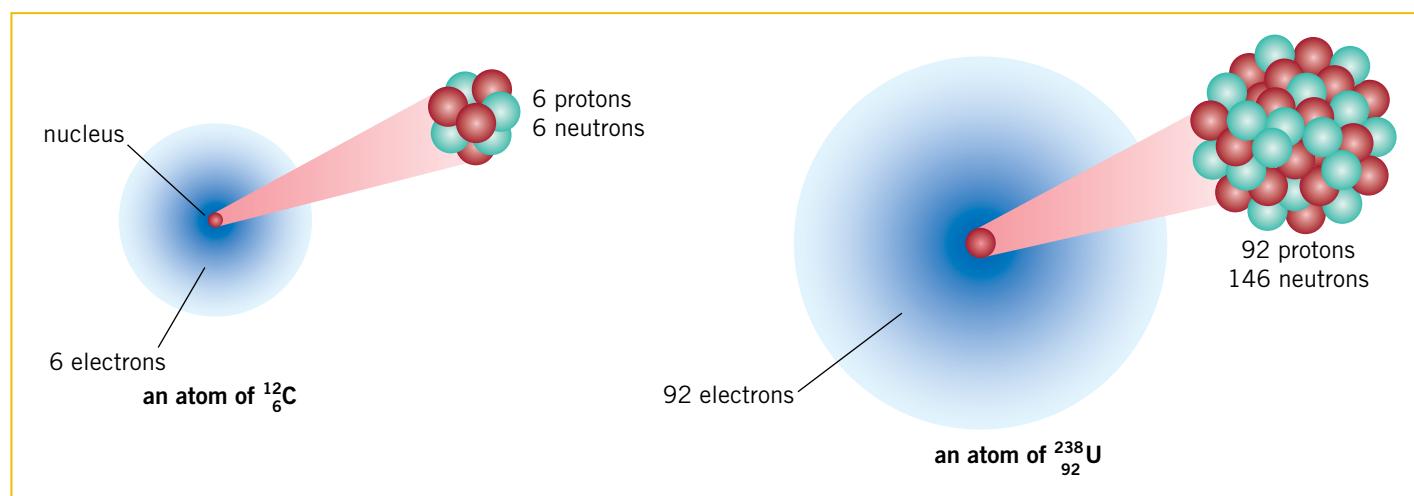


Scientists sometimes represent the structure of an atom using the following convention:



where  $X$  is the symbol of the atom,  $Z$  is the atomic number and  $A$  is the mass number.

From this shorthand representation it is possible to identify the type of atom, the numbers of protons and neutrons in the nucleus, and the number of electrons in the electrically neutral atom. An atom represented as  ${}^{31}_{15}\text{P}$  is a phosphorus atom with an atomic number of 15 and a mass number of 31. This means the neutral phosphorus atom will contain 15 protons, 16 neutrons and 15 electrons. Representations of several other atoms are shown in Figure 1.4.



**Figure 1.4 Examples of neutral atoms.** Representations of a carbon atom with 6 neutrons and a uranium atom with 146 neutrons are shown (the atoms and nuclei are not drawn to scale).

### → Example 1.1

How many protons, neutrons and electrons are in a neutral atom of iron that has a mass number of 56?

### → Solution

Protons: from the periodic table, iron, Fe, has an atomic number of 26 and so there are **26 protons**.

Electrons: because the atom of iron is neutral, the number of positively charged protons will equal the number of negatively charged electrons, that is, there will be **26 electrons**.

Neutrons: mass number = number of protons + number of neutrons, so the number of **neutrons** =  $56 - 26 = 30$

### → Example 1.2

How many protons, neutrons and electrons are in the neutral atom of  $^{109}_{47}\text{Ag}$ ?

### → Solution

Protons: the bottom number of the symbol  $^{109}_{47}\text{Ag}$  is the atomic number, which equals the number of protons. The atom therefore has **47 protons**.

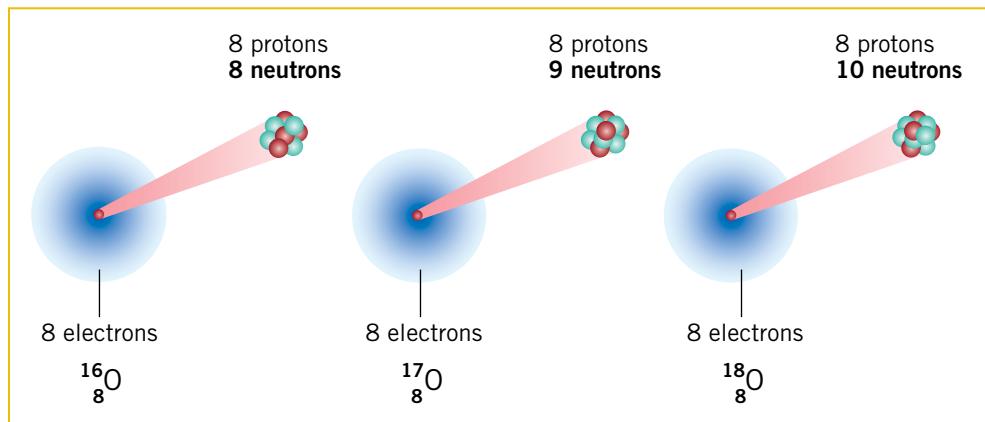
Electrons: because the atom is neutral  
the number of **electrons** = number of protons = **47**.

Neutrons: the top number of the symbol  $^{109}_{47}\text{Ag}$  is the mass number, which equals the (number of protons + number of neutrons). The atom therefore has  $109 - 47 = \mathbf{62 \text{ neutrons}}$ .

## Isotopes



All atoms of the same type, that is, of the same element, have the same number of protons in their nucleus but they do not necessarily have the same number of neutrons. For example, in a sample of oxygen separated from the air, over 99% of the oxygen atoms have 8 neutrons, 0.20% have 10 neutrons and 0.04% have 9 neutrons. All oxygen atoms have 8 protons in their nucleus, so the three different oxygen atoms can be represented as  $^{16}_8\text{O}$ ,  $^{17}_8\text{O}$  and  $^{18}_8\text{O}$ . These oxygen atoms with different mass numbers are called isotopes and are often written as oxygen-16, oxygen-17 and oxygen-18. Representations of these three oxygen isotopes are shown in Figure 1.5.



**Figure 1.5** Three isotopes of oxygen.  
All three isotopes have 8 protons,  
together with electrons, but they have  
differing numbers of neutrons.

**Isotopes** are defined as atoms that have the same number of protons as one another but different numbers of neutrons, or alternatively, atoms with the same atomic number but different mass numbers. Table 1.3 gives a list of some well-known isotopes. The three isotopes of hydrogen are given special names because of their particular importance.

**TABLE 1.3 SOME WELL-KNOWN ISOTOPES**

Type of isotope	Name	Symbol	Number of protons in nucleus	Number of neutrons in nucleus	Number of electrons in neutral atom
Isotopes of hydrogen	hydrogen	${}_1^1\text{H}$	1	0	1
	deuterium	${}_1^2\text{H}$	1	1	1
	tritium	${}_1^3\text{H}$	1	2	1
Isotopes of carbon	carbon-12	${}_6^{12}\text{C}$	6	6	6
	carbon-13	${}_6^{13}\text{C}$	6	7	6
	carbon-14	${}_6^{14}\text{C}$	6	8	6
Isotopes of uranium	uranium-235	${}_{92}^{235}\text{U}$	92	143	92
	uranium-238	${}_{92}^{238}\text{U}$	92	146	92

#### → Example 1.3

Which of the following atoms are isotopes of lithium?

Atom A has an atomic number of 3 and a mass number of 6.

Atom D has 3 neutrons and a mass number of 5.

Atom E is composed of 7 protons, 7 neutrons and 7 electrons.

Atom G is composed of 4 neutrons, 3 protons and 3 electrons.

#### → Solution

Lithium has an atomic number of 3, so all atoms that are isotopes of lithium will contain 3 protons. However, they will have a different number of neutrons compared to one another.

Atom A has 3 protons and  $(6 - 3) = 3$  neutrons.

Atom D has  $(5 - 3) = 2$  protons.

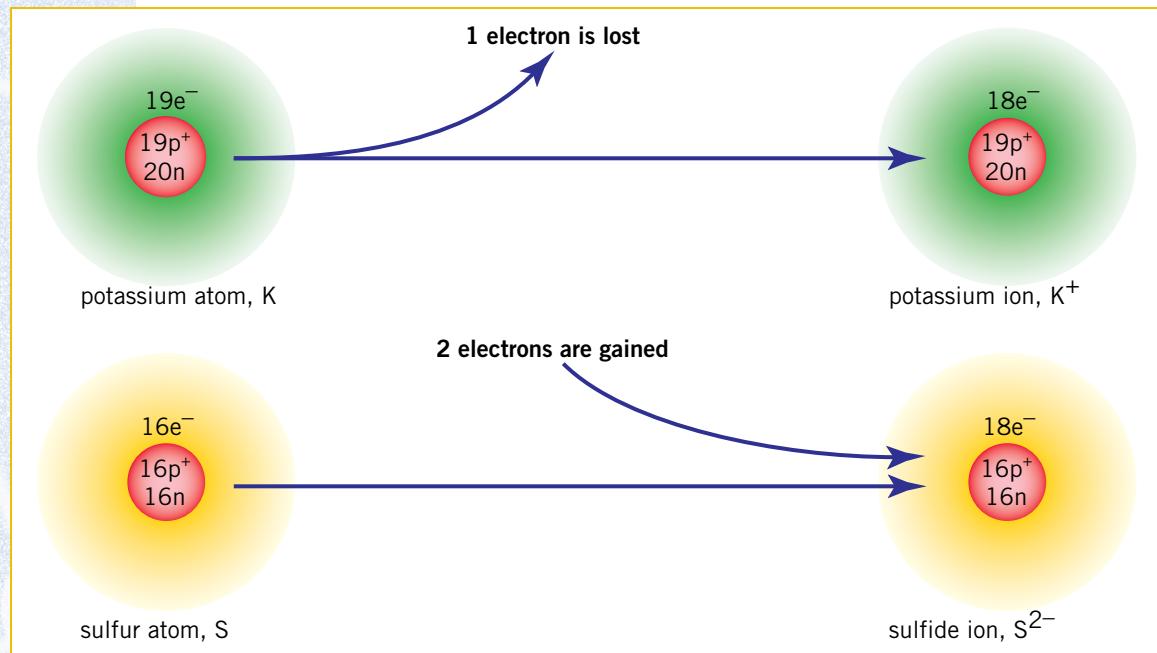
Atom E has 7 protons.

Atom G has 3 protons and 4 neutrons.

**Atoms A and G** are therefore isotopes of lithium.

## Ions

**Ions** are electrically charged species formed when atoms gain or lose electrons. Positively charged ions, or cations, are formed when one or more electrons are removed from an atom. The resulting ion therefore has more positively charged protons than negatively charged electrons. For example, when a potassium atom loses an electron, the potassium ion formed has 19 protons and 18 electrons and has a charge of +1, as shown in Figure 1.6. The potassium ion is represented as  $\text{K}^+$ . When an aluminium atom loses 3 electrons, it forms an aluminium ion with 13 protons and 10 electrons. This ion has a charge of +3 and so is represented as  $\text{Al}^{3+}$ .



**Figure 1.6 Representations of the formation of a positively charged potassium ion and a negatively charged sulfide ion from neutral atoms.**

Negatively charged ions, or anions, are formed when an atom gains one or more electrons. For example, a sulfur atom can gain 2 electrons to form the sulfide ion,  $S^{2-}$ , as shown in Figure 1.6. A sulfide ion contains 16 protons and 18 electrons, giving it a charge of  $-2$ . A fluoride ion with 9 protons and 10 electrons has a formula of  $F^-$ . The formulas, names and formation of ions will be described in more detail in Chapter 3. Examples of some ions found in everyday substances are shown in Table 1.4.

**TABLE 1.4 EXAMPLES OF SOME IONS IN EVERYDAY SUBSTANCES**

Name of ion	Formula of ion	Number of protons	Number of electrons	Where commonly found
Sodium ions	$Na^+$	11	10	in sodium chloride (common name, salt)
Chloride ions	$Cl^-$	17	18	in sodium chloride
Calcium ions	$Ca^{2+}$	20	18	in milk
Iron(III) ions	$Fe^{3+}$	26	23	in rust
Oxide ions	$O^{2-}$	8	10	in soil and rocks

#### → Example 1.4

Give the complete formula, showing the mass number, the atomic number and the charge, of the ion that contains 15 protons, 16 neutrons and 18 electrons.

#### → Solution

Atomic number and identity of the ion: because the ion has 15 protons, its atomic number must be 15, and it must be an ion of phosphorus.

Mass number: the mass number equals the number of protons plus the number of neutrons, that is,  $15 + 16 = 31$ .

Charge: the ion has 15 protons and 18 electrons, that is, it has three more electrons, which are negatively charged, than protons, so it must have a  $-3$  charge.

The formula of the ion is  ${}_{15}^{31}\text{P}^{3-}$ .



**Figure 1.7** The calcium in milk is not present as the metal calcium, but as positively charged calcium ions,  $\text{Ca}^{2+}$ .

### \* Review exercise 1.2

- 1 The symbols of the most abundant types of atoms found in the Earth's crust are listed in Table 1.5, together with their approximate percentage abundances, in terms of number of atoms. Name each of these atoms.

**TABLE 1.5**

Symbol of atom	O	Si	Al	Fe	Ca	Na	K	Mg	Ti	H	P	C
Percentage abundance	47	28	8	5	4	3	3	2	0.6	0.1	0.1	0.1

- 2 The following is a list of ingredients shown on a toothpaste package:

**INGREDIENTS:** dicalcium phosphate dihydrate, water, sorbitol, glycerin, PEG-12, sodium lauryl sulfate, cellulose gum, flavour, sodium monofluorophosphate, tetrasodium pyrophosphate, sodium saccharin

- a From the names of the listed substances, identify seven different types of atoms present in the toothpaste. Give the name, symbol and number of protons in each of these atoms.
- b **RESEARCH** Choose two of these ingredients and find out what their functions are in the toothpaste.
- 3 Copper, a brown-coloured metal, was probably the first useful metal to be discovered in ancient times. Today it is used extensively, for example, in electrical wiring and for water and gas pipes. Copper is composed of two isotopes, copper-63,  ${}_{29}^{63}\text{Cu}$ , and copper-65,  ${}_{29}^{65}\text{Cu}$ . In terms of atomic structure, how are these isotopes similar and how are they different?

*continued*

### Review exercise 1.2 — *continued*

4 **TABLE 1.6** gaps in Table 1.6.

Formula of species	Atomic number	Mass number	Charge	Number of protons	Number of neutrons	Number of electrons
$^{23}_{11}\text{Na}^+$						
	16	32	-2			
				24	28	21
		81			46	36

- 5 The radioactive isotope krypton-85 is used in electric blanket thermostats and in indicator lights in appliances like washing machines, clothes dryers, stereos and coffeemakers. When a krypton-85 atom undergoes radioactive decay, one neutron disintegrates to form a proton and an electron. The electron, together with gamma radiation, is emitted by the atom.
- a How many protons and neutrons are in a krypton-85 atom?
  - b Give the name of the isotope formed when a krypton-85 atom undergoes radioactive decay. How many protons and neutrons will this new isotope have?

## 1.3 Arrangement of electrons in atoms

### Energy levels (shells)

During the past century, a series of models have been developed by scientists in an attempt to explain the arrangement of electrons in atoms. The current model, the quantum mechanical model, is very complex and only certain simplistic ideas derived from it have been described in this section.

In the quantum mechanical model, electrons are considered to exist in energy levels or **shells**. These energy levels or shells are denoted by the numbers 1, 2, 3, 4, ... or alternatively by the letters K, L, M, N, ... The first energy level, or the K shell, is the lowest energy level and is closest to the nucleus. The second energy level, the L shell, is the next energy level, and so on. In successive shells the electrons, in general, have increased energy.

From quantum mechanics it has been calculated that the maximum number of electrons that a shell can accommodate is  $2n^2$ , where n is the shell number. Therefore, the first shell can accommodate up to 2 electrons, the second can accommodate up to 8 electrons and the third can accommodate up to 18 electrons. This means that in shells 1 to 4 the maximum number of electrons will be 2, 8, 18, 32 respectively, as shown in Table 1.7.

**TABLE 1.7 MAXIMUM NUMBER OF ELECTRONS FOR EACH SHELL**

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

## Electron configurations of atoms and ions

In atoms, electrons tend to be in shells with the lowest possible energy, that is, in the shells that are closest to the nucleus. This is called the ground state of the atom. When determining which shell the electrons are in for a particular atom or ion, the electrons are generally ‘added’, beginning with the first shell, then the second shell, and so on. For example, a magnesium atom with 12 electrons will have 2 electrons in the first shell, 8 electrons in the second shell and 2 electrons in the third shell.

The arrangement of electrons in shells, sometimes called the **electron configuration**, for atoms up to an atomic number of 20 are shown in Table 1.8. Electron configurations are sometimes written in a shorthand form showing just the number of electrons in each shell. For example, the electron configuration for an atom with 2 electrons in the first shell, 8 electrons in the second shell and 3 electrons in the third shell can be written as 2, 8, 3.

TABLE 1.8 ELECTRON ARRANGEMENTS IN ATOMS WITH ATOMIC NUMBERS 1 TO 20

Atom	Symbol	Atomic number	Number of protons	Number of electrons in neutral atom	Arrangement of electrons in shells			
					First shell	Second shell	Third shell	Fourth shell
Hydrogen	H	1	1	1	1			
Helium	He	2	2	2	2			
Lithium	Li	3	3	3	2	1		
Beryllium	Be	4	4	4	2	2		
Boron	B	5	5	5	2	3		
Carbon	C	6	6	6	2	4		
Nitrogen	N	7	7	7	2	5		
Oxygen	O	8	8	8	2	6		
Fluorine	F	9	9	9	2	7		
Neon	Ne	10	10	10	2	8		
Sodium	Na	11	11	11	2	8	1	
Magnesium	Mg	12	12	12	2	8	2	
Aluminium	Al	13	13	13	2	8	3	
Silicon	Si	14	14	14	2	8	4	
Phosphorus	P	15	15	15	2	8	5	
Sulfur	S	16	16	16	2	8	6	
Chlorine	Cl	17	17	17	2	8	7	
Argon	Ar	18	18	18	2	8	8	
Potassium	K	19	19	19	2	8	8	1
Calcium	Ca	20	20	20	2	8	8	2

Because filling shells beginning with the first shell, then moving out from the nucleus, is based on a rather simplistic model, there are some discrepancies with the filling of the third shell and beyond. For atoms up to an atomic number of 18, the order of filling the shells is as explained earlier. Then, as shown in Table 1.8, instead of potassium being 2, 8, 9 and calcium being 2, 8, 10, as would be anticipated, the nineteenth and twentieth electrons are ‘added’ to the fourth shell. This results in potassium being 2, 8, 8, 1 and calcium being 2, 8, 8, 2.

Electron configurations of ions are determined in the same way as for neutral atoms. This procedure can be summarised in the following way:

- Determine the number of electrons from the atomic number and, if relevant, the charge on the ion.
- Place these electrons into the shells starting with the first shell, remembering:
  - the maximum number of electrons found in each shell (2 electrons in the first shell, 8 in the second, 18 in the third, and so on)
  - the anomaly that occurs when filling the third shell; 8 electrons are placed in the third shell then 2 electrons in the fourth shell (the next 10 electrons then fill up the third shell).

→ **Example 1.5**

Give the electron configuration of the following atoms and ions:

- a neutral atom with 11 protons
- a neutral silicon atom
- an aluminium ion,  $\text{Al}^{3+}$ .

→ **Solution**

- A neutral atom with 11 protons will have 11 electrons. The electron configuration is therefore **2, 8, 1**.
- Silicon has an atomic number of 14, which means it contains 14 protons. If the atom is neutral, there will be 14 electrons, giving an electron configuration of **2, 8, 4**.
- Aluminium has an atomic number of 13, and so the atoms will contain 13 protons. If the ion has a charge of +3, it must contain 3 more protons than electrons. As a result, there must be 10 electrons, which means an electron configuration of **2, 8**.

Sometimes it is convenient to represent the arrangement of electrons in an atom pictorially. This is often done in a simple way, using circles to represent shells and dots or crosses drawn on the circles to show how many electrons are in each shell, as shown in Figure 1.8.

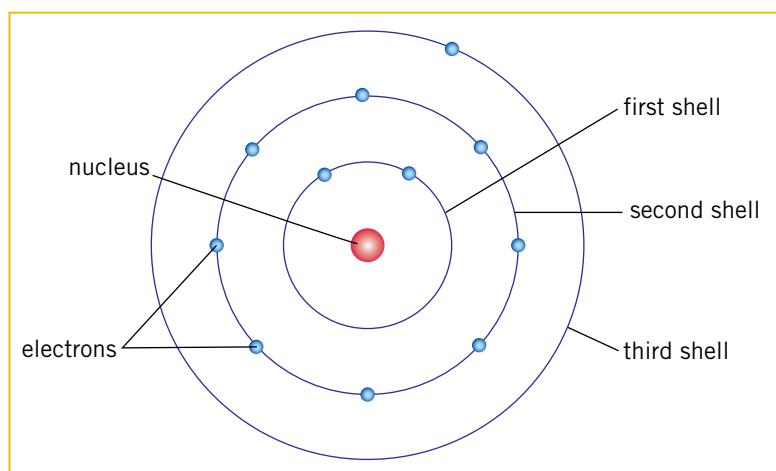


Figure 1.8 A Bohr model representation of the electron configuration of sodium, 2, 8, 1.

This representation showing the arrangement of electrons in an atom is more like the model proposed by Niels Bohr in 1913, rather than the quantum mechanical model. In his theory, Bohr suggested that electrons move around the nucleus in circular orbits, which seems to be suggested in the diagram.

However, according to the quantum mechanical model it is not possible to specify the exact location or path of an electron around the nucleus. All that can be done is to predict the probability of locating an electron in a given region in space. That is, electrons are thought to occupy regions of space, referred to as orbitals, rather than just travel along a specific circular path. These regions of space occupied by electrons are sometimes called **electron clouds**.

### Valence electrons

The electrons in the outer shell of an atom are often called **valence** or outer-shell **electrons**. For instance, sodium, with an electron configuration of 2, 8, 1, has 1 valence electron, and oxygen, with a configuration of 2, 6, has 6 valence electrons. Many of the properties, particularly the chemical properties, of substances are determined by the number of valence electrons in the atoms. This relationship between properties and valence electrons will be examined in later chapters.

### \* Review exercise 1.3

- Iron is probably the most commonly used metal in society, yet it is not often used in its pure state. Usually, small amounts of specific impurities are added to the iron to give it more desired properties. For example, chromium, nickel and carbon are mixed with iron to produce stainless steel. This form, or alloy, of iron is more resistant to rusting, less brittle and more visually attractive than pure iron. Write the electron configurations of neutral atoms of carbon, iron and nickel.
- Give the names and symbols of the neutral atoms that have the following electron configurations:
  - 2, 1
  - 2, 8, 18, 8.
- The sea is like a gigantic soup of ions. Table 1.9 lists some of the more abundant ions dissolved in seawater.

TABLE 1.9 SOME OF THE IONS DISSOLVED IN SEAWATER

Name of the ion	Formula of the ion	Relative amounts, in g per kg of seawater
Chloride ion	$\text{Cl}^-$	19.1
Sodium ion	$\text{Na}^+$	10.8
Sulfate ion	$\text{SO}_4^{2-}$	2.7
Magnesium ion	$\text{Mg}^{2+}$	1.3
Calcium ion	$\text{Ca}^{2+}$	0.41
Potassium ion	$\text{K}^+$	0.39
Hydrogencarbonate ion	$\text{HCO}_3^-$	0.14
Bromide ion	$\text{Br}^-$	0.07

Give the electron configuration of each of the monatomic ions, that is, ions composed of only one atom, shown in Table 1.9.

- What is the difference between the arrangement of electrons in sulfur and chlorine?
- What are the similarities and differences between the electron arrangements of oxygen and sulfur?

## 1.4 Where are all the atoms?

About 74%, by mass, of the atoms making up the universe are estimated to be hydrogen, about 24%, by mass, are helium and the remaining different types of atoms make up only about 2%. Most scientists believe that shortly after the Big Bang, which is thought to have marked the beginning of the universe, much of the mass of the universe existed as hydrogen. In the 10 to 20 billion years since then some of the hydrogen has undergone a complicated series of nuclear reactions in the stars to form helium and the heavier atoms. It is these heavier types of atoms that form the Earth and some of the other planets.

Of the different types of atoms making up the Earth, shown in Figure 1.9, iron (35%), oxygen (30%), silicon (15%) and magnesium (13%) are the most abundant, followed by nickel, sulfur, calcium and aluminium.

In the human body, the distribution of various types of atoms is different again. Humans are made up of 65% oxygen, 18% carbon, 10% hydrogen, 3% nitrogen, 2% calcium and smaller percentages of numerous other types of atoms.

Of the 100 or so different types of atoms known to scientists, eighty-nine are known to occur naturally on Earth. The others have been artificially made and exist for very short times before they undergo radioactive decay. The eighty-nine different types of naturally occurring atoms make up all the substances that exist on Earth, and possibly in the universe.

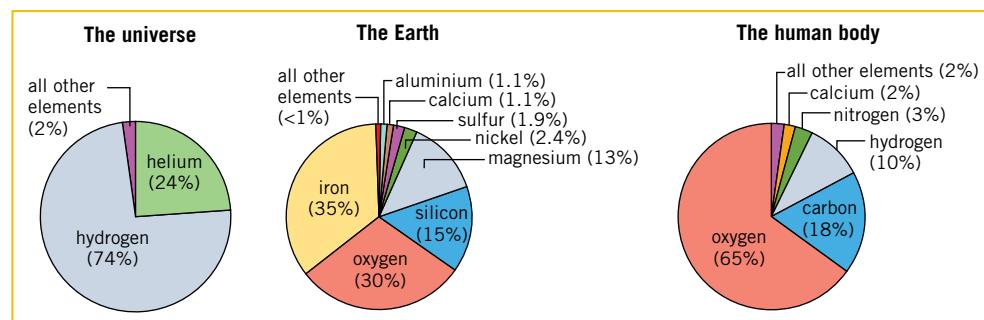


Figure 1.9 The distribution, as mass percentages, of the most abundant types of atoms in nature.

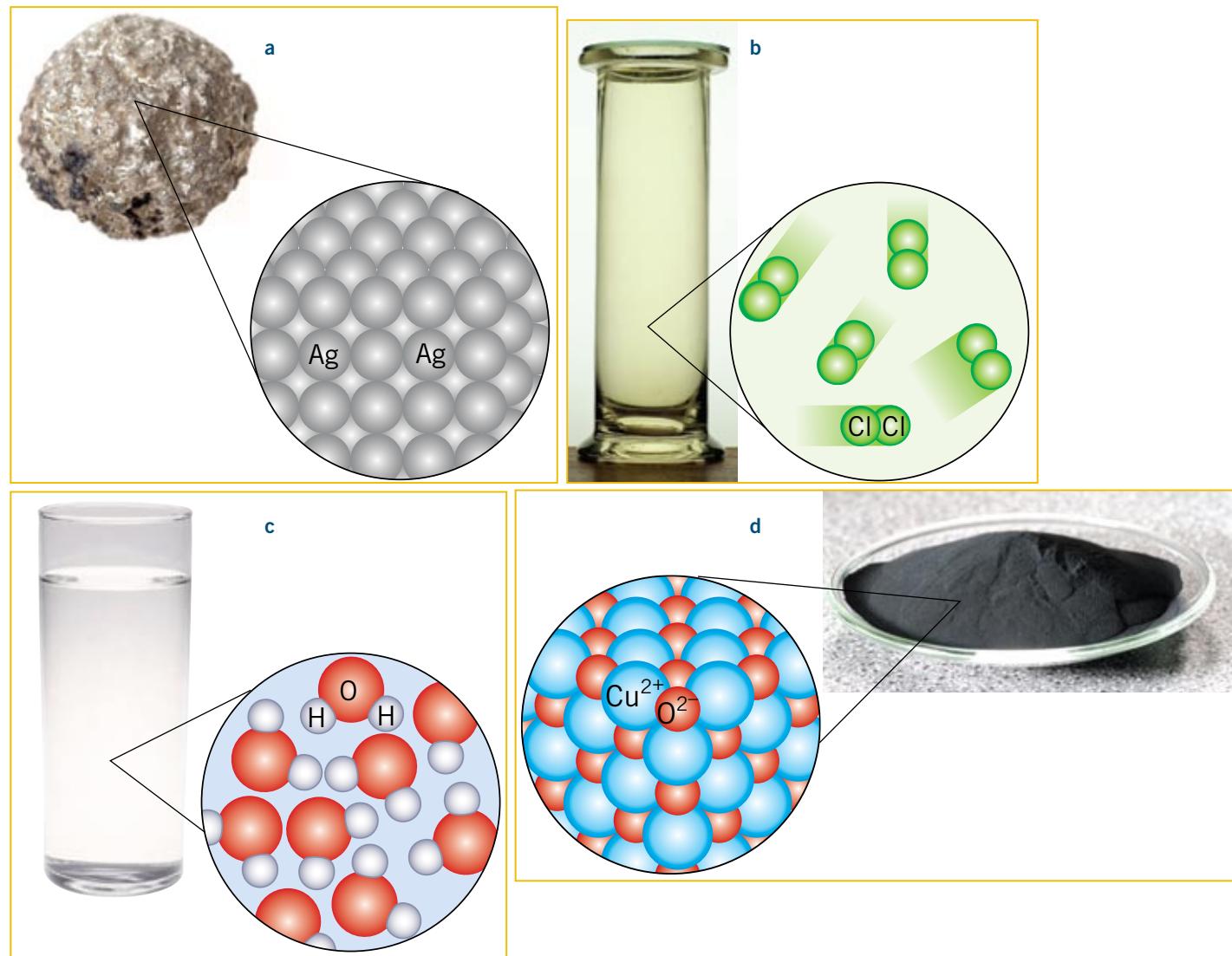
### Elements, compounds and mixtures

It is convenient for chemists to classify all substances into three broad categories: elements, compounds and mixtures.

**Elements** are substances composed of only one type of atom. A bar of pure gold, for example, is classified as an element because it is made up of only gold atoms. All the atoms in a diamond are carbon atoms, so diamond is also regarded as an element. Silver and chlorine, as shown in Figure 1.10, are also elements. All the known elements are listed in the periodic table.

Some substances are composed of two or more different types of atoms strongly bonded together in fixed proportions, as represented in Figure 1.10. Water and copper oxide are examples of **compounds**. Water consists of hydrogen and oxygen atoms bonded together in a 2:1 ratio and copper oxide contains copper and oxide ions bonded together in a 1:1 ratio.

Because elements and compounds have constant compositions, they are known as **pure substances**. However, many of the substances that exist are **mixtures** of pure substances. Seawater, for example, is a mixture of water, sodium chloride and traces of other elements and compounds such as oxygen and carbon dioxide. Air is a mixture of nitrogen, oxygen, water, carbon dioxide and very small amounts of other elements and compounds. Elements, compounds and mixtures will be discussed further in later chapters.



**Figure 1.10** Some examples of elements and compounds. **a** (silver) and **b** (chlorine) show examples of elements that consist of a large collection of atoms of the same type. **c** (water) and **d** (copper oxide) show examples of compounds where two or more different types of atoms are bonded together in fixed ratios.



## \* Review exercise 1.4

- About 90% of the mass of hydrogen and oxygen in the human body exists as water. (The remaining 10% is found in other compounds.) Using the information in Figure 1.9, calculate the approximate percentage of the human body that is water.
- Figures 1.11 i–iv refer to four different substances. The coloured circles represent six different types of atoms. Which substances are:
  - elements?
  - compounds?
  - shown as a solid?

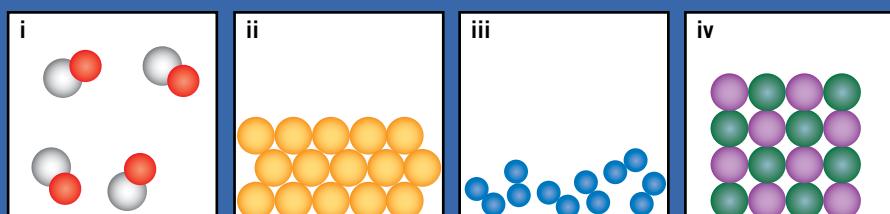


Figure 1.11 Atoms in various elements and compounds.



## 1.5 The periodic table—a preview

To systematise much of what is known about the properties of the known elements, they are often displayed in what is called the **periodic table**. A periodic table is shown in Figure 1.12.

1	2													13	14	15	16	17	18
1																			
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12		13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn		31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd		49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg		81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg								
	*58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm		70 Yb	71 Lu				
	**90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md		102 No	103 Lr				

Figure 1.12 The periodic table of elements.

In the periodic table, the elements are arranged horizontally in order of increasing atomic number. When the elements are ordered in this way, similar outer energy shell electron configurations are observed to recur at regular intervals. As can be seen in Table 1.10, the configuration with 1 electron in the outer shell appears in lithium and then again in sodium. 2 electrons in the outer shell appears in beryllium and then in magnesium. 3 electrons in the outer shell appears in boron and then in aluminium, and so on.

Furthermore, elements with similar electron configurations in their outer shells display similar chemical properties. In the periodic table, these elements with similar outer shell electron configurations, and consequently similar chemical properties, are placed in the same vertical column.

The arrangement of the elements horizontally according to their atomic number and vertically according to their outer shell configuration, leads to two important features of the periodic table. These are the periods and the groups.

**TABLE 1.10 ELECTRON CONFIGURATIONS OF THE ELEMENTS WITH ATOMIC NUMBERS OF 1 TO 14**

Element	H	He	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si
Atomic number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Electron configuration	1	2	2,1	2,2	2,3	2,4	2,5	2,6	2,7	2,8	2,8,1	2,8,2	2,8,3	2,8,4

The horizontal rows in the periodic table are called **periods**. These periods are numbered from the top of the table to the bottom and they vary in the numbers of elements they contain. For example, period 1 is composed of two elements, H and He, period 2 has eight elements, Li to Ne, and period 4 has eighteen elements, K to Kr.

The two rows of elements shown at the bottom of the periodic table are actually part of periods 6 and 7, but the periodic table would be too wide to fit comfortably on one page if they were included in their correct position in the table. The wide form of the periodic table has been shown in Figure 1.13.

**Figure 1.13 The wide form of the periodic table.**

The period number corresponds to the number of the shell in which the outermost electrons are located in the neutral atoms. For example, lithium, with an electron configuration of 2, 1, has its outermost electron in the second shell and it is in period 2. Phosphorus, 2, 8, 5, has its 5 outermost electrons in the third shell and it is in period 3. Iron, 2, 8, 14, 2, has 2 outermost electrons in the fourth shell and it is in period 4.

## Groups

The vertical columns in the periodic table are called **groups**. In the past, the groups were numbered using Roman numerals. The first two columns (groups) on the left-hand side of the periodic table were numbered I and II and the last six columns on the right-hand side were numbered from III to VIII. The ten columns in the middle of the periodic table were (and still are) described as the transition metals, and the two rows at the bottom of the table as the rare earths (or lanthanides and actinides).

A more recent recommendation from the International Union of Pure and Applied Chemistry (IUPAC), for identifying the groups, is to number each column of elements, including the transition metals, from 1 to 18 working from left to right, as shown in Figure 1.12. Using this method, the transition metals are broken up into ten groups, and groups III to VII become groups 13 to 18.

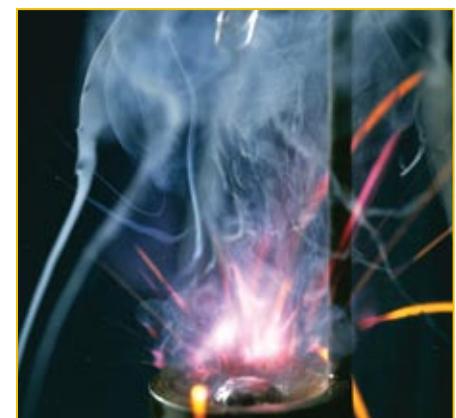
Elements within a particular group have the same number of valence electrons, that is, electrons in their outer shell. For example, group 1 elements have only one electron in their outer shell:

lithium	2, 1
sodium	2, 8, 1
potassium	2, 8, 8, 1
rubidium	2, 8, 18, 8, 1
cesium	2, 8, 18, 18, 8, 1

and group 2 elements have electrons in their outer shell:

beryllium	2, 2
magnesium	2, 8, 2
calcium	2, 8, 8, 2
strontium	2, 8, 18, 8, 2
barium	2, 8, 18, 18, 8, 2

As mentioned earlier, elements with the same number of electrons in their outer shell display similar chemical properties. For example, lithium (Li), sodium (Na) and potassium (K), in group 1, are all soft, reactive metals; and helium, neon and argon, in group 18, are all very unreactive gases.



**Figure 1.14** Similar reactivities within group 1. Both sodium (a) and potassium (b) react vigorously when water is dripped onto them.

## Metals and non-metals

In the periodic table the metals tend to be on the left-hand side of the table and the non-metals on the upper right-hand side of the table. (Hydrogen is an exception to this.) For example, potassium (K), chromium (Cr), silver (Ag) and aluminium (Al) are all metals, and carbon (C), chlorine (Cl) and xenon (Xe) are non-metals.

Some elements, notably boron (B), silicon (Si), germanium (Ge), arsenic (As), antimony (Sb) and tellurium (Te), possess a mixture of both metallic and non-metallic properties. These elements are often referred to as semimetals or metalloids. Figure 1.15 shows the relative positions of the metals, non-metals and metalloids in the periodic table, together with some examples of these three types of elements.



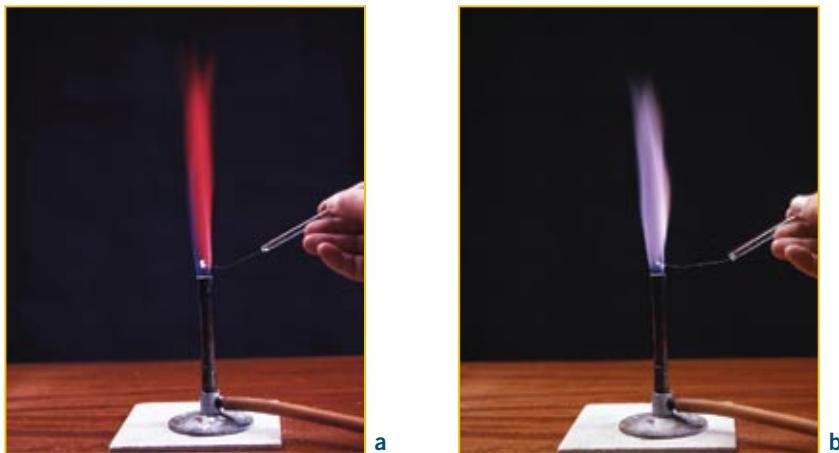
**Figure 1.15** Examples of metals, non-metals and metalloids and their positions in the periodic table. The non-metals shown are, clockwise from top left, sulfur, bromine, phosphorus, iodine and carbon.

## \* Review exercise 1.5

- 1 Give the period and group in the periodic table to which the following elements belong:  
oxygen, krypton, aluminium, potassium, lead, helium.
- 2 The electron configurations of neutral atoms of three different elements are shown below:  
**a** 2, 3                   **b** 2, 8, 7                   **c** 2, 8, 18, 5.  
For each element, give the:  
**i** group number           **iii** atomic number  
**ii** period number          **iv** name.
- 3 The following elements are known to be toxic to humans:  
lead, mercury, fluorine, selenium, barium, arsenic, cadmium, bromine.
  - a** Identify each of these elements as a metal or a non-metal.
  - b** ↗ RESEARCH Choose one of these elements and answer the following questions about this element.
    - i** How might a person be exposed to the element?
    - ii** What effect could this element have on the health of the person?
    - iii** In the case of poisoning, what should be done?
- 4 A particular element found as a compound in some rocks belongs to group 2 in the periodic table.
  - a** How many valence electrons would be present in neutral atoms of this element?
  - b** This element is in period 4 in the periodic table. In its neutral atoms in the ground state, how many shells contain electrons?
  - c** What is the electron configuration of the element?
  - d** What is the element, and how many protons are in its atoms?
  - e** This element does not exist in its elemental form in the Earth's crust. Suggest a reason for this observation.
  - f** ↗ RESEARCH A sedimentary rock containing a compound of this element is found quite extensively in Western Australia and is used in the building of fences, houses and in paving. Name this sedimentary rock and briefly explain how it was formed originally.

## 1.6 Fireworks, fluorescent tubes and flame tests

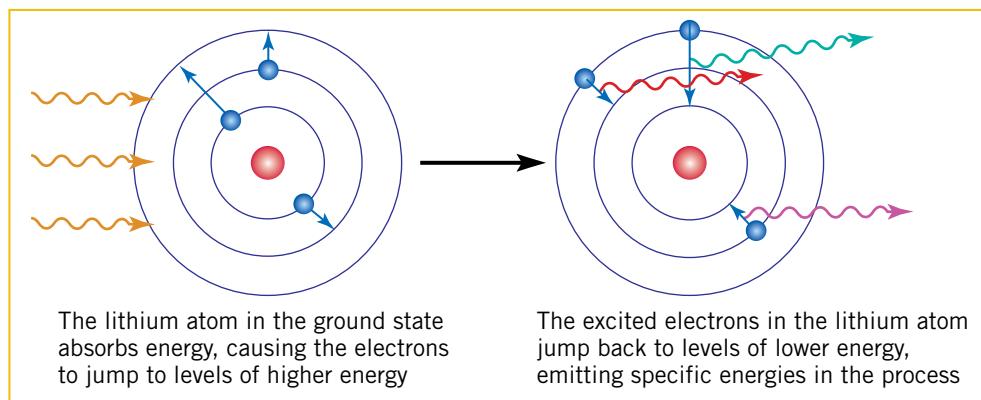
Many atoms emit light of a distinctive colour when they are heated in a flame or their vapours are exposed to an electric discharge. Sodium atoms emit a characteristic orange light, as shown by the sodium vapour lights that are sometimes used in street lighting. Other elements which produce characteristic colours include potassium—violet, copper—green, calcium—red, barium—yellow-green and strontium—scarlet.



QuickTime  
CW  
Video

**Figure 1.16** The characteristic colours produced when (a) strontium and (b) potassium ions are heated in the Bunsen flame.

These characteristic colours arise because electrons in atoms occupy definite energy levels (shells). When a substance is heated to a high temperature, electrons in its atoms may absorb definite amounts of energy and jump from their ground state energy levels to higher energy levels to form excited atoms. These excited atoms are unstable and the electrons move back to lower energy levels. When an electron jumps from a higher energy level to a lower energy level, light (or a photon) of a specific energy is released or emitted, as represented in Figure 1.17. The energy of this emitted light is exactly equal to the difference in energy between the two energy levels in the atom.



**Figure 1.17** Using the Bohr model of electron energy levels, the absorption and emission of light by the lithium atom can be explained. (The colours of the emitted light arrows are not accurately represented.)

The emission of light of characteristic colours, by particular atoms such as neon, argon or mercury, is utilised in the many ‘neon’ signs used in advertising. As well, fireworks often contain small quantities of different metal compounds so that when the fireworks burn, the particular metal atoms emit photons of light with characteristic wavelengths. A further application is in the identification of particular atoms using a ‘flame test’. In a flame test a small sample of the substance adhering to a platinum wire is placed in a non-luminous Bunsen flame. The atoms can be identified from the colours they emit, as shown in Figure 1.16.

Fluorescent lights in the home or office contain low pressure mercury vapour inside the lighting tube which is coated with zinc sulfide. Electricity is used to excite the mercury atoms causing them to emit ultraviolet light. This ultraviolet light then excites the atoms in the zinc sulfide coating. As the excited electrons return to their ground state they release light of many different energies in the visible range to produce white light.

### \* Review exercise 1.6

- 1 An electron in an atom is said to be excited when it moves from its ground state to a higher energy level.
  - a What is meant by the 'ground state' of an atom?
  - b From their electron configuration, decide which of the following atoms are shown in their ground state:

atom A: 2, 8, 4	atom D: 2, 7, 1
atom E: 2, 8, 8, 3	atom G: 2, 1
  - c What is necessary to make an electron move from a lower energy level to a higher energy level?
  - d What happens when an electron moves from a higher energy level to a lower energy level?
- 2 When a neon light is turned on, excited atoms of elements such as neon, argon or krypton, emit colourful light.  
Explain:
  - a why neon lights require an electrical supply
  - b why different elements give rise to different coloured neon lights.
- 3 Atomic absorption spectroscopy can be used to determine the concentration of very dilute solutions of metal ions. In this process, the solution is vaporised and the free ions produced are exposed to visible or ultraviolet radiation of a wavelength absorbed by the ions. The number of ions present is determined by the amount of radiation absorbed. Explain what characteristic of atoms allows the absorption of such radiation.



## MAJOR IDEAS

- Atoms are composed of protons, neutrons and electrons. A proton has a +1 charge, an electron a -1 charge and a neutron is neutral.
- Atoms consist of a nucleus surrounded by electrons.
- In an electrically neutral atom, the number of protons equals the number of electrons.
- The atomic number ( $Z$ ) of an element is the number of protons in the nucleus of an atom of that element.
- The mass number ( $A$ ) of an atom of an element is the sum of the numbers of protons and neutrons in the nucleus of that atom.
- The structure of an atom can be represented as  ${}^A_Z X$  where  $X$  is the element's symbol.
- Isotopes are atoms with the same atomic number but different mass numbers.
- Ions are charged atoms. Positive ions have more protons than electrons and negative ions have more electrons than protons.
- The electrons in an atom can exist in only certain allowed energy levels or shells.
- Each shell can accommodate a maximum number of electrons.
- The electron configuration of an atom can be represented in terms of the number of electrons in each shell, for example, calcium 2, 8, 8, 2.
- Valence electrons are electrons in the outermost shell of an atom.
- Matter can be classified into the following categories:
  - elements—substances made up of only one type of atom
  - compounds—substances composed of two or more elements chemically combined in fixed proportions
  - mixtures—two or more substances mixed together in any proportions.
- The elements are arranged horizontally in the periodic table, in increasing atomic number.
- Periods are horizontal rows of elements in the periodic table.
- Groups are vertical columns of elements in the periodic table. Elements in the same group in the periodic table have the same outer shell electron arrangement and they share some similar properties.

## QUESTIONS

- 1 List the similarities and differences between protons, neutrons and electrons.
- 2 What is the difference between the atomic number and mass number of an atom?
- 3 You want to make an accurate scale model of a hydrogen atom and decide that the nucleus will have a diameter of 1 mm. What would be the diameter of the entire model? Assume the diameter of an actual hydrogen atom is  $1 \times 10^{-8}$  cm and the diameter of its nucleus is  $1 \times 10^{-13}$  cm.
- 4  ${}^{24}_{12} \text{Mg}$        ${}^{27}_{13} \text{Al}$        ${}^{28}_{14} \text{Si}$        ${}^{23}_{11} \text{Na}$        ${}^{25}_{13} \text{Al}$   
Which of the neutral species listed above contain:
  - a the same number of electrons?
  - b the same number of protons?
  - c the same number of neutrons?
- 5 The number of atoms in a  $1 \text{ cm}^3$  cube of aluminium is nearly the same as the number of atoms in the same volume of lead, but the masses of these cubes are very different.
  - a Explain why the masses are different.
  - b Which cube would have the larger mass?
  - c Why do you think aircraft are made out of aluminium and not lead? Give at least two reasons.
- 6
  - a Explain why it is to be expected that the number of electrons in a neutral atom equals the number of protons, but there is no such relationship between the number of neutrons and the other atomic components.
  - b Why is it possible to speak of the atomic number of an element but not the mass number of the element?
- 7 Two atoms both have 18 neutrons in their nuclei. One of these atoms also has 18 protons and the other has 19 protons. Are these atoms isotopes of the same element? Explain your reasoning.
- 8 Calcium oxide, commonly called lime, is one of society's oldest and most vital chemicals. The ancient Romans used lime in building and road construction, uses that continue to the present day. Calcium oxide is composed of calcium ions,  $\text{Ca}^{2+}$ , and oxide ions,  $\text{O}^{2-}$ . Describe how the subatomic particles are arranged in these two ions.

- 9** Write the electron configuration for:
- a neutral atom of atomic number 7
  - a phosphide ion,  $P^{3-}$
  - a neutral atom of the element in period 3, group 14
  - a neutral atom with two more protons than a chlorine atom.
- 10** The radioactive species  $^{131}_{53}\text{I}$  is used in the diagnosis and treatment of thyroid disorders. The iodine in naturally occurring compounds is wholly the stable isotope  $^{127}_{53}\text{I}$ .
- What are the similarities in the atomic structure of these two isotopes?
  - What is the difference in their atomic structure?
- 11** Use information given in Table 1.11 to answer the following questions.
- Identify those species that are:
    - isotopes of the same element
    - neutral atoms
    - positive ions
    - negative ions.
  - Write the complete symbol, including the atomic number, mass number and charge, if appropriate, of each of the species.

TABLE 1.11

Species	Protons	Electrons	Neutrons
A	20	18	20
B	17	18	18
C	20	20	22
D	22	20	26
E	19	18	20
F	18	18	22

- 12** Fill in the gaps in the table below.

Symbol	$^{16}_8\text{O}$	$^{17}_8\text{O}^{2-}$	$^{11}_{11}\text{Na}$	$^{4}_{4}\text{Be}^{2+}$
Protons			17	
Neutrons		12	20	5
Electrons			18	
Net charge	0	1+		
Atomic number			11	
Mass number			23	

- 13** a Name the elements in the following groups and periods in the periodic table:
- group 2, period 2
  - group 14, period 3
  - group 18, period 1
  - group 2, period 6.
- b Which of these elements would you expect to have similar properties to one another?
- c Give the electron configuration of the neutral atoms of elements i, ii and iii.
- 14** Nitrogen and phosphorus are in the same group but different periods in the periodic table.
- Indicate what similarity in electron arrangement is shared by neutral atoms of these two elements.
  - What is the difference between their electron arrangements?
- 15** How would you react to a claim that a new element had been discovered that:
- fits between selenium and bromine in the periodic table?
  - has an atomic number of 122?
- 16** Some isotopes of group 14 elements include carbon-12, silicon-28, germanium-73, tin-118 and lead-208.
- Represent each of these isotopes with its chemical symbol, atomic number and mass number.
  - How does the ratio of neutrons to protons change as the group is descended?
- 17** In 1909, Geiger and Marsden, students of Rutherford, reported the results of experiments in which beams of  $\alpha$ -particles (helium nuclei with a mass number of 4) were fired at very thin metal foils. Most of the  $\alpha$ -particles went straight through the foils without deflection, some were deflected slightly and a very small number were deflected backwards.
- How many protons and neutrons are in an  $\alpha$ -particle?
  - Why were most  $\alpha$ -particles not deflected when fired at the very thin metal foils?
  - Why were a very small number of  $\alpha$ -particles deflected backwards?
  - What do these experiments show about the structure of metal atoms?
  - Geiger and Marsden did not expect the results they obtained. What results did they expect and why?

- 18 One of the major activities of alchemists was to try to produce gold from less valuable metals such as lead and iron. Explain, in terms of the modern atomic theory, why they were not successful.
- 19 Read the following and then answer the questions below.

### States of matter

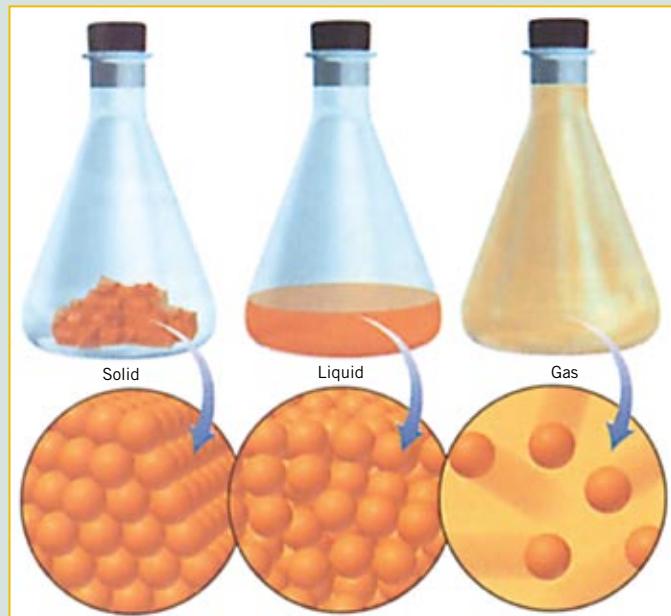
Matter exists in three states—solids, liquids and gases. Water, for example, exists as steam, liquid water and ice. The characteristics of solids, liquids and gases are summarised in Table 1.12. These characteristics reveal some information about the arrangement of particles in the three states of matter.

**TABLE 1.12 CHARACTERISTICS OF SOLIDS, LIQUIDS AND GASES**

	Solid	Liquid	Gas
<b>Shape</b>	definite	variable	variable
<b>Volume</b>	definite	definite	variable
<b>Compressibility</b>	almost incompressible	very slightly compressible	highly compressible
<b>Diffusion</b>	negligible	slow	fast

In solids, the particles are closely packed, held fairly rigidly in position and only vibrate about these fixed positions. In liquids, the particles are still fairly closely packed, but are not held as rigidly in position. This allows the particles to move relative to one another and is why liquids have a variable shape. It is also the reason why diffusion occurs in liquids. When the particles are close together, as in solids and liquids, it is assumed there are electrostatic forces of attraction holding the particles together.

In gases the particles are widely spaced and move virtually independently of one another. Because of this, a gas will become dispersed throughout any container into which it is placed. Also, diffusion can occur rapidly. Gases are highly compressible because the particles are relatively widely spaced compared to their size. The arrangement of particles in solids, liquids and gases is illustrated in Figure 1.18.

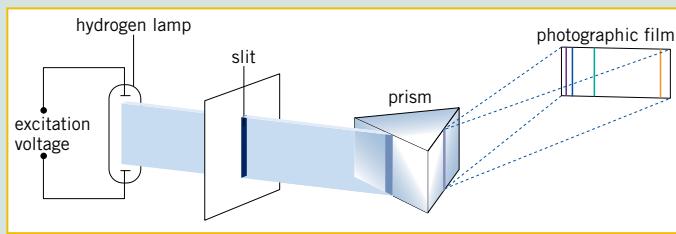


**Figure 1.18** Arrangement of particles in solids, liquids and gases.

- a Briefly describe how the particle theory of gases, liquids and solids presented in Figure 1.18 can account for the observed characteristics of these states of matter.
- b When a substance is heated, its particles move faster. Describe the changes that occur, at the particle level, when water is heated until it boils.
- c Boyle's law describes the relationship between the pressure and volume of a sample of a gas. It states that: 'If the temperature is kept constant, the volume of a given mass of gas is inversely proportional to its pressure'. Explain this law in terms of the particles making up the gas.
- d Plan an experiment to investigate the effect of temperature on the rate of diffusion of liquids.
- e ↗ RESEARCH Is glass a solid or liquid? Justify your answer by giving reasons in terms of both the properties of solids and liquids and the particle theory of matter.

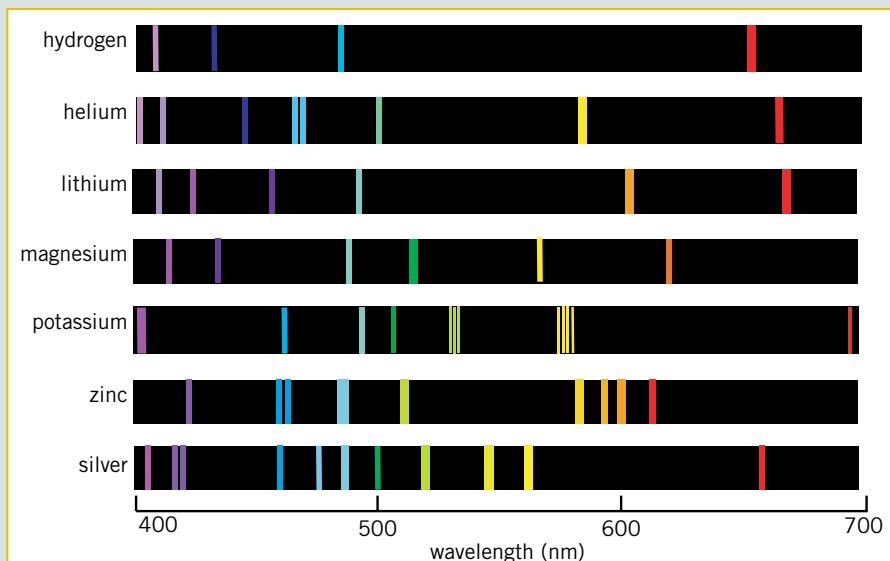
### 20 Analysis using emission spectra

Many elements emit light of a distinctive colour when their compounds are heated to a high temperature. This light emission can be analysed by passing it through a prism to produce a spectrum that can be recorded on a photographic film. The spectrum consists of a pattern of bright lines and is unique to the particular element.



**Figure 1.19** Obtaining an emission spectrum of hydrogen.

The series of emission lines and their corresponding wavelengths produced by some elements are shown below in Figure 1.20.



**Figure 1.20** Line emission spectra of various elements (only the main lines have been shown in some of the spectra).

- a Explain why the emission spectrum of each element consists of a series of lines rather than a continuous spectrum like the one shown in Figure 1.21.



**Figure 1.21** The continuous spectrum of white light.

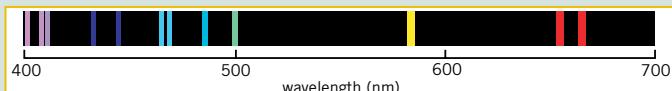
- b Why does each element have a unique set of emission lines?  
c Emission spectra can be used to identify the presence of particular elements in an unknown mixture.

- i The emission spectrum obtained by heating a sample of a metal ore in a flame is shown in Figure 1.22. Identify two of the elements present in the ore sample.

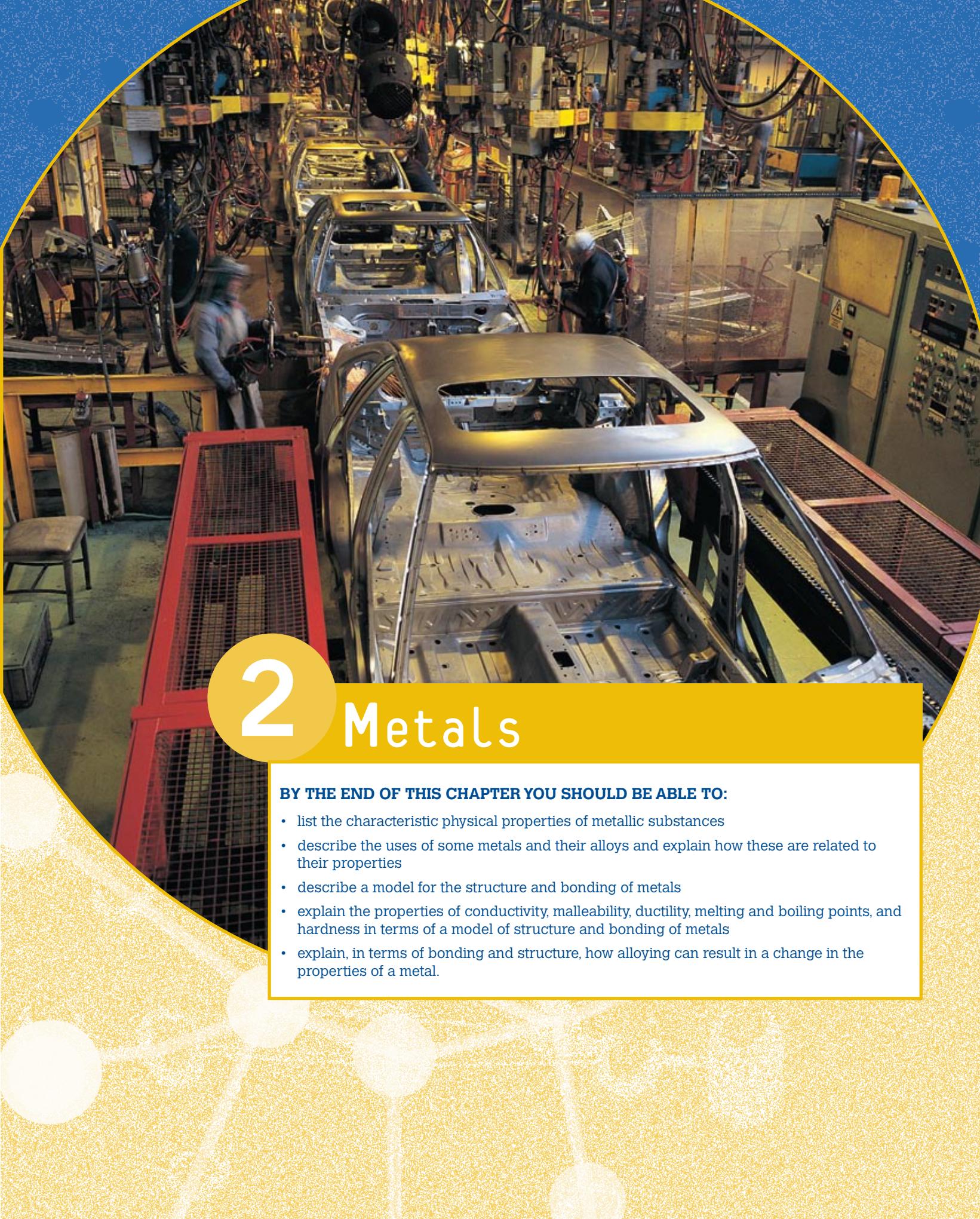


**Figure 1.22** Emission spectrum of a metal ore.

- ii The light from a very distant nebula produced the emission spectra given in Figure 1.23. Determine two elements that are present in this nebula.



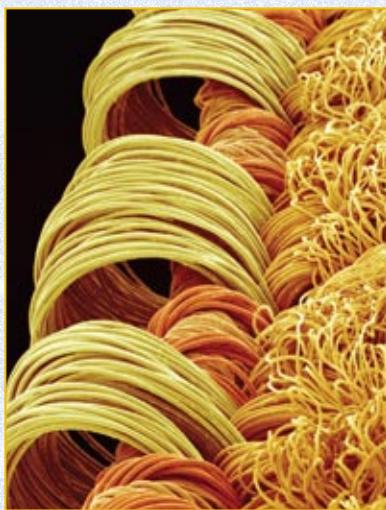
**Figure 1.23** Simplified emission spectrum of a nebula.



## 2 Metals

**BY THE END OF THIS CHAPTER YOU SHOULD BE ABLE TO:**

- list the characteristic physical properties of metallic substances
- describe the uses of some metals and their alloys and explain how these are related to their properties
- describe a model for the structure and bonding of metals
- explain the properties of conductivity, malleability, ductility, melting and boiling points, and hardness in terms of a model of structure and bonding of metals
- explain, in terms of bonding and structure, how alloying can result in a change in the properties of a metal.



**Figure 2.1** Coloured scanning electron micrograph of the synthetic fibres along the edge of a piece of clothing. These fibres help reduce itchiness and discomfort.

## 2.1 Useful materials

Throughout the last century there has been an astounding development in the types of materials used by society. For instance, in the early 1900s, the choice was wool, cotton, silk or linen as fabrics for clothes and furnishings. Today, the selection is from fibres such as polyesters, spandex, nylon, acrylic, olefins, lyocell, viscose, tencel, metallic and triacetate to make clothes stretchy, colourfast, easily cleaned, shrink-resistant, wrinkle-free, shiny, brightly coloured, waterproof, comfortable, warm or cool.

The special characteristics or properties of materials, such as those mentioned above, allow them to be used in specific ways. For example, to manufacture a bolt to be used in a car engine that is going to reach over 200°C, the chosen material would have to have a higher melting point and be considerably stronger than a material chosen to produce a plastic food storage container.

Why do different materials have different properties? It is because the types of particles, the arrangement of these particles and the forces between them vary from one material to the next. It is chemists' understanding of these properties, structures and different types of bonding that has contributed, in a vital way, to the remarkable growth and advances in the materials available for use today. This chapter and the following three chapters will explore the structure, bonding and resulting properties and uses of four classes of substances: metals, ionic, covalent molecular and covalent network.

### \* Review exercise 2.1

- 1 The particular uses of different materials in the manufacture of cars are determined by the properties of the materials.
  - a For each of the materials labelled on the 1950s Holden, describe the function of the material in the car and give the properties relevant to this function.
  - b The windscreens of this car are made from tempered glass, which has been produced by cooling the molten glass very quickly. Tempered glass is extremely strong but under impact it rapidly breaks into countless little cubes of glass. The windscreens in modern cars are made from laminated glass, which is composed of two sheets of glass sandwiched together by a plastic interlayer. Suggest some reasons for why laminated glass has replaced tempered glass in the windscreens of cars.
  - c In most modern cars, a plastic called polypropylene is now used for bumper bars rather than chrome-plated steel. Give some advantages and disadvantages of this change.



**Figure 2.2** A 1950s Holden.

## 2.2 Metals and their properties

Metals are used in an extraordinary number of different ways. Around the home, for example, the sink, cutlery, saucepans, appliances, taps, chair and table legs, roofing, bolts and nails are all made from steel, a mixture, or alloy, of iron, chromium, nickel and a trace of carbon. Aluminium is used to make drink cans, cooking foil, cooking utensils, window frames and gutters. Water pipes and electrical wires are composed of copper; the galvanised iron used for roofing is steel covered with zinc, and lead is used to seal the roof. Silver, gold, palladium and platinum are found in jewellery, and coins are alloys of various metals such as copper, nickel and tin. In the garage, the car body and the engine are steel, and in the sky, the aeroplanes are light-weight alloys of aluminium. Buildings have steel reinforcing in the concrete, steel girders and beams, and some have aluminium frames. The list is almost endless.

Metals are used extensively because they have a range of useful properties. Some properties for a variety of metals are shown in Table 2.1. The properties of several non-metals are also included in the table to enable comparisons to be made between metals and non-metals.



Figure 2.3 The bodies of planes are made from an alloy of aluminium.

TABLE 2.1 SOME PROPERTIES OF A RANGE OF METALS AND SEVERAL NON-METALS

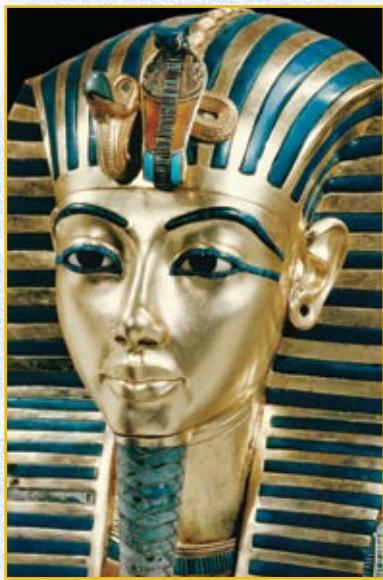
Metal	Melting point (°C)	Boiling point (°C)	Density, at 25°C (g mL <sup>-1</sup> )	Electrical conductivity in solid state (MS m <sup>-1</sup> )	Thermal conductivity (J s <sup>-1</sup> m <sup>-1</sup> K <sup>-1</sup> )	Resistance to corrosion
Aluminium	660	2450	2.70	38	237	high
Copper	1085	2572	8.96	57.9	401	high
Gold	1063	2970	19.30	45	317	very high
Iron	1535	2750	7.86	10.3	80	moderate/low
Magnesium	650	1110	1.74	23	156	low
Platinum	1770	3825	21.40	9.3	73	very high
Sodium	98	883	0.97	21	141	very low
Tin (white)	232	2602	7.30	8.5	67	high
Tungsten	3410	5660	19.30	19	174	high
Zinc	419	907	7.14	16	116	high/moderate
<b>Non-metal</b>						
Carbon (diamond)	>3550	–	3.51	10 <sup>-17</sup>	1000	very high
Phosphorus (white)	44	280	1.82	10 <sup>-15</sup>	0.24	very low

### Characteristic properties of metals

Despite the variation in the properties shown in Table 2.1, it is possible to list some characteristic physical properties that are possessed by most metals.

These characteristic metallic properties are:

- Metals are good conductors of electricity in both the solid and liquid states. In the solid state, conductivity decreases with increasing temperature.



**Figure 2.4** Gold mask of Tutankhamen circa 1300 BC.

- Metals are good conductors of heat in both the solid and liquid states. As a consequence, the solid metals feel cold to touch.
  - Metals are lustrous (shiny) when freshly cut or cleaned.
  - Metals can be worked into different shapes without breaking. Two properties that reflect this behaviour are malleability and ductility. Metals are malleable because they can be hammered, pressed or bent into different shapes without breaking. They are ductile because they can be drawn into thin wires without breaking.
  - At room temperature, many metals are hard, tough and relatively dense solids with high tensile strength. Mercury is the only liquid metal at room temperature. Toughness is the ability of a material to withstand impact. Tensile strength is the ability of the material to be stretched without breaking.
  - Most metals are silver in colour, except gold and copper. Gold is yellow, while copper is a salmon pink colour.
  - The melting points of metals vary over a wide range; nonetheless, most are reasonably high. The boiling points of nearly all metals, however, are very high.
  - Metals are sonorous. This means that when they are manufactured in a shape that allows them to vibrate, most make a pleasant ringing sound when tapped.

## Groups of metals

As indicated in the periodic table in Figure 2.5, the metal elements are shown on the left-hand side of the table. There are many more metals than non-metals. Group 1 metals are commonly called **alkali metals** and group 2 metals are called **alkaline earth metals**. The large collection of metals shown between group 2 and group 13 are commonly called the **transition metals**. The two rows of elements underneath the main body of the periodic table are also metals. The metals in the top of these two rows are called the lanthanides and the metals in the bottom row are called the actinides.

Groups		Periodic Table of Elements																			
1	2	Main groups										H	Noble gases								
Li	Be	Alkaline metals						Alkaline earth metals			Hydrogen		Boron group		Carbon group		Nitrogen group		Oxygen group	F	He
Na	Mg	3	4	5	6	7	8	9	10	11	12	13	B	C	N	O	F	Ne	Ar		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Transition metals										
Lanthanides		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu						
Actinides		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr						

**Figure 2.5** The metals in the periodic table are shaded yellow. The elements shaded pale green exhibit both metallic and non-metallic properties.

When comparing transition metals with group 1 and group 2 metals, there is some variation in their common properties. Groups 1 and 2 metals tend to be softer, a little less dense and have slightly lower melting points than most transition metals, as shown in Table 2.2. Even within the transition metals there are also some variations. For example, mercury has the low melting point of  $-39^{\circ}\text{C}$  but tungsten has a very high melting point of  $3410^{\circ}\text{C}$ .

**TABLE 2.2 SOME PHYSICAL PROPERTIES OF SOME TYPICAL GROUP 1, GROUP 2 AND TRANSITION METALS**

Metal	Atomic number	Group	Melting point ( $^{\circ}\text{C}$ )	Density ( $\text{g mL}^{-1}$ )
Potassium, K	19	1	63	0.86
Rubidium, Rb	37	1	39	1.53
Calcium, Ca	20	2	839	1.54
Barium, Ba	56	2	725	3.50
Titanium, Ti	22	transition metal	1660	4.50
Chromium, Cr	24	transition metal	1860	7.19
Nickel, Ni	28	transition metal	1450	8.90
Silver, Ag	47	transition metal	962	10.50
Tungsten, W	74	transition metal	3410	19.30



**Figure 2.6** Coloured scanning electron micrograph of a tungsten light bulb filament.

### \* Review exercise 2.2

- What properties make each of the metals listed below particularly suited for the described use?
  - copper for making electrical wires
  - gold for jewellery
  - steel for reinforcement rods in concrete
  - zinc for coating steel to make galvanised iron
  - aluminium as a food wrap.
- Use the data presented in Table 2.1 to answer the following questions.
  - i Which metal in the table has the lowest density?  
ii Why is this metal not used for making light metal objects, such as aircraft?
  - i Which two metals in the table are the best conductors of heat?  
ii Why is only one of these metals used for making saucepans?
  - Why is tungsten a suitable metal for use as the filament in a light globe?
- a 'Tin' cans are actually made of steel coated with tin. Using the information in Table 2.1, suggest a way in which the tin could be put on to the steel.  
b **RESEARCH** Find out how modern tin-plating is actually carried out.  
c Suggest reasons for why cans are not made of only steel or of only tin.

*continued*

### Review exercise 2.2 — *continued*

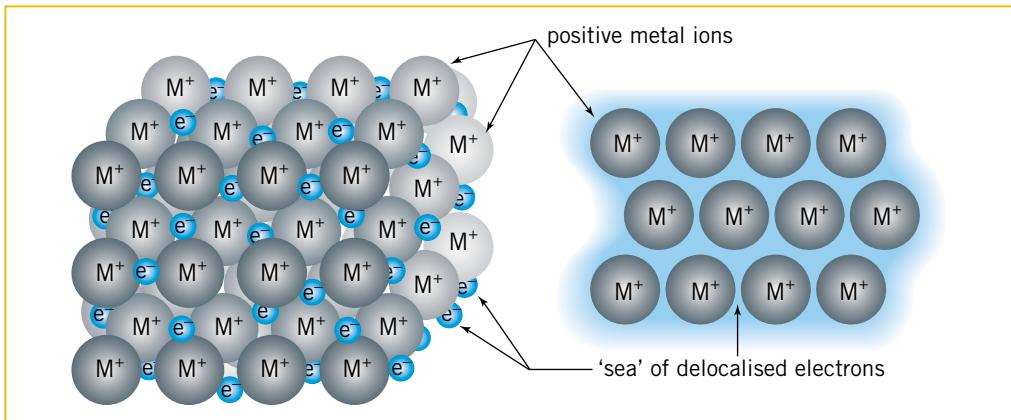
- 4    a Which of groups 1, 2, 13, 14, 15, 16, 17 and 18 in the periodic table contain only metals?  
b Which contain a mixture of metals and non-metals?  
c Name a metal that would have similar properties to magnesium.
- 5    Not only are titanium-based alloys new orthopaedic alloys, but they are rapidly becoming the most widely used alloys in implantable devices. Suggest what properties would be required of a titanium alloy if it were to be used successfully as an artificial hip replacement.
- 6    In 1991, a well-preserved natural mummy of a man from about 3300 BC was found in a glacier of the Ötztal Alps between Austria and Italy. Nicknamed Ötzi the Iceman, he is one of the oldest known human mummies. High levels of arsenic in Ötzi's hair suggest he may have been involved in copper smelting. The axe found with Ötzi had a 0.6 m handle made of wood and a 10 cm blade made of 99.7% pure copper. Why do you think he made the blade of copper and not of wood or stone?



Figure 2.7 The mummy of Ötzi the Iceman.

## 2.3 Metallic bonding

Chemists have developed various models to explain the characteristic properties of metals. In one of these models, it is assumed that the outermost or valence electrons of metal atoms move about freely within a three-dimensional arrangement or lattice of positively charged metal ions. That is, the metal consists of a lattice of positive ions surrounded by a 'sea' of mobile electrons as represented in Figure 2.8. The valence electrons are said to be delocalised as they are not associated with a particular metal ion but can move freely through the lattice of metal ions. The positively charged metal ions in the lattice are attracted to the negatively charged delocalised electrons and these electrostatic attractions hold the metallic lattice together. This type of bonding, that is, the electrostatic attractions between the delocalised electrons and the positive metal ions, is called **metallic bonding**.



**Figure 2.8** A model of the structure of metals. The first diagram shows the three-dimensional lattice of positive ions and the delocalised valence electrons. The second diagram shows one layer of these positive ions surrounded by the 'sea' or cloud of delocalised electrons.

### \* Review exercise 2.3

- 1 Certain inferences about the bonding and structure of metals can be made by examining their physical properties. For each physical property listed below, match up the most appropriate inference.

Physical properties of most metals	Inferences about the structure and bonding of metals
A High melting and boiling points	i The atoms of the metal are tightly packed in the solid lattice
B High densities	ii The forces between the particles in the metallic lattice are able to readjust to a distorting force so the new structure is just as strong
C High electrical and thermal conductivities in solid state	iii There are strong attractive forces between the particles in the solid lattice
D High malleability and ductility	iv The surface structure allows light to be readily reflected
E High lustre	v The solid contains freely moving charged particles

- 2 The properties of calcium indicate that it can be classified as a metal.



**Figure 2.9** Calcium.

- a Calcium has an electron configuration of 2, 8, 8, 2 and so each atom has two valence electrons. When calcium atoms bond together to form a metallic lattice, each atom donates two electrons to form the delocalised electron cloud, and, as a result, becomes a positive ion with a +2 charge. The particles making up calcium are therefore positive ions with a +2 charge and delocalised electrons.
- Draw a representation of the metallic lattice of calcium showing the particles present.
  - Describe the forces that hold the lattice together.
  - What name is given to these forces?

*continued*

### Review exercise 2.3 — *continued*

- b** Despite being the fifth most abundant element in the Earth's crust, the metal calcium has rather limited commercial use. It is sometimes used in small amounts to extract other metals from their compounds and also to remove unwanted chemical impurities in various alloys. Why is calcium not widely used as a metal?
- c** Calcium is only present in the Earth's crust in compound form. Name some of the well-known materials containing compounds of calcium found in the Earth's crust.
- 3 a** Use the information presented in part **a** of question **2** to determine the particles present in each of the following metals:
- i** magnesium                                   **ii** aluminium
- b** Draw a representation of the metallic lattice of aluminium showing the particles present.
- 4 a** Using the data in Table 2.1, list the six best electrical conductors and the six best heat conductors.
- b** What is noticeable about these two lists?
- c** Propose an explanation to explain this connection.

## 2.4 Explaining metallic properties

The ‘electron sea’ model of metallic bonding can be used to explain the common properties of metals.

### Conduction of electricity and heat

Metals are good conductors of electricity because of the mobility of the delocalised electrons within the lattice of positive ions. When a metal is used in an electrical circuit, electrons entering one end of the metal cause a similar number of electrons to be displaced from the other end, and the metal conducts. This is represented in Figure 2.10. In the solid state, the positive ions do not act as charge carriers. They remain vibrating about fixed positions within the lattice, as the delocalised electrons move. However, when a molten metal conducts electricity, both the delocalised electrons and the positive ions are able to move and act as charge carriers.

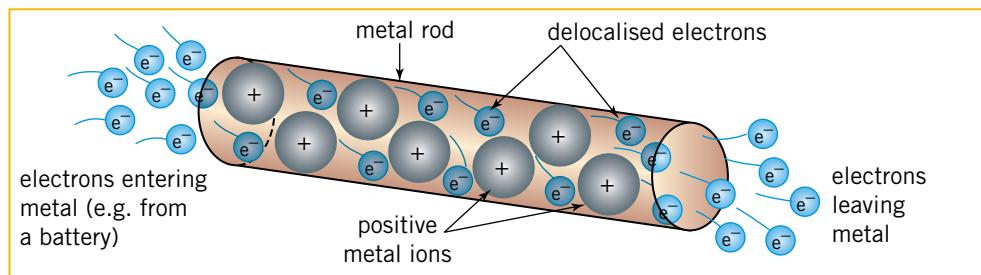


Figure 2.10 Electrical conduction by a metal.

The delocalised electrons are also responsible for the rapid transmission of heat energy in metals. When one end of a piece of metal is heated, the kinetic energy of the positive ions and the delocalised electrons in the heated region increases, that is, their rate of movement increases. The heat energy is conducted along the piece of metal by the more energetic electrons and positive ions colliding with less energetic electrons and ions. However, because the electrons are delocalised, they are able to move quite freely through the lattice and so cause a transfer of the heat energy along the metal that is more rapid than for most other materials.

## Malleability and ductility

The delocalised electrons in metals do not ‘belong’ to any particular positive ion in the lattice, so metallic bonding is said to be non-directional. Therefore, if sufficient force is applied to the metal, one layer of positive ions can slide, or slip, over another without disrupting the metallic bonding. This means that, after the layer of positive ions has moved, there are still attractive forces between the delocalised electrons and the positive ions holding the lattice together in the newly deformed metal. As a result, metals can be hammered readily into sheets or drawn into wires without breaking, as shown in Figure 2.11.

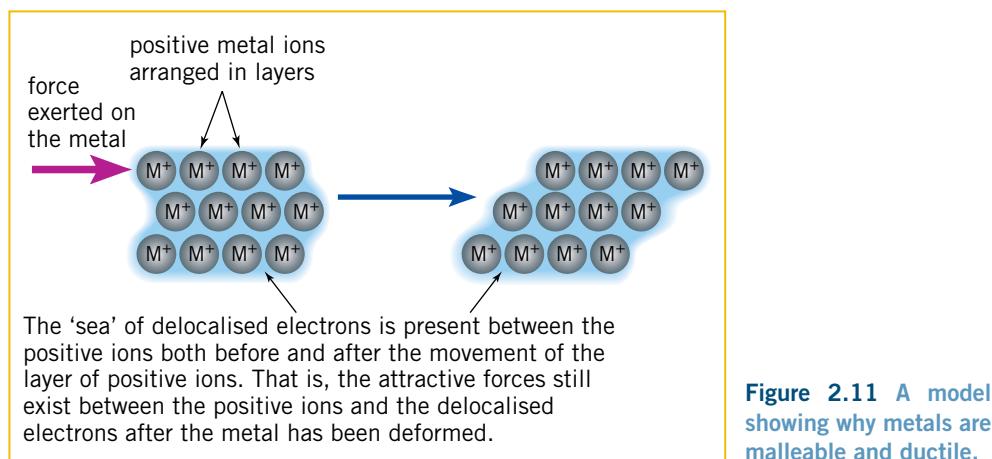


Figure 2.11 A model showing why metals are malleable and ductile.

## Hardness, and melting and boiling points

The relatively high melting and boiling points of most metals are due to the strong electrostatic attraction between the positive metal ions and the delocalised electrons. The stronger the metallic bonds, the greater the amount of heat required to move the ions out of their fixed positions, that is, the higher the melting point.

As shown in Table 2.2, the melting and boiling points of group 1 metals are generally lower than those of group 2 metals, which in turn are lower than those of the transition metals. One possible explanation for this observation can be given in terms of the number of valence electrons the metal atoms readily contribute to form the cloud of delocalised electrons. Group 1 metal atoms have one valence electron that they release to form ions with a +1 charge together with the sea of electrons, as shown for sodium in Figure 2.12. For a group 2 metal, the atoms release their two valence electrons to form the sea of electrons, together with ions with a +2 charge, as shown for magnesium in Figure 2.12. As a result, in group 2 metals there will be more delocalised electrons and the ions will have larger positive charges than for group 1 metals. The expectation is therefore that group 2 metals will have stronger metallic bonds, and consequently higher melting points, than group 1 metals.

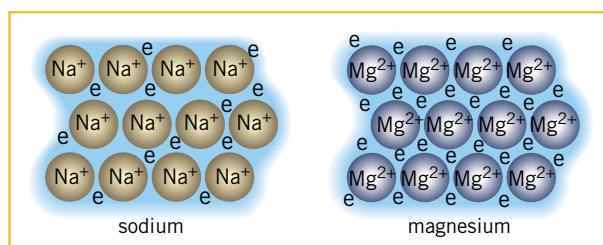


Figure 2.12 The metallic bonding in magnesium, a group 2 metal, is stronger than that in sodium, a group 1 metal, possibly because there are more delocalised electrons and the positive ions have a greater positive charge in magnesium.



**Figure 2.13** Sodium being cut by a knife. The knife is composed of an alloy of several transition metals.

In most transition metals, each atom releases more than two electrons in forming a metallic lattice. This results in more delocalised electrons and ions with greater positive charges compared to the group 1 and group 2 metals. Consequently, the transition metals tend to form even stronger metallic bonds, and have higher melting and boiling points than group 1 and group 2 metals.

The number of electrons that metal atoms contribute to the ‘sea of electrons’ is only one factor that influences the strength of the metallic bonds. Other factors such as the size of the positive ions and the way they are packed together in the metallic lattice also have an influence on the metallic bond strength.

The boiling points of most metals are very high in comparison to their melting points, which can be regarded as moderately high, as seen in Table 2.1. When a metal is melted, the positive ions move out of their lattice positions but there are still metallic bonds between these randomly moving ions and the delocalised electrons. However, boiling requires positive ions and electrons to move apart from one another, consequently breaking the strong metallic bonds. This requires a much larger amount of energy, making the boiling points very high.

Similar reasoning to that used to explain melting points can also be used to explain the hardness of metals. Many metals are hard because of the strong metallic bonds between the positive ions in the metallic lattice and the delocalised electrons. However, as with melting points, there is a variation in hardness. Group 1 metals can be cut with a knife and group 2 metals can be cut easily with scissors, yet many of the transition metals are much harder. The group 2 metals are harder than the group 1 metals, possibly because of the greater number of delocalised valence electrons and ions with larger positive charges in the lattice of group 2 metals. In turn, the transition metals are often harder than the group 2 metals because of the stronger metallic bonds, possibly due to more delocalised electrons and positive ions with larger charges in some transition metals.

### \* Review exercise 2.4

- 1 Read the following description of tantalum then answer the questions.

Tantalum is a silver-grey solid that has a particularly high melting point of  $2996^{\circ}\text{C}$  and is also extremely hard. It is a heavy metal, having a density of  $16.6 \text{ g mL}^{-1}$ . Its ability to be drawn into fine wires and to conduct electricity has led to many commercial uses. Tantalum is used to construct the small but powerful capacitors that are used in miniaturised electronic circuitry in devices such as mobile phones and computers. Resembling gold in its resistance to chemical attack, it also has a host of applications in dental and medical surgery.

- a List the physical properties of tantalum mentioned in the description.
- b Explain these properties in terms of the ‘delocalised electron’ model of metallic bonding and structure.
- 2 Propose an explanation for the trends in the melting and boiling points of the two metals shown in Table 2.3.

TABLE 2.3

Metal	Melting point ( $^{\circ}\text{C}$ )	Boiling point ( $^{\circ}\text{C}$ )
Sodium	98	883
Aluminium	660	2450

- 3 Metals tend to be thought of as hard materials with high melting points yet the group 1 elements all have low melting points and are soft enough to be cut with a knife. Why are the group 1 elements regarded as metals?
- 4 Using a model of metallic bonding, propose explanations for the following observations:
  - a An aluminium drink can is able to be crushed without it breaking or shattering.
  - b A metal spoon used to stir a boiling mixture quickly becomes too hot to hold.
  - c It is dangerous to use a metal knife to remove some burnt material from a toaster that is turned on.
  - d The thermal conductivity at room temperature of aluminium is  $237 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$ , yet the thermal conductivity of magnesium is  $156 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$ .

## 2.5 Uses of metals

In modern society, metals have a vast range of uses closely related to their physical properties. Some of the uses and related properties of metals obtained from ores mined in Western Australia are given in Table 2.4. Because most metals are not used commercially in their pure form, many of the listed uses are of the alloy containing the metal, not the pure metal. An alloy is a mixture of metals and occasionally non-metals.

**TABLE 2.4 USES OF SOME METALS OBTAINED FROM ORES MINED IN WESTERN AUSTRALIA**

Metal	Properties	Uses
Iron	relatively soft, malleable, good thermal and electrical conductor, corrodes fairly readily, readily forms alloys	normally converted to steel to make the iron stronger and more resistant to corrosion; variety of steels used for buildings, bridges, machinery, appliances, tools and drills
Aluminium	low density (lightweight metal), excellent thermal and electrical conductor, malleable and ductile, does not corrode due to protective oxide layer, shiny surface reflects heat and light, readily forms alloys	normally used as an alloy to give it better mechanical properties; used in aircraft, boat and building constructions, electric cables, components for electrical appliances, food packaging, drink cans, cooking utensils, foundry castings, gearboxes and motor parts in vehicles
Zinc	low corrosion rate due to reasonable protection of oxide layer, stronger donator of electrons than iron, low melting point, conducts electricity, readily forms alloys	often used in pure form for galvanising steel to prevent rusting and in batteries, used as an alloy in automotive equipment, household appliances, tools, electrical components, the building industry, computers and medical equipment
Nickel	strong even at high temperatures, corrosion resistant, high ductility, good thermal and electrical conductivities, magnetic, readily forms alloys	used in stainless steel to increase strength and resistance to corrosion, used in other alloys as parts in jet engines, combustion turbines in power generating stations, heating elements, coins and scientific instruments, used in pure form in rechargeable batteries and the electroplating industry
Lead	soft, low melting point, very corrosion resistant, dense, ductile, malleable	often used in its pure form for weatherproofing buildings, as a shield against radiation in the nuclear industry and in hospitals, added to glass in televisions and computer monitors to protect users from radiation, and in lead-acid batteries in vehicles
Gold	bright yellow colour, very dense, unreactive, high electrical conductivity, malleable, ductile	monetary standard, used in jewellery, dentistry, the adornment of buildings and for artistic purposes, electronic and computer circuitry, radar equipment and satellites

## \* Review exercise 2.5

- 1 Identify the particular physical properties that make the following metals suitable for the use identified.
  - a tungsten in electric-light filaments
  - b lead in roof flashing to seal gaps between roof tiles and walls
  - c steel in car bodies
  - d an alloy of tin and lead in solder
  - e mercury in thermometers
- 2 Aluminium, normally in the form of an alloy, is used to manufacture the bottom plate, that is, the ironing surface, on an electric iron.  
Explain, in terms of a metallic bonding model, why aluminium is particularly suited for this use.
- 3 **RESEARCH** Titanium has been hailed as a miracle metal because of its strength, low weight and resistance to corrosion. It is the ninth most abundant element in the Earth's crust and Australia has large reserves of this metal. Western Australia produces approximately 30% of the world supply of titanium.
  - a From what ores is titanium extracted?
  - b Where is titanium mined in Western Australia?
  - c Titanium is an ideal structural metal yet it is not, at the present time, used in large amounts. Why is this?
  - d In what ways is titanium used?
  - e List the properties of titanium that make it suitable for these uses, and where possible explain these properties in terms of the bonding and structure of the metal.



Figure 2.14 Artificial hip joints made from a titanium alloy.

## 2.6 Mixing metals with metals—designer alloys

### What are alloys?

Pure metals seldom have the properties required for particular uses. They may corrode too easily, not be strong enough, or be too brittle or too soft. Chemists have long known that other elements can be added to a metal to alter the metal's properties and as a result expand its range of uses. The homogeneous mixture formed when one or more other elements are added to a metal is called an **alloy**. The elements added to the metal to form the alloy can be either metals or non-metals. For example, steel is an alloy of iron with a little carbon mixed with it, and brass is a mixture of copper and zinc.

Alloys are mixtures because they do not have a constant composition. It is possible to mix the metal with its alloying elements in many different proportions. Often alloys are formed by melting the metal present in the largest amount, then mixing in the small amounts of the other elements and allowing the mixture to cool and solidify. Through experimentation the best proportions of the constituent metals and non-metals are found to suit the required need.



Figure 2.15 Stainless steel kitchen equipment.

For instance, stainless steel is effectively iron that has been modified by the addition of other metals such as 10% to 25% chromium and 4% to 22% nickel. The result is a corrosion-resistant alloy that is suitable for kitchen sinks, surfaces, appliances and cutlery.

In general, alloys are harder than pure metals. This is thought to be because the different-sized ions or atoms of other elements interrupt the orderly arrangement of ions in the lattice and prevent them from sliding over each other easily. For example, bronze, an alloy of copper and tin, is harder than either pure copper or pure tin. The tin ions prevent layers of copper ions from being displaced easily. This is illustrated in Figure 2.16.

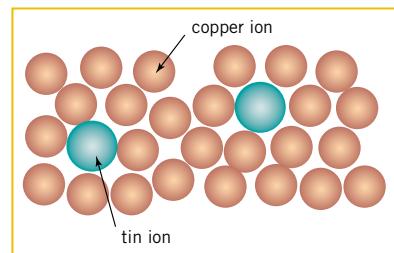
In some alloys such as carbon steels, depending on the proportion of the elements present and the conditions under which the alloy was formed, the elements form microcrystals that harden the alloy by interfering with the way the planes of ions slip past each other.

## Uses of alloys

Many thousands of different alloys are in use in today's world. To estimate how many there are is difficult because their numbers increase daily. Some examples of alloys and their uses are given in Table 2.5.

**TABLE 2.5 EXAMPLES OF COMMONLY USED ALLOYS**

Parent metal	Alloy	Composition	Properties	Uses
Silver	dental amalgam	60% Ag, 28% Sn, 12% Cu, 0.05% Pt dissolved in Hg	flexible when first mixed, expands as it hardens to fill cavity	filling teeth
Aluminium	Al 3003 alloy	97% Al, 1.5% Mn, <1% of Fe, Si, Zn	corrosion-resistant, lightweight, malleable, reasonably strong	cooking utensils, drink cans
Gold	9-carat yellow gold	38% Au, 12% Ag, 44% Cu, 6% Zn	gold colour, unreactive, harder and stronger than pure gold, easily worked	jewellery
Iron	C steel—mild steel	<0.3% C	cheap, easily welded, ductile and malleable	drink cans, car bodies, chains, wire
	C steel—tool steel	0.9%–1.5% C	very hard and strong, wear-resistant, slightly brittle	axes, scissors, drills, hammers
Lead	solder	67% Pb, 33% Sn (other proportions are also used)	low melting point, 'wets' and adheres to other metals, strong joints	joining pipes and wires, used in electronics industry
Nickel	nickel/steel alloy	48% Ni, 52% Fe	low expansion rate similar to that of soda glass	used in equipment with metal/glass seals, such as oven doors
Titanium	titanium/aluminium alloy	95% Ti, 3% Al, 2% V	biocompatible, very corrosion-resistant, strong, lightweight	bone and joint replacements
Zinc	zinc die-cast alloys	92% Zn, 8% Al (other proportions also used)	high strength, hard, wear-resistant, melts at sufficiently low temperature	precision parts for household appliances, vehicles, aircraft



**Figure 2.16** In bronze, the larger tin ions block the slip planes of copper and so increase copper's hardness.

## \* Review exercise 2.6

- 1 The following was presented in an information brochure about pewter:

Pewter is an alloy of tin with varying quantities of copper, bismuth, lead and antimony. The metal present in largest amount is always tin. The advantages of using tin are that it does not oxidise readily, and it has a low melting point of 232°C. However, it is quite soft. Alloying tin with some of the other metals overcomes this problem. Copper, bismuth and antimony are hardening agents, while lead is a relatively low-cost bulking agent. The melting point of pewter is low, about 170–180°C, which makes it easy to melt for casting.

- a Explain why adding other metals to tin to form pewter should produce a harder material than pure tin.
  - b Historically, pewter was an alloy of tin and lead and it became popular in the manufacture of kitchenware such as plates, mugs and utensils. But by the mid-1700s new non-leaded forms of pewter were being developed. Today, most of the pewter alloys used, particularly those for food vessels, contain no lead. Explain why lead was removed from the pewter alloys.
  - c ‘Britannia Metal 92’, one of the ‘leadless’ pewter alloys used for casting, is composed of 92% tin with 6% copper and 2% antimony. Assuming these values are percentages by mass, calculate the masses of copper and of antimony needed to be mixed with 1 kg of tin to form a sample of ‘Britannia Metal 92’.
  - d In the process to make a pewter cast, the pewter is first melted and then poured into the mould. After the liquid pewter has solidified, it is removed from the mould. Explain the changes that occur to the structure and bonding of the pewter during this cast-producing process.
- 2 The alloy used to make Australian ‘silver’ coins is composed of 25% nickel and 75% copper.
- a Draw a small section of the metallic lattice of this alloy showing the particles present.
  - b Which properties of copper would you expect to change when it is alloyed with nickel?
  - c Why is a copper–nickel alloy used for the ‘silver’ coins rather than silver?
- 3
- a What properties of stainless steel make it suitable for a kitchen sink?
  - b Why would pure iron not be suitable for a kitchen sink?
  - c How is iron modified to make stainless steel?
- 4 **RESEARCH**
- a Explain how the properties and structure of dental mercury amalgam impact on its use.
  - b Why do many dentists no longer use mercury amalgams?



Figure 2.17 Pewter teapot.

## 2.7 Copper—a profile

Copper, the reddish-coloured metal, permeates daily life in an enormous variety of ways. In an average home there is approximately 200 kg of copper, in a medium-sized car there is about 20 kg of copper and in a large aeroplane there is about 4000 kg of copper. Yet despite its widespread use, copper is a rather rare element, making up only 0.007% of the Earth's crust. Native copper, that is, copper in its elemental form, can be found occasionally in the Earth's crust, but more common sources of copper are in ores such as chalcopyrites,  $\text{CuFeS}_2$ , and chalcocite,  $\text{Cu}_2\text{S}$ . Most of the copper ore is currently obtained by open-pit mining. The ore is roasted, or heated in air, to produce impure copper, which is then purified by electrolysis to form 99% pure copper. Even though the copper ore is usually of a low grade, in other words, it does not contain a large percentage of copper, the extraction process does not consume a large amount of energy. As a consequence, the cost of producing copper is reasonably low compared with some other metals. However, it is still more costly than the other commonly used metals like iron, zinc, lead and aluminium.

Because copper is one of the best conductors of electricity and is soft and ductile it is an ideal material for making electrical wires. Copper wires are used extensively in household, vehicle and aircraft electric circuits, electric generators, electrical appliances, computers, lights, motors, telephone cables, radios and television sets. Copper's ability to conduct heat means it is used for home heating systems, steam-producing boilers, car radiators, air-conditioners and refrigeration systems. It is also ideal for the bases of cooking pots.

Although copper is relatively unreactive, it corrodes slowly in the atmosphere to form a green-coloured complex mixture of substances, commonly called patina, which protects the copper underneath from further corrosion. Many people consider this green-coloured patina that covers old copper structures, such as the Statue of Liberty, beautiful. Modern architects often choose copper plates for

roofs and facades of buildings with the expectation that the copper will corrode and change from its pleasant shiny salmon colour to a beautiful green colour. Perth's Bell Tower, shown in Figure 2.20, is an example of this, where the architects are expecting the copper to turn green and, consequently, complement the green colour of the glass in the tower.

As copper does not readily corrode or react with water, and is easily shaped, it is used for making pipes to convey water and gas in buildings and homes. Using copper for water pipes dates back to the Romans and ancient Egyptians. Health issues concerning copper in drinking water were raised in the 1980s. Copper is an essential element for all known living organisms, including humans. However, very



Figure 2.18 Large reels of copper wire.



Figure 2.19 The copper dome of a parliament building in Canada has turned green due to the slow corrosion of the copper.

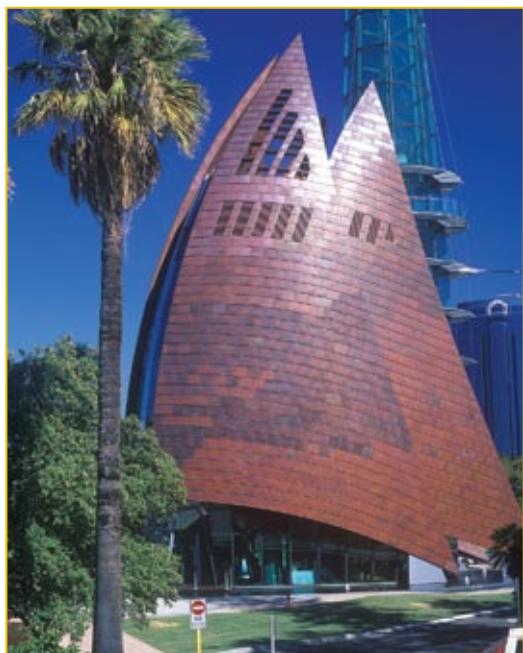


Figure 2.20 Perth's Bell Tower. The 'sails' are made from pure copper, which will corrode over the years to form a green coating.

large single or long-term intakes of copper, in the form of ions, may be harmful to health, particularly for young children. It has been shown that if the water delivered through copper pipes is corrosive, or remains motionless in the pipe for six hours or so, the level of dissolved copper ions in the water increases. It must also be recognised that, on average, drinking water accounts for less than 5% of a human's daily copper intake. Nonetheless, it remains a contentious issue as to whether or not the amount of copper in the drinking water that runs through copper pipes may be dangerous to health.

When copper is combined with other metals to form alloys, the resulting metal is normally harder and tougher than any of the original metals used in the alloys. Copper alloys are widely used in coins because they do not react readily with air and water. Most of the Australian coins are either an alloy of copper with nickel or an alloy of copper, aluminium and nickel, as shown in Figure 2.21.

Brass is an alloy of 65% copper and 35% zinc. Bronze is an alloy of approximately 90% copper and 10% tin. Bronze was used to make tools and weapons before the smelting of iron was discovered. Today, bronze is used to make objects such as springs, screws, wires, bearings, and top-quality bells and cymbals. Because brass has a yellow colour, somewhat similar to gold, it is often used as a decoration, for example, in brass door handles, lights and taps. Brass is particularly corrosion-resistant and so is also used to make hardware for marine craft. Due to its malleability and acoustic properties brass is the preferred metal for making musical instruments such as the trumpet and tuba.



Figure 2.21 The copper alloys used in Australian coins.

Chemists, and other scientists, are continually looking for new ways in which copper can be used for society's benefit. One potential use recently investigated applies the ability of copper to inhibit the growth of microbes, in particular, harmful bacteria. Scientists have found that the survival rates of deadly bacteria, such as the antibiotic resistant 'superbugs', on copper-alloy surfaces are significantly decreased compared with the survival rate on stainless steel surfaces. The recommendation from this research is that the healthcare industry should evaluate and begin to use copper-alloy work surfaces and door handles, especially in high human-contact areas, instead of stainless steel.

## \* Review exercise 2.7

- 1 **a** Draw a representation of a portion of copper at the atomic level.  
**b** Describe the bonding between the particles making up copper.
- 2 **a** In a table, list the properties of copper described in ‘Copper—a profile’.  
**b** Include an explanation, where possible, of the properties.  
**c** Give some examples of the uses of copper which rely on each of the properties.
- 3 **RESEARCH**  
**a** Find an example where copper has been used to produce, compared with what previously existed:
  - i a more energy-efficient machine, motor or process, or
  - ii a more sustainable process.

Explain the property or properties of copper that led to this improvement.

**b** The minimum amount of energy required to extract each of the three most used metals from their ores is given in Table 2.6.  
Suggest reasons to explain why copper is used less extensively than aluminium and iron and yet a smaller amount of energy is required to extract it from its ores, compared with the other two metals.
- c** Although copper is an essential mineral in the diet, there are concerns about the toxicity of copper.
  - i What are these concerns?
  - ii What is being done by the copper industry and health authorities to prevent any damage to life and the environment caused by the use of copper?

TABLE 2.6

Metal	Minimum energy required to produce 1 kg of metal (kJ)
Aluminium	31 100
Iron	7 400
Copper	2 500



## MAJOR IDEAS

- The characteristic physical properties of metals include:
  - good conductors of electricity in both the solid and liquid states
  - good conductors of heat
  - shiny when freshly cut or cleaned
  - malleable and ductile
  - many are hard, tough and relatively dense solids with high tensile strength
  - silver in colour, except gold and copper
  - melting points vary over a wide range but most are reasonably high
  - sonorous.
- A metal consists of a lattice of positive ions surrounded by a 'sea' of mobile delocalised valence electrons.
- Metallic bonding is the electrostatic attraction between the delocalised electrons and the positive ions in the metallic lattice.
- The metallic bonding model can be used to explain the properties of metals as shown in Table 2.7.

TABLE 2.7

Property	Explanation
Relatively high density	positive ions tightly packed in the lattice
Malleability and ductility	layers of positive ions can slip over one another without disrupting the metallic bonding; metallic bonding is non-directional
Conductivity of electricity and heat	mobile, delocalised electrons transfer charge and heat energy
High melting and boiling points	strong metallic bonding exists throughout the entire lattice

- An alloy is a homogenous mixture formed when one or more elements are added to a metal.

## QUESTIONS

1 Aluminium is a silvery-white, lightweight, relatively soft metal with a moderately high melting point. It is a good conductor of electricity and heat, an excellent reflector of radiation and highly malleable and ductile. When exposed to air it forms an oxide coating, which prevents further atmospheric corrosion. In addition, it is tasteless, odourless and is claimed by some to be non-toxic.

- a Which of the properties described above make aluminium suitable for the following uses?
- i aluminium foil used to wrap food
  - ii high-voltage electrical transmission lines

- iii cooking utensils such as kettles
- iv roofing on houses and factories.

- b For most of the uses listed in part a, aluminium is not used as the pure metal, but as an alloy. Why is the pure metal not very useful?
- c Explain why aluminium is malleable.
- d Environmentally there is a negative effect resulting from one of the properties of aluminium described above.
- i What property is this?
  - ii Explain how aluminium, because it possesses this property, causes harm to the environment.
  - iii What is being done to help prevent this environmental damage?
- e  RESEARCH Is aluminium non-toxic?
- 2 For an element to be a metal, what is the major characteristic of the valence electrons of the element?
- 3 In which of the following substances are the atoms held together by metallic bonding?
- brass   diamond   iodine   calcium   nickel*
- 4
- a To which group does rubidium belong in the periodic table?
  - b Using the assumption that elements in the same group have the same number of valence electrons, how many valence electrons does each rubidium atom have?
  - c Draw a representation of rubidium, at the atomic level, showing the particles present and the arrangement of these particles.
  - d Explain how the particles are held together in rubidium.
  - e Compared with most other metals, rubidium is very soft. Propose an explanation for this.
- 5
- a Gold is very reflective, so it is used to protect spacecraft from solar radiation. It is also used in the electronic components of spacecraft. One of the properties of gold is a drawback for its use in space. What is this property and why is it a problem?
  - b For hundreds of years gold prospectors have used the property referred to in part a to separate the gold from dirt and sand. Describe how they used this property.
  - c The densities of gold and two other metals are given as follows:

Metal	Gold	Aluminium	Iron
Density at 25°C (g cm <sup>-3</sup> )	19.3	2.7	7.87

- i** If a rectangular bar of gold has the dimensions of  $255 \times 80 \times 35$  mm, calculate its mass.
- ii** Calculate the mass of a bar of the same dimensions of the other two metals.
- iii** **RESEARCH** At today's prices, approximately how much would each of these three bars of metal be worth?
- iv** Briefly explain why there is a difference in monetary value between the three bars of metal.
- d** In earlier days, goldminers would test a specimen, to determine whether or not it was gold, by either biting it or hitting it with a rock.
- i** If the specimen was gold, what would you expect the results to be for each of these two tests?
  - ii** What properties of gold enable it to be tested in these ways?
  - iii** Explain why gold possesses these properties.
- e** Pure gold is not often used for making jewellery because of its properties referred to in part **d**.
- i** What is done to pure gold to make it more suitable for the jewellery industry?
  - ii** What effect does this have on the properties of gold?
  - iii** Explain these property changes in terms of a metallic bonding model.
- f** The purity of gold is measured in carats, where pure gold is said to be 24-carat gold. A 12-carat sample of gold would contain 50%, by mass, of gold. A ring of mass 5.3 g is composed of 18-carat white gold, an alloy of gold, silver, copper and zinc. What mass of gold must be in the ring?
- g** Approximately 83 000 000 troy ounces of gold are mined worldwide each year. What sized cube would this make if it was all in one piece?  
 $1 \text{ troy oz} = 31.10 \text{ g}$
- h** Possibly gold's most useful property has not been mentioned in any of the previous parts to this question.
- i** What is this property?
  - ii** Which of the uses mentioned in this question rely on gold possessing this property?
- 6** A metal can be described in the following way:
- A metal is an orderly crystalline packing of positive ions surrounded by delocalised electrons. The particles making up the metal are held together by metallic bonding.*
- a** Explain the meaning of the term 'delocalised electrons'.
- b** Which electrons are delocalised in a metal?
- c** What is meant by the term 'metallic bonding'?
- 7** Mercury is a heavy, silver-coloured metal that is a good conductor of electricity but, unlike most metals, it is a rather poor conductor of heat. It has a melting point of  $-38.9^\circ\text{C}$  and a boiling point of  $357^\circ\text{C}$ . Mercury is rarely found as a pure metal in nature, but it can be readily extracted from its ore, cinnabar, by heating the ore in air and condensing the mercury vapour.
- a** Mercury has been used in thermometers since the 1700s. Why is it a suitable metal to be used in this way?
- 
- Figure 2.22** Drops of mercury and a thermometer.
- b** In Antarctica, the temperatures can get as low as  $-60^\circ\text{C}$ . Could you use a mercury thermometer to measure these temperatures? Explain your answer.
- c** Explain in terms of the particle theory of matter how a thermometer works.
- d** The use of mercury in thermometers is now being phased out. Suggest why this is happening.
- e** The thermometers commonly used in school laboratories contain coloured alcohol instead of mercury. The alcohol is ethanol, which has a melting point of  $-114^\circ\text{C}$  and a boiling point of  $78^\circ\text{C}$ . If you were making toffee and wanted to use a thermometer to indicate when the toffee mixture had reached the required temperature of approximately  $150^\circ\text{C}$ , would you use a mercury thermometer or an alcohol thermometer?
- f** Suggest why mercury is a rather poor conductor of heat for a metal.
- 8** For each of the following metals, what significant property do you think has led to its widespread use? Justify your answer.
- a** iron
  - b** aluminium
  - c** copper

## 9 Heat and electrical conductivity

- a Plan an experiment to investigate how the electrical conductivity of copper is affected by temperature. Remember to consider safety issues.
- b A similar experiment to the one referred to in part a was carried out for aluminium. The following results were obtained.

### Conductivity of aluminium at different temperatures

Temperature (°C)	25	60	100	150	220
Electrical conductivity (MS m <sup>-1</sup> )	38	33	29	24	20

Propose an explanation of these results in terms of the ‘delocalised electron’ model of metals.

## 10 Determining the percentage of copper in an alloy using electrolysis

The following experiment describes the determination of the percentage by mass of copper in a sample of brass, using electrolysis. Read the information and then answer the questions.

### Background information

Brass is a homogeneous mixture of copper and zinc. In this experiment, the brass sample is reacted with acid to form a solution containing copper ions, Cu<sup>2+</sup>, and zinc ions, Zn<sup>2+</sup>. Electricity is then passed through the solution. In the electrolysis process, the copper ions gain electrons, at the negative electrode, to form copper metal. The zinc ions remain in the solution.

### Experiment

The following method was followed for the experiment:

- i Accurately weigh out about 1 g of brass into a 150 mL beaker. Add 10 mL of water followed by 15 mL of concentrated nitric acid.
- ii When the vigorous reaction is over, accurately dilute the solution with water, using a volumetric flask, to form a 100 mL solution.
- iii Set up the electrolysis equipment as shown in Figure 2.23. Accurately weigh the dry platinum gauze electrode.
- iv Using a pipette, transfer 50 mL of the solution to the electrolysis vessel.
- v Using a voltage of 2–3 volts, pass electricity through the solution until all the colour disappears.

- vi Carefully remove the copper-coated platinum gauze electrode and gently wash it, first with water and then with acetone.
- vii Dry the copper-coated electrode at 100–110°C for 3–4 minutes. Weigh the cooled electrode.

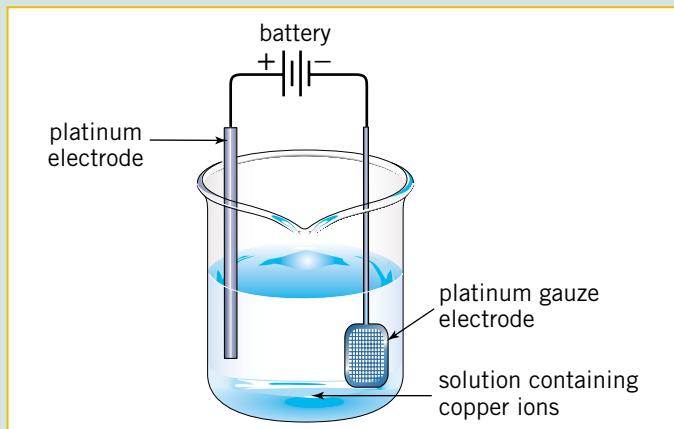


Figure 2.23 Electrolysis equipment.

### Results

Mass of brass = 1.04 g

Mass of dry platinum gauze electrode before the experiment = 50.24 g

Mass of dry platinum gauze electrode coated with copper = 50.55 g

- a From the above results, calculate the percentage by mass of copper in the sample of brass.
- b Compare this answer to the approximate amount of copper normally in brass.
- c What colour was the solution before the electrolysis step?
- d Why did this colour disappear during the electrolysis process?
- e Suggest any experimental errors that may have occurred during the experiment.
- f Suggest some ways in which the experimental method could be improved.

- 11 The first ionisation energies of the elements in the third period are given in Table 2.8. The first ionisation energy of an element is the energy required to remove the outermost electron from  $6.022 \times 10^{23}$  atoms (1 mole) of the element.
  - a Which of the elements listed in Table 2.8 are metals and which are non-metals, according to their position on the periodic table?

- b** After considering the ionisation energy data given in Table 2.8, propose an explanation for why phosphorus, sulfur, chlorine and argon do not exist as metallic lattices, that is, as a lattice of positive ions surrounded by delocalised electrons.
- c** Silicon is an unusual element because even though it tends to behave as a non-metal, it acts as a semiconductor when it has small amounts of boron or arsenic added to it. What modern industry is based on this semi-metallic property of silicon?

## 12 RESEARCH Building with metals

Metals are used extensively in the building industry. In homes, nails, bolts, roofs, reinforcement in concrete, structural beams, roof and wall insulation, gas and water pipes, electrical wiring, window and door frames, roof flashing and gutters are examples of objects made from metal.

Choose a variety of metal objects used in the construction of a house. For each of these objects:

- a** identify the metal or metals used in its manufacture
- b** justify, in terms of its properties, why the metal was chosen for the particular use
- c** explain these properties in terms of the bonding and structure of the metal

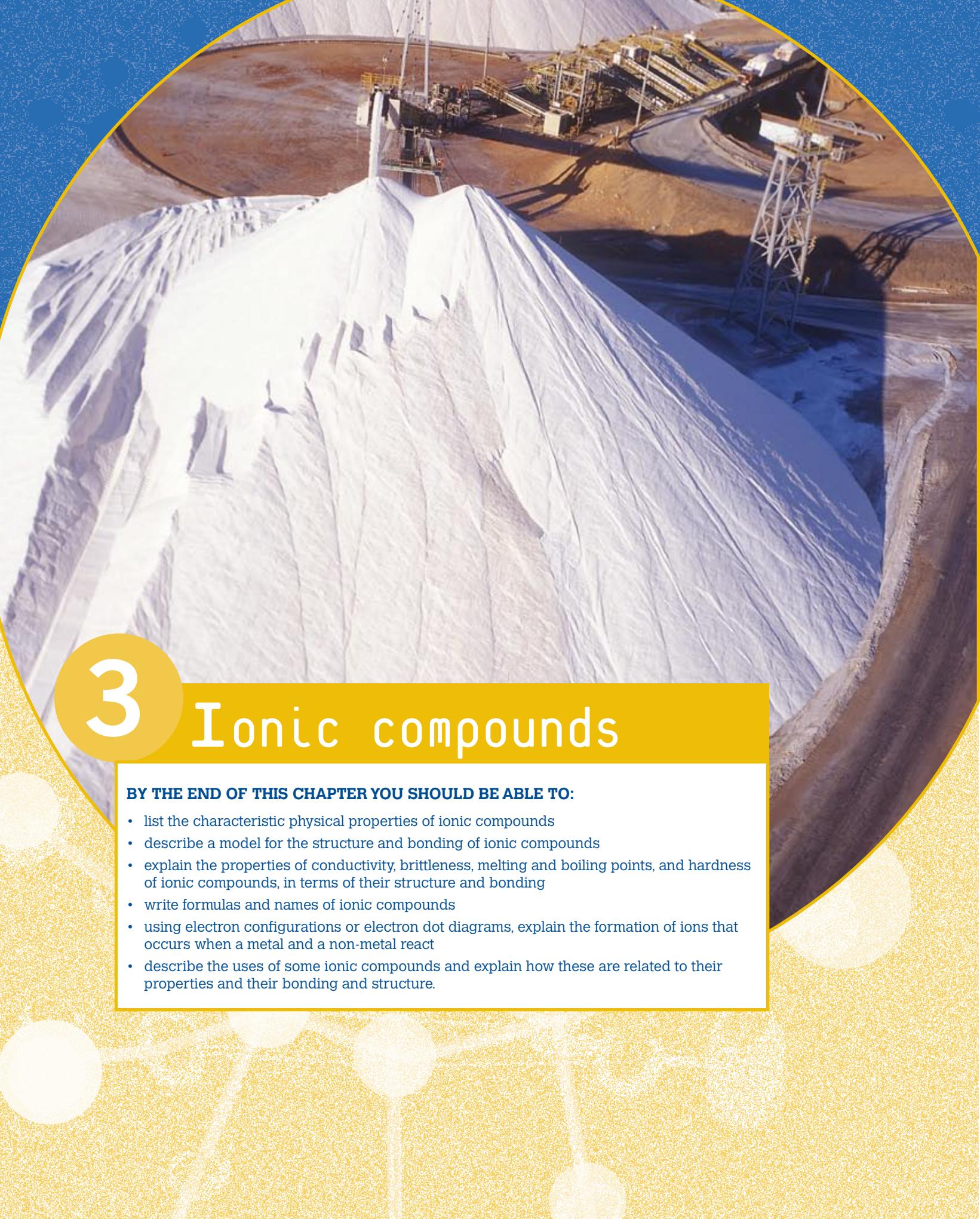
- d** investigate the history of the object and discuss any changes that have been made over time to improve its function
- e** predict any future developments in its use
- f** discuss any environmental issues involved with the use of the object.

**13 RESEARCH** In 1991, just off the coast from Perth, the bow of a fully laden oil tanker named *Kirki* broke off. Around 17 770 tonnes of crude oil were spilt in the sea but fortunately little reached the coastline. The ship's crew was rescued by helicopter and after salvage and anti-pollution arrangements were put in place, the *Kirki* was towed to Dampier where a ship-to-ship transfer of the remaining crude-oil cargo took place. The investigation into the cause of the incident concluded that the failure was due to excessive metal corrosion and metal fatigue in the vessel.

- a** What is metal fatigue and what is thought to cause it?
- b** Profile another real disaster that is thought to have occurred because of metal fatigue.
- c** What are some of the recommendations made by metal experts in the attempt to prevent metal fatigue from causing a disaster?

TABLE 2.8

Third-period element	Na	Mg	Al	Si	P	S	Cl	Ar
First ionisation energy (MJ mol <sup>-1</sup> )	0.502	0.744	0.584	0.793	1.018	1.006	1.257	1.527

The background image shows a massive, white, crystalline mound of salt or similar mineral at an industrial extraction site. In the foreground, there's a large, dark, curved structure, possibly a conveyor belt or storage tank. The background features more industrial equipment, including pipes, scaffolding, and smaller piles of material under a clear blue sky.

# 3

## Ionic compounds

**BY THE END OF THIS CHAPTER YOU SHOULD BE ABLE TO:**

- list the characteristic physical properties of ionic compounds
- describe a model for the structure and bonding of ionic compounds
- explain the properties of conductivity, brittleness, melting and boiling points, and hardness of ionic compounds, in terms of their structure and bonding
- write formulas and names of ionic compounds
- using electron configurations or electron dot diagrams, explain the formation of ions that occurs when a metal and a non-metal react
- describe the uses of some ionic compounds and explain how these are related to their properties and their bonding and structure.

## 3.1 Properties of ionic compounds

Millions of different compounds exist on Earth, being made from the eighty-nine different naturally occurring elements combining together in varying amounts. For each of these compounds, the elements making them up are present in fixed proportions. For example, in sodium chloride, the sodium ions and the chloride ions are always present in a ratio of 1:1, as shown in its formula of NaCl. In water, the hydrogen atoms and oxygen atoms are always present in a ratio of 2:1, which means the formula of water is H<sub>2</sub>O. The formulas of compounds contain the symbols of the elements involved and the subscripts indicate the relative numbers of atoms of each element in the compound.

Each compound has its own characteristic properties, which are different from the properties of the elements that combined to form it. Magnesium chloride, for example, is a white solid that is not very reactive, but magnesium is a moderately reactive grey solid and chlorine a highly reactive yellow-green gas at room temperature.



**Figure 3.1** The appearance of the compound magnesium chloride is quite different from the appearances of the metal magnesium and the non-metal chlorine.

Compounds that are composed of positive and negative ions are called **ionic compounds**. Many familiar substances such as salt (sodium chloride), marble (calcium carbonate), potash (potassium carbonate), baking soda (sodium hydrogencarbonate) and lime (calcium hydroxide) are ionic compounds.

## Properties of ionic compounds

Some physical properties of a selection of ionic compounds that are found in commercially available products are given in Table 3.1.

**TABLE 3.1 PHYSICAL PROPERTIES OF SOME IONIC COMPOUNDS**

Ionic compound	Formula	Description	Melting point (°C)	Conductivity			Solubility in water at 25°C (g/100 g water)	Example of commercially available product containing the compound
				Solid	Liquid	Aqueous solution (0.1 mol L <sup>-1</sup> )		
Copper sulfate	CuSO <sub>4</sub> ·5H <sub>2</sub> O	blue crystals	decomposes 110	no	yes	yes	22	bluestone spray (used to kill pathogens on fruit)
Sodium chloride	NaCl	white crystals	801	no	yes	yes	36	food salt
Calcium carbonate	CaCO <sub>3</sub>	white powder	1339 <sup>#</sup>	no	yes	–	0.0013	main component in marble
Potassium nitrate	KNO <sub>3</sub>	colourless crystals	334 <sup>#</sup>	no	yes	yes	38	plant fertiliser
Zinc oxide	ZnO	white powder	1975	no	yes	–	insoluble	zinc cream
Sodium hydroxide	NaOH	white solid	318	no	yes	yes	114	oven cleaner

# Melting point determined under pressure to prevent decomposition of compound.

As with metals there are variations in the properties of individual ionic compounds, but some generalisations can be made about the physical properties characteristic of ionic compounds.

- Ionic compounds have high melting and boiling points. They are all solids at room temperature.
- They are made up of hard crystals.
- They are neither malleable nor ductile, but are brittle.
- In the solid state they are non-conductors of electricity.
- They are good conductors of electricity in the liquid state.
- The solutions formed from soluble ionic compounds are good conductors of electricity.
- Their solubilities in water vary from very soluble to insoluble. They are not soluble in non-polar solvents, such as oil.
- Ionic solids formed from group 1 and 2 metals are white or colourless while those formed from transition metals are usually coloured.



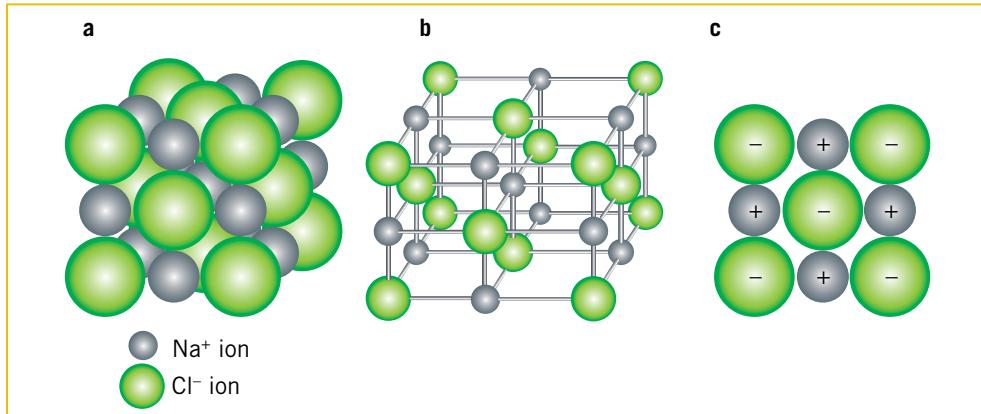
## \* Review exercise 3.1

- 1 Identify the following substances as either a metal, an ionic compound or neither.
  - a A silvery-grey solid that conducts electricity. It melts at 660°C and the liquid formed is also a good electrical conductor.
  - b A brittle, yellow solid that melts at 113°C. Both solid and liquid forms are non-conductors of electricity.
  - c A hard, brittle, white solid that melts at 620°C. The solid does not conduct electricity but the liquid does.
  - d A hard, white, crystalline solid that melts at 1610°C. Neither the solid nor liquid conducts electricity.
- 2 a Explain the difference in meaning of the two terms ‘sodium chloride in its liquid state’ and ‘a solution of sodium chloride’.  
b Several other words or terms are used instead of the term ‘liquid state’. What are these alternative words or terms?
- 3 Sketch the equipment that could be used to test the electrical conductivity of a molten ionic compound.
- 4 Use the solubility data in Table 3.1 to answer the following questions.
  - a What mass of potassium nitrate would dissolve in 250 g of water at 25°C?
  - b Describe and explain a procedure that could be used to separate a mixture of sodium chloride and calcium carbonate. Include a sketch of the equipment used in the procedure.
- 5 You are given unlabelled samples of:  
sugar      sodium chloride      potassium nitrate      copper sulfate      zinc oxide      calcium  
Describe how you would identify each sample using only the physical properties of the substances.
- 6 Predict and compare the physical properties of copper and of copper oxide.

## 3.2 Structure and bonding of ionic compounds

The electrical conductivity of molten ionic compounds suggests that ionic compounds are composed of positively and negatively charged ions.

The positive and negative ions in these compounds are thought to be arranged in an orderly three-dimensional lattice. The structure of sodium chloride is shown in Figure 3.2. In the lattice, each positive sodium ion is surrounded by six negative chloride ions and each negative chloride ion is surrounded by six positive sodium ions. The position of the ions is fixed and apart from vibration about these fixed positions no other movement of the ions occurs in the solid compound.



**Figure 3.2** Three models used to represent a small portion of the crystal lattice of sodium chloride.

Each ion in an ionic solid is held in the crystal lattice by strong electrostatic attractions to the oppositely charged ions around it. These electrostatic attractive forces between the positive and negative ions are called **ionic bonds**. Because ionic compounds have high melting points and boiling points, in other words considerable energy is required to disrupt the attractive forces between the positive and negative ions, **ionic bonding** is regarded as an example of strong bonding.

## \* Review exercise 3.2

- 1 Sodium fluoride is an ionic compound used in toothpaste as a cavity-preventing ingredient. It is composed of sodium ions,  $\text{Na}^+$ , and fluoride ions,  $\text{F}^-$ .

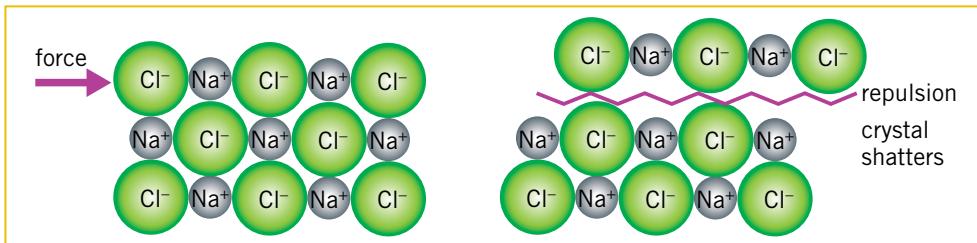
    - a Using sketches, describe the structure of:

      - i solid sodium fluoride,  $\text{NaF}$
      - ii molten sodium fluoride.
    - b Describe the bonding between the particles in solid sodium fluoride and molten sodium fluoride.
  - 2 Compare the similarities and differences between the structure and bonding of the solids sodium chloride and sodium.

### 3.3 Explaining some properties of ionic compounds

## Hardness and brittleness

The strong, electrostatic attractions between the oppositely charged ions in the three-dimensional lattice result in ionic solids being hard and difficult to cut. The brittleness of an ionic compound results from the orderly arrangement of ions in a crystal being disturbed after a layer of ions is forced to slide past another layer. This is shown in Figure 3.3. Because of the displacement, ions of similar charge are forced closer to one another with an increase in repulsive forces and a decrease in attractive forces. As a result, the crystal will shatter.



**Figure 3.3** Ionic solids are brittle. An applied force causes the crystal to shatter.

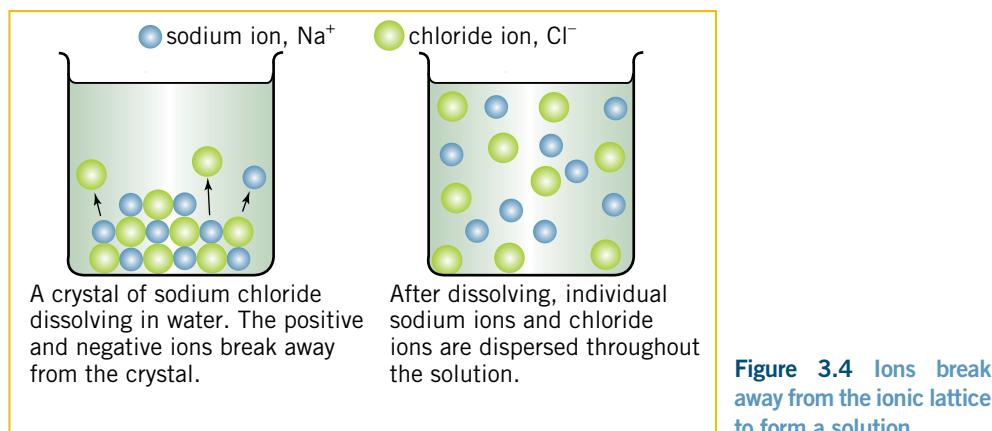
### High melting and boiling points

The forces of attraction between the oppositely charged ions in ionic compounds are so strong that large quantities of heat energy must be supplied to disrupt the crystal lattice and separate the ions. Consequently, ionic solids have high melting points.

In the liquid state, the ions have sufficient energy to move around randomly, but they are still close together. As a result, the attractive forces between the positive and negative ions in the liquid state are still strong. These attractive forces will be broken when the ionic compound boils to form a gas. In other words, molten ionic compounds have high boiling points (even though many decompose before they reach their boiling temperatures).

### Solubility

When a soluble ionic compound is added to water, the ions break away from the ionic lattice and mix with the water molecules, as shown in Figure 3.4.



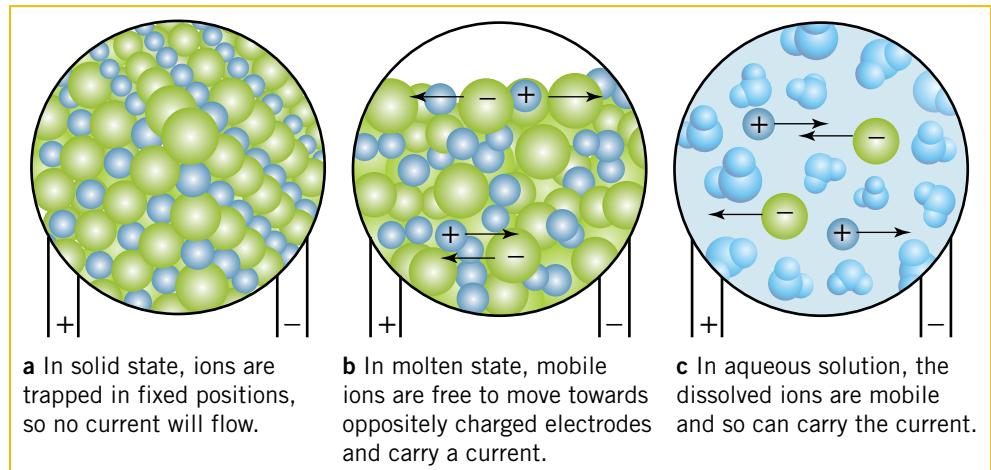
**Figure 3.4** Ions break away from the ionic lattice to form a solution.

If an insoluble ionic compound is added to water, the ions essentially remain bonded together in the ionic lattice. There is no simple explanation for why some ionic compounds are soluble and others are insoluble in water, but further discussion of the solubilities of substances will occur in Chapter 8.

### Electrical conductivity

Ionic solids do not conduct electricity because, although they contain charged particles, these ions occupy fixed positions and are not free to move through the solid lattice. Molten ionic compounds do conduct electricity because in the molten state the positive and negative ions are no longer strongly bonded in fixed positions in a lattice but are able to move through the liquid. Although molten ionic compounds conduct an electric current, they do not conduct as well as metals. This suggests that electrons in metals are much more mobile than ions in the molten state.

Pure water does not conduct an electric current to an appreciable extent, but when an ionic compound is dissolved in it the resulting solution conducts quite well. When a soluble ionic compound is added to water its ions break away from their fixed positions in the ionic lattice and are able to move around randomly in the solution. Consequently, the positive and negative ions in a solution are able to act as the charge carriers and conduct the electric current through the solution (see Figure 3.5). Mobile positive and negative ions are therefore responsible for the conduction of an electric current in an aqueous solution as well as in the molten state, for ionic compounds.



**Figure 3.5 Electrical conductivity and ion mobility for an ionic compound.**

### \* Review exercise 3.3

- 1 Potassium chloride, KCl, is made up of potassium ions,  $K^+$ , and chloride ions,  $Cl^-$ . Explain why molten potassium chloride conducts an electric current but solid potassium chloride does not.
- 2
 

*Useful seashells*

Due to their variety of shapes, shells of marine molluscs have often been used as tools. Giant clams have been used as bowls and even as bathtubs. Many bivalves were used as scrapers and blades. Some gastropods that have the shape of a snail shell have been used for oil lamps with the oil being poured in the cavity and the opening of the shell acting as a holder for the wick.

  - a Identify the physical properties that must be possessed by seashells if they can be used in the ways described above.
  - b The substance present in the largest amount in seashells is an ionic compound. What is the name of this compound?
  - c Where possible, explain the properties identified in part a, in terms of the bonding and structure of the ionic compound making up the shells.
  - d Bowls can be made from metals, such as copper, by hammering a piece of the metal into the required shape. Explain why you would not expect to be able to create a bowl from a seashell in this way.
  - e Would a seashell be an electrical conductor or an insulator? Explain your answer.

- 3** Sodium fluoride has a melting point of  $993^{\circ}\text{C}$  and magnesium oxide has a melting point of  $2852^{\circ}\text{C}$ . In both of these solids, the ions are organised in similar ways.
- Propose an explanation for why one of these melting points is much higher than the other.
  - What other physical properties, apart from high melting points, would the two compounds be expected to have in common?
  - Could a crystal of magnesium oxide be used to scratch a crystal of sodium fluoride? Justify your answer.
- 4** Which would you expect to be a better electrical conductor, a solid metal or an aqueous solution of an ionic compound? Justify your answer in terms of the bonding and structure of the two types of substances.

## 3.4 Names and formulas of ionic compounds

### Names and formulas of positive ions

A list of positive ions (cations) commonly found in ionic compounds is shown in Table 3.2. These positive ions, with the exception of the ammonium ion, are all derived from metallic elements.



**TABLE 3.2 COMMON POSITIVE IONS**

+1	+2	+3
lithium, $\text{Li}^{+}$	magnesium, $\text{Mg}^{2+}$	aluminium, $\text{Al}^{3+}$
sodium, $\text{Na}^{+}$	calcium, $\text{Ca}^{2+}$	iron(III), $\text{Fe}^{3+}$
potassium, $\text{K}^{+}$	strontium, $\text{Sr}^{2+}$	chromium(III), $\text{Cr}^{3+}$
rubidium, $\text{Rb}^{+}$	barium, $\text{Ba}^{2+}$	gold(III), $\text{Au}^{3+}$
caesium, $\text{Cs}^{+}$	manganese(II), $\text{Mn}^{2+}$	
silver, $\text{Ag}^{+}$	iron(II), $\text{Fe}^{2+}$	
copper(I), $\text{Cu}^{+}$	cobalt(II), $\text{Co}^{2+}$	
gold(I), $\text{Au}^{+}$	nickel(II), $\text{Ni}^{2+}$	
ammonium, $\text{NH}_4^{+}$	copper(II), $\text{Cu}^{2+}$	
	zinc, $\text{Zn}^{2+}$	
	mercury(I), $\text{Hg}_2^{2+}$	
	mercury(II), $\text{Hg}^{2+}$	
	tin(II), $\text{Sn}^{2+}$	
	lead(II), $\text{Pb}^{2+}$	
	cadmium(II), $\text{Cd}^{2+}$	

The monatomic positive ions have been formed when atoms have lost electrons. They are named after the element from which they were derived, for example,  $\text{Ba}^{2+}$  is called a barium ion and  $\text{Ag}^{+}$  is called a silver ion.

Some elements can form more than one positive ion. For example, iron forms two common ions: the iron(II) ion,  $\text{Fe}^{2+}$ , and the iron(III) ion,  $\text{Fe}^{3+}$ . To distinguish between these ions, Roman numerals are placed in brackets after the element's name to indicate the charges on the ions. The ions are called the iron-two ion and the iron-three ion respectively.

Most positive ions are formed from metallic elements. An exception to this is the ammonium ion,  $\text{NH}_4^+$ . The ammonium ion is an example of a **Polyatomic ion**. These ions are made up of two or more atoms strongly bonded to one another. The nitrogen atom and four hydrogen atoms in each ammonium ion are joined together by covalent bonds. Covalent bonds are of similar strength to ionic bonds and they will be discussed in more detail in Chapter 4. The superscript ‘+’ in the chemical formula represents the +1 charge on the ammonium ion. This indicates that there is one less electron in the ion than the total number of protons possessed by the five atoms.

### Names and formulas of negative ions

Negative ions, or anions, commonly found in ionic compounds are listed in Table 3.3. These ions are derived from mainly non-metals that occur on the right-hand side of the periodic table.

TABLE 3.3 COMMON NEGATIVE IONS

-1	-2	-3
hydride, $\text{H}^-$	oxide, $\text{O}^{2-}$	nitride, $\text{N}^{3-}$
fluoride, $\text{F}^-$	sulfide, $\text{S}^{2-}$	phosphide, $\text{P}^{3-}$
chloride, $\text{Cl}^-$	carbonate, $\text{CO}_3^{2-}$	phosphate, $\text{PO}_4^{3-}$
bromide, $\text{Br}^-$	sulfate, $\text{SO}_4^{2-}$	
iodide, $\text{I}^-$	sulfite, $\text{SO}_3^{2-}$	
hydroxide, $\text{OH}^-$	peroxide, $\text{O}_2^{2-}$	
nitrate, $\text{NO}_3^-$	hydrogenphosphate, $\text{HPO}_4^{2-}$	
nitrite, $\text{NO}_2^-$	dichromate, $\text{Cr}_2\text{O}_7^{2-}$	
hydrogencarbonate, $\text{HCO}_3^-$	chromate, $\text{CrO}_4^{2-}$	
hydrogensulfate, $\text{HSO}_4^-$	oxalate, $\text{C}_2\text{O}_4^{2-}$	
dihydrogenphosphate, $\text{H}_2\text{PO}_4^-$		
acetate (ethanoate), $\text{CH}_3\text{COO}^-$		
cyanide, $\text{CN}^-$		
permanganate, $\text{MnO}_4^-$		
hypochlorite, $\text{ClO}^-$		
chlorite, $\text{ClO}_2^-$		
chlorate, $\text{ClO}_3^-$		
perchlorate, $\text{ClO}_4^-$		

Monatomic negative ions are named by adding the suffix ‘-ide’ to the stem of the element’s name. Fluoride ions are formed when fluorine atoms gain electrons and so have the formula of  $\text{F}^-$ , and sulfide ions have the formula  $\text{S}^{2-}$  because they form when sulfur atoms gain electrons.

Many of the negative ions are polyatomic ions which, as described previously, are groups of atoms strongly bonded to one another and having an overall charge. Most of the polyatomic anions shown in Table 3.3 contain oxygen and so their name ends in either ‘-ite’ or ‘-ate’. For example, the  $\text{NO}_3^-$  ion is called the nitrate ion and the  $\text{NO}_2^-$  ion is called the nitrite ion. If there are two ions composed of the same element together 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’. Representations at the atomic level of some positive and negative ions are shown in Figure 3.6.

Atomic model	$\text{Fe}^{2+}$			
Name and formula	iron(II) ion $\text{Fe}^{2+}$	ammonium ion $\text{NH}_4^+$	carbonate ion $\text{CO}_3^{2-}$	phosphide ion $\text{P}^{3-}$
Number of protons	26	11	30	15
Number of electrons	24	10	32	18

Figure 3.6 Some positive and negative ions, showing the atoms present.

## Formulas of ionic compounds

Ionic compounds contain oppositely charged ions that are arranged in three-dimensional lattices. Because ionic compounds are electrically neutral, the number of positive charges must equal the number of negative charges. Common salt, sodium chloride, consists of sodium ions,  $\text{Na}^+$ , and chloride ions,  $\text{Cl}^-$ . Since these two ions have equal but opposite charges, the numbers of sodium ions and of chloride ions present in sodium chloride are always equal, that is, they are present in a 1:1 ratio. This ratio is expressed in the chemical formula of the substance. The formula of sodium chloride is therefore represented as  $\text{NaCl}$ . For ionic compounds, the formula of the positive ion is written before the formula of the negative ion. Also the charges of the ions are not shown in the formula of the compound.

If the charges on the individual ions in an ionic compound are not equal in magnitude, then to preserve electrical neutrality there will be more ions with the smaller charge. For example, the formula of the compound formed between calcium ions,  $\text{Ca}^{2+}$ , and chloride ions,  $\text{Cl}^-$ , is  $\text{CaCl}_2$ . This formula indicates that in calcium chloride there are two chloride ions for every calcium ion. Two chloride ions are necessary to ‘provide’ a  $-2$  charge to balance out the  $+2$  charge on each calcium ion. The formula of an ionic compound therefore indicates the relative numbers of ions of each type in the compound. The writing of formulas of several other ionic compounds is shown in Figure 3.7.

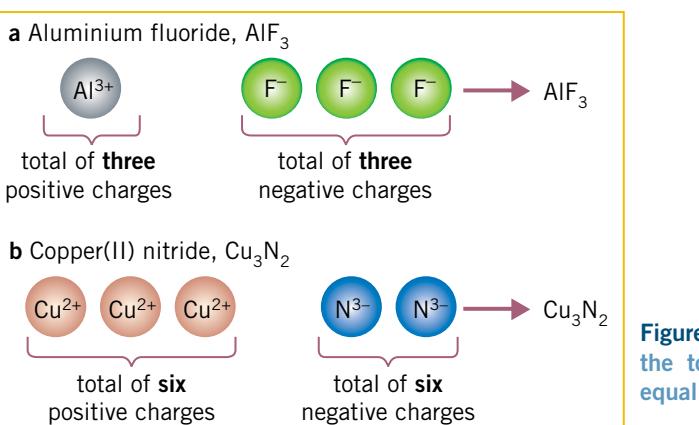
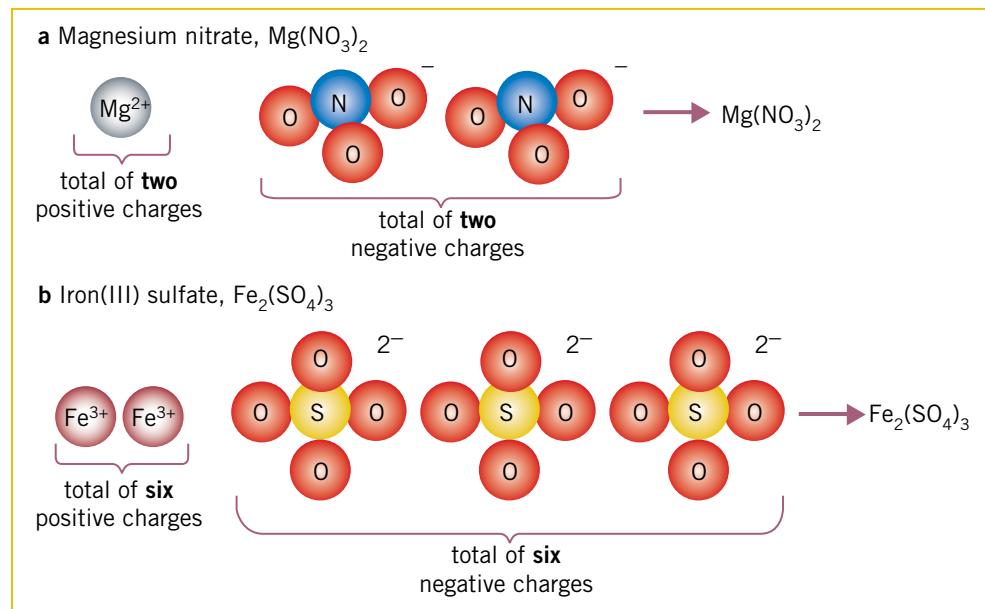


Figure 3.7 In an ionic compound the total positive charge must equal the total negative charge.

When there are two or more units of a polyatomic ion in a formula, the polyatomic ion is enclosed in brackets to show that the subscript applies to the entire ion. For example, the formula of a compound composed of copper ions,  $\text{Cu}^{2+}$ , and hydroxide ions,  $\text{OH}^-$ , is  $\text{Cu}(\text{OH})_2$  and the formula of a compound composed of ammonium ions,  $\text{NH}_4^+$ , and phosphate ions,  $\text{PO}_4^{3-}$ , is  $(\text{NH}_4)_3\text{PO}_4$ . Other examples are shown in Figure 3.8.



**Figure 3.8 Examples of formulas involving polyatomic ions, showing that the total number of positive charges must equal the total number of negative charges.**

→ **Example 3.1**

1 Write formulas for the compounds formed between:

- a sodium ions ( $\text{Na}^+$ ) and oxide ions ( $\text{O}^{2-}$ )
- b calcium ions ( $\text{Ca}^{2+}$ ) and phosphate ions ( $\text{PO}_4^{3-}$ ).

2 Write the formulas for:

- a gold(III) carbonate
- b potassium peroxide.

→ **Solution**

1 a **Ions:**       $\text{Na}^+$      $\text{O}^{2-}$        $2 \times \text{Na}^+ + 1 \times \text{O}^{2-} = \text{Na}_2\text{O}$

**Charge:**    +1    -2       $2 \times (+1) + 1 \times (-2) = 0$

For the compound to be electrically neutral there must be two sodium ions for every oxide ion. The formula will therefore be  $\text{Na}_2\text{O}$ .

b **Ions:**       $\text{Ca}^{2+}$      $\text{PO}_4^{3-}$        $3 \times \text{Ca}^{2+} + 2 \times \text{PO}_4^{3-} = \text{Ca}_3(\text{PO}_4)_2$

**Charge:**    +2    -3       $3 \times (+2) + 2 \times (-3) = 0$

For the compound to be electrically neutral there must be three calcium ions for every two phosphate ions. The formula is  $\text{Ca}_3(\text{PO}_4)_2$ .

2 a **Ions:**       $\text{Au}^{3+}$      $\text{CO}_3^{2-}$        $2 \times \text{Au}^{3+} + 3 \times \text{CO}_3^{2-} = \text{Au}_2(\text{CO}_3)_3$

**Charge:**    +3    -2       $2 \times (+3) + 3 \times (-2) = 0$

For the compound to be electrically neutral there must be two gold(III) ions for every three carbonate ions. The formula is  $\text{Au}_2(\text{CO}_3)_3$ .



Charge: +1    -2     $2 \times (+1) + 1 \times (-2) = 0$

For the compound to be electrically neutral there must be two potassium ions for every peroxide ion. The formula is  $\text{K}_2\text{O}_2$ .

## Names of ionic compounds

When naming ionic compounds the following procedure is followed.

### Procedure

- 1 The name of the positive ion is written first.
- 2 The name of the negative ion is written after the positive ion.

### Example: naming $\text{Fe}(\text{MnO}_4)_3$

iron(III)

iron(III) permanganate



Note that in naming ionic compounds:

- the word 'ion' does not appear in the name
- prefixes like 'di' and 'tri' are not used to identify the relative numbers of ions in the compound.

Some ionic compounds have water molecules bonded to the positive ions in the lattice. The number of water molecules—often called water of crystallisation—associated with the ions in the compound can be shown as part of the formula. For example, the formula  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  means that there are five water molecules for every copper(II) ion. The name of this compound is written as copper(II) sulfate-5-water.

### → Example 3.2

What are the names of the following ionic compounds?



### → Solution

#### a Positive ion:

$\text{Mg}^{2+}$ , magnesium ion

#### Negative ion:

$\text{H}_2\text{PO}_4^-$ , dihydrogenphosphate ion

The name is therefore **magnesium dihydrogenphosphate**.

#### b Positive ion:

one of  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$   
Because each of the three  
negative ions has a charge of  
-2, to give -6 in total, each of  
the two positive ions must have  
a charge of +3.

The positive ion is  $\text{Fe}^{3+}$ ,  
iron(III) ion.

#### Negative ion:

$\text{SO}_4^{2-}$ , sulfate ion

#### Water of crystallisation:

$\text{H}_2\text{O}$ , water  
There are  
9 water  
molecules.

The name is therefore **iron(III) sulfate-9-water**.

## \* Review exercise 3.4

- 1 Give the names and formulas of the ions in the familiar mixtures shown in Table 3.4.

TABLE 3.4

	Name	Formula
a The positive ion in milk that is 'good for strong bones'.		
b The positive ion that contributes to the red colour of blood.		
c The negative ion in marble.		
d The negative ion added to drinking water to prevent tooth decay.		
e A negative ion in sherbet and 'fizzy' lollies.		
f A negative ion in sulfuric acid.		
g The positive polyatomic ion often found in plant fertilisers.		
h The negative ion in a solution of Condy's crystals, which can be used, with care, to disinfect feet.		
i The positive ion in bauxite ore.		

- 2 Given the atomic numbers and mass numbers of the elements, determine the numbers of protons, neutrons and electrons in the following ions:
- a  $\text{S}^{2-}$ , Z = 16, A = 32      b  $\text{Sc}^{3+}$ , Z = 21, A = 45.
- 3 Give the total number of protons and the total number of electrons in the following polyatomic ions:
- a ammonium ion      b dichromate ion.
- 4 Write the formulas for the ionic compounds that form between the following ions:
- |                                       |   |
|---------------------------------------|---|
| a $\text{Hg}^{2+}$ and $\text{CN}^-$  | d $\text{NH}_4^+$ and $\text{SO}_4^{2-}$  |
| b $\text{Al}^{3+}$ and $\text{OH}^-$  | e $\text{Fe}^{3+}$ and $\text{O}^{2-}$    |
| c $\text{Ca}^{2+}$ and $\text{ClO}^-$ | f $\text{Mg}^{2+}$ and $\text{PO}_4^{3-}$ |
- 5 What are the names of the following ionic compounds?
- |   |                         |
|---|-------------------------|
| a $\text{KMnO}_4$                                     | d $\text{NaHSO}_3$      |
| b $\text{Ni}(\text{HSO}_4)_2$                         | e $\text{Cu}_2\text{O}$ |
| c $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ | f $\text{Fe(OH)}_3$     |
- 6 What are the formulas of the following ionic compounds?
- |                           |                     |
|---------------------------|---------------------|
| a ammonium sulfide        | d barium nitride    |
| b potassium nitrite       | e sodium dichromate |
| c calcium sulfate-2-water | f tin(II) carbonate |

- 7** What would you expect the formulas of the following compounds to be?

**a** zinc phosphite                   **d** rubidium carbonate  
**b** magnesium hydrogensulfite     **e** mercury(I) chloride where the  
**c** aluminium hypobromite               formula of the mercury(I) ion is  $\text{Hg}_2^{2+}$

**8** ↳ RESEARCH The following is a list of substances as they were presented in a fireworks manufacturer's handbook.

## Materials used in fireworks manufacture

<b>Oxidants</b>	Chlorates(V) of potassium and barium Chlorates(VII) of potassium and ammonium Nitrates of potassium, barium and strontium Peroxides of barium and strontium
<b>Colouring agents</b>	Barium nitrate and chlorate(V) for green Strontium carbonate, ethanedioate, nitrate for red Sodium ethanedioate, cryolite for yellow Copper(II) oxide, carbonate and chloride for blue
<b>Fuels</b>	Accaroid resin, gum copal, shellac for colours Charcoal and sulfur for non-colours Antimony sulfide
<b>Other materials</b>	PVC, titanium, aluminium, magnesium, antimony, lampblack, dextrin, gum arabic, starch, barium carbonate, calcium phosphate(V)

Give the formulas of the nineteen different ionic compounds mentioned in this list of materials. A book or website may need to be consulted to determine the formulas of some of the ions whose names are unfamiliar or have been expressed using a different naming system.

## 3.5 Formation of ionic compounds

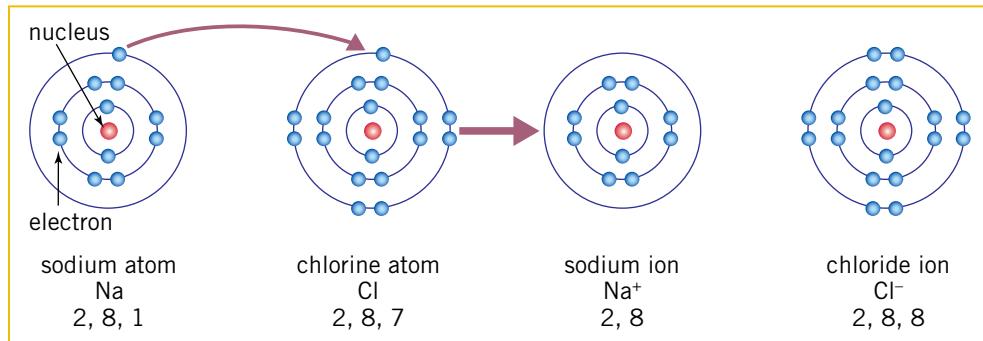
The group 18 elements (the noble gases), other than helium, have an outer shell or valence electron configuration of eight electrons. Because these elements are very unreactive, it can be inferred that an outer shell configuration of eight electrons is very stable. Many elements attain eight electrons in their outer shell when they react to form compounds. This is sometimes referred to as the **octet rule**.

An ionic compound forms when metal and non-metal elements react. During such a reaction, the metal atoms lose electrons to form positive ions and the non-metal atoms gain electrons to form negative ions. In this exchange of electrons, both the metal and non-metal atoms achieve a noble gas electron configuration, that is, eight electrons in their outer shell.

## Formation of sodium chloride

In the case of sodium chloride, the sodium electron configuration of 2, 8, 1 is one electron more than the neon electron configuration of 2, 8. When sodium's one valence electron is removed, the resulting species, a sodium ion ( $\text{Na}^+$ ), has the stable electron configuration of neon.

Chlorine, with an electron configuration of 2, 8, 7, is one electron short of the stable argon electron configuration of 2, 8, 8. When it reacts with sodium, chlorine acquires an electron and forms a chloride ion ( $\text{Cl}^-$ ), which has the electron configuration of argon, as shown in Figure 3.9.



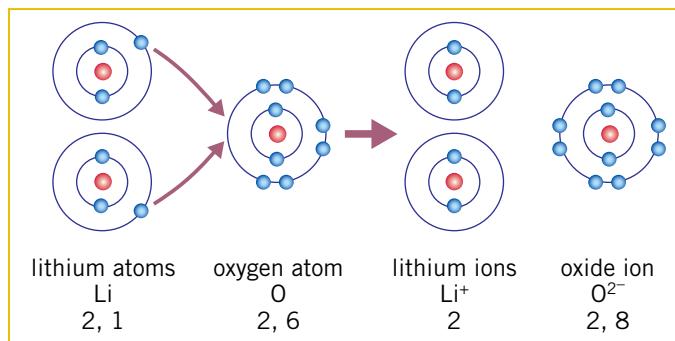
**Figure 3.9** A Bohr-model representation can be used to show the transfer of electrons between sodium and chlorine to form sodium ions and chloride ions.

Because in this reaction every sodium atom loses one electron and every chlorine atom gains one electron, the atoms will react in a 1:1 ratio. As a result, the sodium and chloride ions formed will be present in a 1:1 ratio. This is represented in the formula of sodium chloride, which is written as  $\text{NaCl}$ .

The positive sodium ions and negative chloride ions produced in the electron transfer reaction electrostatically attract each other to build up the regular three-dimensional ionic lattice shown in Figure 3.2.

### Formation of lithium oxide

As with the reaction between sodium and chlorine, when the metal lithium reacts with the non-metal oxygen, electrons are transferred from the metal atoms to the non-metal atoms to form ions, as shown in Figure 3.10.



**Figure 3.10** A Bohr-model representation of the electron transfer reaction between lithium and oxygen atoms.

In this reaction every lithium atom gives up one electron and every oxygen atom gains two electrons to form  $\text{Li}^+$  and  $\text{O}^{2-}$  respectively. Consequently, for every one oxygen atom there will need to be two lithium atoms to provide sufficient electrons. That is, the lithium and oxygen will react in a 2:1 ratio. The lithium oxide formed in this reaction will therefore be made up of lithium ions,  $\text{Li}^+$ , and oxide ions,  $\text{O}^{2-}$ , present in a ratio of 2:1, and its formula will be  $\text{Li}_2\text{O}$ .

### Predicting the formulas of some monatomic ions

Using the inference that atoms achieve a noble gas electron configuration when they form ions, the periodic table can be used to predict the formulas of ions formed by the elements of groups 1 and 2 and groups 13 to 17.

- Group 1 metals Li, Na, K, Rb and Cs all have one electron in their outermost shell. If they lose one electron, the +1 ions they form will have a noble gas configuration. These ions will be  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$ .

- Group 2 metals Be, Mg, Ca, Sr and Ba all have 2 valence electrons, which they lose to form ions with a +2 charge. These ions are  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ .
  - Group 13 metals, with 3 valence electrons, form +3 ions, for example,  $\text{Al}^{3+}$  and  $\text{Ga}^{3+}$ .
  - Group 14 elements have 4 valence electrons. These atoms can, in theory, achieve a noble gas configuration by either losing 4 electrons or gaining 4 electrons. The first two non-metal elements, C and Si, and the metalloid element Ge, tend not to form ions, but the metal elements, Sn and Pb, form both +2 and +4 ions.
  - Group 15 non-metal elements N, P and As have 5 valence electrons. Non-metal elements gain electrons when they react with metals. These group 15 elements therefore will gain 3 electrons to achieve a noble gas configuration. The ions formed will be  $\text{N}^{3-}$ ,  $\text{P}^{3-}$  and  $\text{As}^{3-}$ .
  - Group 16 non-metal elements have 6 valence electrons, so they gain 2 electrons to form ions with a -2 charge, for example,  $\text{O}^{2-}$  and  $\text{S}^{2-}$ .
  - Group 17 elements have 7 valence electrons, and they gain 1 electron to form ions with a -1 charge, for example,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ .

These points are summarised in the periodic table shown in Figure 3.11.

**Figure 3.11** The formulas of the ions formed by some elements can be predicted from their position in the periodic table.

The transition metals all lose electrons to form positive ions, but it is not possible to predict the charge on these ions by consulting the periodic table. Most form ions with a +2 charge because they have 2 electrons in their outer shell, but most of them also form ions with other charges. For example, iron forms both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions.

## \* Review exercise 3.5

- 1 Why do atoms become positively or negatively charged when they lose or gain electrons?
- 2
  - a Explain why sodium and potassium atoms both form ions with a +1 charge.
  - b Oxygen and fluorine are both non-metal elements, yet oxygen forms ions with a -2 charge and fluorine forms ions with a -1 charge. Explain why these two elements form ions with different charges.
- 3 Using a Bohr model representation, show what happens to the valence electrons of the atoms when aluminium atoms react with fluorine atoms.
- 4 When barium reacts with chlorine, a compound with the formula  $\text{BaCl}_2$  forms. However, when barium reacts with sulfur, the compound that forms has a formula of  $\text{BaS}$ . Explain why the ratio of the atoms shown in each of these formulas is different.
- 5 Atom X, having three electrons in its outer shell, reacts with atom Z, which has six electrons in its outer shell.
  - a Write the formula of the compound formed. Explain your reasoning.
  - b What type of bonding holds the particles together in the compound?
  - c Predict three general physical properties of the compound.

## 3.6 Electron dot diagrams of ionic compounds

**Electron dot diagrams** are a simple way of showing the arrangement of electrons around atoms and the changes that occur as atoms react with one another. In electron dot diagrams only the valence, or outer shell, electrons are shown and a dot or some other marker is used to represent each of these electrons. The symbol of the atom is also shown and it can be thought of as representing the nucleus plus the electrons in the inner shells of the atom. For example, the electron dot diagrams for hydrogen, sodium, magnesium, chlorine and oxygen atoms are shown below.



The number of valence electrons for an atom can be determined from its electron configuration. However, generalisations can be made concerning the number of valence electrons for the main group elements, as shown in Table 3.5.

**TABLE 3.5 THE NUMBER OF VALENCE ELECTRONS FOR THE MAIN GROUP ELEMENTS**

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

For example, magnesium is in group 2 and has 2 valence electrons, and oxygen is in group 16 and has 6 valence electrons.

Electron dot diagrams can be used to represent the formation of ions in a reaction of a metal with a non-metal. For example, the formation of potassium ions and bromide ions in the reaction of potassium atoms with bromine atoms is shown as follows.



Square brackets are often placed around the electron dot diagram of an ion, and the charge on the ion is given outside the brackets. Also, the dots are only used as a means of counting electrons; they do not show the location of electrons.

Two other examples of the reactions of metals with non-metals to form ions are barium atoms reacting with fluorine atoms



and magnesium atoms reacting with phosphorus atoms.



The electron dot diagrams of ionic compounds are also sometimes drawn using subscripts to show the relative numbers of ions present. The electron dot diagrams of calcium iodide,  $\text{CaI}_2$ , and aluminium sulfide,  $\text{Al}_2\text{S}_3$ , are as follows:



### → Example 3.3

Draw the electron dot diagrams of the following:

- a selenium atom      c strontium ion
- b chloride ion,  $\text{Cl}^-$       d calcium nitride.

### → Solution

- a Selenium is in group 16 and it has 6 valence electrons.

The electron dot diagram is:



- b Chlorine is in group 17, so the neutral atom has 7 valence electrons. The chloride ion has a charge of  $-1$ , which means it has one more electron than the neutral atom, that is, 8 valence electrons. The electron dot diagram of the ion is:



- c Strontium is in group 2, so it will form ions with a  $+2$  charge. That is, the formula of the strontium ion is  $\text{Sr}^{2+}$ .

As a group 2 element, the neutral strontium atom has 2 valence electrons. Because the strontium ion has a  $+2$  charge (that is, it has 2 more protons than electrons) the neutral atom has lost the 2 valence electrons in forming the ion. The electron dot diagram of the ion is:



*continued*

- d Calcium nitride is composed of calcium ions,  $\text{Ca}^{2+}$ , and nitride ions,  $\text{N}^{3-}$ , so its formula will be  $\text{Ca}_3\text{N}_2$ .

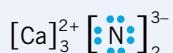
As a group 2 element, the neutral calcium atom has 2 valence electrons. In forming an ion with a +2 charge these 2 electrons are lost. The electron dot diagram of the calcium ion is:



Nitrogen is in group 15, so the neutral atom has 5 valence electrons. Because the nitride ion has a charge of -3, it has 8 valence electrons. The electron dot diagram of the nitride ion is:



The electron dot diagram of calcium nitride is therefore:



### \* Review exercise 3.6

- 1 What evidence is there that the electron configurations of the noble gases are particularly stable?
- 2 Draw electron dot diagrams illustrating the valence electrons in the following:
  - a potassium atoms and iodine atoms
  - b potassium ions and iodide ions in potassium iodide.
- 3 Draw electron dot diagrams for the following ionic compounds:

a sodium fluoride	c aluminium bromide
b calcium oxide	d barium phosphide.



Figure 3.12 Household products containing sodium carbonate and sodium hydrogencarbonate.

## 3.7 Uses of ionic compounds

Ionic compounds have innumerable uses or functions. They are used as building materials, in food preparation and preservation, in beauty products and medicines, as fertilisers and cleaners, and in industrial processes, to name a few. Also they play vital roles in the biochemical processes that occur in all living things. Many of these uses and functions can be understood in terms of the physical and chemical properties of the ionic compounds.

A variety of uses of ionic compounds are given in Table 3.6.

TABLE 3.6 USES OF IONIC COMPOUNDS

Name	Uses	Related properties
Ammonium chloride	in the moist paste in a torch battery	conducts electricity as a solution
Ammonium nitrate	in fertilisers	soluble in water, provides nitrogen in compound form for plant growth
Calcium phosphate	in bones and teeth, in ceramics used for surgical and dental implants, in the manufacture of superphosphate	hard, insoluble in water, reacts with sulfuric acid to form water-soluble, phosphorus-containing compounds
Corundum (crystals of aluminium oxide)	as an abrasive on sandpaper and grinding tools, used to make firebricks to line furnaces, with impurities present it is a gemstone	extremely hard, very high melting point
Gypsum (calcium sulfate)	in the manufacture of plaster for walls and plaster of Paris	when added to water the powder forms a hard material
Potassium nitrate	in fireworks, gunpowder, fertilisers	oxidant, soluble source of nitrogen and potassium
Silver chloride	in photochromic spectacles	forms silver when exposed to light
Sodium carbonate	as washing soda, as a cleaning agent, in the manufacture of glass, paper and ceramics	forms an insoluble substance with calcium ions, acts as a weak base
Sodium chloride	as a food flavouring agent and preservative, as a reactant for production of chlorine and sodium hydroxide by electrolysis	tastes salty, dehydrates bacteria, solution conducts electricity
Sodium hydrogencarbonate	as baking soda, as a cleaning agent, in fizzy lollies and drinks, in fire extinguishers	a weak base, produces carbon dioxide when heated or added to acid
Sodium hydroxide	as a drain and oven cleaner, used in the manufacture of soap	acts as a strong base, reacts with fats to make them more water-soluble
Sodium hypochlorite	as a pool chlorinator, in bleaching and in disinfectant mixtures	acts as an oxidant to kill bacteria and algae, bleaches coloured materials
Sodium nitrite	as a food preservative	stops the growth of bacteria
Titanium oxide	the ore from which titanium is extracted, white pigment in paint, used as sunscreen	pure white colour, good endurance, high opacity
Zinc oxide	as sunscreen, as a white pigment in paint, in photocopiers	insoluble in water, makes white opaque paste with water/oil, absorbs UV light, solid conducts electricity when exposed to light

## \* Review exercise 3.7

- 1 The following is a glaze recipe for pottery:

Bright green glaze	
Feldspar	39%
Strontium carbonate	33%
Clay	12%
Zinc oxide	9%
Whiting	7%
TOTAL	100%
add Cobalt carbonate	3%
OR a Rutile	2%
OR add Red iron oxide	2%

- 2 a Give the formulas of the ionic compounds listed in Table 3.6.  
b From Table 3.6, select a variety of uses of ionic compounds and explain these uses in terms of the bonding and structure of the compounds.



Figure 3.13 Dead trees encrusted with salt.



Figure 3.14 Cubic-shaped crystals of sodium chloride.

## 3.8 Sodium chloride

Sodium chloride, common salt, is an important ionic compound in human health, in the environment and as an industrial raw material. Adult humans need about 2 g of sodium (as  $\text{Na}^+$ ) per day to maintain appropriate levels of salt in their body fluids. This equates to about 5 g of sodium chloride per day. Most of this requirement is supplied naturally in food and drink, without the need for adding extra sodium chloride. In the body, sodium ions are essential for the passage of nerve impulses and they help control the movement of water in and out of cells, as well as many other functions. Sodium ions are excreted by the kidneys in urine and lost during perspiration. A deficiency in sodium chloride can lead to muscular cramps, lethargy, dizziness and reduced brain function. However, it has been estimated that the average Australian consumes over 10 g of sodium chloride per day. There are concerns about a possible link between high intakes of sodium chloride and high blood pressure. Many doctors now advocate limited amounts of sodium chloride in the diets of their patients. As a result, increasing numbers of 'salt-reduced' foods are now available.

Sodium chloride is added to food to act as a preservative and, for the misinformed reason, to improve 'flavour'. Before the invention of refrigeration, salt was added to meat to prevent the growth of bacteria and to increase its durability. Even today salted meats, such as salami, ham and bacon, are still part of the diets of many people.

Within the environment, increased salinity, due to the presence of sodium chloride, can make some rivers and streams unsuitable as a source of water for irrigation and drinking. In addition, increasing soil salinity reduces crop yields and the amount of useful land available for agriculture.

Sodium chloride is usually harvested from salt lakes or the sea. These sources depend on evaporation to concentrate the salt to sufficiently high levels for it to crystallise from solution. The photograph on the first page of this chapter shows salt that has been harvested from seawater lagoons at Dampier, Western Australia.

As well as its use in the food industry, sodium chloride is an important raw material used in the production of sodium, sodium hydroxide, hydrogen, chlorine and subsequently bleach, hydrochloric acid and poly(vinylchloride).

When viewed under the microscope, sodium chloride can be seen to be made up of cubic-shaped crystals, as shown in Figure 3.14. If these crystals are accidentally spilt on a hot element of a stove, or heated in a Bunsen burner flame, they do not melt because of the high melting point of sodium chloride. The crystals are also very hard. To break up sea-salt crystals to sprinkle over food, a grinder or a mortar and pestle are necessary rather than just crumbling the crystals with fingers. Also, when hit, for instance with a pestle, the sea-salt crystals shatter into small pieces rather than flatten like a malleable metal might. Solid sodium chloride does not conduct electricity, but once dissolved in water the solution is a good conductor of electricity. When monitoring heartbeats or brainwaves, a sodium chloride water-based gel is used to provide better electrical contact between the patient's skin and the electrode.

### \* Review exercise 3.8

- 1 The sodium (as  $\text{Na}^+$ ) content in some food is listed in Table 3.7.

TABLE 3.7 SODIUM CONTENT OF SOME FOODS

Food	Sodium content (g sodium/100 g food)	Food	Sodium content (g sodium/100 g food)
Beef	0.06	Milk	0.05
Chicken	0.08	Banana	0.001
Fish	0.08	Tomato	0.003
Lettuce	0.009	Tomato sauce	1.04
Carrot	0.04	Cheese, tasty	0.64
Ice-cream	0.087	Potato, boiled	0.006
Strawberries	0.001	Potato chips	1.00
Salad dressing	approx. 0.1	Butter/Margarine	0.90

- a Using these figures, determine the total sodium content of the following meal.  
grilled beef (120 g)    potato chips (100 g)    salad (100 g)    tomato sauce (30 g)  
ice-cream (60 g)    strawberries (70 g)

- b If a person consumed the meal described in part a, how much more sodium could they consume for the rest of the day and still remain below the required daily sodium level?

*continued*

### Review exercise 3.8 — *continued*

- 2 **RESEARCH** Since before written history, the need for salt (sodium chloride) in the diet has been recognised. Due to this need, salt has greatly influenced the political, economic and social history of the world.
- a Describe several ways in which ancient societies used sodium chloride.
  - b Salt deficiency is thought to have had tragic effects on Napoleon's army in their great retreat from Moscow. The diet of the defeated soldiers lacked salt because the army's precious supply had to be left behind. This contributed significantly to the heavy death toll of the exhausted soldiers.

Give another example of a way in which the need for salt had an effect on history.

## 3.9 Calcium carbonate

Calcium carbonate is a common ionic compound found in the Earth's crust. It is also the main component of eggshells of birds, coral reefs produced by cnidarians, and shells of molluscs such as snails, oysters and barnacles. Rocks and minerals composed of calcium carbonate include limestone, marble, chalk and calcite. Stalactite and stalagmite formations in caves are also composed of calcium carbonate.

Pearls produced by pearl oysters are composed of 82–92% calcium carbonate. If an irritant such as a parasite enters the oyster, the oyster reacts by slowly coating the irritant, layer by layer, with a pearly substance known as 'nacre'. This process gives rise to a natural pearl. Cultured pearls are created by the irritant, often a tiny part of a mussel shell together with some nacre-producing cells, being inserted into the oyster by a technician. The seeded oyster is then put back into the water and after approximately two years of intensive care by the pearl-farm workers, the pearl is removed from the oyster.

The main use of calcium carbonate is in the construction industry, either as a building material in its own right, for example, as limestone or marble, or as an ingredient of cement. Portland cement, the most commonly used type of cement, is produced by heating limestone with clay or sand and then grinding the product with gypsum (calcium sulfate). The resulting powdered cement crystallises to form a hard solid when mixed with water.



Figure 3.15 A pearl in an oyster shell.

A variety of other uses of calcium carbonate include:

- as an antacid to relieve indigestion. The calcium carbonate reacts with excess acid in the stomach to form carbon dioxide, water and a solution containing calcium ions.
- as a calcium supplement to assist in the prevention of, for example, osteoarthritis in elderly people
- in the paper industry, where it is used as an inexpensive filler to make paper bright, smooth and opaque
- in the manufacture of optical glass and soda glass. It is used to lower the melting point of the glass mixture, that is, it acts as a flux, and also to lower the water solubility of the glass
- as limestone in the blast furnace to extract iron from its ore. Its two main functions in the blast furnace are to form calcium oxide, which reacts with impurities to form slag, and to act as a porous packing agent for the furnace
- in the production of lime, CaO, which is used extensively in industry as a chemical reagent.



Figure 3.16 A marble quarry in Italy.



### \* Review exercise 3.9

- 1 **a** Summarise the properties of sodium chloride and calcium carbonate described in sections 3.8 and 3.9.  
**b** For the two substances, list the similarities and differences in their properties.

## MAJOR IDEAS

- Ionic compounds have characteristic physical properties as listed in Table 3.8.
- Ionic substances consist of positive ions and negative ions arranged in a regular lattice.
- Ionic bonding is the electrostatic attraction between oppositely charged ions.
- The ionic bonding model can be used to explain the properties of ionic crystals as shown in Table 3.8.

TABLE 3.8

Property	Explanation
high melting and boiling points, hardness	strong attractive forces between the positive and negative ions
brittleness	when a layer of ions moves, repulsion between ions of similar charge occurs and the crystal shatters
non-conductor of electricity in solid state	positive and negative ions are held by strong ionic bonds in a lattice
conductor in molten state and aqueous solution	positive and negative ions are no longer arranged in a rigid lattice, they are relatively free to move

- Positive ions are named after the element from which they were derived, for example,  $\text{Fe}^{2+}$  is the iron(II) ion.
- Negative ion names usually end in 'ide'; or, if oxygen is present, 'ite' or 'ate'.
- When writing the formula of an ionic compound the following must be remembered:
  - the formula of the positive ion is written before the formula of the negative ion. The charges of the ions are not shown in the formula.
  - the total positive charge must equal the total negative charge. In the formula, subscripts are used to indicate the relative numbers of ions required for neutrality.
  - when there are two or more units of a polyatomic ion in a formula the polyatomic ion formula is enclosed in brackets.
- When writing the name of an ionic compound, the name of the positive ion is given first, followed by the name of the negative ion.
- Ions can be formed by the transfer of electrons from atoms of a metal element to atoms of a non-metal element.
- Electron dot diagrams can be used to show the arrangement of valence electrons in atoms, ions and ionic compounds. Square brackets are usually drawn around the electron dot diagram of an ion.

## QUESTIONS

- 1 A certain solid is a non-conductor of electricity and has a melting point of  $470^\circ\text{C}$ . What further test or tests could be performed in order to decide whether or not the solid is an ionic compound?
- 2 Identify the charged species that conduct the electric current in the following substances:
  - a molten  $\text{NaI}$
  - b molten  $\text{Cu}$
  - c solid  $\text{Al}$
  - d molten  $\text{Mg}(\text{NO}_3)_2$
  - e an aqueous solution of  $\text{Al}(\text{NO}_3)_3$ .
- 3 Write the formulas of the following compounds and explain your reasoning:
  - a iron(III) selenide
  - b caesium phosphate
  - c chromium(III) hydrogensulfide
  - d silver chromite.
- 4 Sodium hydrogencarbonate is a white powder made up of tiny crystals. It is used as an 'environmentally friendly' cleaner in the kitchen and the bathroom. Explain why sodium hydrogencarbonate can be used as an abrasive to clean pots, surfaces and even teeth.
- 5
  - a If the formula of the selenate ion is  $\text{SeO}_4^{2-}$ , what is the formula of copper(II) hydrogenselenite?
  - b Given that the name of the ion  $\text{VO}_4^{3-}$  is vanadate, what is the name of  $(\text{NH}_4)_3\text{VO}_3$ ?
  - c If the formula of calcium azide is  $\text{Ca}(\text{N}_3)_2$ , what is the formula of aluminium azide?
- 6 Consider the following substances:  
 $\text{CO}_2$ ,  $\text{Zn}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{CH}_4$ , brass,  $\text{KF}$ ,  $\text{I}_2$ ,  $\text{Fe}$ . Identify the substances that are:
  - a ionic compounds
  - b metals.
- 7 When a piece of lead is struck with a hammer, a dent is left in the surface of the lead. However, when a piece of lead sulfide is struck with a hammer, it breaks into many little pieces. Explain this difference in behaviour in terms of the bonding and structure of the two substances.
- 8 For samples of molten magnesium chloride and solid magnesium answer the following questions.
  - a Predict which sample would be a better electrical conductor. Explain your reasoning.

- b** What particles in each sample conduct the electric current?
- c** Will any change take place in the samples while they are conducting electricity?
- 9** Neither solid sodium chloride nor liquid water are electrical conductors. However, when sodium chloride dissolves in water it forms a conducting solution. Explain.
- 10** The mineral magnesite is magnesium carbonate,  $MgCO_3$ . Magnesite is used to line furnaces, kilns and incinerators that operate at high temperatures.
- a** What properties must magnesite possess to be used in this way?
- b** Explain these properties in terms of the bonding and structure of magnesite.
- 11** Compare the number of positive ions with the number of negative ions in the ionic lattices composed of the following pairs of ions:
- a** potassium ions and iodide ions  
**b** calcium ions and chloride ions  
**c** aluminium ions and oxide ions.
- 12** A label on a bottle of mineral water claims that the following ions are dissolved in the drink:
- |                        |                |               |
|------------------------|----------------|---------------|
| calcium ions           | magnesium ions | sodium ions   |
| hydrogencarbonate ions | chloride ions  | sulfate ions  |
| potassium ions         | fluoride ions  | lithium ions. |
- Give the names and formulas of the ionic compounds that could possibly have been used by the manufacturers to produce this mineral water.
- 13** Explain why it is not possible to form an ionic compound between two atoms of the same element.
- 14** Using your knowledge of electron configurations, predict the charges of the ions in the following ionic compounds. Explain your reasoning.
- a** sodium selenide      **b** gallium chloride
- 15** Chemicals are often known by their common name rather than their chemical name. Give the chemical names of the following ionic compounds:
- a** potash,  $K_2CO_3$   
**b** rutile,  $TiO_2$   
**c** gypsum,  $CaSO_4 \cdot 2H_2O$   
**d** slaked lime,  $Ca(OH)_2$ .
- 16** **a** Give the formulas of the ions in the following compounds. Assume there is only one type of positive ion and one type of negative ion in each compound.
- i** uranyl sulfate,  $UO_2SO_4$   
**ii** thorium nitrate,  $Th(NO_3)_4$   
**iii** sodium tetrahydrogentellurate,  $Na_2H_4TeO_6$   
**iv** potassium pyrosulfate,  $K_2S_2O_7$   
**v** potassium ferrocyanide,  $K_4Fe(CN)_6$
- b** Some ionic compounds called double salts have two different positive ions in their crystal lattice. Give the formulas of the ions present in the following double salts:
- i** ammonium cobalt(II) sulfate-6-water,  $(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$   
**ii** chrome alum,  $KCr(SO_4)_2 \cdot 12H_2O$ .
- 17** Draw electron dot diagrams showing the valence electrons for the following:
- a** a calcium atom      **c** an oxygen atom  
**b** a calcium ion      **d** an oxide ion.
- 18** Element M has an electron configuration of 2, 8, 18, 8, 2 and element Z has an electron configuration of 2, 8, 18, 7.
- a** Draw the electron dot diagram of a compound formed between these two elements.  
**b** Predict the electrical conductivity properties of this compound. Explain your predictions in terms of the bonding and structure of the compound.
- 19** Draw electron dot diagrams for the following ionic compounds:
- a** magnesium sulfide      **c** strontium chloride  
**b** potassium oxide      **d** barium arsenide.
- 20** The general formulas of ionic compounds can be written using X as the symbol for the metal ion and Y as the symbol for the non-metal ion. For each of the general formulas given below, refer to a periodic table to identify two elements from different periods that will react to form an ionic compound with that formula:
- a**  $XY_2$       **b**  $X_2Y_3$
- 21** Equal numbers of formula units (the group of ions shown in the formula of the ionic compound) of three different ionic compounds were added to equal volumes of water. The mixtures were stirred until all of the solid dissolved. The three solutions formed were: copper(II) nitrate solution, sodium phosphate solution, zinc sulfate solution.
- a** The electrical conductivities of each of these solution was measured. Predict the order of conductivity of these solutions. Show the solutions in order of increasing conductivity.

- b** Explain this order in terms of the number of ions making up each substance.
- c** If a mixture of aluminium oxide and water was prepared in the same way as the three solutions referred to at the beginning of the question, would you expect the mixture to conduct electricity? Explain your answer.
- 22** A student made the following predictions about the properties of tin(IV) iodide, an orange crystalline solid:
- Tin(IV) iodide will not conduct electricity in the solid state, but molten tin(IV) iodide will be a good conductor of electricity.
  - Tin(IV) iodide will be a hard, brittle solid.
- a**
- i Describe an experiment that could be carried out to test each of these predictions. Include a sketch of the equipment that could be used.
  - ii What should be done before beginning any experiments involving an unfamiliar substance?
- b** The student's predictions were tested and it was found that the tin(IV) iodide did not conduct electricity in either the solid or molten states, and a gentle tap with a hammer caused the crystals to shatter.  
From these observations could it be concluded that tin(IV) iodide is an ionic compound? Explain your answer in terms of the structure and bonding of an ionic compound.
- 23** Use the ionic bonding model to explain the following observations.
- a** A marble bench top remained unmarked when a hot saucepan was accidentally placed on it.
- b** Crystals of rock salt cannot be crushed between the fingers, but they can be ground to a powder using a mortar and pestle.
- c** Soapy water is a better conductor of electricity than pure water.
- 24** Sometimes a compound called 'Fool's gold' tricks inexperienced miners into believing they have found real gold. 'Fool's gold' is a compound with a formula of FeS.
- a** Suggest some procedures a chemist could use, without chemically changing the specimen, to decide whether or not the collected specimen is gold or 'Fool's gold'.
- b** In terms of the bonding and structure of gold and the 'Fool's gold', explain why these procedures should be successful in distinguishing between the two substances.
- 25** **a** Compare the way in which an artist might sculpt a shape from marble to the way in which an ornament might be formed from copper.
- b** In terms of their bonding and structure, explain any differences in the way in which the two different materials would be shaped.
- 26** **▷ RESEARCH** Ionic compounds are commonly used as food additives. Food additives are substances added to food in small amounts to prevent food deterioration or to enhance the texture, flavour or appearance of the food. These food additives are shown as E numbers on the food's label.
- Table 3.9 shows some food additives that are ionic compounds.

TABLE 3.9

Code number	Name of food additive	Code number	Name of food additive
559	aluminium silicate	250	sodium nitrite
264	ammonium acetate	329	magnesium lactate
510	ammonium chloride	337	potassium sodium tartrate
952	calcium cyclamate	341	calcium phosphate
302	calcium ascorbate	402	potassium alginate
213	calcium benzoate	509	calcium chloride
171	titanium oxide	512	stannous chloride
223	sodium bisulfite	621	monosodium glutamate

Choose a selection of these additives, and for each:

- a** give the reason for the additive being added to the food
- b** give an example of the type of food it would be added to
- c** describe any health risks associated with the additive
- d** decide whether or not you think this additive should be added to the food. Justify your decision.

- 27** ☐ RESEARCH The following ionic compounds are used in soaps, detergents and shampoos:

ammonium laural sulfate	calcium stearate
sodium perborate	selenium sulfide.
sodium xylene sulfonate	

For each compound:

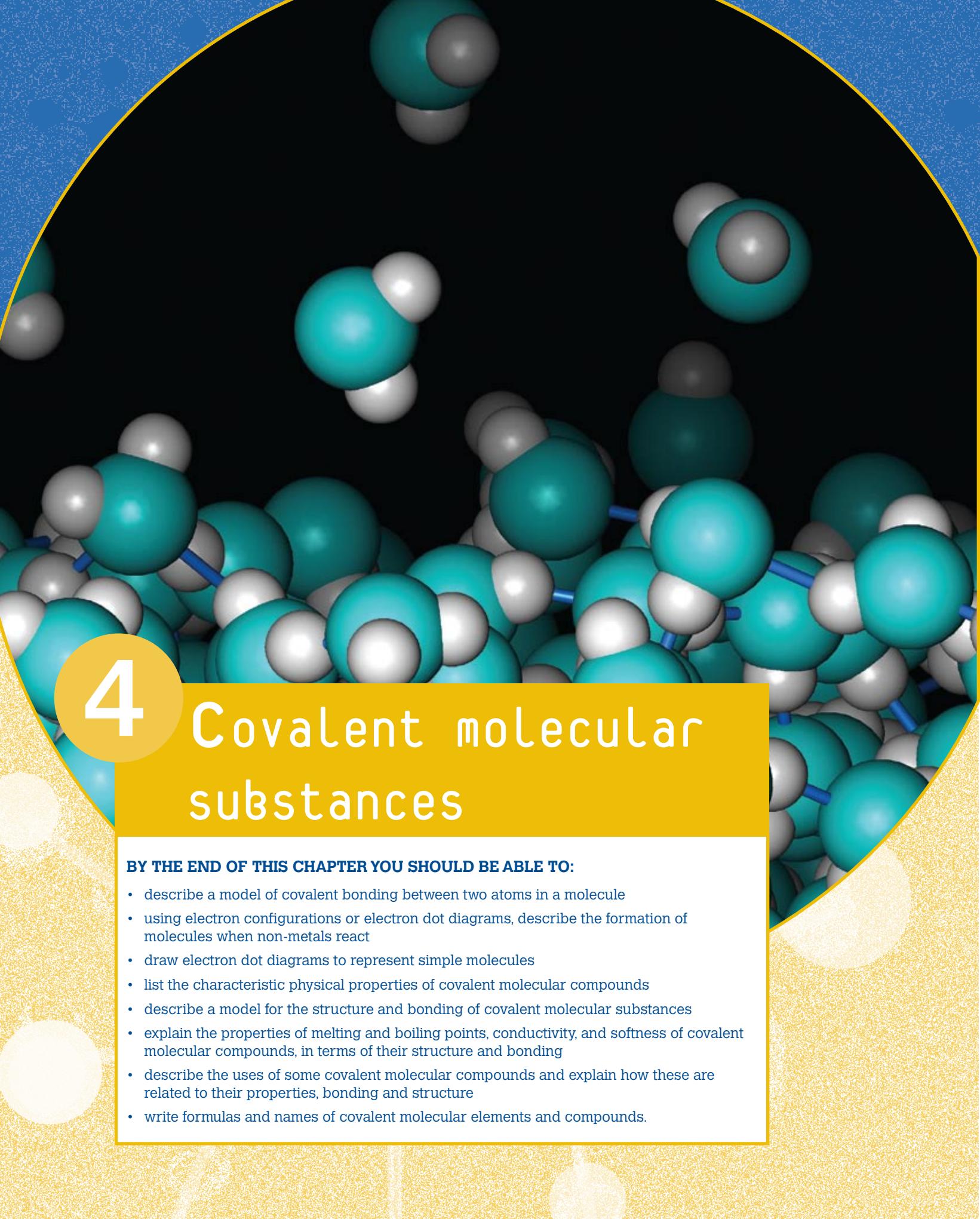
- a give its formula
- b describe what kinds of cleaning products it is used in
- c explain its function in the cleaning product
- d list any health problems that may arise from its use
- e describe any environmental damage that may occur because of its use.

- 28** ☐ RESEARCH The following is a label on the side of a box of Aquasol, the 'fast acting soluble fertiliser with trace elements' for use on plants.

**GUARANTEED ANALYSIS**

Nitrogen (N) as mono-ammonium phosphate	1.8%
Nitrogen (N) as potassium nitrate	2.6%
Nitrogen (N) as urea	18.6%
<b>Total Nitrogen (N)</b>	<b><u>23.0%</u></b>
<b>Total Phosphorus (P)</b> —water soluble as mono-ammonium phosphate	<b><u>4.0%</u></b>
Potassium (K) as potassium nitrate	7.8%
Potassium (K) as potassium chloride	10.2%
<b>Total Potassium (K)</b>	<b><u>18.0%</u></b>
Zinc (Zn) as sulfate	0.05%
Copper (Cu) as sulfate	0.06%
Molybdenum (Mo) as sodium molybdate	0.0013%
Manganese (Mn) as sulfate	0.15%
Iron (Fe) as sodium ferric EDTA	0.06%
Boron (B) as sodium borate	0.011%

- a Give the formulas of the ionic compounds in this fertiliser.
- b Why are fertilisers added to plants?
- c Why is it important that the ionic compounds in this fertiliser are soluble in water?
- d Why are three elements, nitrogen, phosphorus and potassium, present in much larger amounts in this fertiliser than the other elements?
- e i Describe the damage to the environment that can be caused by fertilisers.  
ii How can this damage be prevented?



# 4

# Covalent molecular substances

## BY THE END OF THIS CHAPTER YOU SHOULD BE ABLE TO:

- describe a model of covalent bonding between two atoms in a molecule
- using electron configurations or electron dot diagrams, describe the formation of molecules when non-metals react
- draw electron dot diagrams to represent simple molecules
- list the characteristic physical properties of covalent molecular compounds
- describe a model for the structure and bonding of covalent molecular substances
- explain the properties of melting and boiling points, conductivity, and softness of covalent molecular compounds, in terms of their structure and bonding
- describe the uses of some covalent molecular compounds and explain how these are related to their properties, bonding and structure
- write formulas and names of covalent molecular elements and compounds.

## 4.1 Covalent bonding

The formation of an ionic compound, from the reaction of a metal with a non-metal, was discussed in Chapter 3. In this process, the metal atoms give up their valence electrons to form positive ions and the non-metal atoms gain these electrons to become negative ions. A transfer of electrons occurs between the metal and non-metal atoms to form ions with 8 electrons in their outermost shell.

In a reaction between non-metals, it is not energetically favourable for any of the atoms to lose electrons. Nonetheless, the non-metal atoms do react, but rather than forming ions, they often form molecules. A **molecule** is a small group of atoms strongly bonded together. Water, carbon dioxide, methane, chlorine, sulfur and ethanol are examples of substances composed of molecules.

### Covalent bond model

In 1916, the American chemist Gilbert N. Lewis suggested that the atoms in a molecule share electrons. These atoms, he proposed, are held or bonded together by electrostatic attractions between the shared electrons and their positive nuclei. This form of bonding between atoms in a molecule is called **covalent bonding**.

A covalent bond can form when two hydrogen atoms interact. Each hydrogen atom with only 1 electron in its first shell would be more stable with 2 electrons, giving each of them the same electron configuration as the noble gas helium. A transfer of an electron from one atom to another does not occur; instead, each hydrogen atom shares its single valence electron with the other. These 2 shared electrons move about both nuclei so that each atom has a share of 2 electrons. In effect, each hydrogen atom has the stable electron configuration of a helium atom.

Figure 4.2 shows the formation of a hydrogen molecule from two hydrogen atoms. In the hydrogen molecule, the shared pair of electrons would be in the region between the two nuclei most of the time, that is, there is a greater probability of finding the bonding electrons in this region. The density of the electron cloud is therefore greater between the two nuclei in the molecule. The two positively charged nuclei are held together by their mutual attraction to the two shared electrons, or in other words, they are held together by a **covalent bond**.



Figure 4.1 Chocolate, marshmallows and nuts are all mixtures of substances composed of molecules.



The electron cloud, composed of 2 electrons, is more dense between nuclei. The shared electrons spend more time in this region than in other areas of the molecule.

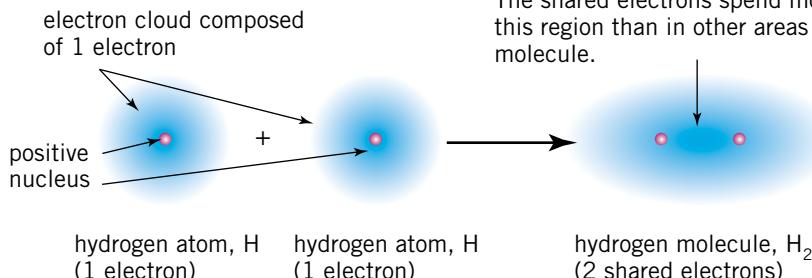
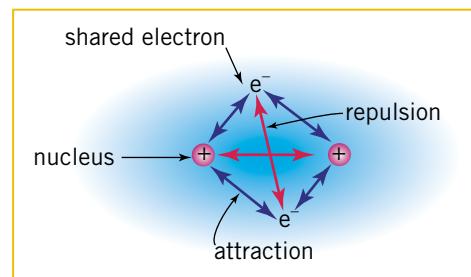


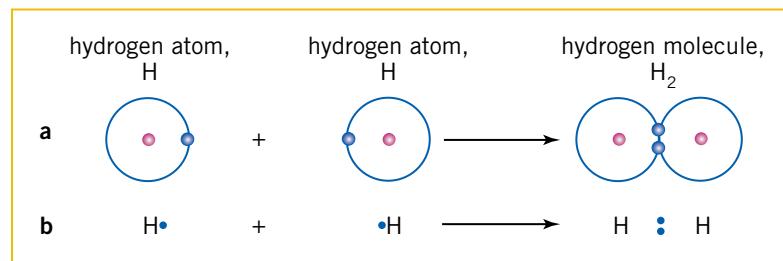
Figure 4.2 The formation of a hydrogen molecule from two hydrogen atoms, using the electron cloud model. In the molecule, the two positively charged nuclei are held together by the electrostatic attractions between them and the shared electrons.

Because the hydrogen molecule is stable, the electrostatic attractive forces between the two positive nuclei and the shared electrons must balance the repulsive forces between the nuclei and between the electrons, as shown in Figure 4.3.



**Figure 4.3** The attractive forces between the nuclei and shared electrons balance the repulsive forces between the nuclei and between the electrons in the stable hydrogen molecule.

Covalent bond formation in a hydrogen molecule can also be illustrated using the Bohr-model representation of atoms (see Figure 4.4a) and electron dot diagrams (see Figure 4.4b).

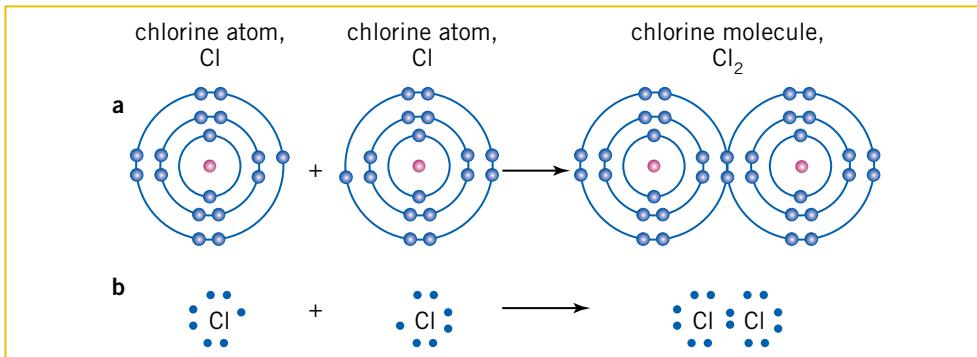


**Figure 4.4** The formation of a hydrogen molecule using: **a** the Bohr model; **b** electron dot diagrams.

A covalent bond in which 2 electrons are shared is called a **single covalent bond** and it can be represented by a line drawn between the atoms. Hence a hydrogen molecule can be represented as H–H.

### The chlorine molecule

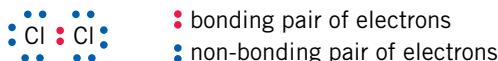
When two chlorine atoms, with electron configurations of 2, 8, 7, combine to form a chlorine molecule, the chlorine atoms share a pair of electrons. In this way, each chlorine atom obtains a share in 8 valence electrons and acquires the electron configuration of the noble gas argon. As with ionic compounds, the octet rule is ‘obeyed’ in many covalent molecular substances. The formation of a chlorine molecule,  $Cl_2$ , is shown in Figure 4.5 using the Bohr model (a) and electron dot diagrams (b).



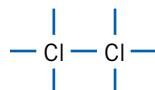
**Figure 4.5** The formation of a chlorine molecule using: **a** the Bohr model; **b** electron dot diagrams.

The two chlorine atoms in the molecule are held together by the attractive forces between their nuclei and the pair of shared electrons. That is, there is a single covalent bond between the atoms in the  $\text{Cl}_2$  molecule.

In the chlorine molecule, 2 electrons are shared, but the other valence electrons are not involved in the bonding. The electron pairs forming covalent bonds in molecules are called **bonding electron pairs**. The remaining valence electron pairs, if any, are called **non-bonding electron pairs or lone pairs**. The one bonding pair and six non-bonding pairs of valence electrons in a chlorine molecule are shown below.



The chlorine molecule can also be shown using a line to represent each pair of valence electrons around each atom:



Chemists sometimes find it convenient to build or present molecules using two further models: the ball-and-stick model and the space-filling model. In both of these models, the non-bonding electrons are not shown.



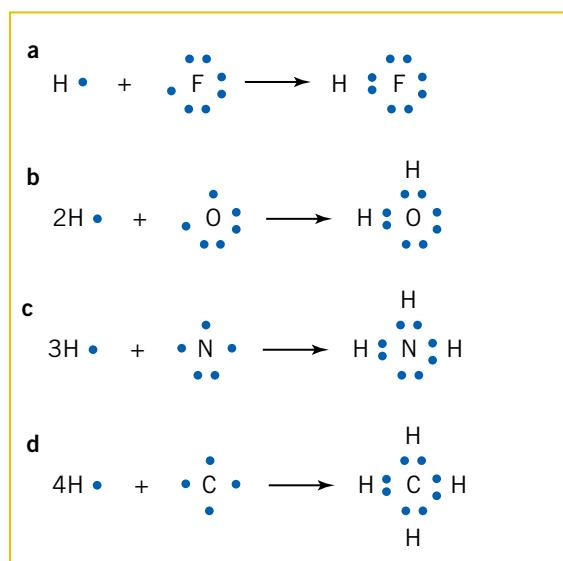
### Covalent bonds and valence electrons

The number of covalent bonds formed by an atom of an element depends on the number of electrons in its valence or outer shell. The electron dot diagrams for the non-metallic elements in the second period of the periodic table are shown below.



Neon atoms have the electron configuration 2, 8. Both electron shells of neon are fully occupied and so no covalent bond formation is possible between neon atoms. This explains why neon exists as a monatomic gas.

Fluorine, with an electron configuration of 2, 7, requires 1 more electron to achieve 8 electrons in its outermost shell. Consequently, it will form one single covalent bond in molecules and so have a share in 8 valence electrons. For example, when it combines with a hydrogen atom, it forms HF not H<sub>2</sub>F as shown in Figure 4.6a.



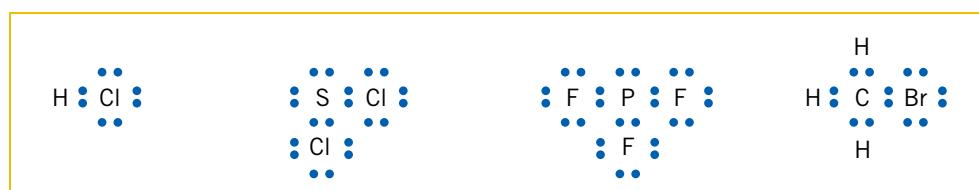
**Figure 4.6** Using electron dot diagrams to show the formation of molecules: a formation of hydrogen fluoride, HF; b formation of water, H<sub>2</sub>O; c formation of ammonia, NH<sub>3</sub>; d formation of methane, CH<sub>4</sub>.

Oxygen, with 6 valence electrons, requires 2 more electrons to achieve a complete octet. Oxygen will therefore tend to form two covalent bonds when it forms molecules. For example, when oxygen combines with hydrogen, water, H<sub>2</sub>O, can form, as shown in Figure 4.6b.

Similarly, nitrogen and carbon will tend to form three and four covalent bonds respectively as shown when they combine with hydrogen, to form ammonia, NH<sub>3</sub>, and methane, CH<sub>4</sub> (Figures 4.6c and 4.6d).

Elements in the same group in the periodic table have the same valence electron configuration. Consequently, they will tend to form the same number of covalent bonds. For example, the group 17 elements tend to form one covalent bond in their molecules and the group 16 elements tend to form two covalent bonds. Carbon and silicon, in group 14, form four covalent bonds.

Figure 4.7 shows more examples of electron dot diagrams for some simple molecules. Notice that in the simple molecules each atom has a share in 8 valence electrons, or for hydrogen, 2 valence electrons. Therefore each atom has a stable valence electron configuration.



**Figure 4.7** Electron dot diagrams of HCl, SCl<sub>2</sub>, PF<sub>3</sub> and CH<sub>3</sub>Br.

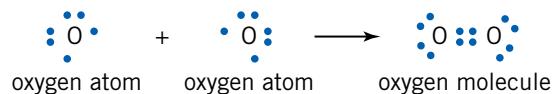
## \* Review exercise 4.1

- 1 In many substances, the atoms are bonded together in the form of discrete (independent) particles called molecules.
  - a Describe the forces that are responsible for holding the atoms together in a simple molecule such as  $\text{F}_2$ .
  - b How many valence electrons does an atom usually attain when it combines with other atoms?
  - c What evidence exists to show that this number of valence electrons is generally stable?
  - d Draw an electron dot diagram of  $\text{F}_2$ .
  - e Identify the bonding and non-bonding electron pairs in  $\text{F}_2$ .
  - f Where are the bonding electrons in  $\text{F}_2$  localised most of the time?
- 2 Molecules with the formula of  $\text{NH}_3$  are formed when hydrogen atoms join up with nitrogen atoms. In these molecules there is a covalent bond between each hydrogen atom and the nitrogen atom.
  - a What is a covalent bond?
  - b Draw a line structure of a  $\text{NH}_3$  molecule showing the bonding and non-bonding pairs of electrons.
  - c Explain why nitrogen and hydrogen form molecules with the formula of  $\text{NH}_3$  rather than molecules with the formula of  $\text{NH}_2$  or  $\text{NH}$ .
- 3 Chloroform,  $\text{CHCl}_3$ , was used as an anaesthetic in the early twentieth century, but when its toxicity was discovered it was replaced by ether.
  - a Draw the electron dot diagram for a  $\text{CHCl}_3$  molecule.
  - b How many electrons are there in the valence shell of each carbon, hydrogen and chlorine atom in the  $\text{CHCl}_3$  molecule? Which noble gas electron configuration does each atom resemble?
- 4 Draw electron dot diagrams for the following substances:

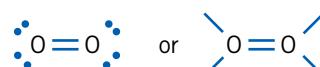
a $\text{SiCl}_4$	d $\text{SF}_2$
b $\text{Cl}_2\text{O}$	e $\text{CH}_3\text{CH}_2\text{CH}_3$
c $\text{NF}_3$	
- 5 In the molecules  $\text{Cl}_2\text{O}$ ,  $\text{NF}_3$  and  $\text{SiCl}_4$  in question 4, identify the bonding and non-bonding electron pairs.
- 6 Write formulas, using a straight line between atoms to represent a covalent bond, for the substances  $\text{SF}_2$  and  $\text{CH}_3\text{CH}_2\text{CH}_3$  in question 4.
- 7 Mobile charged particles, either electrons or ions, need to be present for conduction of electricity. Solid iodine is made up of molecules with the formula of  $\text{I}_2$ . Would you expect solid iodine to be able to conduct electricity? Explain your reasoning.

## 4.2 Multiple covalent bonds

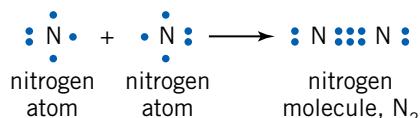
Oxygen atoms have an electron configuration 2, 6, which means they are 2 electrons short of a valence electron octet. In forming the molecule  $O_2$ , each oxygen atom accepts a share of 2 electrons belonging to the other oxygen atom. Hence, 4 electrons are shared by the two oxygen atoms.



A covalent bond comprising two shared pairs of electrons is called a **double covalent bond** and can be represented by two lines joining the atoms. An oxygen molecule may be shown as:



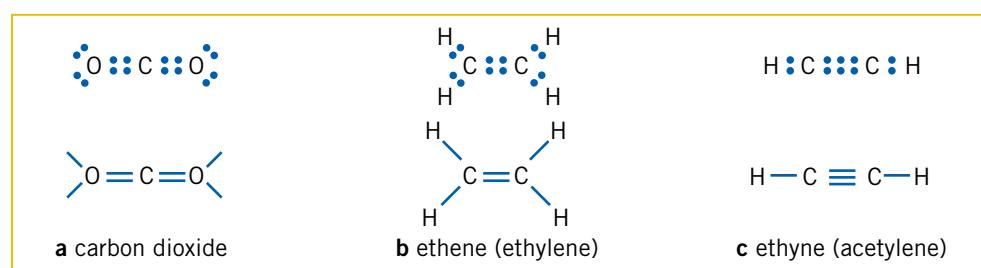
Nitrogen atoms that have the electron configuration 2, 5 are 3 electrons short of a valence electron octet. By sharing three pairs of electrons between two nitrogen atoms, a nitrogen molecule,  $N_2$ , is formed.



A bond in which three pairs of electrons are shared is called a **triple covalent bond** and is represented by three parallel lines joining the atoms. A nitrogen molecule may therefore be drawn as:



Figure 4.8 shows some other molecules containing multiple covalent bonds.



**Figure 4.8** Electron dot diagrams and line structures of simple molecules involving multiple covalent bonds.

## \* Review exercise 4.2

- 1 **a** How many electrons are shared in the formation of each of the following?
  - i** a single covalent bond
  - ii** a double covalent bond
  - iii** a triple covalent bond
- b** Give the name and formula of a substance in the air whose atoms are bonded together in molecules by:
  - i** single covalent bonds
  - ii** double covalent bonds
  - iii** triple covalent bonds.
- 2 **a** Using the electron dot notation, show the valence electron configurations for the uncombined atoms and the diatomic molecules of fluorine, oxygen and nitrogen.  
**b** Show that the atoms in the molecules conform to the octet rule.
- 3 Cigarette smoke contains over 4000 chemical compounds, many of which are toxic and some are known carcinogens. Most of these compounds are covalent molecular substances. Table 4.1 lists some of the compounds composed of smaller molecules contained in the ‘mainstream’ smoke from a Benson & Hedges 100’s deluxe ultra-light cigarette.

TABLE 4.1

Name	Formula	Name	Formula
Formaldehyde	HCHO	Carbon monoxide	CO
Acetaldehyde	CH <sub>3</sub> CHO	Hydrogen cyanide	HCN
Acetone	CH <sub>3</sub> COCH <sub>3</sub>	Buta-1,3-diene	CH <sub>2</sub> CHCHCH <sub>2</sub>

For each of these compounds draw the:

- a** electron dot diagram      **b** line structure diagram.

- 4 The distance between the two nuclei of the atoms in a diatomic molecule is called the bond length.
  - a** The bond length in a fluorine molecule, F<sub>2</sub>, is 143 pm but the bond length in an oxygen molecule, O<sub>2</sub>, is 121 pm (pm = picometres = 10<sup>-12</sup> m). Explain this observation.
  - b** Would you expect the bond length in a nitrogen molecule, N<sub>2</sub>, to be larger or smaller than 121 pm?
- 5 In a fluorine molecule there is a single bond between the two atoms. In an oxygen molecule there is a double bond and in a nitrogen molecule there is a triple bond. Suggest a reason for why carbon does not form a diatomic molecule of C<sub>2</sub>, with a ‘quadruple’ bond between the two atoms.
- 6 The four most abundant gases in the air are given in Table 4.2.

TABLE 4.2

Name	Formula	Percentage by volume
Nitrogen	N <sub>2</sub>	78.08
Oxygen	O <sub>2</sub>	20.95
Argon	Ar	0.93
Carbon dioxide	CO <sub>2</sub>	0.03

Why does the formula of argon show only one atom when all of the other formulas show two or more atoms?

## 4.3 Covalent molecular substances



Figure 4.9 Commonly used items that contain covalent molecular substances.

Over 90% of the 10 million or so compounds and elements that have been identified to date can be classified as covalent molecular substances. That is, substances made up of atoms covalently bonded together in molecules. Many of these substances are found in living things and in products derived from remains of living things. These include proteins, carbohydrates, fats and compounds made from the substances in coal, crude oil and natural gas. Some commonly used covalent molecular substances are described in Table 4.3.

Many substances used domestically are mixtures of covalent molecular compounds. These include wood, paper, wool, cotton, most plastics, oils, butter, starch, meat, fruit, vegetables, chocolate, kerosene, candle wax and turpentine. Covalent molecular substances include both non-metallic elements, such as nitrogen,  $N_2$ , and ozone,  $O_3$ , and compounds formed from non-metals, such as water,  $H_2O$ , and carbon dioxide,  $CO_2$ .

### Properties of covalent molecular substances

Substances made up of molecules have the following properties in common:

- They have low melting and boiling points; many are liquids or gases at room temperature.
- They are non-conductors of electricity in both the solid and liquid states. The aqueous solutions of some compounds are weak conductors of electricity. A few compounds in aqueous solution are good conductors of electricity.
- They form solids that are generally quite soft, are easily scratched and often have a waxy appearance.
- Many solids are malleable when bent and do not shatter when hit.
- Many are insoluble in water, but are soluble in non-polar solvents such as petrol and kerosene.
- Many have an odour.

**TABLE 4.3 EXAMPLES OF COMMONLY USED COVALENT MOLECULAR SUBSTANCES**

Name	Formula	Description	M. pt (°C)	B. pt (°C)	Use
Acetylsalicylic acid (aspirin)	C <sub>9</sub> H <sub>8</sub> O <sub>4</sub>	white crystals	136	140 d	relieving pain
Ammonia	NH <sub>3</sub>	colourless gas, pungent odour	-78	-33	in solution form as a floor cleaner
Carbon dioxide	CO <sub>2</sub>	colourless, odourless gas	-57*	-78 s	provides the fizz in carbonated drinks, reactant in photosynthesis
Citric acid	C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	white crystals	153	175 d	food flavouring
Ethanol (methylated spirits)	CH <sub>3</sub> CH <sub>2</sub> OH	colourless liquid	-114	78	solvent, antiseptic, in alcoholic drinks
Ethyne (acetylene)	C <sub>2</sub> H <sub>2</sub>	colourless gas	-81*	-84 s	welding
Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	white crystals	146 d	-	food sweetener
Hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	colourless liquid	-0.4	150	bleach
Iodine	I <sub>2</sub>	black-purple solid	114	184	in solution form as an antiseptic (e.g. Betadine)
Methane (natural gas)	CH <sub>4</sub>	colourless gas	-183	-162	a fuel to heat food and homes
Nitrogen	N <sub>2</sub>	colourless, odourless gas	-210	-196	makes up 80% of the atmosphere, used in the manufacture of fertilisers
Oxygen	O <sub>2</sub>	colourless, odourless gas	-219	-183	necessary for respiration and combustion
Polythene	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>n</sub> CH <sub>3</sub> (where n is a large number)	colourless, flexible solid	approx. 130	-	plastic bags, bottles, pipes
Sucrose (sugar)	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	white crystals	192	-	food sweetener
Water	H <sub>2</sub> O	colourless liquid	0	100	drinking, solvent, cleaning

s sublimation point

d decomposes when heated strongly

\* under pressure

## \* Review exercise 4.3

- 1 Complete the gaps in Table 4.4 by predicting for each substance whether it has a high or low melting point and its electrical conductivity properties.

TABLE 4.4

Substance	Formula	Melting point (high or low?)	Electrical conductivity	
			Solid	Molten
Copper bromide	$\text{CuBr}_2$			
Copper	Cu			
Bromine	$\text{Br}_2$			
Carbon tetrabromide	$\text{CBr}_4$			
Helium	He			

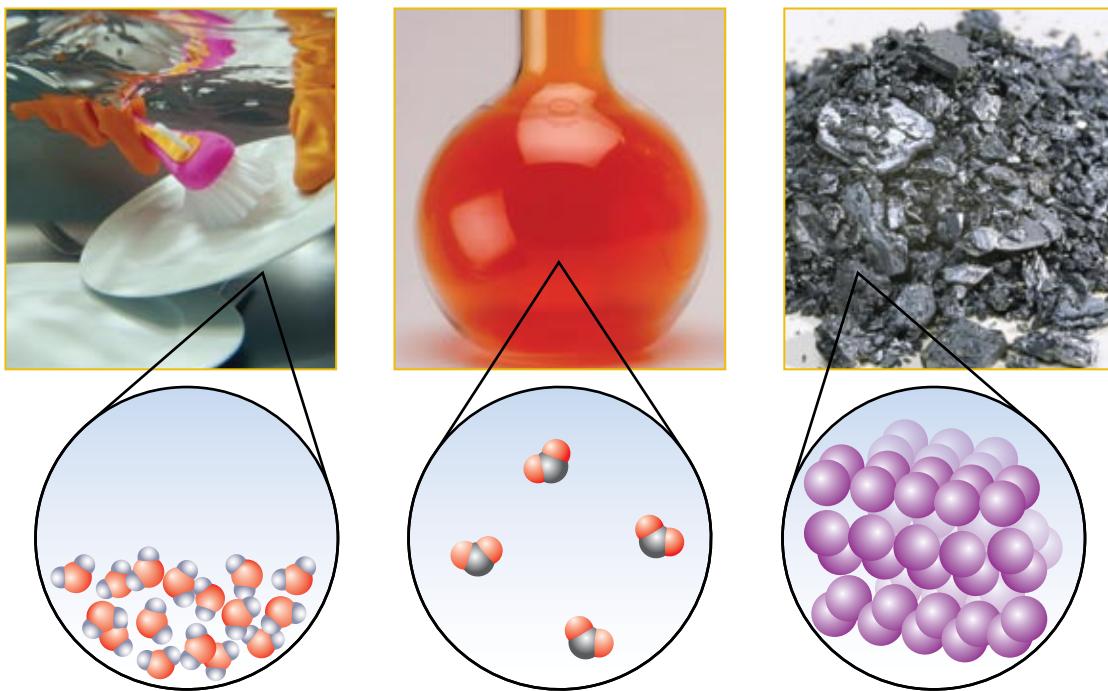
- 2 What physical properties of the following covalent molecular substances make them suitable for the specified use?
- a Plasticine is used by young children to make different shapes.
  - b Wax is used to seal the tops of jars of home-made jams.
  - c Ethanol is used as the solvent in some perfumes.
  - d Poly(ethene) is used to make squeezable toothpaste tubes.
  - e Kerosene can be used to clean the grease from car engines.
  - f The outer casing of a hair-dryer is made of plastic and not of metal.
  - g Vanilla essence is put into cake mixtures.
- 3 Three unlabelled substances are known to be magnesium chloride, magnesium and sugar. Describe how the three solids could be identified by safe experiments.

## 4.4 Explanation of properties

### Composition and structure of covalent molecular substances

Experimental evidence indicates that covalent molecular substances consist of neutral molecules. As defined earlier, a molecule is a group of two or more atoms held together by covalent bonds. Representations of molecules making up three covalent molecular substances are shown in Figure 4.10.

For a covalent molecular substance in the solid state, the neutral molecules are organised in an orderly lattice structure. In the liquid and gas states, the molecules are arranged randomly. In the gas state, however, the molecules are much further apart from each other than in the liquid state.



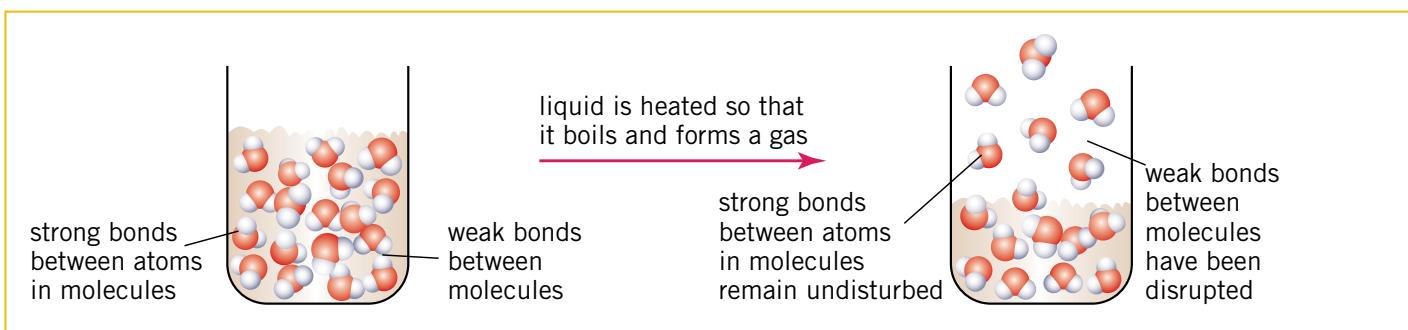
**Figure 4.10** Water ( $\text{H}_2\text{O}$ ), nitrogen dioxide ( $\text{NO}_2$ ) and iodine ( $\text{I}_2$ ) are three examples of covalent molecular substances. As the magnified views show, they are composed of molecules.

### Melting and boiling points

Generally, the attractive forces between the molecules of covalent molecular substances are weak, as indicated by the low melting points of these substances. For example, ice has the low melting point of  $0^\circ\text{C}$  because the attractive forces between the water molecules, the intermolecular forces, are relatively weak. However, a large amount of energy is required to break up water molecules into individual hydrogen and oxygen atoms. For the process  $\text{H}_2\text{O(g)} \rightarrow 2\text{H(g)} + \text{O(g)}$  to occur to a significant extent, a temperature of over  $2000^\circ\text{C}$  is required. This indicates that the covalent bonds between the hydrogen and oxygen atoms within water molecules must be strong. The nature of the weak intermolecular forces between molecules, often called van der Waals forces, will be discussed in Unit 3A.

As with melting, when a covalent molecular substance is boiled, it is the weak intermolecular forces between the molecules that are disrupted, not the covalent bonds between the atoms in the molecules. A molecular view of the boiling of water is illustrated in Figure 4.11.

**Figure 4.11** When water boils, only the weak bonds between the molecules are broken. The strong covalent bonds between the atoms in the molecules remain undisturbed.



The bonds between the neutral molecules of many covalent molecular substances are so weak that the substances exist as gases or volatile liquids at room temperature. In other words, their melting and possibly boiling points are less than room temperature. This is particularly true for substances composed of small molecules, such as methane,  $\text{CH}_4$ , oxygen,  $\text{O}_2$ , and ethanol,  $\text{C}_2\text{H}_5\text{OH}$ . Covalent molecular substances composed of larger molecules tend to have stronger forces between their molecules and so are often solids at room temperature, for example, iodine,  $\text{I}_2$ , sulfur,  $\text{S}_8$ , and sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ . However, in all covalent molecular compounds, the intermolecular bonding, that is, the bonding between the molecules, is much weaker than the covalent bonding between the atoms within the molecules.

### Softness

Covalent molecular solids such as wax, chocolate and butter are soft and can be cut easily. As with the low melting and boiling points, this property can also be explained in terms of the weak attractive forces between the molecules. Very little force is required to push the neutral molecules in the solid lattice past one another. Even with ice, which is possibly one of the harder molecular substances, it can be crushed fairly easily, compared with, for example, the ionic substance marble and the metal steel.

### Malleability

Many covalent molecular substances, particularly those made up of larger molecules such as petroleum jelly and some of the plastic materials, can be bent or pushed into another shape without the solid shattering. When a force is exerted on a molecular substance, the molecules can be pushed past one another easily because of the weak forces between them. But once the molecules reach their new positions, weak forces still exist between them and they remain held together in the new shape.

### Non-conductor of electricity

For a substance to conduct electricity, mobile charged particles capable of conducting electricity must be present. These charged particles include electrons and positive and negative ions. In covalent molecular substances, there are no ions because the molecules are neutral. Also, in the molecules the valence electrons are localised between or around atoms, as either shared or unshared pairs, and so are not free to move throughout the solid lattice or the liquid. As a result, covalent molecular substances are non-conductors of electricity in the solid and liquid states.

When dissolved in water some covalent molecular substances conduct electricity. These substances form or break up into ions (ionise) when added to water. The mobile ions in the aqueous solutions are then able to act as the charge carriers of the electric current.

A small number of the soluble covalent molecular substances, such as hydrogen chloride,  $\text{HCl}$ , nitric acid,  $\text{HNO}_3$ , and sulfuric acid,  $\text{H}_2\text{SO}_4$ , ionise completely in water to form solutions which are good conductors of electricity. Many of the other soluble substances only partially ionise, which means only a few of the dissolved molecules break up into ions. Solutions of these substances, for example, ammonia,  $\text{NH}_3$ , and acetic acid,  $\text{CH}_3\text{COOH}$ , are poor conductors of electricity. Some covalent molecular substances, when dissolved in water, remain as the neutral molecules. For example, when ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , or

glucose,  $C_6H_{12}O_6$ , dissolve in water, the solution formed only contains neutral molecules and therefore will not conduct electricity. More detail concerning the electrical conductivity of solutions of covalent molecular substances is in Chapter 8.

## Solubility

The solubility properties of covalent molecular compounds vary considerably. Some are very soluble in water, others slightly soluble, but many are insoluble. For example, ethanol and sugar are soluble in water but butter, chocolate and olive oil are insoluble in water. Numerous covalent molecular substances are soluble in non-polar solvents such as oil and kerosene. For example, cooking oil and petrol are soluble in kerosene. The solubilities of covalent molecular substances will be discussed in more detail in Chapter 8.



Figure 4.12 Environmental problems caused by oil being insoluble in water.

## \* Review exercise 4.4

- 1 ‘In covalent molecular substances the intramolecular forces are strong but the intermolecular forces are weak?’ Explain what is meant by this statement, illustrating your answer with chlorine ( $\text{Cl}_2$ ), which has a melting point of  $-101^\circ\text{C}$  but does not break up into separate atoms except at very high temperatures.
- 2 It has been found that most substances that have an odour are covalent molecular substances. Suggest a reason for this observation.
- 3 Explain the following observations in terms of the bonding and structure of the substances.
  - a Margarine can be spread on a piece of bread but a lump of copper cannot.
  - b When iodine crystals,  $\text{I}_2$ , are gently heated a purple vapour is produced.
  - c Plastics, such as high-density polythene, which can be regarded as covalent molecular compounds, are often used as coatings wrapped around electrical wires.
  - d Cooking oil is a liquid at room temperature but salt (sodium chloride) is a solid.
- 4 The boiling points of some covalent molecular liquids are given in Table 4.5. Use this information to answer the questions below.

TABLE 4.5

Name	Formula	Boiling point ( $^\circ\text{C}$ )
Propanol	$\text{C}_3\text{H}_7\text{OH}$	97
Diethyl ether	$(\text{CH}_3\text{CH}_2)_2\text{O}$	35
Hexane	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	69

- a Predict which substance has the strongest intermolecular forces. Justify your answer.
- b Can any comment be made about the relative strengths of the covalent bonds in the molecules of these three substances? Explain your answer.
- c Which of the three substances would be the most volatile?
- 5 The gas phosphine, composed of phosphorus and hydrogen atoms, is used as a fumigant to protect stored grain from pests. It is generated in situ by adding water to solid aluminium phosphide or solid magnesium phosphide.
  - a Predict the formula of phosphine, and draw its electron dot diagram.
  - b Give the formula of aluminium phosphide and draw its electron dot diagram.
  - c Explain why phosphine is a gas at room temperature but the two phosphides are solids.

## 4.5 Names and formulas of covalent molecular substances

### Covalent molecular elements

In covalent molecular elements the molecules consist of two or more atoms of the same type covalently bonded together. Nearly all non-metallic elements are covalent molecular substances. Most of these are composed of diatomic molecules, such as hydrogen,  $\text{H}_2$ , and a few are composed of polyatomic molecules, as shown in Table 4.6. The noble gas elements (group 18 elements) are also usually classified as covalent molecular elements although they exist as monatomic gases. They have very weak forces between their individual atoms and so have the same general physical properties as substances made up of molecules.

**TABLE 4.6 THE NAMES, MOLECULAR FORMULAS AND STATES AT 25°C OF SOME COVALENT MOLECULAR ELEMENTS**

Name	Formula	State at 25°C	Name	Formula	State at 25°C
Argon	Ar	gas	Krypton	Kr	gas
Bromine	Br <sub>2</sub>	liquid	Neon	Ne	gas
Chlorine	Cl <sub>2</sub>	gas	Nitrogen	N <sub>2</sub>	gas
Fluorine	F <sub>2</sub>	gas	Oxygen	O <sub>2</sub>	gas
Helium	He	gas	Ozone	O <sub>3</sub>	gas
Hydrogen	H <sub>2</sub>	gas	Phosphorus	P <sub>4</sub>	solid
Iodine	I <sub>2</sub>	solid	Sulfur	S <sub>8</sub>	solid

### Covalent molecular compounds

The formula of a covalent molecular compound shows the number of atoms of each element in one molecule of the compound. For example, the formula of water is H<sub>2</sub>O, which indicates that each molecule of water contains 2 hydrogen atoms and 1 oxygen atom covalently bonded together. Similarly, the formula of sucrose is C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, which shows that each sucrose molecule consists of 12 atoms of carbon, 22 atoms of hydrogen and 11 atoms of oxygen.

There is a systematic procedure for naming molecular compounds formed between non-metallic elements. This systematic procedure is:

#### Procedure

- 1 The name of the element closer to the bottom or left-hand side of the periodic table is written first.
- 2 The second part of the name is obtained by adding the suffix '-ide' to the stem of the name of the second element.
- 3 Where a molecule contains more than one atom of one type, the number of atoms is indicated by the prefixes 'mono-', 'di-', 'tri-', 'tetra-', 'penta-' and 'hexa-', which stand for 1, 2, 3, 4, 5 and 6 respectively. The prefix 'mono-' is used for the second-named element only.

#### Example: naming N<sub>2</sub>O<sub>4</sub>

- |   |  |
|---|--|
| Nitrogen                                      | Nitrogen   |
| Nitrogen oxide<br>(the oxygen becomes ox-ide) | Dinitrogen tetraoxide<br>(there are 2 nitrogen atoms and 4 oxygen atoms) |

Some familiar molecular substances are known by their common names rather than the name derived using the above method. These include ammonia, NH<sub>3</sub>, water, H<sub>2</sub>O, hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, methane, CH<sub>4</sub>, and hydrogen chloride, HCl.

The formulas and names of some molecular compounds are shown in Table 4.7. The common names are provided for compounds known by these names.

**TABLE 4.7 THE NAMES OF SOME COVALENT COMPOUNDS**

Molecular formula	Systematic name	Common name
CO	carbon monoxide	–
CO <sub>2</sub>	carbon dioxide	–
N <sub>2</sub> O	dinitrogen monoxide	nitrous oxide
NO	nitrogen monoxide	nitric oxide
NO <sub>2</sub>	nitrogen dioxide	–
N <sub>2</sub> O <sub>4</sub>	dinitrogen tetraoxide	–
SO <sub>2</sub>	sulfur dioxide	–
SO <sub>3</sub>	sulfur trioxide	–
H <sub>2</sub> O	–	water
H <sub>2</sub> O <sub>2</sub>	–	hydrogen peroxide
H <sub>2</sub> S	–	hydrogen sulfide
HF	–	hydrogen fluoride
HCl	–	hydrogen chloride
NH <sub>3</sub>	–	ammonia
CH <sub>4</sub>	–	methane

### \* Review exercise 4.5

1 Complete the gaps in Table 4.8.

**TABLE 4.8**

Name	Formula	Description/Uses
Carbon disulfide		colourless, smelly, flammable liquid, used in some solvents, cleaners and waxes
	NO	colourless gas, a pollutant in car exhausts
	NO <sub>2</sub>	brown gas, smog pollutant
Ammonia		colourless gas, pungent odour, solution used as cleaning agent
	P <sub>4</sub> O <sub>10</sub>	white, crystalline solid
	HCl	colourless gas, pungent odour, dissolves in water to form hydrochloric acid
Phosphorus		white, waxy solid, odour similar to garlic, ignites spontaneously in air
	CCl <sub>4</sub>	smelly liquid once used as drycleaning fluid until it was found to be a carcinogen
Sulfur pentafluoride		colourless liquid with an odour like sulfur dioxide, causes lung damage if inhaled

2 Some formulas of compounds are given below. For each:

- a identify it as an ionic compound or a covalent molecular compound
- b name the compound.



## 4.6 Compounds with both ionic and covalent bonding

Ionic compounds composed of polyatomic ions, such as calcium carbonate,  $\text{CaCO}_3$ , contain both ionic and covalent bonds. There are ionic bonds between the positive calcium ions,  $\text{Ca}^{2+}$ , and the negative carbonate ions,  $\text{CO}_3^{2-}$ , but the carbon and oxygen atoms making up the carbonate ions are held together by covalent bonds. Ionic compounds containing polyatomic ions have the same properties as any other ionic compound. They have high melting and boiling points, are hard and brittle, and only conduct electricity in the molten state and in aqueous solution.

Electron dot diagrams can be drawn for polyatomic ions in the same way as for polyatomic molecules. Again, the atoms tend to acquire a noble gas valence electron configuration, usually an octet, by sharing electrons. The only difference is that in a polyatomic negative ion there are more electrons than protons and in a polyatomic positive ion there are fewer electrons than protons.

A useful procedure for drawing electron dot diagrams is to determine the number of valence electrons in the ion or molecule, remembering to consider the charge on the ion, then ‘position’ them around the atoms so that each atom has a share of 8 electrons, or 2 electrons for hydrogen. This can be done by first showing a bonding pair of electrons between atoms, then including lone pairs around each atom. If there seems to be insufficient electrons, the possibility of multiple covalent bonds should be considered. An example of this procedure is given below for the nitrate ion,  $\text{NO}_3^-$ .

- 1 Draw the atoms in their most probable arrangement.

For example, for the nitrate ion,  $\text{NO}_3^-$ , the central atom is N, and the three oxygen atoms are arranged around this central atom:



- 2 Add up the number of valence electrons for each atom in the molecule, and add or subtract electrons if the species is an ion, for example, for the nitrate ion:

nitrogen—group 15:	5 valence electrons
3 × oxygen—group 16:	$3 \times 6 = 18$ valence electrons
-1 charge:	1 electron
	total = 24 electrons

- 3 Position these electrons around the atoms, perhaps first joining up the atoms with a pair of electrons, for example:



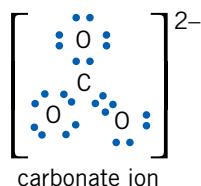
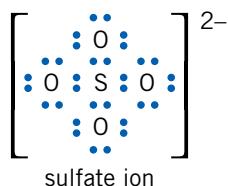
- 4 Rearrange the electrons so that each atom has 8 electrons ‘around’ it (or 2 electrons for H), for example:



- 5 If the molecule is an ion, put it in square brackets and include its charge, for example:



The electron dot diagrams for some other polyatomic anions are shown below.



### \* Review exercise 4.6

- 1 Use electron dot diagrams to represent the following:
  - a  $\text{ClO}_3^-$
  - b  $\text{PO}_4^{3-}$
  - c  $\text{SO}_3^{2-}$
  - d  $\text{Mg}(\text{NO}_2)_2$
  - e  $\text{Ba}(\text{OH})_2$
  - f  $\text{SO}_2$
- 2 For each of the elements and compounds listed in Table 4.9 give the formulas of the molecules or ions present, describe how they are organised and explain what types of bonds are present. The first two examples have been completed.

TABLE 4.9

Name of substance	Formulas of particles	How particles are organised (at 25°C)	Types of bonds present
Oxygen	$\text{O}_2$	random arrangement (because it is a gas)	covalent bonds between O atoms in molecules and weak bonds between molecules
Sodium sulfate	$\text{Na}^+$ , $\text{SO}_4^{2-}$	in an ionic lattice	ionic bonds between positive and negative ions, covalent bonds between S and O atoms in sulfate ion
Sulfur			
Carbon dioxide			
Ammonium chloride			
Potassium hydrogencarbonate			
Chlorine			
Methane			

- 3 Sulfur dioxide has a low melting point of  $-73^\circ\text{C}$  and there are covalent bonds between the sulfur and oxygen atoms. In barium sulfate the sulfur and oxygen atoms also have covalent bonds between them; however, barium sulfate has a very high melting point of  $1580^\circ\text{C}$ . Account for the difference in melting points despite the sulfur and oxygen atoms being covalently bonded in both substances.

## 4.7 Three useful covalent molecular liquids

Ethanol, acetic acid and kerosene are examples of organic compounds. Of all the known covalent molecular substances, approximately 99% are known as organic compounds. The study of the compounds of carbon is often described as organic chemistry, with the study of all the other compounds and elements being called inorganic chemistry.

All three liquids, ethanol, acetic acid and kerosene, are readily available chemicals. Methylated spirits is almost pure ethanol, and alcoholic drinks contain ethanol. Vinegar is a solution of acetic acid that can be obtained in various concentrations. Kerosene is purchased in an undiluted form.

Ethanol has the formula  $C_2H_5OH$ , which is also sometimes written as  $CH_3CH_2OH$ , and the formula of acetic acid is  $CH_3COOH$ . Kerosene is a complex mixture of hydrocarbons, some of which have formulas of  $C_9H_{20}$ ,  $C_{12}H_{26}$  and  $C_{16}H_{34}$ . The electron dot diagrams and line structures of ethanol, acetic acid and nonane,  $C_9H_{20}$ , are shown in Figure 4.14.



Figure 4.13 Domestic products containing ethanol or acetic acid.

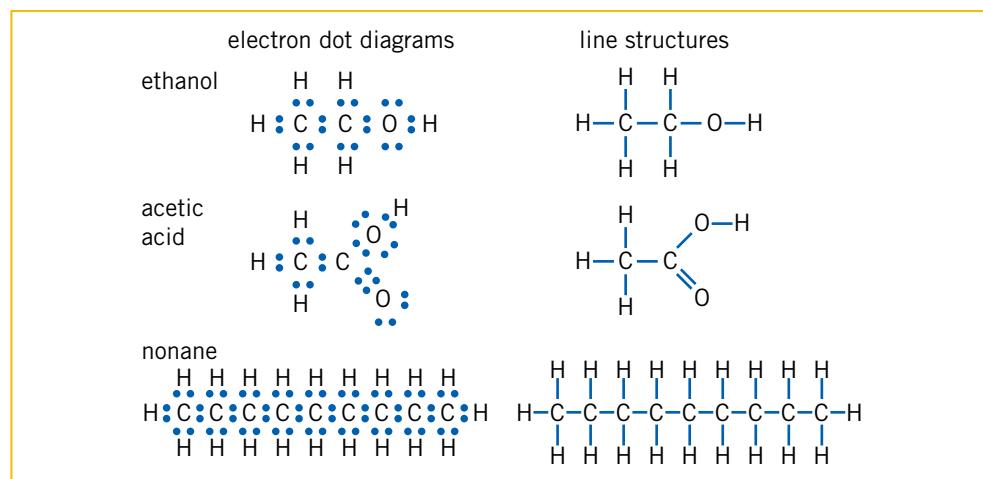


Figure 4.14 Electron dot structures and line structures of ethanol, acetic acid and a molecule from kerosene. (Lone pairs have been omitted in the line structures.)

A selection of properties of these three liquids is shown in Table 4.10.

**TABLE 4.10 PROPERTIES OF THREE COVALENT MOLECULAR LIQUIDS**

Property	Ethanol	Acetic acid	Kerosene
Appearance at 25°C	colourless liquid	colourless liquid	colourless liquid
Melting point (°C)	-114	16.7	approx. -25
Boiling point (°C)	78.3	118	approx. 200
Odour	slight fruity odour	sharp vinegar odour	strong odour
Taste	burning taste	sour taste	poisonous, 'not so nice' taste
Solubility in water	very soluble	very soluble	insoluble
Acid/base properties	neither acid nor base	weak acid	neither acid nor base
Density at 25°C, 1 atm (g mL <sup>-1</sup> )	0.785	1.044	approx. 0.78
Flammability	highly flammable	flammable	flammable
Toxicity	toxic	as a dilute solution not toxic	toxic particularly when consumed

Since ancient times, ethanol has been made by the fermentation of sugars. All alcoholic drinks and about half of the alcohol used in industry today is made this way. In the fermentation process an enzyme from yeast changes the sugars contained in or produced from plant material such as grapes, wheat, barley, potatoes and corn into ethanol and carbon dioxide. This process can produce ethanol up to concentrations of about 12–18%, by volume, before the yeast dies. Distillation is used to obtain ethanol up to 96% pure. Much of the ethanol not intended for drinking is now made synthetically from substances obtained from the petroleum industry. To prevent most of the commercially available or industrial ethanol from being used as a beverage, it is denatured. This means it contains small amounts of several different unpleasant, poisonous substances.

Acetic acid, as the defining ingredient in vinegar, has also been produced since ancient times and, as with ethanol, the process used to make it can be regarded as a natural process. Bacteria in dilute solutions of ethanol such as wine and cider can cause a reaction between the ethanol and oxygen to produce acetic acid. The name vinegar comes from the French term *vin aigre*, which means 'sour wine'. Industrially, acetic acid is produced by the reaction of carbon monoxide with methanol, CH<sub>3</sub>OH, in the presence of a catalyst. Pure acetic acid is also called glacial acetic acid.

Kerosene is also obtained from natural resources, but this time they are non-renewable resources. It can be extracted from coal and wood, but primarily it is one of the products obtained from the fractional distillation of petroleum.

A selection of uses of ethanol, acetic acid and kerosene is summarised in Table 4.11.

**TABLE 4.11 SELECTION OF USES OF ETHANOL, ACETIC ACID AND KEROSENE**

	Uses	Related properties
Ethanol	<ul style="list-style-type: none"> <li>• as methylated spirits, used in the home for cleaning purposes</li> <li>• in the manufacture of paints, dyes, varnishes</li> <li>• in medicine as a disinfectant</li> <li>• in thermometers</li> <li>• in spirit lamps</li> <li>• used as a fuel in portable stoves, and as substitute fuel in vehicles</li> <li>• main component of alcoholic beverages such as rum, whisky and beer</li> <li>• used industrially in the preparation of other chemicals such as chloroform and ether</li> </ul>	<ul style="list-style-type: none"> <li>• polar solvent, but less polar than water, evaporates readily</li> <li>• being less polar than water, it mixes more readily with non-polar materials, volatile</li> <li>• kills bacteria and fungi, but not spores or viruses</li> <li>• liquid at room temperature, low melting point</li> <li>• burns, giving off light energy</li> <li>• produces heat when burnt, low emission of CO during burning</li> <li>• traditional drink, it is a central nervous system depressant, slows down both physical and mental activity, can cause alcoholism, which is often fatal</li> <li>• reasonably reactive organic chemical</li> </ul>
Acetic acid	<ul style="list-style-type: none"> <li>• used as vinegar (dilute solution of acetic acid), a flavouring agent for foods</li> <li>• used as a food preservative, e.g. in tomato sauce</li> <li>• domestically used to remove mineral deposits in water systems, kettles</li> <li>• important industrial chemical, used in the manufacture of plastics, synthetic fibres, insecticides and pharmaceuticals, e.g. aspirin</li> </ul>	<ul style="list-style-type: none"> <li>• sour taste</li> <li>• acidic conditions inhibit bacterial growth</li> <li>• as a weak acid it reacts with carbonates</li> <li>• reactive organic chemical</li> </ul>
Kerosene	<ul style="list-style-type: none"> <li>• used as a cleaning agent and a solvent</li> <li>• used as aviation fuel for jet engines and as a heating fuel in portable stoves and home heaters</li> <li>• used as a propellant in insecticide sprays</li> <li>• at one time used in kerosene lamps</li> </ul>	<ul style="list-style-type: none"> <li>• readily available solvent of non-polar substances such as grease</li> <li>• releases large amount of heat when burnt, i.e. its combustion reaction is highly exothermic</li> <li>• dissolves non-polar insecticide chemicals</li> <li>• produces light energy when burnt</li> </ul>

## \* Review exercise 4.7

- 1 **a** Explain why ethanol, acetic acid and kerosene are liquids and not solids at room temperature.  
**b** **i** Describe in terms of its molecules, and their bonding, what would happen if pure acetic acid is placed in the refrigerator.  
**ii** What happens to pure acetic acid in the refrigerator does not happen when vinegar or salad dressing are stored there. Propose a reason for this.  
**c** Would ethanol have weaker or stronger intermolecular bonds compared with carbon dioxide?
- 2 **a** One of the advantages of using ethanol as a cleaner and as a solvent in varnishes and paints is that it evaporates readily. Explain in terms of its bonding why ethanol is a volatile liquid.  
**b** Acetic acid is not as volatile as ethanol. Which of the two liquids, ethanol or acetic acid, has the stronger intermolecular forces?
- 3 Lubricating oil or grease is composed of long-chain hydrocarbon molecules similar to those in kerosene. Explain, in terms of the bonding between these molecules, how the oil or grease lubricates.
- 4 **a** Explain, in terms of its bonding, why ethanol is a suitable substance to be used, instead of mercury, in a thermometer.  
**b** Why have mercury thermometers been replaced by alcohol thermometers for use in school laboratories?
- 5 Organic chemists use a systematic method for naming compounds. For example, if a molecule contains one carbon atom, its name contains the prefix 'meth'; if it contains two carbon atoms, its name contains the prefix 'eth'; if three carbons 'prop' and if four carbons 'but'. For example, ethanol contains two carbon atoms.
  - a** Ethanol,  $C_2H_5OH$  or  $CH_3CH_2OH$ , belongs to an organic family of compounds called alcohols. All alcohols contain an OH group in their molecules.
    - i** Predict the formulas of methanol and propanol.
    - ii** Draw electron dot diagrams of these two alcohols.
  - b** Acetic acid, or according to its systematic name ethanoic acid, belongs to the carboxylic acid group of compounds. The carboxylic acid,  $HCOOH$ , with only one carbon in its chain, is produced by ants. What would you expect the systematic name of this acid to be?
- 6 **a** Predict whether or not pure ethanol, glacial acetic acid and kerosene will conduct electricity. Explain your predictions in terms of the bonding and structure of the substances.  
**b** When added to water, ethanol acts as a non-electrolyte and acetic acid as a weak electrolyte. Would either of the solutions of these two substances conduct electricity? Explain your answer.
- 7 In an acrylic ceiling paint, water is used as the solvent or diluent, as it is called in the paint industry. In an enamel paint, the diluent is a mixture of compounds with formulas like  $CH_3(CH_2)_7CH(CH_3)_2$ . Could kerosene be used to clean brushes that have been used for painting with the:
  - a** acrylic paint?
  - b** enamel paint?Justify your answers.
- 8 When a flammable substance is in its liquid state, it will not burn. It will ignite and burn only when it is in a gaseous state. Flammable liquids undergo evaporation to produce vapours that can ignite and burn when an ignition source such as a lighted match or spark is present.  
Use this information, and an understanding of the bonding in the substances, to explain why ethanol is classified as very flammable, but acetic acid and kerosene are only classified as flammable.



## MAJOR IDEAS

- Within molecules, atoms are held together by the electrostatic attraction between shared electrons and the nuclei of atoms. This form of bonding is called covalent bonding.
- When atoms combine to form molecules they often share electrons so that their outer shell has eight electrons or a noble gas electron configuration.
- Electron dot diagrams can be drawn to show the formation of a molecule and to represent molecules.
- A single covalent bond is formed when two atoms share a pair of valence electrons.
- A double covalent bond is formed when two atoms share two pairs of valence electrons. A triple covalent bond is formed when two atoms share three pairs of valence electrons.
- The electron pairs forming covalent bonds in molecules are called bonding electron pairs. The remaining valence electron pairs, if any, are called non-bonding electron pairs or lone pairs.
- In covalent molecular substances, the atoms in the molecules are held together by covalent bonds. (Covalent bonds are strong bonds.) But between the molecules there are weak attractive forces, sometimes called intermolecular forces or van der Waals forces.
- The properties of covalent molecular substances are listed and explained in Table 4.12

TABLE 4.12

Property	Explanation
low melting and boiling points	forces between molecules are weak
non-conductors of electricity when solid or liquid	the molecules are uncharged and electrons are localised in covalent bonds or in the atoms
the solids are generally soft	forces between molecules are weak

- When naming covalent molecular compounds, the prefixes 'mono-', 'di-', 'tri-', 'tetra-', 'penta-' and 'hexa' are often used to indicate how many of each type of atom are in a molecule of the compound.
- Compounds comprising polyatomic ions, contain both ionic and covalent bonds.

## QUESTIONS

- 1 Table 4.13 shows a list of additives commonly used in foods.

TABLE 4.13

Name of food additive	Formula	Function of additive in food
Ammonium chloride	$\text{NH}_4\text{Cl}$	bulking agent
Aluminium	$\text{Al}$	colouring agent
Ascorbic acid (vitamin C)	$\text{C}_6\text{H}_8\text{O}_6$	antioxidant
Nitrous oxide	$\text{N}_2\text{O}$	propellant
Sulfur dioxide	$\text{SO}_2$	preservative
Calcium phosphate	$\text{Ca}_3(\text{PO}_4)_2$	anticaking agent
Potassium chloride	$\text{KCl}$	gelling agent
Sodium sulfate	$\text{Na}_2\text{SO}_4$	acidity regulator
Aspartame	$\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_5$	sweetener

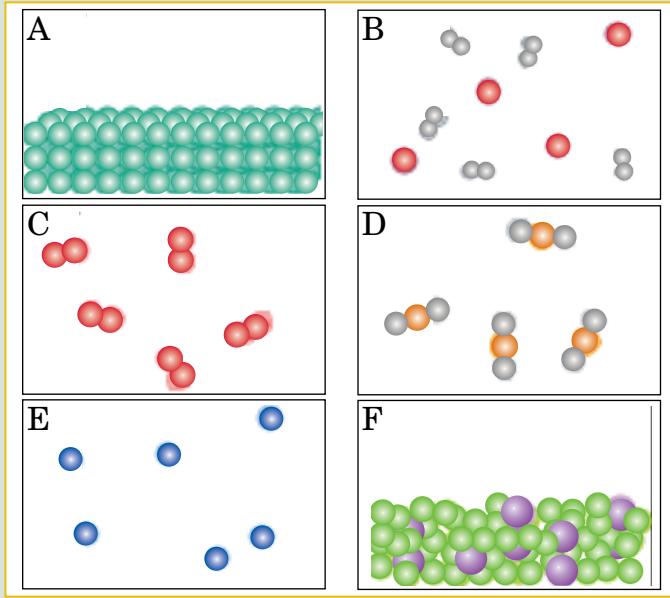
- a Which of these substances are covalent molecular compounds?  
b Which substances contain both covalent bonds and ionic bonds?

- 2 A typical analysis of the gases in natural gas from northern Western Australia is shown in Table 4.14.

TABLE 4.14

Chemicals in natural gas	Percentage proportion, by number of particles
Methane ( $\text{CH}_4$ )	88.0
Ethane ( $\text{C}_2\text{H}_6$ )	5.5
Propane ( $\text{C}_3\text{H}_8$ )	2.0
Butane ( $\text{C}_4\text{H}_{10}$ )	0.8
Carbon dioxide ( $\text{CO}_2$ )	3.0
Nitrogen ( $\text{N}_2$ )	0.7

- a Explain why these substances are gases at room temperature.  
b Draw electron dot diagrams for methane, ethane, propane, carbon dioxide and nitrogen gases.  
c Draw line structures for ethane and butane.  
d i Give some domestic uses of natural gas.  
ii What chemical property of the hydrocarbons enables natural gas to be used in these ways?



**Figure 4.15**

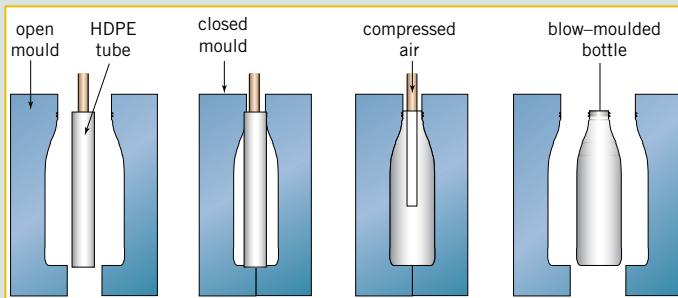
- 3 Figure 4.15 shows diagrams A–F depicting various substances at the atomic level. Choose the correct diagram or diagrams for each of the descriptions a–h:
- a gaseous element
  - a gaseous compound
  - a solid element
  - a gaseous mixture of two elements
  - a covalent molecular compound
  - a covalent molecular element
  - a gas composed of diatomic molecules
  - a monatomic gas.
- 4 Draw electron dot diagrams for the following:
- ICl
  - $\text{SO}_3^{2-}$
  - $\text{KNO}_3$
- 5 Hydrogen sulfide is known as ‘rotten egg gas’. It is a toxic gas and even though it has an unpleasant smell, after an initial strong exposure to the gas it paralyses the olfactory nerve and so the odour is no longer noticed. Continued inhalation of the gas can cause death.
- Use the electron configurations of hydrogen and sulfur to predict the formula of this ‘rotten smelling’ compound.
  - Draw an electron dot diagram of a molecule of hydrogen sulfide.
  - How many lone pairs and bonding pairs of electrons are in a molecule of hydrogen sulfide?
  - Describe the bonding between the hydrogen atoms and the sulfur atom in a molecule of hydrogen sulfide.
- 6 Consider the information below:
- | Compound             | Boiling point (°C) |
|----------------------|--------------------|
| $\text{SO}_2$        | -10                |
| $\text{NH}_3$        | -33                |
| $\text{CH}_4$        | -162               |
| $\text{H}_2\text{O}$ | 100                |
- Name the four substances.
  - Order the substances in increasing strength of intermolecular forces.
- 7 Solid crystals are composed of particles organised in an orderly lattice. These particles can be neutral atoms, ions or molecules.
- Name and give the formulas of the particles present in the solid crystal lattices of the following:
- sodium
  - sodium chloride
  - zinc carbonate
  - carbon dioxide.
- 8 When sulfur is ignited it burns with a blue-purple flame to produce sulfur dioxide, a pungent-smelling gas.
- What is the formula of sulfur dioxide?
  - Draw an electron dot diagram for sulfur dioxide.
  - Argon is the group 18 element in the same period of the periodic table as sulfur. When argon is heated it does not react with oxygen to form an oxide. Explain this observation.
- 9 Explain the following in terms of the bonding and structure of the substances involved:
- Potassium nitrite,  $\text{KNO}_2$ , is a solid at room temperature, but nitrogen dioxide,  $\text{NO}_2$ , is a gas.
  - A steel knife can be used to cut candle wax.
  - Ice does not conduct electricity but copper does.
  - A solution of sodium chloride conducts electricity but a solution of sucrose (sugar) does not.
- 10 Historically, the metalloid arsenic was the poison of choice for many murderers, both in fiction and in reality. Arsenic is a group 15 element and has five valence electrons.
- What are valence electrons and why is the number of them significant?
  - When arsenic reacts with chlorine, it forms a compound with a melting point of  $-16^\circ\text{C}$  and a boiling point of  $130^\circ\text{C}$ .

- i** What type of substance would you expect this chloride of arsenic to be? Justify your answer.
- ii** Would you expect the liquid chloride of arsenic to conduct electricity?
- iii** Predict the formula of this chloride of arsenic and draw an electron dot diagram of it.
- iv** What would the name of this chloride of arsenic be?
- 11** Molecules of hydrogen peroxide,  $\text{H}_2\text{O}_2$ , have one more oxygen atom than molecules of water,  $\text{H}_2\text{O}$ . This extra oxygen atom in the hydrogen peroxide molecule causes it to have vastly different properties from those of water. For example, hydrogen peroxide is used as a rocket fuel and as a bleach that removes colours from materials.
- a** Draw an electron dot diagram for a hydrogen peroxide molecule.
- b** Predict the physical properties you would expect hydrogen peroxide to have. Justify your predictions in terms of the bonding and structure of hydrogen peroxide.
- c** Some websites claim that because hydrogen peroxide is composed of ‘only water and oxygen’ it is therefore safer to use than other toxic substances often used in the home. They also claim that hydrogen peroxide has many therapeutic uses.
- i** Explain why some people may think that hydrogen peroxide is composed of only water and oxygen.
- ii** Is hydrogen peroxide composed of only water and oxygen? Explain your answer.
- iii** **RESEARCH** List some of the claimed therapeutic uses of a hydrogen peroxide solution and comment on whether or not you think each use is actually safe.
- 12** **a** Tetraphosphorus trisulfide is used in the tips of ‘strike anywhere’ matches. Give the formula of tetraphosphorus trisulfide.
- b** Registered as an antimicrobial pesticide,  $\text{ClO}_2$ , has many uses including disinfecting meat and poultry and treating medical wastes. Give the name of this compound.
- c**  $\text{Ca(OCl)}_2$  is used to chlorinate swimming pools. What is the name of this compound?
- d** Would you expect  $\text{ClO}_2$  and  $\text{Ca(OCl)}_2$  to be a solid, liquid or gas at room temperature? Justify your answer.
- 13** Elements E, Q and Z occur in the same period of the periodic table and have two, five and seven electrons respectively in their valence shell. For the compounds that form between **i** E and Q, and **ii** Q and Z:
- a** write the chemical formulas
- b** predict and describe the bonding
- c** draw the electron dot diagrams.
- 14** Naphthalene,  $\text{C}_{10}\text{H}_8$ , is a white crystalline solid that was once used for protecting clothes from being eaten by moths. It has quite a strong odour and sublimes readily without creating a messy liquid. However, it has now been classified as a possible human carcinogen.
- a** Explain in terms of its bonding and structure why naphthalene can be smelt, and why it sublimes at room temperature.
- b** Would you expect naphthalene to be soluble in water or in kerosene?
- c** Predict whether or not solid or liquid naphthalene would conduct electricity. Explain your answer in terms of the bonding and structure of naphthalene.
- 15** Consider the following substances, all in the solid state— $\text{Cu}$ ,  $\text{I}_2$  and  $\text{NaF}$ . Match each of these solids with one of the following statements.
- a** This high melting point solid conducts electricity only in the molten state.
- b** This solid is a good electrical conductor.
- c** Of the three solids, this one could be scratched by the other two.
- d** This solid has a low melting point.
- 16** What attractive forces must be overcome in the following processes?
- a** The sublimation of iodine,  $\text{I}_2$ .
- b** Gaseous iodine ( $\text{I}_2$ ) is very strongly heated until it forms individual iodine atoms.
- c** The melting of ice.
- d** Cutting margarine with a knife.
- e** Shattering a sodium chloride crystal with a hammer.
- f** Bending an iron nail until it breaks in half.
- 17** Is there any such thing as a sodium chloride molecule? Explain your answer.

- 18** Chlorine atoms react with magnesium atoms to form  $MgCl_2$ . Chlorine atoms can also react with oxygen atoms to form  $Cl_2O$ .
- Compare what happens to the valence electrons of the reacting atoms during these two reactions. Include electron dot diagrams of the two compounds in your answer.
  - Name the two compounds,  $MgCl_2$  and  $Cl_2O$ .
  - Compare the physical properties of the two compounds  $MgCl_2$  and  $Cl_2O$  formed in the reactions and explain any differences in terms of their bonding and structure.
- 19** Which is which?
- The properties of a substance act a little like a ‘fingerprint’ in that they are essentially unique for the substance and also enable it to be identified. The properties of ten pure substances A–J are given in Table 4.15.
- Identify each of these substances by choosing your answer from the names given in the box below:
- |                           |                 |                |
|---------------------------|-----------------|----------------|
| decane ( $C_{10}H_{22}$ ) | iron(III) oxide | lead bromide   |
| glucose                   | copper sulfate  | sulfur dioxide |
| aluminium iodide          | silver          | methane        |
| propanol ( $C_3H_7OH$ )   |                 |                |
- 20** A fuel safety tip given on a brochure advised:
- Kerosene should never be stored or carried in a container that has contained gasoline because the residual gasoline is enough to increase the flammability of the kerosene.*
- Would you expect this safety tip to be true? Explain your reasoning.
- 21** ↗ RESEARCH Plastic milk bottles are made from high-density polythene (poly(ethene)). A hollow tube of the polythene is heated until it is quite soft. It is then placed inside the open mould, as shown in Figure 4.16. The two halves of the mould are closed together and air is blown into the hollow polythene tube. The softened polythene blows up like a balloon so that it fits the mould and forms the shape of the bottle. After cooling, the mould is opened to release the bottle.
- Explain what happens, at the molecular level, to the molecules in the polythene tube when they are heated and then put through the shaping process, to finally form the bottle.
  - In an attempt to ‘help the environment’ many plastic containers, bottles and products are now recycled. Many containers and bottles have a small symbol marked on them to show what type of plastic they are made from and whether or not they can be recycled. What do these small symbols look like?
  - Why are we encouraged to recycle plastic containers and bottles?

TABLE 4.15

	Colour	M. pt (°C)	B. pt (°C)	Solubility in		Conductivity		
				Water	Kerosene	Solid	Liquid	Aqueous solution
A	white	146	–	soluble	insoluble	nil	nil	nil
B	colourless	-73	-10	soluble	insoluble	nil	nil	very poor
C	white	191	386	soluble	insoluble	nil	good	good
D	white/grey	962	2212	insoluble	insoluble	good	good	–
E	colourless	-30	174	insoluble	soluble	nil	nil	–
F	blue	d110	–	soluble	insoluble	nil	–	good
G	colourless	-183	-162	insoluble	soluble	nil	nil	–
H	white	373	914	insoluble	insoluble	nil	good	–
I	colourless	-126	97	soluble	slightly soluble	nil	nil	nil
J	brown	1565	–	insoluble	insoluble	nil	good	–



**Figure 4.16** The production of high-density polythene bottles by blow moulding.

**22 RESEARCH** More and more of the food and drink consumed today contains artificial sweeteners.

- Give some reasons for why artificial sweeteners, rather than sucrose (sugar), are being used in food and drink.
- Name some of the commonly used artificial sweeteners, and give their formulas.
- Are the structures of the molecules of the artificial sweeteners given in part **b** similar to the molecular structures of sucrose or glucose?
- Choose several of the artificial sweeteners and find out how and when they were discovered.
- Do you think artificial sweeteners should be used in food and drink? Justify your answer.

The background of the slide features a wide-angle aerial photograph of a sandy beach. The sand is light beige and shows distinct wavy patterns from the tides. The ocean water is a vibrant turquoise color, with white foam from breaking waves along the shore. The horizon is visible in the distance where the sea meets the sky.

# 5

# Covalent network substances

## BY THE END OF THIS CHAPTER YOU SHOULD BE ABLE TO:

- give examples of covalent network substances
- list the characteristic physical properties of covalent network substances
- describe a model for the structure and bonding of covalent network substances
- explain the properties of electrical conductivity, melting and boiling points, hardness and brittleness of covalent network substances, in terms of their structure and bonding
- describe the uses of some covalent network substances and explain how these are related to their properties
- compare the bonding and structure, and physical properties of ionic, metallic, covalent molecular and covalent network substances
- explain the use of filtration, crystallisation, solvent extraction, distillation and chromatography in obtaining pure substances.

## 5.1 Covalent network substances

Most substances formed when non-metal atoms combine are covalent molecular substances. That is, substances in which the atoms are covalently bonded in small groups called molecules. However, a few non-metallic substances have quite different properties compared with those of covalent molecular substances. For example, both carbon and silicon, which are group 14 elements, form oxides with formulas of  $\text{CO}_2$  and  $\text{SiO}_2$  respectively, yet the physical properties of these two compounds are somewhat different, as shown in Table 5.1.

TABLE 5.1 A COMPARISON OF PROPERTIES OF CARBON DIOXIDE AND SILICON DIOXIDE

Name, formula	Appearance at room temperature	Melting point (°C)	Boiling point (°C)	Hardness of solid	Electrical conductivity	Solubility in water
Carbon dioxide, $\text{CO}_2$	colourless gas	−57 (under pressure)	sublimes at −78	not very hard	does not conduct in solid or liquid states	slightly soluble
Silicon dioxide, $\text{SiO}_2$	colourless solid	1610	2230	very hard, can scratch glass	does not conduct in solid or liquid states	insoluble

Carbon dioxide is a covalent molecular compound and because it has weak forces between each of its molecules, it has low melting and boiling points and does not form a very hard solid. However, the carbon and two oxygen atoms in each molecule are held together by double covalent bonds, which are strong bonds, as shown in Figure 5.2.

The high melting point of silicon dioxide suggests that it may be an ionic compound although the lack of conductivity in the liquid state implies that ions are not present. In silicon dioxide, the silicon atoms share electrons with the oxygen atoms to form covalent bonds, but, unlike in carbon dioxide, the atoms are not covalently bonded in discrete molecules.

Silicon, having an electron configuration of 2, 8, 4, needs to gain 4 electrons to attain 8 electrons in its outermost shell. Oxygen, with an electron configuration of 2, 6, needs to gain 2 electrons to complete its outermost shell. As a result, in silicon dioxide, each silicon atom forms single covalent bonds with four oxygen atoms and each oxygen atom forms single covalent bonds with two silicon atoms. But these atoms are not bonded in small molecules, instead they are covalently bonded in a network lattice, or a giant molecule. Therefore, in silicon dioxide each atom is strongly held by covalent bonds in a large lattice structure. A small portion of the network lattice arrangement of silicon and oxygen atoms is shown in Figure 5.3.

Silicon dioxide is called a covalent network substance. Other examples of covalent network substances include the elements diamond and silicon and the compound silicon carbide,  $\text{SiC}$ .

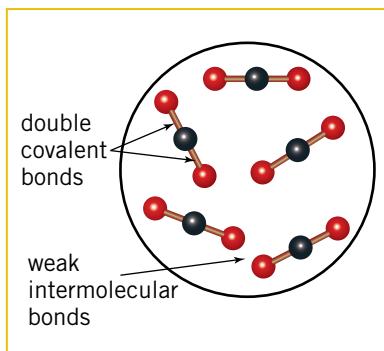


Figure 5.2 Bonding and structure of carbon dioxide.



Figure 5.1 Quartz crystals, composed of pure silicon dioxide.

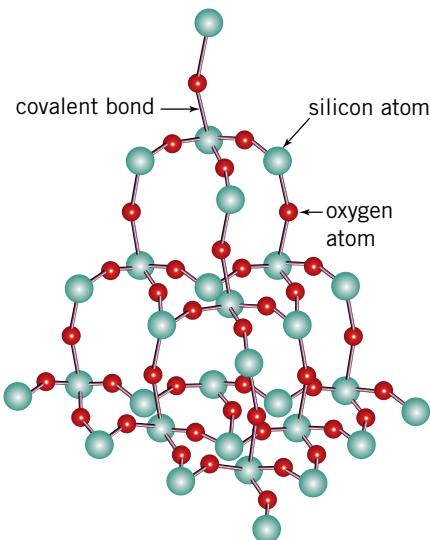


Figure 5.3 Silicon and oxygen atoms covalently bonded in a network lattice.

## \* Review exercise 5.1

- 1
  - a When solid carbon dioxide is hit gently with a hammer, it breaks into small pieces. What type of bond is broken in this process?
  - b If a small piece of silicon dioxide is placed in a vice, it can be crushed into small pieces. What type of bond is being broken in this crushing process?
- 2
  - a Silicon dioxide, or quartz, is a mineral used as a gemstone. When it contains a small amount of impurity it sometimes is coloured, for example, the amethyst gemstone is silicon dioxide with a trace of iron ions in its lattice (Figure 5.4). What properties of silicon dioxide make it suitable for use as a gemstone?
  - b The grains in most types of sand are small crystals of silicon dioxide. Many different uses are made of sand, several of which are listed below. What properties of silicon dioxide make it suitable for each of these uses?
    - i Used to make sandpaper.
    - ii Used as a water filter.
    - iii Used to make moulds for molten metals.

## 5.2 Properties of covalent network substances

Covalent network substances have the following characteristic properties:

- very high melting and boiling points
- non-conductors of electricity in the solid and liquid states
- extremely hard and brittle
- reasonably chemically inert
- insoluble in water and most other solvents.

Covalent network substances have very high melting points and are very hard because each atom is held in the rigid lattice by the strong covalent bonds. To break these bonds requires a very large amount of energy. However, if some of the covalent bonds are broken, the network lattice is placed under stress and rather than it changing shape or becoming distorted, the solid shatters.

In a covalent network substance, the electrons are either inner-shell electrons or localised in the bonding and non-bonding pairs around each atom. As a result, these electrons cannot act as charge carriers in the conduction of electricity. There are also no ions present in the lattice. It therefore follows that pure substances, with atoms covalently bonded in a three-dimensional lattice, are not expected to be conductors of electricity.

A few other elements, apart from carbon and silicon also form covalent network substances. These elements are shown in the periodic table in Figure 5.5.



Figure 5.4 A mass of amethyst crystals. Amethyst is a slightly impure form of silicon dioxide.

H																He	
Li	Be																
Na	Mg																
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				

Figure 5.5 The elements shaded orange form covalent network solids.

### \* Review exercise 5.2

- 1 Compare the characteristic properties of covalent network substances with those of:
  - ionic compounds
  - metals.
- 2 Silicon tetraiodide and silicon dioxide are both solids at room temperature. However, silicon tetraiodide has a melting point of 120°C and silicon dioxide has a melting point of 1610°C. Explain, in terms of bonding and structure, why these melting points differ. As part of your answer, use diagrams of the particles present in each compound, showing the bonds that are broken in the melting process.
- 3 The properties of two group 14 elements, germanium and tin, are shown in Table 5.2.

TABLE 5.2

	Description	Melting point (°C)	Boiling point (°C)	Hardness (Mohs scale)	Electrical conductivity (MS m <sup>-1</sup> )	Brittleness/ Malleability
Germanium	silvery-grey solid	937	2830	6	$10^{-6}$	brittle
Tin (white form)	silvery-white solid	232	2602	1.5–1.8	8.5	soft, pliable

- a Predict and describe the bonding and structure of germanium and tin.
- b Justify your predictions (made in part a) by explaining the properties of the two elements in terms of their predicted bonding and structure.
- c During the last century, the tin organ pipes in cold northern European cathedrals slowly disintegrated because of what was known as tin disease or tin plague. If white tin is kept for a long period of time at temperatures less than 13°C, it begins to change into a grey, crumbly powder called grey tin. This grey tin is made up of microcrystals, which have a crystal structure different to that of the white form of tin, but similar to that of diamond (shown in Figure 5.7).
  - i Draw a small portion of the crystal lattice of grey tin.
  - ii Would you expect grey tin to conduct electricity?

## 5.3 Allotropes of carbon

As the pure element, carbon exists in a number of different forms. For instance, it can be seen as the black soot in a fireplace, as a clear, sparkling diamond in a necklace, as the lead in a pencil and as a more recently discovered black crystalline powder called buckminsterfullerene. These different forms, or allotropes, of carbon have quite different properties and uses because the carbon atoms are arranged in different ways. However, in each of these allotropes, the carbon atoms are covalently bonded in an extensive lattice arrangement.

Diamond and graphite are two crystalline allotropes of carbon and their properties are summarised in Table 5.3.



Figure 5.6 Two allotropes of carbon.

TABLE 5.3 PROPERTIES OF TWO ALLOTROPES OF CARBON: DIAMOND AND GRAPHITE

Diamond	Graphite
melting point: >3550°C boiling point: – normally colourless clear reflects and refracts light extremely hard, brittle not very reactive non-conductor of electricity insoluble in polar and non-polar solvents  undergoes combustion if heated to a high temperature	melting point: 3727°C (under pressure) boiling point: sublimes at 3642°C black opaque lustrous slippery, flaky not very reactive conductor of electricity insoluble in polar solvents but slightly soluble in non-polar solvents undergoes combustion if heated to a high temperature

### Diamond

Diamonds are found naturally on Earth but they are very rare. However, cheaper industrial-quality diamonds can be made artificially. Experimental evidence indicates that in diamond all the C–C bonds are of the same length and all the bond angles are 109.5°. In view of this information, a diamond crystal can be pictured as a single giant molecule made up of a regular network of carbon atoms extending throughout the crystal. Each carbon atom can be imagined to be at the centre of a regular tetrahedron, surrounded by four other carbon atoms at the corners of the tetrahedron as illustrated in Figure 5.7.

In this three-dimensional network of atoms, each carbon atom forms four covalent bonds by sharing electrons with each of its four nearest neighbours. The bonding electrons are tightly bound and highly localised between pairs of atoms and so cannot drift throughout the lattice under the influence of an electric field. Diamonds are therefore non-conductors of electricity.

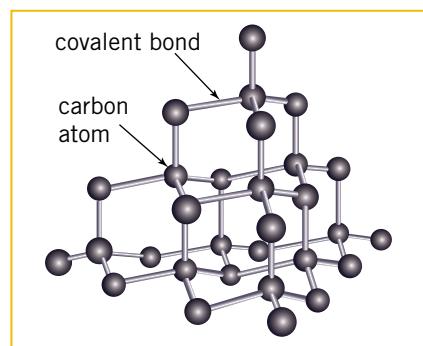


Figure 5.7 The structure of diamond.

It is very difficult to break or cut diamond since this would involve breaking many covalent bonds. Consequently, diamond is extremely hard and has a very high melting point. If the highly directional bonds in diamond are subjected to extreme stress, the crystal is unable to deform in shape and so it shatters. Diamond is the hardest known naturally occurring substance.

Since early times, diamonds have been prized as gemstones mainly because of their hardness and optical properties. As gems, they are cut and polished into a number of faceted, or angled, shapes to accentuate their attractiveness. The extreme hardness of diamond means that it resists scratching and therefore maintains its polished surface. The extraordinary brilliance of a cut diamond is due to its high refractive index, which is greater than that of any other naturally occurring gemstone. This means that light entering the diamond will be bent significantly. As a consequence, much of the light entering the front of a diamond ends up being reflected from the back surface of the crystal, giving the diamond its characteristic 'sparkle'. Also, because the different wavelengths of white light are refracted by differing amounts, flashes of rainbow colours can be seen when looking at the diamond. At temperatures normally experienced in everyday life, diamond is very unreactive and insoluble in common liquids; consequently, diamonds worn as jewellery have almost an indefinite lifetime. However, because diamond undergoes combustion at high temperatures to form carbon dioxide, in the same way as charcoal does, jewellery may not last 'for a lifetime' if dropped into a hot fire.

Due to its extreme hardness, diamond can be used to cut through or scratch any material. As a result, diamond is extensively used in industry as an abrasive and in cutting, grinding and drilling tools. With improved technology, as artificial diamonds become more readily and cheaply available, the number of everyday tools relying on the hardness of diamond will increase. Some articles and appliances presently in use include nailfiles impregnated with diamond grit, glass cutters, diamond grinding wheels, diamond saw blades, dentists' drills, diamond-encrusted drill bits and diamond sharpening tools, for example, to sharpen knives, scissors and axes.

A technology that is rapidly emerging centres on the use of thin films of diamond, produced by chemical vapour deposition (CVD) techniques. These very thin diamond films are composed of many tiny coalesced diamonds and have the same properties—hardness, wear resistance, high melting point, chemical inertness and optical transparency from UV to IR light—as the larger diamond crystals. A number of areas of application, such as on cutting tools, tweeters in stereo speakers and as scratch-proof coatings on watches, are gradually beginning to appear on the market. Some possible future uses of diamond films are wear-resistant coatings on car engine parts, gears, windows, knife blades, sunglasses, ophthalmic lenses, razor blades, surgical blades, DVDs and diamond-coated fibres.

### The 4 Cs

More than ten factors determine the value of a diamond, with the four most important ones being cut, carat weight, clarity and colour. These factors are often called the 4 Cs. The cut refers to the shape, proportions and polish of the diamond. The weight of a diamond is measured in carats where 1 carat is equal to 0.2 g. Because they are a natural substance, most diamonds have flaws in them. Clarity grades are assigned to each diamond to describe how flawed or flawless it is. Diamonds vary in colour from colourless (highest quality) to many shades of yellow (less rare).

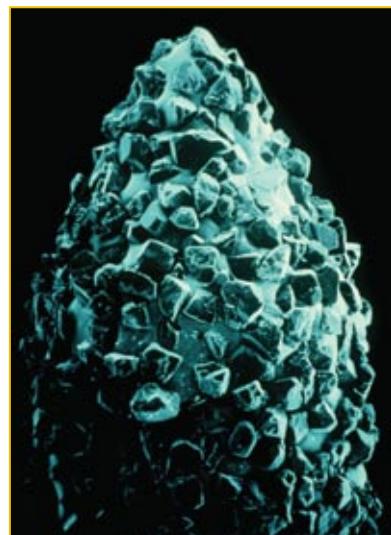


Figure 5.8 Scanning electron microscope image of the tip of a diamond dental drill, showing the tiny diamond crystals.

## Graphite

Like diamond, graphite is composed of only carbon atoms. However, because graphite's atoms are strongly bonded in flat layers rather than in a three-dimensional lattice, some of its properties are quite different from those of diamond. Both diamond and graphite have high melting and boiling points but graphite is soft and is a good conductor of electricity. Figure 5.9 shows the arrangement of carbon atoms in graphite.

Within the flat parallel layers of graphite, each carbon atom is covalently bonded to three other atoms, forming a hexagonal arrangement. Every layer can be considered as a two-dimensional network of carbon atoms. Each carbon atom shares one of its valence electrons with each of its three neighbouring atoms within the layer. The fourth electron is delocalised. The delocalised electrons are free to move in between the layers of carbon atoms and are responsible for the electrical conductivity of graphite.

The high electrical conductivity of graphite

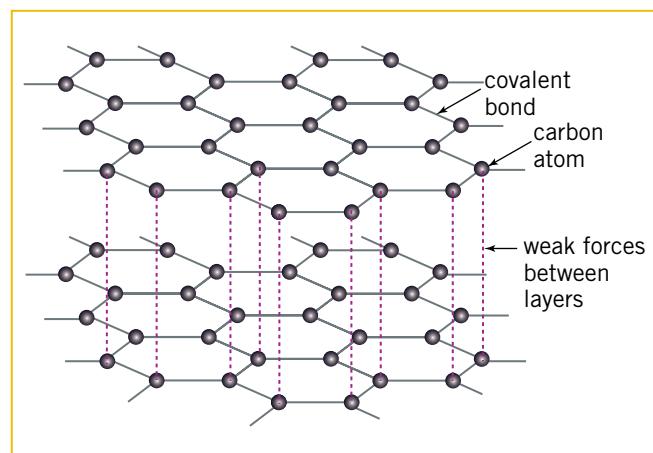


Figure 5.9 Model showing the arrangement of carbon atoms in graphite.

and its good heat and chemical stability are attractive features for its use as carbon brushes in electric motors and in galvanic and electrolytic cells. As the pure solid or mixed with other chemicals, it is used as an electrode in a wide range of cells that produce electricity. These cells include the dry cell, alkaline cells, rechargeable lithium cells (that are used in portable electronic devices such as mobile phones, portable computers and laptops), and fuel cells. It is also used as electrodes in cells that require electricity for their operation, including the Hall-Héroult cell in which aluminium is produced.

Graphite has a very high melting point because in the melting process it is necessary to separate the carbon atoms. The carbon atoms are held together in the layers by strong covalent bonds, and these bonds require a very high temperature to disrupt them.

The bonding between the layers in graphite is quite weak, being only van der Waals forces. As a result, the layers can slide easily over each other. This accounts for the softness and slippery feel of graphite and its use as a dry lubricant and in 'lead' pencils. Because of its high melting point, graphite is also used as a lubricant in high-temperature machinery.

The lead in 'black lead' pencils is actually a mixture of graphite and clay. When the lead is pushed along a piece of paper, layers of carbon atoms are left behind on the paper. The more graphite present in the lead, the softer the lead and the blacker the line produced by the pencil. The more clay present, the harder the lead. This hardness and blackness of the lead is often marked on the pencil using the letters 'H' and 'B'. For example, a 4H pencil is used for light-coloured lines that are easy to erase, but a 2B pencil, having a softer lead, produces a thicker, darker line.

### Other slippery layers

Other substances such as the minerals talc and mica also have a layered structure like graphite. These two substances are composed of layers built up from silicate (silicon and oxygen) units and metals ions. Within each layer the atoms are held together by strong bonds, but between the layers there are only weak bonds. Talc, the softest known mineral, is used as a body powder because of its slippery texture and softness to the touch. Mica can be split into very thin sheets and because it is an insulator it is used as the material around which the electric wire is wound to produce the element in an electric toaster.

## Amorphous carbon

Variations in the graphite structure can occur depending on how the graphite is formed. When the size of the layers is small and the separation between them becomes large, the graphite is referred to as amorphous carbon. Soot, charcoal, coke and activated carbon are all examples of amorphous carbon. One of the earliest uses of amorphous carbon was for drawing on the walls of caves and as a colouring agent. The carbon materials in these applications were most likely derived from soot. When a fire, or even a candle burns in air, because there is a limited supply of oxygen, the black smoke produced is mainly composed of soot, that is, small powdery flakes of amorphous carbon. Carbon black, a soot-like form of amorphous carbon, is used as the black pigment in paints and inks, toners for photocopying and in ink-jet and laser printers. The black colour of automobile tyres is also due to carbon black, which is added to rubber in the manufacturing process. The carbon improves wear and abrasion resistance and therefore extends the usable life of the tyre.

Cigarette smoke contains soot that clogs up the lungs and damages them. This can cause the lung tissue to be scarred, reducing its elasticity and thus its surface area. Consequently, the gas exchange that takes place in the lungs becomes very inefficient. This condition is called emphysema and it can eventually cause death.

Activated carbon is charcoal that has been treated with oxygen to open up millions of tiny pores, called micropores, on its surface, as shown in Figure 5.11. This form of graphite plays a major role in the purification of water, food, pharmaceuticals and air because it has the ability to adsorb many unwanted substances. Adsorption is a process that involves an attractive interaction between the substance and the carbon resulting in the unwanted substance ‘sticking’ onto the surface of the activated carbon. Because activated carbon is very porous and its surface is covered with the micropores, it has a very large surface area. One teaspoon of activated carbon is thought to have a surface area of a football oval. Consequently, it is ideal for adsorbing and removing many unwanted substances.

Not all chemicals are adsorbed by activated carbon. It tends to best adsorb molecular substances such as chlorine and organic molecules that can cause taste and odour, but not ionic compounds. New composite materials containing activated carbon are continually being developed that enable the adsorption of a wider range of substances. In the home, the uses of activated carbon include in water filters, in air filters, to purify water in aquariums, as a deodoriser for shoes, and, with precautions, as an antidote for swallowed poisons. Once the activated carbon’s adsorption capacity has been exhausted, usually it can be reactivated by heating. This means it is regarded as a reusable and an environmentally friendly material. As a result, some inventive uses of activated carbon are beginning to emerge. One such use involves embedding it in material used for making clothes. When the clothes are worn, any body odours are adsorbed by the material. After washing, the clothes are then heated in a clothes dryer to remove the ‘smelly’ molecules and so reactivate the carbon.

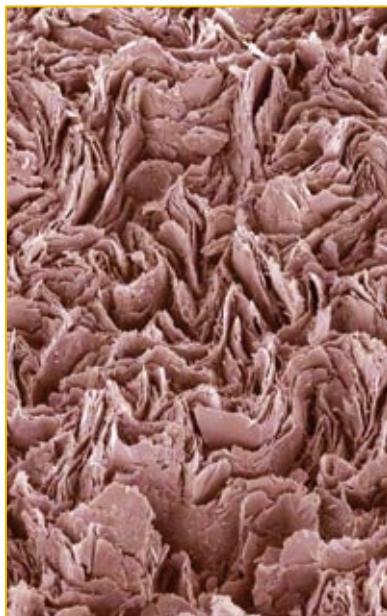


Figure 5.10 Coloured scanning electron micrograph of layers of graphite mixed with clay, in the lead of a pencil. Because graphite is soft, the layers in the tip of the pencil break off under pressure to leave marks on paper.



Figure 5.11 Artificially coloured scanning electron micrograph of coconut shell charcoal from a water filter, showing the micropores in its surface. Magnification: approx.  $\times 1500$ .



Figure 5.12 Carbon fibre.

### Carbon fibre

Late last century, a new type of graphite, called carbon fibre, was developed. Where graphite is flaky and breaks apart very easily, carbon fibre is strong and does not break until a large force is applied. Carbon fibre is produced by strongly heating an organic polymer, such as poly(acrylonitrile), under controlled conditions.

The carbon layers making up the carbon fibre are thought to be tangled, therefore preventing the layers from slipping over one another. As a consequence, carbon fibre has the property of incredible strength and is unreactive, lightweight and resistant to stretching and compression. This fibre is finding increased application in items such as tennis rackets, golf clubs, bicycles, cars, and hip and knee ligament replacements where improved mechanical strength is required.

### Fullerenes

In the 1980s, a new allotrope of carbon was identified. This allotrope comprises a group of structures called fullerenes. Fullerenes of various shapes and sizes have since been made, including spherical fullerenes, and cylindrical fullerenes, which are called nanotubes.

One of the more stable fullerenes to be isolated is  $C_{60}$ , which has been given the name buckminsterfullerene after the noted American engineer R. Buckminster Fuller.  $C_{60}$  is often referred to as 'buckyball'. Buckyball molecules have a similar structure to the segments on a soccer ball. They consist of twelve five-membered or pentagon rings of carbon and twenty six-membered or hexagon rings of carbon arranged in a spherical shape as shown in Figure 5.13.

In a molecule of  $C_{60}$  each carbon atom is covalently bonded to three other carbon atoms in much the same way as in graphite. This leaves one delocalised electron for each carbon atom in the molecule. Buckminsterfullerene is a covalent molecular substance. It is a fine, black, crystalline powder, insoluble in water but soluble in non-polar solvents and stable at normal conditions; however, it is flammable.

Fullerenes are found in small amounts in soot and new ways of producing larger quantities are in the process of being developed. Investigations into the properties and possible uses of the new fullerenes are also progressing at a rapid pace. Examples of some possible future uses of the spherical fullerenes include as lubricants, in batteries, as superconductors when doped with potassium, as a trap for radioactive atoms used in radiotherapy, for mopping up harmful chemicals in the body, as possible molecular sieves that allow biological chemicals to flow through but not viruses, and as toner in photocopier machines to produce better resolution.

Tube-shaped fullerenes were discovered in 1991. These nanotubes or buckytubes can be pictured as a layer of graphite wrapped in a cylinder, as shown in Figure 5.14. They can exist as single-walled tubes, that is, one carbon atom thick, or multi-walled tubes. Nanotubes can also be extremely long, for example, a tube might contain 1 000 000 carbon atoms. Experiments show that nanotubes are incredibly tough, and that properties such as electrical conductivity vary with the particular geometry of the tube. The potential applications of nanotubes in areas widely ranging from medicine to construction are presently being investigated.

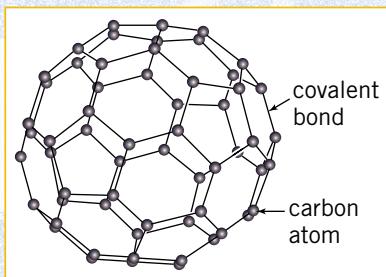


Figure 5.13 The structure of a  $C_{60}$  buckyball molecule.

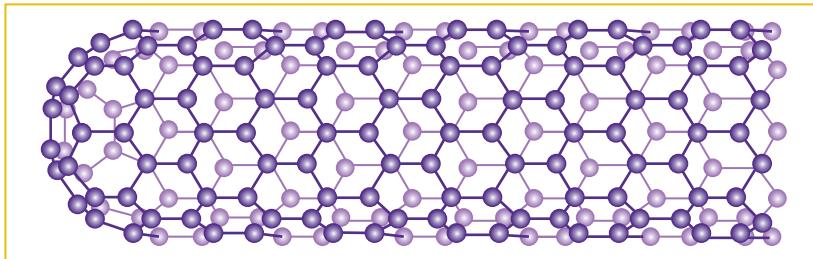


Figure 5.14 Representation of a nanotube.

Research into the fullerene family is still very much in its infancy and only the future will determine the full extent to which these substances with exceptional properties will be used.

### \* Review exercise 5.3

- 1 What are allotropes? Give examples of other elements apart from carbon that exist as allotropes.
- 2 Name the type, or types, of bonds broken when:
  - a writing with a black lead pencil
  - b diamond sublimes
  - c a sodium chloride crystal is ground to a powder
  - d wax melts
  - e diamond is cut to form an attractive shape.
- 3 a Explain the structural and bonding differences between diamond and methane,  $\text{CH}_4$ .  
b What differences and similarities in properties would be expected between these two substances?
- 4 Even though both diamond and graphite are composed of carbon atoms covalently bonded together, diamond is an insulator of electricity, but graphite is a conductor of electricity. Explain this difference in terms of their bonding and structure.
- 5 Graphite as a powder or mixed with a small amount of oil is commonly used as a lubricant on domestic items such as locks, food-handling equipment, electrical appliances and door hinges.
  - a List the properties of graphite that make it suitable for this use. Where possible, explain these properties in terms of graphite's bonding and structure.
  - b Describe any advantages a graphite lubricant might have compared with a hydrocarbon oil or grease, such as petroleum jelly.
- 6 a Explain, in terms of the bonding and structure, why coating the blade of a kitchen knife with a thin film of diamond would produce a 'better' knife.  
b ↗ RESEARCH If diamond is the hardest known natural material, how are rough diamonds shaped, or cut, to form the attractive gem shapes?
- 7 ↗ RESEARCH Carbon fibre is used in the construction of the chassis of racing cars. Explain in terms of its properties, and where possible its bonding and structure, why carbon fibre has been chosen for this use.

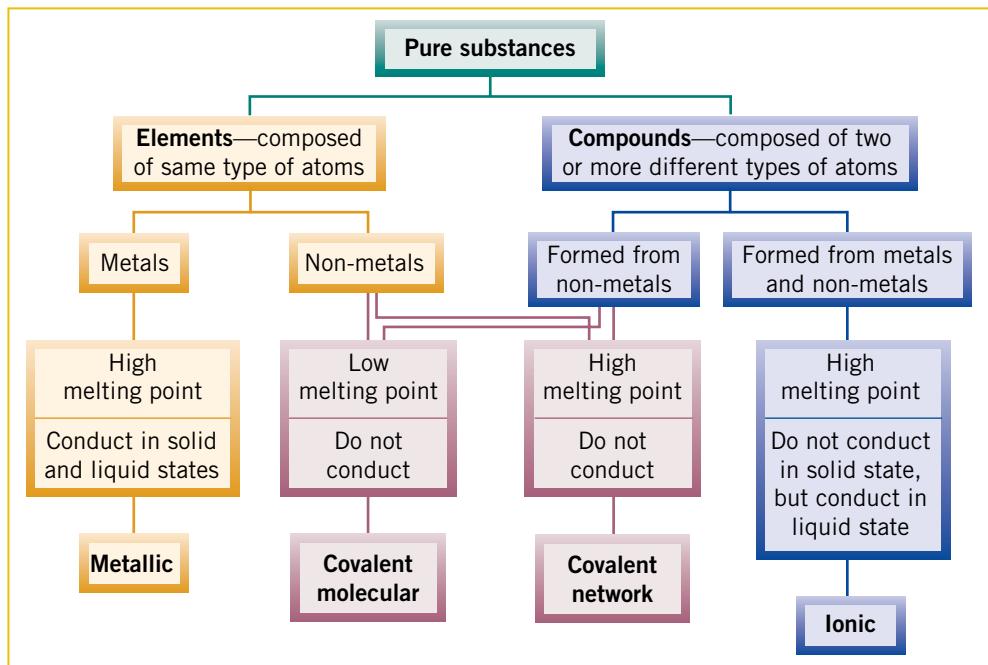
## 5.4 Comparing the four classes of substances

The structure, bonding and properties of the four classes of substances examined in Chapters 2, 3, 4 and 5 are compared in Table 5.4.

**TABLE 5.4 THE STRUCTURE, BONDING AND PROPERTIES OF THE FOUR CLASSES OF SOLID SUBSTANCES**

	Metallic	Ionic	Covalent molecular	Covalent network
<b>Examples</b>	Cu, Al, Zn, Ca, Na	NaCl, CaCO <sub>3</sub> , MgO, CuSO <sub>4</sub>	NH <sub>3</sub> , H <sub>2</sub> O, HCl, SO <sub>2</sub> , Ne, Cl <sub>2</sub> , CCl <sub>4</sub> , C <sub>2</sub> H <sub>5</sub> OH	diamond, Si, SiC, SiO <sub>2</sub> , graphite
<b>1 Types of elements forming the substance</b>	metal elements	formed between metal and non-metal elements	formed between non-metal elements	most are formed by non-metal elements of group 14
<b>2 Structure</b>				
a Constituent particles	positive ions and delocalised electrons	positive and negative ions	neutral molecules	atoms
b Arrangement of particles in solid	lattice of positive ions, sea of delocalised electrons around ions	lattice of positive and negative ions	molecules organised in a lattice, each molecule composed of atoms bonded together	atoms organised in a lattice
<b>3 Bonding</b>				
a Principal attractive forces between particles	electrostatic attraction between delocalised electrons and positive metal ions, called metallic bonding	electrostatic attraction between positive and negative ions, called ionic bonding	i within molecules, electrostatic attraction between shared electrons and nuclei, called covalent bonding ii weak bonds (intermolecular forces) between molecules	electrostatic attraction between shared electrons and nuclei, called covalent bonding
b Strength of bonds	strong	strong	covalent bonds are strong, intermolecular forces are weak	strong
<b>4 Properties</b>				
a Melting and boiling points	most are high	high	low	very high
b Electrical conductivity	good conductors in solid and liquid states	non-conductors in solid state, good conductors in liquid state and in aqueous solution	non-conductors in solid and liquid states	non-conductors in solid and liquid states (except graphite)
c Hardness and malleability	most are hard, malleable and ductile	hard and brittle	most are soft	very hard and brittle

A summary of the melting point and electrical conductivity properties of these four classes of substances can also be represented in a flow chart, shown in Figure 5.15.



**Figure 5.15** Summary of the patterns shown in the melting points and electrical conductivities of different types of elements and compounds.

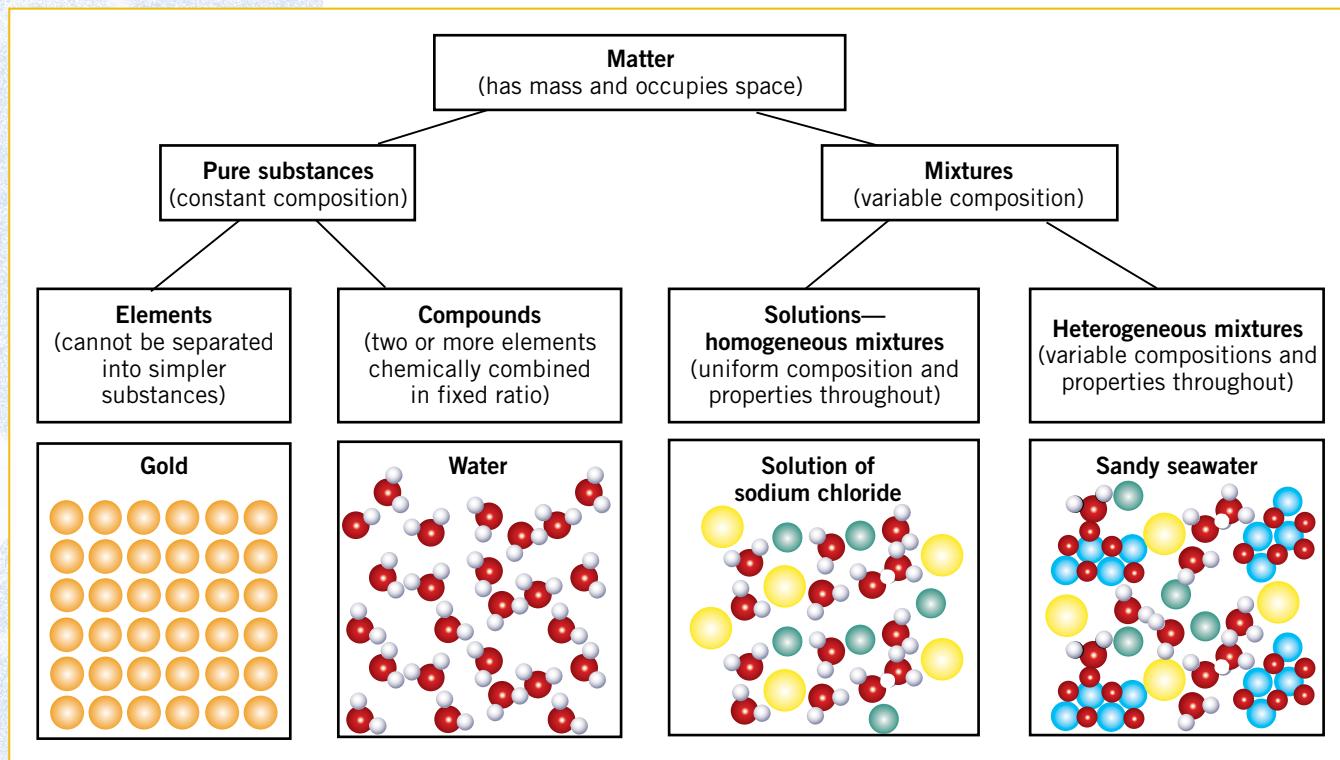
### \* Review exercise 5.4

- 1    a    Describe, generally, how the melting points change across the periodic table for the:  
 i    period 3 elements              ii    oxides of the period 3 elements.  
 b    Explain, in terms of their bonding and structure, these changes or trends in melting points of the:  
 i    period 3 elements              ii    oxides of the period 3 elements.
- 2    a    For each of the period 2 elements in the periodic table predict the formula of its chloride.  
 b    Classify each of these chlorides as an ionic, covalent molecular or covalent network compound  
 c    Draw electron dot diagrams for the chlorides.  
 d    Compare the electrical conductivity properties of the chlorides.
- 3    Crayons, like the ones used by children, are made of a mixture of paraffin wax and coloured pigments, which are normally ionic or covalent molecular compounds. Compare what is happening at the molecular level when writing with a black lead pencil, a crayon and a felt-tip pen.
- 4    Explain the following uses in terms of the properties and, where possible, the bonding and structure of the substances.
  - a    The handle of a saucepan is made from a carbon-based plastic polymer but the body of the saucepan is made from stainless steel.
  - b    The legs of a school chair are made from steel but the seat is made from high-density PVC.
  - c    The small decorative part of a ring is a diamond, but the band of the ring is 18-carat gold.
  - d    For a plug on the end of an electrical cord, the three prongs in the plug are made of steel but the body of the plug holding these prongs is made of a carbon-based polymer material.

## 5.5 Pure substances and mixtures

As explained in Chapter 1, chemists classify all matter into two broad categories—pure substances and mixtures. This classification scheme is shown in Figure 5.16.

The ionic compounds, covalent molecular elements and compounds, covalent network elements and compounds and metallic elements examined in Chapters 2 to 5 are all examples of pure substances.



**Figure 5.16 Classification of matter. A scheme for classifying matter showing, at an ‘atomic level’, an example of each type of substance.**

Pure substances consist of matter that is homogeneous and has a definite, fixed composition. Elements are pure substances that cannot be separated by chemical change into simpler substances. Carbon, oxygen and gold are examples of elements. Compounds are pure substances composed of two or more elements chemically combined in fixed proportions. Water, silicon dioxide and sodium chloride are examples of compounds.

Matter composed of two or more pure substances is described as a mixture. Mixtures can contain different proportions of the same component substances but pure substances, on the other hand, always have the same composition. Seawater is an example of a mixture because the amount of salt dissolved in the water can vary. However, water is a pure substance because it always contains hydrogen and oxygen in the same proportions, as shown in its formula of  $\text{H}_2\text{O}$ .

Mixtures can be homogeneous or heterogeneous. Homogeneous mixtures have uniform composition and properties throughout and are known as solutions. For example, when sugar is dissolved in water it forms a solution in which the sugar and water are uniformly mixed. Air is another homogeneous mixture because the gases are uniformly mixed.

Heterogeneous mixtures are not uniform in composition and properties throughout. For example, fruit cake is a heterogeneous mixture that consists of cake mix, fruit and possibly nuts. It is usually possible to identify these separate components in fruit cake by observation. Concrete, which consists of cement, sand and rock aggregate, is another example of a heterogeneous mixture.

### \* Review exercise 5.5

- 1 Identify each of the following as an element, a compound, a solution or a heterogeneous mixture:  

a magnesium	f carbon dioxide
b sodium chloride	g muddy sea water
c lemonade (without bubbles)	h clear sea water
d wood	i glucose ( $C_6H_{12}O_6$ )
e mercury	j air.
- 2 Place a tick or a cross in the appropriate columns for each substance shown in the table below:

TABLE 5.5

Substance	Mixture	Pure substance	Heterogeneous	Homogeneous	Solution	Element	Compound
nitrogen gas							
copper sulfate							
multigrain bread							
blood							
calcium							
raspberry cordial							
methane ( $CH_4$ )							

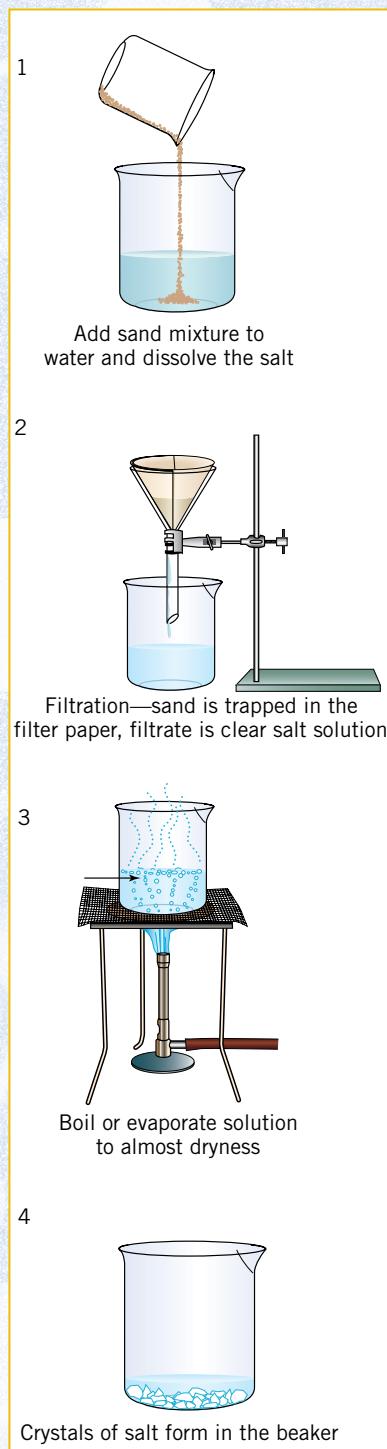
## 5.6 Obtaining pure substances

Very few elements or compounds occur naturally in the pure state. They are found mostly as mixtures. To make use of the properties discussed in Chapters 2–5, it is often necessary to use pure substances. Five commonly used techniques for separating the components of mixtures are filtration, crystallisation, solvent extraction, distillation and chromatography. In choosing a method to separate a particular mixture, the macroscopic properties, such as solubility and boiling points, of the components of the mixture need to be considered.

### Filtration

Filtration is used to separate components of a mixture on the basis of difference in particle size. Most often it is used to separate a liquid, or a solution, from an insoluble solid. A mixture of sand and salt (sodium chloride), for example, can be separated easily in this way. Salt is quite soluble in water but sand is insoluble.

If water is added to the mixture the salt will dissolve but not the sand. The sand grains, being larger than the ions from the dissolved salt, can then be filtered off from the solution using a filter paper, as shown in Figure 5.17. Evaporation of the filtrate will allow salt crystals to form. Separating tea-leaves during tea-making, separating dust from air during vacuuming and purification of water in fish tanks are further examples of filtration.



**Figure 5.17** Separation of sand and salt mixture by filtration and crystallisation.

### Crystallisation

The crystallisation technique depends on the components of a mixture having different solubilities in a selected liquid. For example, a mixture of salt and baking soda can be separated by dissolving in hot water and then cooling the resultant solution. While both substances are soluble in hot water, the baking soda is much less soluble in cold water and most of it will crystallise from the solution when it is cooled. This can then be filtered off leaving all the salt and a small amount of baking soda in solution.

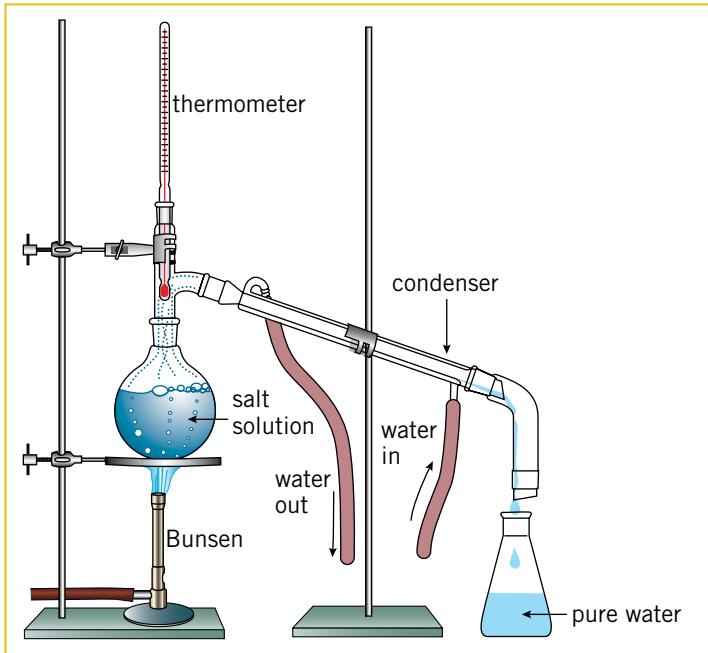
A similar technique, sometimes referred to as recrystallisation, is also often used to purify an impure substance. An appropriate solvent for this process is one in which the substance to be purified is highly soluble at high temperatures but not very soluble at low temperatures. The impure substance is dissolved in a minimum amount of this solvent at a high temperature, and then the hot mixture is filtered to remove any insoluble impurities. The filtrate is cooled, causing crystals of the pure substance to form. These can then be filtered off, leaving any soluble impurities in the filtrate. Because these impurities are normally present in only small amounts, even though they may be less soluble than the substance being purified, they will remain dissolved in the solution during the cooling stage. Sugar is purified using a recrystallisation process.

### Solvent extraction

Solvent extraction is a process in which substances are separated because of their differing solubilities in two immiscible liquids. For example, to separate a mixture of salt and a trace of iodine by this method, the mixture is first dissolved in water and the resulting solution added to a separating funnel, like the one shown in Figure 5.18. A non-polar solvent, such as hexane, is also added to the separating funnel, and the mixture shaken. When the mixture is allowed to settle, the salt will be dissolved in the lower aqueous layer and the iodine dissolved in the upper hexane layer. The two liquid layers can be separated by running the lower layer through the tap at the bottom of the separating funnel. Evaporation of the water will produce the pure salt. Solvent extraction is used industrially, for example, to separate the organic contaminants in paint wastes, wood-treatment wastes, pesticide/insecticide wastes and petroleum refinery oil wastes.

### Distillation

Distillation is used commonly in the purification of liquids. It is most effective when the components in a mixture have very different boiling points. When the mixture is heated, the component with the lowest boiling point boils off first. Its vapour is cooled in a condenser and collected as a pure liquid as shown in Figure 5.19. The components with higher boiling points remain in the distillation flask.



**Figure 5.19** A simple distillation procedure to obtain pure water from a salt solution.



**Figure 5.18** A student using a separating funnel to separate two immiscible liquids.

Pure water can be obtained from seawater using the process of distillation. Water boils at a much lower temperature than salt, leaving the salt in the distillation flask.

Distillation is used in the manufacture of spirits such as brandy and whisky. These spirits are obtained by the distillation of wines and fermented grains respectively. In the petroleum industry, repeated fractional distillation is used to separate the components of crude oil into petroleum, diesel fuel, kerosene, lubricating oil, waxes and bitumen. Fractional distillation is used to separate liquids with similar boiling points. The gas produced from the boiling mixture is allowed to pass through a column, the temperature of which gradually decreases along its length. Liquids with the higher boiling points condense in the column and run back into the boiling mixture. The vapour of the liquid with the lowest boiling point passes through the column and after cooling is collected as a liquid.

### Chromatography

Chromatography is particularly useful for separating components present in small quantities of mixtures. There are several different chromatographic techniques including column chromatography, paper chromatography and gas chromatography. In each of these techniques the mixture is passed over the surface of an inert substance such as alumina, silica or chromatography paper. The separation of the components in the mixture occurs because the components adhere, or cling, to the surface of the inert substance with different strengths.

Column chromatography can be used, for example, to separate the various pigments found in plant matter. A solution of the pigments is passed through a column packed with a porous gel, for example, alumina. The different pigments will pass through the column at different speeds depending on the strength with which they adhere to the alumina. The less strongly adsorbed pigments pass more quickly through the column compared to the more strongly adsorbed pigments. The pigments can be collected as they wash out of the column.



**Figure 5.20** The separation of several red/brown substances by column chromatography.

In paper chromatography a solution of the mixture is allowed to move up strips of chromatography paper. Chromatography paper is very much like filter paper. Again, the components in the mixture that adhere more strongly to the paper will move more slowly up the paper strip. This technique is sometimes used to detect food additives and dyes or particular drugs that are only present in small quantities in mixtures.

Gas chromatography is used to detect the components present in a gas mixture. The gas mixture is passed through a tube containing a particular solid such as carbon or silica. The different gaseous components present pass through the tube at different rates and can be detected as they emerge from the tube. The components of cigarette smoke are separated, and then identified, this way.

### \* Review exercise 5.6

- 1 How could the following separations be achieved?
  - a Water from muddy water.
  - b Water from a sugar solution.
  - c Alcohol from wine.
  - d Salt from a mixture of salt and charcoal.
- 2 What property of the substances allows the following separations to be successful?
  - a Water from vinegar by distillation.
  - b Solid salt from seawater, by evaporation.
  - c Oil from water, using a separating funnel.
  - d Sugar from sand by filtration.



## MAJOR IDEAS

- In covalent network substances, every atom is covalently bonded to other atoms, forming a giant network lattice. No separate molecules can be distinguished.
- The properties of covalent network substances are listed and explained in Table 5.6.

TABLE 5.6

Property	Explanation
very high melting and boiling points	strong covalent bonding extending throughout the lattice
non-conductors of electricity in the solid and liquid states	electrons localised (except in graphite) in covalent bonds
hard and brittle	atoms strongly bonded, distortion breaks covalent bonds

- The structure, bonding and properties of the four classes of substances are summarised in Table 5.4.
- Mixtures can be separated by the following processes:
  - Filtration, crystallisation and solvent extraction*—depend on the components having different solubilities.
  - Distillation*—depends on the components having different boiling points.
  - Chromatography*—depends on the components adhering with different strengths to an inert substance when the mixture is passed over the surface of the substance.

## QUESTIONS

- Explain the following uses in terms of the structure and bonding of the substances:
  - Diamond is used as an edge on drill bits.
  - Graphite is used as a lubricant in engines that reach high temperatures.
  - Sand (silicon dioxide) is used to make moulds for molten metal.
  - Silicon carbide is used to make grinding wheels that can be used to sharpen tools.
- Toner is used to produce the images in photocopiers and laser printers. The toner particles comprise powdered graphite blended with a covalent molecular polymer. This polymer melts on heating, binding it, together with the black graphite, to the paper, as shown in Figure 5.21. Why is a blend of graphite with a polymer used as the toner, rather than just graphite? Explain your answer in terms of the bonding and structure of graphite and the polymer.

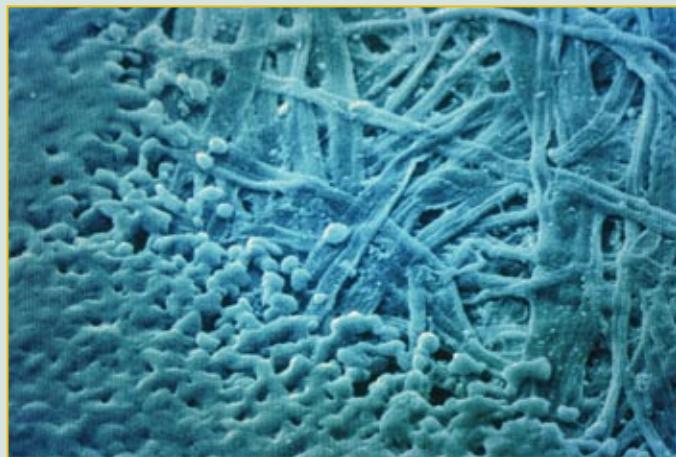


Figure 5.21 Coloured scanning electron micrograph showing part of a character made by a laser printer on a piece of paper. The fibres of the paper are seen in the upper right of the photo, the melted toner (containing the graphite) used to create the character is seen in the lower left. Magnification: approx.  $\times 200$ .

- What is a molecule?
- Each year the journal *Science* selects a ‘Molecule of the Year’. In 1990, diamond was declared the ‘Molecule of the Year’ due to its ability to be made into thin films. Does this title make sense for diamond, based on the definition of the word ‘molecule’ given in part a? Explain your answer.
- In 1991, the buckyball was given the title ‘Molecule of the Year’. Explain if this was an accurate title for the buckyball.
- Aluminium is produced by passing an electric current through a molten mixture containing aluminium oxide at a temperature of about  $1000^{\circ}\text{C}$ . A diagram of a typical electrolytic cell used for this process is shown in Figure 5.22.

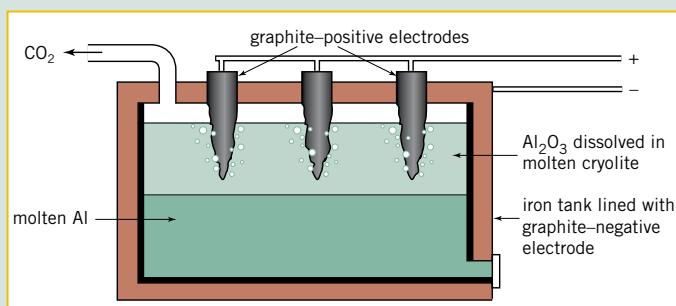


Figure 5.22 Electrolysis cell used for the production of aluminium.

In this cell, graphite is used as both the positive and negative electrodes. The electrodes are the parts of the cell through which the electricity flows to reach the liquid or solution in the cell. Explain in terms of its bonding and structure why graphite can be used as the electrode material in the aluminium-producing cell.

- 5 The melting point properties of three compounds with covalent bonds between some or all of their atoms are given in the following table.

Compound	Melting point (°C)
Silicon carbide	2986 (decomposes)
Carbon monoxide	-205
Sodium carbonate	851

- a Explain why these compounds have very different melting points, in terms of their bonding and structure.
  - b Predict and compare the electrical conductivity properties of these compounds.
  - c Draw electron dot representations of these three compounds.
- 6 On the Mohs scale the hardness of three substances are given as follows:
- quartz 7 calcium fluoride 4 magnesium 2.5
- a For each substance, predict whether or not it could be scratched by the other two.
  - b Explain your predictions in terms of the structure and bonding of the three substances.
- 7 Compare the three different types of strong bonds—ionic, metallic and covalent—in terms of the particles being held together by the bonds and the forces ‘creating the bond’.
- 8 What type or types of bonds are disrupted in the following processes? Choose from metallic, ionic, covalent and intermolecular bonds.
- a Cutting a piece of magnesium.
  - b Crushing ice.
  - c Dissolving sugar in water.
  - d Dissolving sodium chloride in water.
  - e Grinding a silicon dioxide crystal to a powder.
  - f Burning methane,  $\text{CH}_4$ , to form carbon dioxide and water.

- 9 Consider the following common substances at room temperature:

marble ( $\text{CaCO}_3$ )	brass (alloy of Zn, Cu)
ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ )	graphite.

Using circles to represent atoms, draw representations of the particles present in these substances:

- a showing their approximate arrangement
- b labelling the bonds present, identifying whether they are weak or strong bonds.

- 10 Classify the following solid substances as ionic, covalent molecular, covalent network or metallic.

- a A lattice consisting of atoms covalently bonded to neighbouring atoms.
- b A solid only at extremely low temperatures.
- c A good conductor of heat and electricity.
- d A good conductor of electricity only in the molten state.
- e A lattice consisting of positive ions sharing electrons with neighbouring positive ions.
- f Ammonium nitrate.
- g Iodine.
- h Silicon.
- i Stainless steel.

- 11 Consider the substances potassium bromide, gold, silicon carbide and graphite.

- a Which of these solid substances will conduct electricity?
- b Which of these substances will conduct electricity in the liquid state but not the solid state?
- c How does the ‘mode’ of electrical conduction in molten potassium bromide differ from that in solid gold?

- 12 The properties of six substances A–F are given in Table 5.7.

TABLE 5.7

Substance	Melting point (°C)	Boiling point (°C)	Electrical conductivity	
			In solid state	In liquid state
A	2986 (decomposes)	–	not conduct	not conduct
B	30	2403	conducts	conducts
C	approx. 190	decomposes	not conduct	not conduct
D	734	1435	not conduct	conducts
E	–114	78	not conduct	not conduct
F	1495	2870	conducts	conducts

- a Classify each substance as a metal, ionic substance, covalent network substance or covalent molecular substance.  
 b Which substance would be suitable for manufacturing:  
   i electrical wiring in an engine that can reach temperatures of approximately 500°C?  
   ii insulating handles for pliers for electricians, where the handles are to be shaped by pouring the liquid substance into a mould?  
 c By considering the composition of each of the substances, predict the relative melting point and electrical conductivity properties to complete the gaps in Table 5.8. Choose from the alternatives given in the heading for each column.

TABLE 5.8

Name of substance	Formula	Melting point (very high, relatively high or low?)	Conductivity (conductor or non-conductor?)	
			In solid state	In liquid state
Sulfur dioxide	SO <sub>2</sub>			
Potassium fluoride	KF			
Nickel	Ni			
Calcium phosphate	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>			
Silicon dioxide (sand)	SiO <sub>2</sub>			
Octane	C <sub>8</sub> H <sub>18</sub>			
Stainless steel	mixture of Fe, C, Cr and Ni			

- 14 The element iridium has the following properties:

Density (g mL <sup>-1</sup> )	Melting point (°C)	Boiling point (°C)
22.5	2450	4500

- a Chemists often classify solids into four major groups: metallic, ionic, covalent molecular and covalent network. From the properties given above, it can be inferred that iridium is one of two different types of solids. What are these two types of solids?  
 b What further test could be performed in order to make a definite decision about the type of solid?

- c The position of iridium in the periodic table gives an indication of its solid type. What type of solid would you expect iridium to be, based on its position on the periodic table?  
 d A bar made of a mixture of platinum and iridium, whose length was defined as the standard metre, was kept in Paris between the years of 1889 and 1960. (This bar has since been replaced by a standard for length based on the wavelength of krypton-86 radiation.) What property or properties is iridium likely to possess if it could be used as one of the substances in this ‘standard’ bar?

## 15 Building with network lattices

Construction with or maintaining timber in the home may involve the application of covalent network substances for a particular purpose. If a piece of timber needs to be cut to a certain size a pencil might be used to mark where the saw cut needs to be made. The pencil is made from graphite and leaves some of the carbon on the timber.

In order to smooth the timber prior to painting or varnishing it might be necessary to use sandpaper or carborundum paper. Sandpaper has silicon dioxide (silica) grains glued onto the paper, while carborundum uses silicon carbide rather than silica to act as the abrasive.

If it is stonework rather than timber that needs to be cut then saw blades tipped with diamond may be used.

In terms of their bonding and structure, explain why each of the covalent network substances, mentioned in the description given above, is used for the particular purpose.

## 16 Separating a mixture

The following six substances have been mixed together. The approximate amounts of each substance in this mixture is also given.

water (500 mL)  
cyclohexane, C<sub>6</sub>H<sub>12</sub> (500 mL)  
naphthalene, C<sub>10</sub>H<sub>8</sub> (15 g)  
sodium chloride (20 g)  
sand, SiO<sub>2</sub> (40 g)  
iron filings (30 g)

Some physical properties of cyclohexane and naphthalene are shown in the following table.

	Cyclohexane	Naphthalene
Melting point (°C)	6.6	80.3 (sublimes when gently heated)
Boiling point (°C)	80.7	217.9
Density at 25°C (g mL <sup>-1</sup> )	0.774	1.18
Solubility in water	not soluble	not soluble
Solubility in cyclohexane	–	soluble

- a Describe, using a labelled sketch, what this mixture of the six substances might look like.
- b **RESEARCH** Before any experiment is undertaken, the dangers involved in handling the chemicals needs to be assessed. Consult the Materials Safety Data sheets for cyclohexane and naphthalene and summarise the dangers involved in using these chemicals in a school laboratory.
- c i Describe a safe experimental method that could be used to separate these six substances, so that a pure sample of each of the substances is obtained.  
ii Include any necessary safety warnings in this method.  
iii Include diagrams showing the equipment to be used.
- d Explain, where possible in terms of the properties, bonding and structure of the substances, why your suggested method should be successful in obtaining a pure sample of each substance in the mixture.
- 17 **RESEARCH** Choose a commonly used item or appliance that is made up of at least three of the following different types of substances: ionic, metallic, covalent molecular and covalent network.
- a Name and, if possible, give the formula of the example of each type of substance present in the item or appliance.
- b Sketch a diagram or plan of the item or appliance, showing where each of these substances are positioned.
- c List the properties of each of these substances that are relevant to its use in the item or appliance.
- d If possible, explain these properties in terms of the bonding and structure of the substance.
- e Choose one or two of the substances and draw a flowchart briefly describing how they were produced, starting from the original material obtained from the Earth's crust, atmosphere or hydrosphere.



# 6

# Introducing the mole

**BY THE END OF THIS CHAPTER YOU SHOULD BE ABLE TO:**

- explain the terms relative atomic mass, relative molecular mass and molar mass
- calculate the relative atomic mass of an element
- perform calculations related to number of particles and amount of substance in mole or gram
- calculate the amount of ions or atoms, in gram or mole, present in a given amount of a substance
- calculate the percentage composition of the elements in a compound.

## 6.1 Masses of atoms

Chemistry is the study of substances and their reactions. To obtain more information about chemical reactions and chemical compounds it is essential that chemists have a means of counting the particles involved in reactions, or present in the compounds. If the relative masses of particles are known then chemists can count particles by weighing the chemicals.

Virtually all of an atom's mass is contained in its nucleus. Since the nucleus consists of protons and neutrons, which have almost identical masses, the mass of an atom will depend mainly on the number of protons and neutrons in the nucleus. Hydrogen atoms, with just 1 proton in the nucleus, are the lightest atoms. Helium atoms, with 2 protons and 2 neutrons in the nucleus, have a mass about four times that of hydrogen atoms. Similarly, carbon atoms with 6 protons and 6 neutrons in the nucleus are about twelve times heavier than hydrogen atoms.

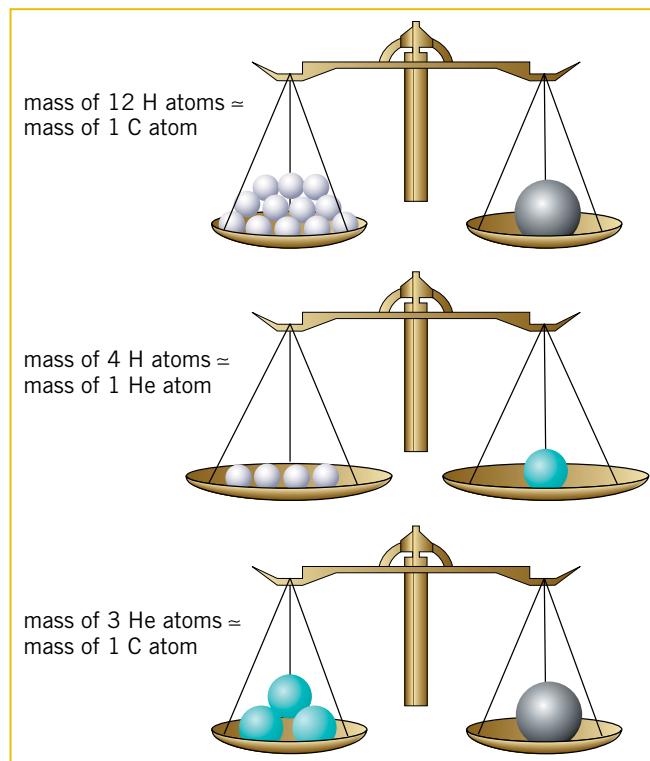


Figure 6.1 Relative masses of different atoms.

The isotopes of an element have different masses as they contain different numbers of neutrons in the nucleus. Carbon-12, carbon-13 and carbon-14 atoms contain 6, 7 and 8 neutrons respectively. Atoms of these isotopes are about twelve, thirteen and fourteen times, respectively, the mass of a hydrogen atom.

The actual mass of an atom is exceedingly small. Even the heaviest naturally occurring atom, an isotope of uranium with 92 protons and 146 neutrons, only has a mass of approximately  $4 \times 10^{-22}$  or 0.0000000000000000000004 g, while an atom of the isotope carbon-12 has a mass of  $1.99 \times 10^{-23}$  g. Because the masses of atoms are too small for practical purposes, chemists use the relative masses of atoms in calculations. In order to determine the relative masses of atoms, it is necessary to select a standard atom to which the masses of other atoms can be compared. In 1961, the International Union of Pure and Applied Chemistry (IUPAC), chose carbon-12 ( $^{12}\text{C}$ ), the isotope of carbon that has 6 protons and 6

neutrons in its nucleus, to be the standard. Carbon-12 was assigned a relative atomic mass, or atomic weight, of exactly 12. The relative atomic masses of other atoms are then based on this reference mass. For example, an atom will have a relative atomic mass of 24 if it has a mass twice that of a carbon-12 atom.

The relative atomic mass,  $A_r$ , of an atom is defined as the mass of the atom compared with  $\frac{1}{12}$ th of the mass of an atom of carbon-12. It can also be referred to as ‘atomic weight’. The relative atomic masses of the isotopes of some common elements are shown in Table 6.1.

**TABLE 6.1 RELATIVE ATOMIC MASSES OF ISOTOPES OF SOME COMMON ELEMENTS**

Element	Isotope	Atomic number	Mass number	Relative atomic mass	Percentage abundance	Mass in grams of atom
Hydrogen	$^1\text{H}$	1	1	1.00783	99.989	$1.67 \times 10^{-24}$
	$^2\text{H}$	1	2	2.01410	0.0115	$3.34 \times 10^{-24}$
	$^3\text{H}$	1	3	3.01605	0.0001	$5.01 \times 10^{-24}$
Carbon	$^{12}\text{C}$	6	12	12 exactly	98.93	$1.99 \times 10^{-23}$
	$^{13}\text{C}$	6	13	13.00335	1.07	$2.16 \times 10^{-23}$
	$^{14}\text{C}$	6	14	14.00324	approx. $10^{-10}$	$2.33 \times 10^{-23}$
Magnesium	$^{24}\text{Mg}$	12	24	23.98504	78.99	$3.98 \times 10^{-23}$
	$^{25}\text{Mg}$	12	25	24.98584	10.00	$4.15 \times 10^{-23}$
	$^{26}\text{Mg}$	12	26	25.98260	11.01	$4.31 \times 10^{-23}$
Copper	$^{63}\text{Cu}$	29	63	62.92960	69.15	$1.04 \times 10^{-22}$
	$^{65}\text{Cu}$	29	65	64.92780	30.85	$1.08 \times 10^{-22}$

As can be seen from the data given in Table 6.1, because the relative masses of a proton and a neutron are approximately 1, the relative atomic mass of an isotope is approximately equal to its mass number. Also, the relative atomic masses of isotopes are very close to whole number values.

Relative atomic masses are usually thought of as not having a unit but often they are designated as atomic mass units or unified atomic mass units, u. For example, the relative atomic mass of  $^1\text{H}$  can be written as 1.00783, 1.00783 u or 1.00783 atomic mass units. These units are essentially meaningless and serve only as a reference to the arbitrary atomic mass scale.

According to the IUPAC recommendations:

- the relative atomic mass of an atom is defined as the ratio of the mass of the atom to the unified atomic mass unit
- the unified atomic mass unit, u, is the non-SI unit of mass defined as one twelfth of the mass of a carbon-12 atom, where  

$$u \approx 1.6605402 \times 10^{-24} \text{ g.}$$

### \* Review exercise 6.1

- The carbon-12 isotope is assigned a mass of 12 exactly. Use this information to explain why the atomic mass of a proton and a neutron will be approximately 1 on this scale.
- In a very small sample of 1000 atoms of magnesium, approximately how many atoms will have a relative atomic mass of 24?
- a Why is the mass of an atom of magnesium-24 approximately twice the mass of a carbon-12 atom?  
continued

### Review exercise 6.1 — *continued*

- b If the standard carbon-12 isotope had been assigned a value of exactly 100 instead of exactly 12, what would the approximate relative atomic mass of the magnesium-24 isotope be on this different scale?
- 4 The relative atomic mass of the isotope nickel-60 is approximately 60.
- How much heavier is an atom of nickel-60 compared with an atom of carbon-12?
  - How much heavier would two atoms of nickel-60 be compared with two atoms of carbon-12?
  - How much heavier would a sample containing 100 atoms of nickel-60 be compared with a sample containing 100 atoms of carbon-12?
  - If a sample of  $1 \times 10^{23}$  atoms of nickel-60 has a mass of 10 g, how many atoms of carbon-12 would be in a sample of carbon-12 that has a mass of 2 g? Explain your reasoning.

## 6.2 Relative atomic masses of elements

Naturally occurring elements generally consist of a mixture of two or more isotopes each with a different relative atomic mass. The percentage abundances of these isotopes of an element are usually constant within the precision of normal chemical experiments. For example, naturally occurring copper consists of 69.15% of an isotope with a relative atomic mass of 62.93 and 30.85% of a second isotope with a relative atomic mass of 64.93. The relative atomic mass of an element is an average of the relative atomic masses of all the naturally occurring isotopes present in the element, taking into account their percentage abundance. This leads to the definition:

The **relative atomic mass**,  $A_r$ , of an element is the weighted average of the relative atomic masses of the isotopes compared to  $\frac{1}{12}$ th the mass of an atom of carbon-12.

The relative atomic masses of some common elements are given in Table 6.2, and a complete list of the relative atomic masses of all the elements is given in the periodic table on the reverse side of the front cover of this textbook.

TABLE 6.2 RELATIVE ATOMIC MASSES ( $A_r$ ) OF SOME COMMON ELEMENTS

Element	Symbol	Relative atomic mass*	Element	Symbol	Relative atomic mass*
Aluminium	Al	26.98	Lead	Pb	207.2
Barium	Ba	137.3	Magnesium	Mg	24.31
Boron	B	10.81	Mercury	Hg	200.6
Bromine	Br	79.90	Nitrogen	N	14.01
Calcium	Ca	40.08	Oxygen	O	16.00
Carbon	C	12.01	Phosphorus	P	30.97
Chlorine	Cl	35.45	Potassium	K	39.10
Chromium	Cr	52.00	Silicon	Si	28.09
Copper	Cu	63.55	Silver	Ag	107.9
Gold	Au	197.0	Sodium	Na	22.99
Helium	He	4.003	Sulfur	S	32.06
Hydrogen	H	1.008	Tin	Sn	118.7
Iodine	I	126.9	Zinc	Zn	65.38
Iron	Fe	55.85			

\* Also known as the atomic weight of the element.

Some relative atomic masses of elements are almost whole numbers but others are not close to a whole number value. For example, the relative atomic mass of hydrogen is 1.008; however, magnesium has a relative atomic mass of 24.31. This occurs because some elements are only composed of one isotope or one of their isotopes is by far the most abundant, but other elements are composed of two or more isotopes present in significant proportions.

The relative atomic mass of a naturally occurring element can be calculated from the relative atomic masses and percentage abundances of its isotopes using the following equation:

$$\text{relative atomic mass of element} = \frac{\text{sum of (percentage abundance} \times \text{relative atomic mass of each isotope)}}{100}$$

#### → Example 6.1

Naturally occurring copper consists of two isotopes with relative atomic masses of 62.93 and 64.93. If the percentage abundance of the lighter isotope is 69.15%, what is the relative atomic mass of naturally occurring copper?

#### → Solution

$$\text{percentage abundance of heavier isotope} = 100 - 69.15 = 30.85\%$$

$$\begin{aligned}\text{relative atomic mass of copper} &= 69.15\% \text{ of } 62.93 + 30.85\% \text{ of } 64.93 \\ &= \frac{(69.15 \times 62.93) + (30.85 \times 64.93)}{100} \\ &= \mathbf{63.55}\end{aligned}$$

#### \* Review exercise 6.2

- 1 Magnesium is a silvery-white, light-weight metal that is often used, when alloyed with other metals, to produce useful items such as automobile and aircraft parts, power tools and racing bikes. Calculate the relative atomic mass of magnesium from the following data:

Isotope	Abundance (%)	Relative atomic mass
$^{24}\text{Mg}$	78.99	23.99
$^{25}\text{Mg}$	10.00	24.99
$^{26}\text{Mg}$	11.01	25.98

- 2 Fluorine occurs as only one isotope in nature and has a relative atomic mass of 19.00. If the relative atomic mass scale was defined relative to  $\frac{1}{19}$ th the mass of a fluorine-19 atom, what effect would this have on the relative atomic masses of the elements?

## 6.3 Relative molecular and formula mass

Whereas the relative atomic mass describes the mass of an atom, the relative molecular mass describes the mass of a molecule. That is:

The **relative molecular mass** ( $M_r$ ) of a substance is the mass of a molecule of that substance compared to  $\frac{1}{12}$ th the mass of an atom of carbon-12.

The symbol used for relative molecular mass is  $M_r$ , and it can be shown with no units or the atomic mass unit, u. The relative molecular mass of a substance is calculated by adding the relative atomic masses of the atoms shown in the molecular formula of the substance.

### → Example 6.2

Calculate the relative molecular mass of sucrose, table sugar, which has a molecular formula of  $C_{12}H_{22}O_{11}$ .

### → Solution

$$\begin{aligned}\text{relative molecular mass of sucrose} &= 12 \times A_r(C) + 22 \times A_r(H) + 11 \times A_r(O) \\ &= (12 \times 12.01) + (22 \times 1.008) + (11 \times 16.00) \\ &= \mathbf{342.3}\end{aligned}$$



Ionic compounds and covalent network compounds are not composed of discrete molecules and so the term 'relative molecular mass' is not appropriate for these compounds. Ionic compounds exist as a lattice of positive and negative ions and covalent network compounds as a covalently bonded lattice of atoms. Chemical formulas are still used to represent these compounds, but instead of showing the atoms present in a discrete molecule, the chemical formulas of ionic and network compounds show the atoms present in the compound, in their simplest ratio. For example, aluminium oxide is an ionic compound and its formula of  $Al_2O_3$  shows that the aluminium ions and oxide ions are present in the ratio of 2:3 respectively.

Sometimes when referring to the relative atomic masses of the atoms in ionic and covalent network compounds, the term 'relative formula mass' is used rather than relative molecular mass. The relative formula mass of a compound is calculated in the same way as a relative molecular mass, that is, by adding together the relative atomic masses of the atoms shown in the chemical formula of the compound. The symbol used to represent the relative formula mass is the same as that used for the relative molecular mass, that is,  $M_r$ .

### → Example 6.3

Calculate the relative formula mass of washing soda, sodium carbonate-10-water.

### → Solution

$$\begin{aligned}M_r(Na_2CO_3 \cdot 10H_2O) &= 2 \times A_r(Na) + 1 \times A_r(C) + 3 \times A_r(O) + 20 \times A_r(H) + 10 \times A_r(O) \\ &= (2 \times 22.99) + (1 \times 12.01) + (3 \times 16.00) + (20 \times 1.008) + (10 \times 16.00) \\ &= \mathbf{286.2}\end{aligned}$$

### \* Review exercise 6.3

- 1 Calculate the relative molecular mass of each of the following covalent molecular substances:
  - a carbon dioxide
  - b nitrogen gas, N<sub>2</sub>
  - c ethanol, C<sub>2</sub>H<sub>5</sub>OH, the alcohol present in alcoholic drinks
  - d cholesterol, C<sub>27</sub>H<sub>46</sub>O.
- 2 Calculate the relative formula mass of the following compounds:
  - a silicon dioxide, a naturally occurring covalent network substance commonly called sand
  - b hydrated copper sulfate, CuSO<sub>4</sub>·5H<sub>2</sub>O, a blue-coloured salt often used in school laboratories
  - c calcium phosphate, an ionic compound that is used to prevent and treat calcium deficiencies.
- 3 A gas in a sample of polluted city air is found to have a relative molecular mass of 44. Which of the following gases could it be: N<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>, NO<sub>2</sub>, O<sub>3</sub>?

## 6.4 The mole and number of particles

The mole is a chemist's measure of the amount of substance and it is defined according to the number of particles the substance contains.

One **mole** (mol) is the amount of substance that contains the same number of particles, or entities, as there are atoms in exactly 12 g of carbon-12.

Experiment shows that the number of atoms in 12 g or 1 mole of carbon-12 is approximately  $6.022 \times 10^{23}$ . This means that one mole of any substance contains  $6.022 \times 10^{23}$  particles of that substance. This number is called the Avogadro constant ( $N_A$ ), named after the Italian scientist Amedeo Avogadro.

The Avogadro constant is difficult to comprehend. It is so large that even all the sand grains in the beaches around Australia do not make a mole of sand. However, it is a unit of measurement that represents the amount of substance or a specific number of things in the same way as the unit 'dozen' represents 12 objects, 'gross' represents 144 objects and 'ream' represents 500 pages of paper.



Figure 6.2 This is a real mole, but it is not a chemist's mole.



Figure 6.3 A mole of rice grains would cover Australia to a depth of about 1 km.

When quoting the amount of a substance in mole, the particles being counted should be identified as atoms, molecules, formula units or ions.

For example:

1 mole of aluminium consists of  $6.022 \times 10^{23}$  atoms of aluminium

1 mole of carbon dioxide,  $\text{CO}_2$ , consists of  $6.022 \times 10^{23}$  molecules of carbon dioxide

1 mole of calcium chloride,  $\text{CaCl}_2$ , consists of  $6.022 \times 10^{23}$  formula units of calcium chloride

1 mole of sodium ions,  $\text{Na}^+$ , consists of  $6.022 \times 10^{23}$  sodium ions.

The term ‘formula unit’ is used for ionic compounds and for some network substances, such as  $\text{SiO}_2$ , which do not exist as simple molecules. The formula unit of a substance is the group of atoms shown in the chemical formula.



**Figure 6.4** One mole of some substances. From left to right: tin, magnesium, iodine and copper. Each of these samples contains  $6.022 \times 10^{23}$  atoms.

The mathematical relationship between the amount of substance in mole,  $n$ , and the number of particles,  $N$ , of the substance is given by:

$$\begin{aligned}\text{amount of a substance in mole} &= \frac{\text{number of particles of the substance}}{\text{number of particles in 1 mole}} \\ n &= \frac{N}{6.022 \times 10^{23}}\end{aligned}$$

#### → Example 6.4

A small ice block contains  $2.70 \times 10^{23}$  molecules of water,  $\text{H}_2\text{O}$ . How many mole of water molecules does this represent?

#### → Solution

$$\begin{aligned}\text{amount of H}_2\text{O (in mole)} &= \frac{\text{number of molecules of H}_2\text{O}}{6.022 \times 10^{23}} \\ &= \frac{2.70 \times 10^{23}}{6.022 \times 10^{23}} = 0.448 \text{ mol of H}_2\text{O molecules}\end{aligned}$$

### → Example 6.5

An aluminium drink can is made from approximately 0.55 mole of aluminium.

How many atoms of aluminium is this?

### → Solution

$$\text{mol (Al)} = \frac{\text{number of atoms of Al}}{6.022 \times 10^{23}}$$

$$0.55 = \frac{\text{number of atoms of Al}}{6.022 \times 10^{23}}$$

$$\text{number of atoms of Al} = 0.55 \times 6.022 \times 10^{23} = 3.3 \times 10^{23}$$

Note: The answer is quoted to two significant figures because the mole figure (the least accurate measurement) given in the question was only quoted to two significant figures.

### \* Review exercise 6.4

- 1 If there are  $4.13 \times 10^{23}$  molecules of acetic acid in a bottle of vinegar, how many mole of acetic acid molecules does this represent?
- 2 A balloon contains 1.20 mole of helium. How many atoms of helium are present?
- 3 The World Health Organisation has set a limit for the sulfur dioxide (the main cause of 'acid' rain) content of clean air of  $3.10 \times 10^{-6}$  mole of  $\text{SO}_2$  per cubic metre. How many molecules of  $\text{SO}_2$  would be present per cubic metre of this air?
- 4 The oceans of the Earth are estimated to contain  $1.36 \times 10^{18} \text{ m}^3$  of water. If 5.00 mole of sugar molecules was dissolved in the Pacific Ocean and they became uniformly distributed throughout all the oceans, what would be the average number of sugar molecules in a  $1 \text{ m}^3$  sample of seawater?

## 6.5 The mole and mass

It is not possible for chemists to count atoms, ions and molecules directly. However, the number of particles can be counted by weighing in the same way as a bank teller counts coins by weighing. For example, it is quicker for a bank teller to count a large number of 5-cent coins by weighing them and comparing their mass with that of a standard 100-coin roll rather than counting the large number of coins one by one.

As defined in the previous section, 1 mole of carbon-12 atoms has a mass of 12 g, or expressed in an alternative way,  $6.022 \times 10^{23}$  atoms of carbon-12 have a mass of 12 g. Using this information and the relative atomic masses of other atoms, the mass of 1 mole of other substances such as magnesium can be inferred.



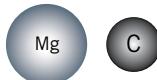
Figure 6.5 One mole of carbon has a mass of 12 g.

For example,

A **magnesium-24 atom** has a relative atomic mass of **24** (quoted to two significant figures).

A **carbon-12 atom** has a relative atomic mass of **12**.

This means that the mass of a magnesium-24 atom is **twice** the mass of a carbon-12 atom.



It therefore follows that:

100 magnesium-24 atoms will be twice as heavy as 100 carbon-12 atoms  
or

$6.022 \times 10^{23}$  atoms of magnesium-24 will have a mass twice that of  $6.022 \times 10^{23}$  atoms of carbon-12.

Because the mass of  $6.022 \times 10^{23}$  or 1 mole of carbon-12 atoms is 12 g  
then

the mass of  $6.022 \times 10^{23}$  or 1 mole of magnesium-24 atoms will be  
 $2 \times 12 = 24$  g.

That is, the mass of 1 mole of magnesium-24 atoms is equivalent to its relative atomic mass expressed in grams.

The same argument can be applied to all elements and compounds.

That is:

The mass of 1 mole of any substance is equal to its relative atomic mass, relative molecular mass or relative formula mass, expressed in grams.

For example:

the mass of 1 mole of calcium, Ca, is 40.08 g

the mass of 1 mole of carbon dioxide, CO<sub>2</sub>, is  $12.01 + (2 \times 16.00) = 44.01$  g

the mass of 1 mole of potassium chloride, KCl, is  $39.10 + 35.45 = 74.55$  g

(where the atomic masses of Ca = 40.08, C = 12.01, O = 16.00, K = 39.10, Cl = 35.45).

The mass of one mole of a substance is known as the **molar mass** (M) of the substance. As explained in Section 6.1, relative atomic mass, relative molecular mass and relative formula mass have no units, but molar mass has the unit of g mol<sup>-1</sup>. For example, the relative formula mass of potassium chloride, KCl, is 74.55, and its molar mass is 74.55 g mol<sup>-1</sup>.

The relationship between the amount of a substance in mole (n), its mass (m) and molar mass (M) is given by:

$$\text{amount of the substance in mole} = \frac{\text{mass of the substance}}{\text{molar mass of the substance}}$$

$$\text{or} \qquad n = \frac{m}{M}$$

where n is the amount of substance in mole (mol)

m is the mass (g) of the substance

M is the molar mass (g mol<sup>-1</sup>) of the substance.

→ **Example 6.6**

In a 1 L bottle of methylated spirits there is 780 g of ethanol,  $\text{C}_2\text{H}_5\text{OH}$ . How many mole of ethanol molecules are in the bottle?

→ **Solution**

$$\text{mol of } \text{C}_2\text{H}_5\text{OH} = \frac{\text{mass of } \text{C}_2\text{H}_5\text{OH}}{\text{molar mass of } \text{C}_2\text{H}_5\text{OH}}$$

$$\begin{aligned}\text{molar mass of } \text{C}_2\text{H}_5\text{OH} &= (2 \times 12.01) + (6 \times 1.008) + (1 \times 16.00) \\ &= 46.068 \text{ g mol}^{-1}\end{aligned}$$

$$\text{mol of } \text{C}_2\text{H}_5\text{OH} = \frac{780}{46.068} = \mathbf{16.9 \text{ mol}}$$

→ **Example 6.7**

A sample of seawater contains 0.0392 mol of sodium chloride dissolved in it. What is the mass of this amount of sodium chloride?

→ **Solution**

$$\text{mol of NaCl} = \frac{\text{mass of NaCl}}{\text{molar mass of NaCl}}$$

$$\text{molar mass of NaCl} = 22.99 + 35.45 = 58.44 \text{ g mol}^{-1}$$

$$0.0392 = \frac{\text{mass of NaCl}}{58.44}$$

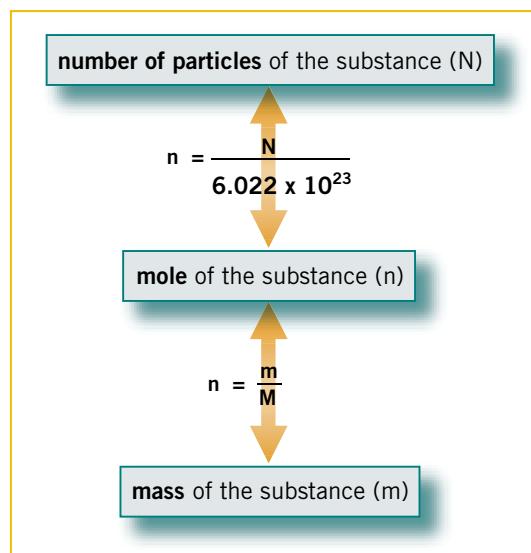
$$\text{mass of NaCl} = 0.0392 \times 58.44 = \mathbf{2.29 \text{ g}}$$

✳ **Review exercise 6.5**

- 1 Distinguish between the terms relative atomic mass, relative molecular mass and molar mass. State the units for each of these.
- 2 Determine, using appropriate units:
  - a the relative atomic mass of nitrogen
  - b the molar mass of nitrogen atoms
  - c the relative molecular mass of nitrogen gas
  - d the molar mass of nitrogen gas.
- 3 A car travelling at 20 km per hour emits about 0.0750 kg of carbon monoxide per kilometre. How many mole of carbon monoxide are emitted per kilometre under these conditions?
- 4 Infants and children require a daily allowance of  $8.00 \times 10^{-6}$  mole of copper per kilogram of body weight. Calculate, for a 10 kg infant, the mass of copper required per day.
- 5 83.3 mol of acetylsalicylic acid (aspirin),  $\text{C}_9\text{H}_8\text{O}_4$ , was used to manufacture  $5.00 \times 10^4$  aspirin tablets. What mass of acetylsalicylic acid is present in each tablet?

## 6.6 The mole, mass and number of particles

It is possible to link the number of particles of the substance to its mass using the two formulas introduced in the previous two sections. This relationship is shown in the following flowchart:



The flowchart can be used to identify the steps involved in a calculation. For example, if the problem requires the mass of a certain number of particles of a substance to be calculated, the first step is to determine the amount of substance in mole, and then the second step is to determine the mass.

### → Example 6.8

A typical human cell contains approximately  $5 \times 10^{-10}$  g of water. How many molecules is this?

### → Solution

The problem involves two steps:

mass of water → mole of water → number of molecules of water

#### Step 1

$$\text{mole of H}_2\text{O} = \frac{\text{mass of H}_2\text{O}}{\text{molar mass of H}_2\text{O}}$$

$$\text{molar mass of H}_2\text{O} = (2 \times 1.008) + 16.00 = 18.016 \text{ g mol}^{-1}$$

$$\text{mole of H}_2\text{O} = \frac{5 \times 10^{-10}}{18.016} = 2.8 \times 10^{-11} \text{ mol}$$

#### Step 2

$$\text{mole of H}_2\text{O} = \frac{\text{number of molecules of H}_2\text{O}}{6.022 \times 10^{23}}$$

$$2.8 \times 10^{-11} = \frac{\text{number of molecules of H}_2\text{O}}{6.022 \times 10^{23}}$$

$$\text{number of molecules of H}_2\text{O} = 2.8 \times 10^{-11} \times 6.022 \times 10^{23} = 2 \times 10^{13}$$

Note: In this problem, because the least accurate value used in the problem (the mass of the water) was quoted to only one significant figure, the final answer should only be quoted to one significant figure. Throughout the problem, the answer to each calculation step can be rounded off to two significant figures, or unsimplified numerical expressions can be carried throughout the problem with the rounding off being done in the final step.

### → Example 6.9

Calculate the mass of one molecule of carbon dioxide.

### → Solution

The problem involves two steps:



#### Step 1

$$\begin{aligned}\text{mole of CO}_2 &= \frac{\text{number of molecules of CO}_2}{6.022 \times 10^{23}} \\ &= \frac{1}{6.022 \times 10^{23}} = 1.6606 \times 10^{-24}\end{aligned}$$

#### Step 2

$$\text{mole of CO}_2 = \frac{\text{mass of CO}_2}{\text{molar mass of CO}_2}$$

$$\text{molar mass of CO}_2 = 12.01 + (2 \times 16.00) = 44.01 \text{ g mol}^{-1}$$

$$1.6606 \times 10^{-24} = \frac{\text{mass of CO}_2}{44.01}$$

$$\text{mass of CO}_2 = 1.6606 \times 10^{-24} \times 44.01 = 7.308 \times 10^{-23} \text{ g}$$

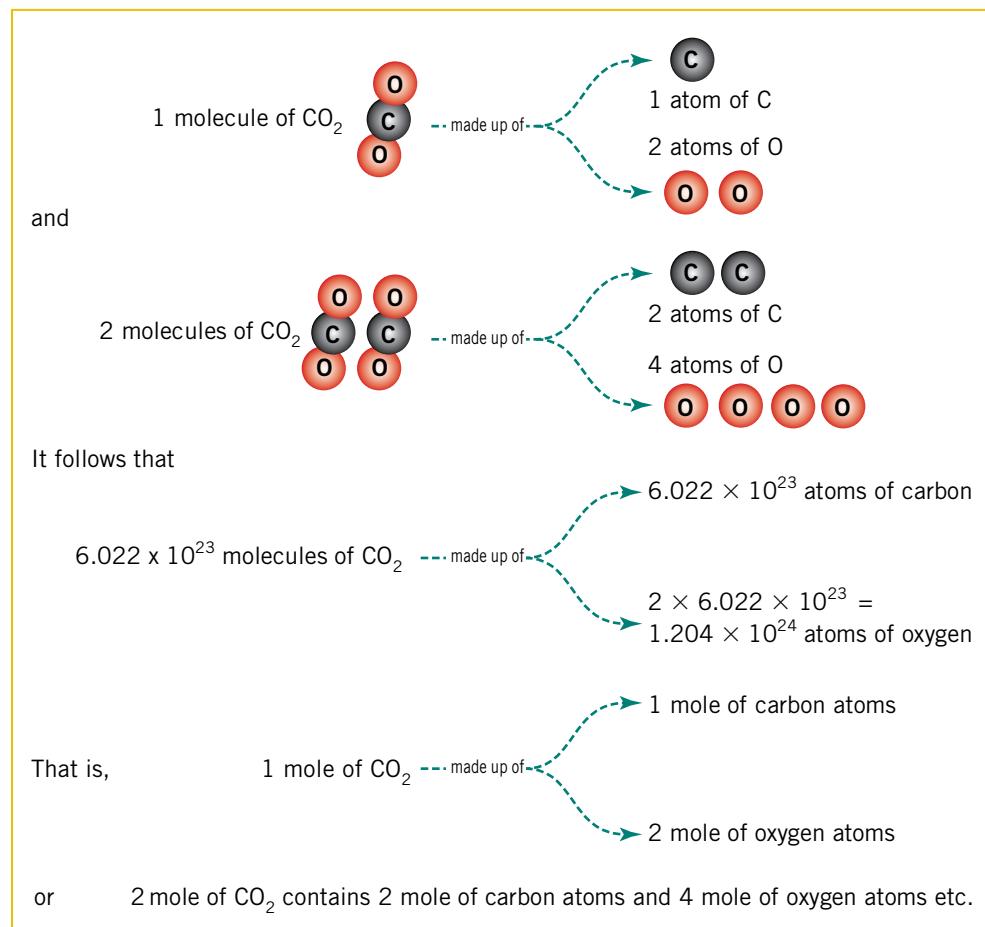
Note: Four significant figures are quoted in the final answer, and five significant figures are carried throughout the calculations because the least accurate data, the Avogadro constant and the atomic masses, are quoted to four significant figures.

### \* Review exercise 6.6

- 1 A crystal of sugar (sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) has a mass of 1.30 mg. How many molecules of sucrose are in the crystal?
- 2 Calculate the mass of  $2.73 \times 10^{24}$  molecules of water.
- 3 An Australian 20-cent coin is made up of a mixture of 75%, by mass, of copper and 25%, by mass, of nickel. If the coin has a mass of 11.3 g:
  - a how many atoms of copper are in the coin?
  - b how many atoms in total, that is, copper and nickel atoms, are present in the coin?
- 4 Hydrogen sulfide, rotten egg gas, is a very poisonous gas. It can be present in volcanic gases in fatal concentrations, and the presence of 68.0 g of the gas in a large hall could well exceed the toxicity limits. In 68.0 g of  $\text{H}_2\text{S}$  there are how many:
  - a mole of  $\text{H}_2\text{S}$ ?
  - b molecules of  $\text{H}_2\text{S}$ ?
- 5 The female American cockroach (*Periplaneta americana*) secretes a material of molecular formula  $\text{C}_{11}\text{H}_{18}\text{O}_2$ , to which the male of the species is attracted. It is reported that the male will respond to as few as sixty molecules of this material. To what mass (in grams) of the material does this correspond?
- 6 The maximum safe mass of mercury in the body is thought to be 0.3 mg. What would be the average number of mercury atoms in each of the  $10^{14}$  cells of a person's body if the person contained this mass of mercury?
- 7 A soft, black pencil is used to draw a line on paper. Consider a pencil line 10.0 cm long, 0.0500 cm wide and 0.0100 cm thick. The black material may be assumed to be entirely carbon. How many atoms of carbon are there in the line? (Density of carbon =  $2.30 \text{ g cm}^{-3}$ .)

## 6.7 Chemical formulas and the mole

The subscripts in a chemical formula of a molecular substance show the number of each type of atom present in a molecule of the substance. For example, the formula for carbon dioxide is  $\text{CO}_2$  and it shows that in every molecule of carbon dioxide there is one atom of carbon and two atoms of oxygen. The chemical formula also provides information about the mole ratio of atoms present in a mole of the substance, as shown below.



So, as well as showing how many of each type of atom is present in a molecule of the substance, the subscripts in a chemical formula represent the amount in mole of the different types of atoms that are present in 1 mole of the substance. For instance, in 1 mole of carbon dioxide ( $\text{CO}_2$ ) there is 1 mole of carbon atoms together with 2 mole of oxygen atoms, and in 1 mole of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) molecules there are 6 mole of carbon atoms, 12 mole of hydrogen atoms and 6 mole of oxygen atoms.

The same situation applies for ionic compounds. Specifically the subscripts in the chemical formula of an ionic compound represent the amount in mole of ions present in 1 mole of the compound. For example, 1 mole of potassium carbonate ( $\text{K}_2\text{CO}_3$ ) formula units contains 2 mole of potassium ions ( $\text{K}^+$ ) and 1 mole of carbonate ions ( $\text{CO}_3^{2-}$ ). Other examples of the amount in mole of atoms or ions present in 1 mole of a substance are given in Table 6.3.

**TABLE 6.3 EXAMPLES SHOWING THE AMOUNT, IN MOLE, OF ATOMS OR IONS IN 1 MOLE OF THE SUBSTANCE**

1 mole of sodium chloride, NaCl	has	1 mole of $\text{Na}^+$ ions and 1 mole of $\text{Cl}^-$ ions
1 mole of octane, $\text{C}_8\text{H}_{18}$	has	8 mole of C atoms and 18 mole of H atoms
1 mole of aluminium sulfate, $\text{Al}_2(\text{SO}_4)_3$	has	2 mole of $\text{Al}^{3+}$ ions and 3 mole of $\text{SO}_4^{2-}$ ions or 2 mole of Al atoms, 3 mole of S atoms and 12 mole of O atoms
1 mole of iron(III) nitrate-9-water, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	has	1 mole of $\text{Fe}^{3+}$ ions, 3 mole of $\text{NO}_3^-$ ions and 9 mole of $\text{H}_2\text{O}$ molecules or 1 mole of Fe atoms, 3 mole of N atoms, 18 mole of H atoms and 18 mole of O atoms

→ **Example 6.10**

How many mole of the following will be in 3.0 mol of ammonium carbonate?

- a  $\text{NH}_4^+$  ions
- b hydrogen atoms

→ **Solution**

- a The formula of ammonium carbonate is  $(\text{NH}_4)_2\text{CO}_3$ .  
1 mol of  $(\text{NH}_4)_2\text{CO}_3$  contains 2 mol of  $\text{NH}_4^+$  ions  
so  
3.0 mol of  $(\text{NH}_4)_2\text{CO}_3$  contains  $2 \times 3.0 = \mathbf{6.0 \text{ mol of } \text{NH}_4^+ \text{ ions}}$
- b 1 mol of  $(\text{NH}_4)_2\text{CO}_3$  contains 8 mol of H atoms  
so  
3.0 mol of  $(\text{NH}_4)_2\text{CO}_3$  contains  $8 \times 3.0 = \mathbf{24 \text{ mol of H atoms}}$

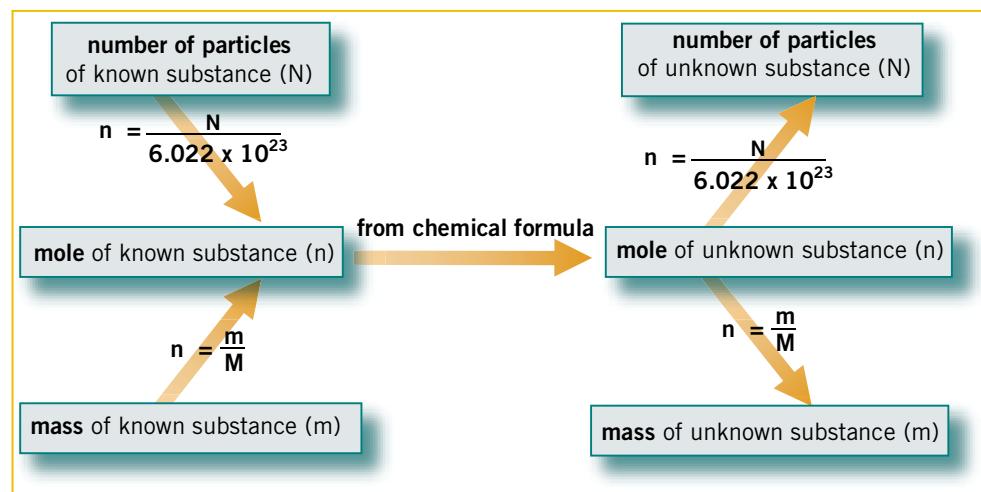
→ **Example 6.11**

How many mole of aluminium oxide will be required to supply 125 mol of oxide ions?

→ **Solution**

- The formula of aluminium oxide is  $\text{Al}_2\text{O}_3$ .  
1 mol of  $\text{Al}_2\text{O}_3$  contains 3 mol of  $\text{O}^{2-}$  ions  
that is  
 $\frac{1}{3}$  mol of  $\text{Al}_2\text{O}_3$  contains 1 mol of  $\text{O}^{2-}$  ions  
so  
 $\frac{1}{3} \times 125 \text{ mol of } \text{Al}_2\text{O}_3 \text{ contains } 125 \text{ mol of } \text{O}^{2-} \text{ ions}$   
 $= \mathbf{41.7 \text{ mol of } \text{Al}_2\text{O}_3}$

The mass and number of atoms or ions in a molecular or ionic compound can also be calculated. The flowchart shown in Section 6.6 can be extended to show the steps involved in such a calculation.

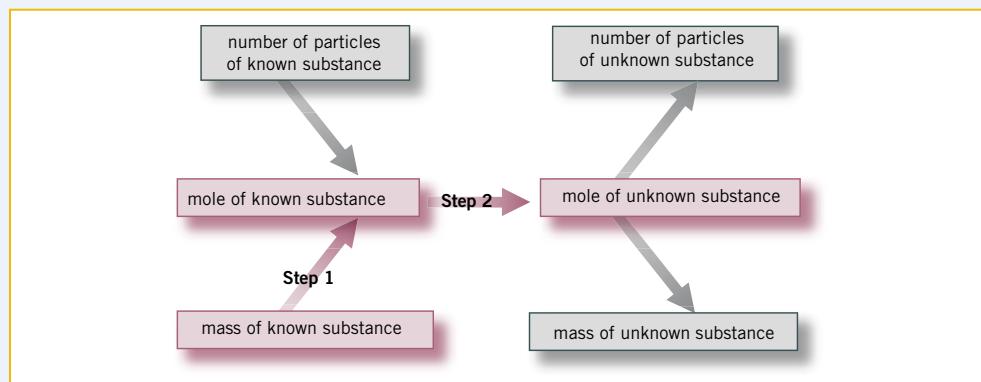


#### → Example 6.12

Nonane,  $C_9H_{20}$ , is a hydrocarbon in the solvent used in enamel house paints. How many moles of nonane will contain 115 g of carbon atoms?

#### → Solution

This calculation will involve two steps, as shown on the flowchart below:



That is,

**Step 1:** mass of C (known substance) → mole of C

**Step 2:** mole of C → mole of  $C_9H_{20}$  (unknown substance)

#### Step 1

$$n(C) = \frac{\text{mass}(C)}{M(C)}$$

$$M(C) = 12.01 \text{ g mol}^{-1}$$

$$n(C) = \frac{115}{12.01} = 9.575 \text{ mol of C}$$

## Step 2

1 mole of  $\text{C}_9\text{H}_{20}$  contains 9 mole of C atoms

$\frac{1}{9}$  mole of  $\text{C}_9\text{H}_{20}$  contains 1 mole of C atoms

$\frac{1}{9} \times 9.575$  mole of  $\text{C}_9\text{H}_{20}$  contains  $9.575$  mole of C atoms

$$= 1.06 \text{ mol of } \text{C}_9\text{H}_{20}$$

### → Example 6.13

The label on a packet of Rennie indigestion tablets shows that:

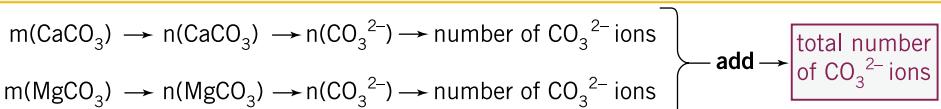
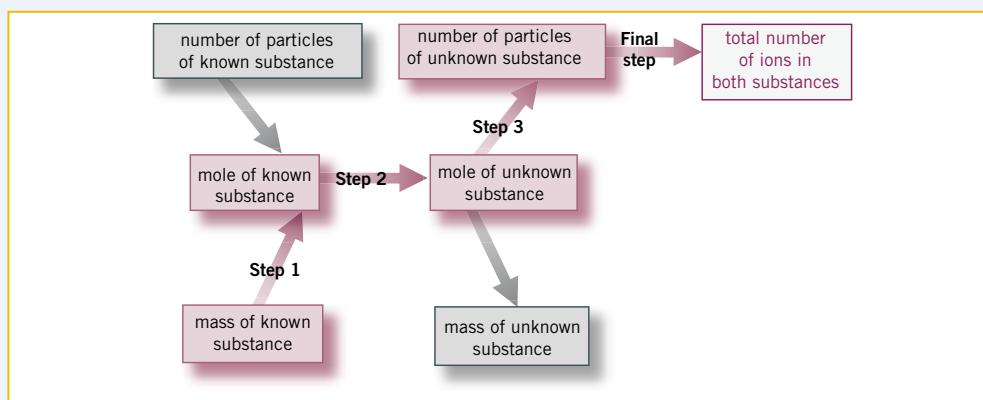
**Each tablet contains:** Calcium carbonate 680 mg and magnesium carbonate 80 mg.

**Each tablet also contains:** Sucrose, glucose (250 mg), spearmint flavour, talc, povidone, sodium saccharin, magnesium stearate.

Calculate the number of carbonate ions, in total, in one tablet.

### → Solution

For each of the two carbonate-containing compounds, a 3-step mole calculation (shown below on the flowchart) will be required, followed by a final step to find, by addition, the total number of carbonate ions.



### Step 1

$$n(\text{CaCO}_3) = \frac{m(\text{CaCO}_3)}{M(\text{CaCO}_3)}$$

$$m(\text{CaCO}_3) = \frac{680}{1000} = 0.680 \text{ g} \text{ (conversion from mg to g)}$$

$$M(\text{CaCO}_3) = 40.08 + 12.01 + (3 \times 16.00) = 100.09 \text{ g mol}^{-1}$$

$$n(\text{CaCO}_3) = \frac{0.680}{100.09} = 6.79 \times 10^{-3} \text{ mol of CaCO}_3$$

### Step 2

1 mole of  $\text{CaCO}_3$  contains 1 mole of  $\text{CO}_3^{2-}$

$6.79 \times 10^{-3}$  mole of  $\text{CaCO}_3$  contains  $6.79 \times 10^{-3}$  mole of  $\text{CO}_3^{2-}$

*continued*

**Step 3**

$$n(\text{CO}_3^{2-}) = 6.79 \times 10^{-3} = \frac{\text{number of } \text{CO}_3^{2-} \text{ ions}}{6.022 \times 10^{23}}$$
$$\text{number of } \text{CO}_3^{2-} \text{ ions} = 6.79 \times 10^{-3} \times 6.022 \times 10^{23} = 4.09 \times 10^{21}$$

**MgCO<sub>3</sub>****Step 1**

$$n(\text{MgCO}_3) = \frac{m(\text{MgCO}_3)}{M(\text{MgCO}_3)}$$
$$m(\text{MgCO}_3) = \frac{80}{1000} = 0.0800 \text{ g}$$

$$M(\text{MgCO}_3) = 24.31 + 12.01 + (3 \times 16.00) = 84.32 \text{ g mol}^{-1}$$

$$n(\text{MgCO}_3) = \frac{0.0800}{84.32} = 9.49 \times 10^{-4} \text{ mol of MgCO}_3$$

**Step 2**

1 mole of MgCO<sub>3</sub> contains 1 mole of CO<sub>3</sub><sup>2-</sup>

9.49 × 10<sup>-4</sup> mole of MgCO<sub>3</sub> contains 9.49 × 10<sup>-4</sup> mole of CO<sub>3</sub><sup>2-</sup>

**Step 3**

$$n(\text{CO}_3^{2-}) = 9.49 \times 10^{-4} = \frac{\text{number of } \text{CO}_3^{2-} \text{ ions}}{6.022 \times 10^{23}}$$

$$\text{number of } \text{CO}_3^{2-} \text{ ions} = 9.49 \times 10^{-4} \times 6.022 \times 10^{23}$$
$$= 5.71 \times 10^{20}$$

**Final step** (for both CaCO<sub>3</sub> and MgCO<sub>3</sub>)

$$\text{total number of } \text{CO}_3^{2-} \text{ ions} = 4.09 \times 10^{21} + 5.71 \times 10^{20}$$

$$= 4.7 \times 10^{21} \text{ ions}$$

(An alternative method would involve adding together the mole of carbonate ions from the two compounds after Step 2, then carrying out only one final calculation step to determine the total number of carbonate ions, as shown below:

$$\text{mole of } \text{CO}_3^{2-} \text{ from CaCO}_3 = 6.79 \times 10^{-3} \text{ mol}$$

$$\text{mole of } \text{CO}_3^{2-} \text{ from MgCO}_3 = 9.49 \times 10^{-4} \text{ mol}$$

$$\text{total mole of } \text{CO}_3^{2-} = 7.74 \times 10^{-3} \text{ mol}$$

$$\text{number of } \text{CO}_3^{2-} \text{ ions} = 7.74 \times 10^{-3} \times 6.022 \times 10^{23}$$
$$= 4.7 \times 10^{21} \text{ ions})$$

## \* Review exercise 6.7

- 1 a How many mole of  $\text{Fe}^{3+}$  ions and of  $\text{CO}_3^{2-}$  ions are contained in 6.0 mol of iron(III) carbonate,  $\text{Fe}_2(\text{CO}_3)_3$ ?  
b How many mole of ammonium hydrogenphosphate contains 5.60 mol of ammonium ions?  
c How many mole of oxygen atoms are in 0.500 mol of calcium hydrogencarbonate?
- 2 Why is the final answer to Example 6.13 only quoted to two significant figures?
- 3 Which of the following contains the greatest number of carbon atoms:  
12.01 g of carbon, 1.000 mole of carbon monoxide or  $6.022 \times 10^{23}$  molecules of carbon dioxide?
- 4 The average person needs 1000 mg of calcium per day. For people unable to eat foods that are rich in calcium (such as milk and cheese), what mass of calcium carbonate do they need to take to provide this calcium?
- 5 While resting, the lungs absorb about 25 g of oxygen gas every 10 minutes. How many molecules of oxygen is this?
- 6 Some of the recycled scrap aluminium is converted into alum, which is used as a food preservative and a dye fixative. Alum is potassium aluminium sulfate-12-water and it has a formula of  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . Calculate the maximum amount of alum, in tonne, that can be prepared from 20.0 tonne of scrap aluminium (1 tonne =  $10^6$  g).
- 7 The pharmaceutical instructions for making soda water are:

**Aqua sodae (Soda water)**

Sodium bicarbonate	0.034 g
Sodium chloride	0.017 g
Sodium sulfate	0.006 g
Distilled water	to 100.000 mL

Dissolve the salts in the distilled water, and saturate the solution with carbon dioxide under pressure.

- a What are the formulas of the ionic compounds used to make the soda water?  
b How many sodium ions in total will be in 100 mL of the soda water?
- 8 The fertiliser superphosphate contains approximately 36%, by mass, of calcium dihydrogen-phosphate,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ . If a certain agricultural crop requires 5.00 kilograms of phosphorus per hectare, what mass of superphosphate must be applied per hectare to yield this amount of phosphorus?

## 6.8 Percentage composition of compounds

Specifying the percentage by mass of each element in the compound is a common way of describing the composition of a compound. This is called the **percentage composition** of the compound. For example, because 100 g of aluminium oxide,  $\text{Al}_2\text{O}_3$ , is made up of 52.9 g of aluminium and 47.1 g of oxygen, the percentage composition of aluminium oxide is 52.9% aluminium and 47.1% oxygen.

The percentage composition of a compound can be calculated from the chemical formula of the compound by comparing the mass of each element present in 1 mole of the compound to the total mass of 1 mole of the compound.

→ **Example 6.14**

Calculate the percentage composition of glucose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>.

→ **Solution**

1 mole of C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> contains 6 mole of C atoms, 12 mole of H atoms and 6 mole of O atoms.

$$M(C_6H_{12}O_6) = 180.156 \text{ g mol}^{-1}$$

So, 180.156 g of C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> contains (6 × 12.01) g of C, (12 × 1.008) g of H, (6 × 16.00) g of O.

$$\%C = \frac{6 \times 12.01}{180.156} \times 100 = 40.00\%$$

$$\%H = \frac{12 \times 1.008}{180.156} \times 100 = 6.714\%$$

$$\%O = \frac{6 \times 16.00}{180.156} \times 100 = 53.29\%$$

The solution to this problem suggests a general mathematical formula that can be used to calculate the percentage composition of the different elements in a compound:

For a general compound A<sub>w</sub>B<sub>z</sub>:

$$\% \text{ A in the compound} = \frac{w \times \text{relative atomic mass of A}}{\text{relative formula mass of compound}} \times 100$$

$$\text{and } \% \text{ B in the compound} = \frac{z \times \text{relative atomic mass of B}}{\text{relative formula mass of compound}} \times 100$$

→ **Example 6.15**

Some ionic compounds crystallise from an aqueous solution to form a hydrated ionic compound. In these compounds, water molecules are included in the crystal lattice structure. This water is called water of crystallisation. The blue hydrated copper sulfate often used in the school laboratory is an example of a hydrated ionic compound. It has the formula of CuSO<sub>4</sub>·5H<sub>2</sub>O. Calculate the percentage of water of crystallisation in the compound.

→ **Solution**

$$\begin{aligned} \text{percentage of water} &= \frac{5 \times \text{relative molecular mass of H}_2\text{O}}{\text{relative formula mass of CuSO}_4 \cdot 5\text{H}_2\text{O}} \times 100 \\ &= \frac{5 \times 18.016}{249.69} \times 100 = 36.08\% \end{aligned}$$

Knowledge of the percentage compositions of compounds can be quite useful. Many industries ranging from health to mining often use percentages composition data to compare the amount of the element of interest in a range of compounds. For example, from the data in Table 6.4, it is apparent that of the three compounds often used in iron supplement medicines, iron(II) sulfate contains the greatest percentage of iron.

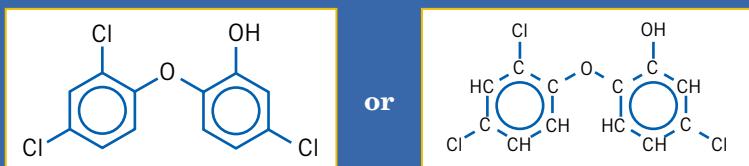
**TABLE 6.4 PERCENTAGE OF IRON IN THREE COMPOUNDS USED IN IRON-SUPPLEMENT MEDICINES**

Iron compound	Formula	Percentage composition of iron
Iron(II) fumarate	$\text{FeC}_4\text{H}_2\text{O}_4$	32.9
Iron(II) sulfate	$\text{FeSO}_4$	36.8
Iron(II) gluconate	$\text{FeC}_{12}\text{H}_{22}\text{O}_{14}$	12.5

### \* Review exercise 6.8

- Calculate the percentage composition of the following:
  - methane,  $\text{CH}_4$
  - calcium hydroxide.
- a Calculate the percentage by mass of nitrogen in ammonium nitrate and ammonium sulfate.  
b Assuming all the nitrogen in each compound is equally accessible to plants, which compound would be most effective, on a mass of nitrogen per gram of compound basis, as a nitrogenous fertiliser?
- Hexachlorophene, an anti-bacterial agent used in hospital washing liquids, shampoos and deodorants, has the molecular mass of 406.9 and contains six chlorine atoms per molecule. Calculate the percentage, by mass, of chlorine in hexachlorophene.
- Triclosan is an anti-fungal agent and a broad-spectrum anti-bacterial agent. It is a white powder that kills germs by interfering with the enzyme necessary for fatty acid synthesis. Its uses include in toothpaste, detergents, laundry soaps, cosmetics and mouthwashes.

The structure of triclosan is:



- What is the chemical formula of triclosan?
- Calculate the percentage composition of this compound.



## MAJOR IDEAS

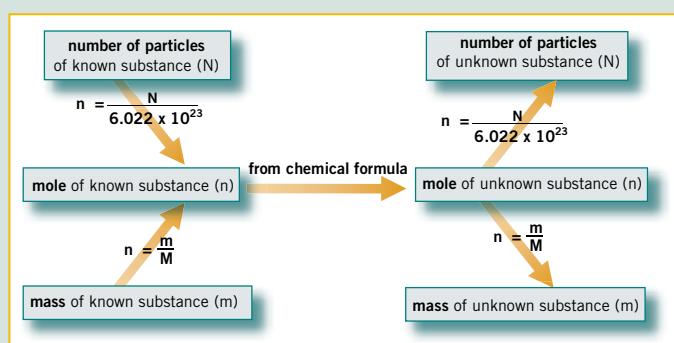
- The relative atomic mass ( $A_r$ ) of an atom is its mass compared with  $\frac{1}{12}$ th the mass of an atom of carbon-12.
- The relative molecular or formula mass ( $M_r$ ) of a substance is the mass of a molecule or formula unit of that substance compared with  $\frac{1}{12}$ th the mass of an atom of carbon-12.
- A mole of any substance is the amount of substance that contains  $6.022 \times 10^{23}$  (the Avogadro constant) atoms, molecules or formula units of that substance.
- One mole of any substance has a mass equal to its relative atomic, molecular or formula mass expressed in grams. This is the molar mass ( $M$ ) of the substance.
- The relationship between the amount in mole ( $n$ ) of a substance and the number of atoms, molecules or formula units ( $N$ ) of the substance is:

$$n = \frac{N}{6.022 \times 10^{23}}$$

- The relationship between the amount in mole ( $n$ ), mass ( $m$ ) and molar mass ( $M$ ) of any substance is:

$$n = \frac{m}{M}$$

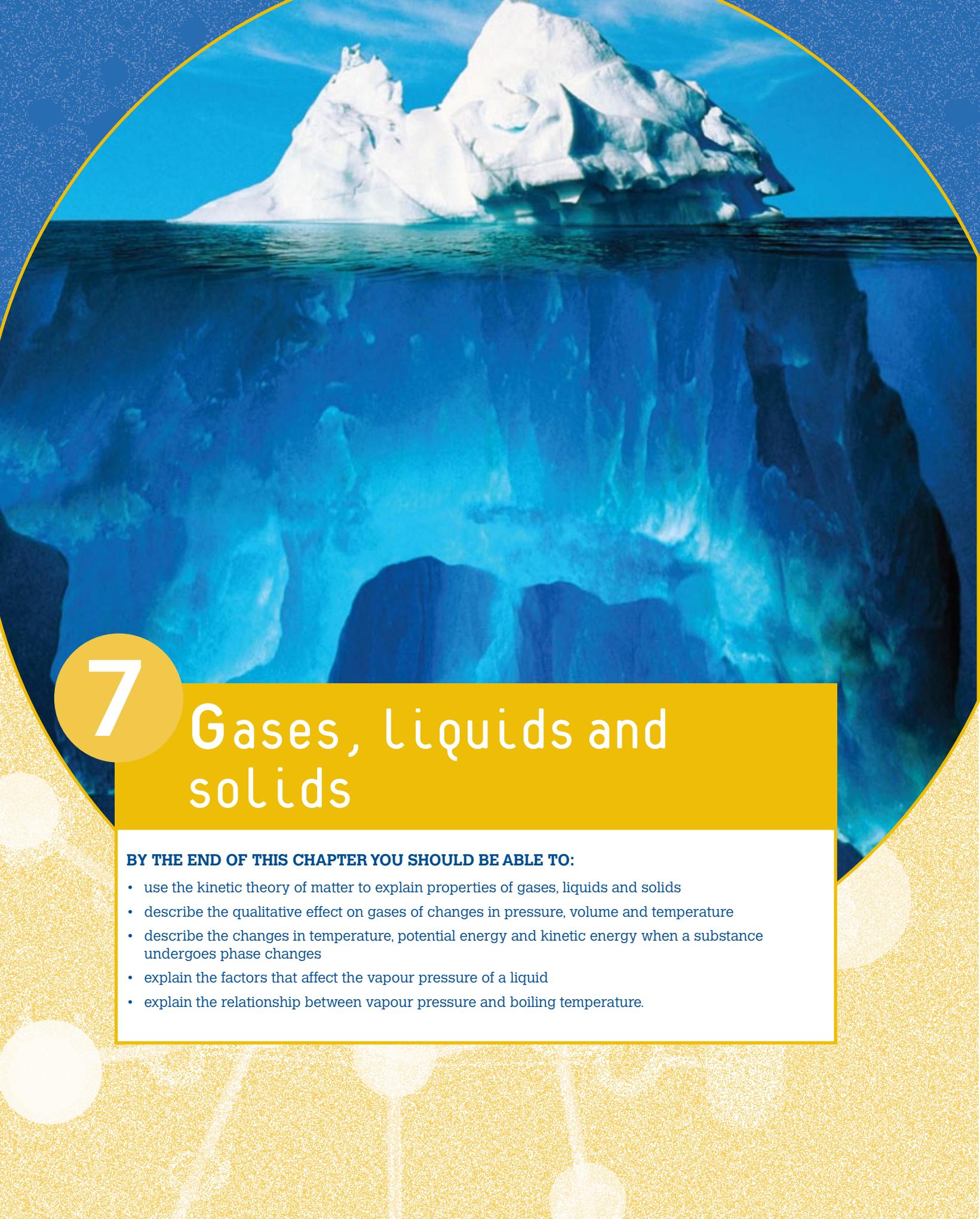
- The percentage composition of a chemical compound specifies the percentage, by mass, of each of the different elements in the compound.
- Different calculations involving chemical formulas are possible as summarised below.



## QUESTIONS

- A silver atom is about nine times heavier than a carbon-12 atom. What would be the relative atomic mass of this silver atom?
- What is the approximate relative atomic mass of sodium-23?
  - Using the data given in Table 6.1, calculate the approximate mass, in grams, of an atom of sodium-23.
- The noble gas neon is well known for its emitted orange light seen in 'neon signs'. It occurs naturally as three isotopes with the following abundances: Ne-20 is 90.9%, Ne-21 is 0.3%, and Ne-22 is 8.8%. Calculate the relative atomic mass of the element neon.
- Bromine is one of the two elements that are liquids at 25°C. Bromine exists in nature as isotopes  $^{79}\text{Br}$  and  $^{81}\text{Br}$ .
  - Given that the relative atomic mass of the element bromine is 79.9, what is the percentage abundance of each of these isotopes in a sample of bromine?
  - What is the name of the other liquid element?
    - Approximately how much heavier are its atoms compared with bromine atoms?
- Calculate the relative molecular or formula masses of the following:
    - ozone ( $\text{O}_3$ )
    - ammonium phosphate
    - cisplatin,  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ , a platinum-based chemotherapy drug used to treat various types of cancers.
  - Calculate the molar mass of:
    - calcium acetate,  $\text{Ca}(\text{CH}_3\text{COO})_2$ , a food additive that acts as a preservative, stabiliser, thickener or acidity regulator in food such as margarine, chocolate milk and fruit yoghurt
    - penicillin V,  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_5\text{S}$ , an antibiotic used to treat tonsillitis.
- A typical silicon chip has a mass of 5.70 mg. How many silicon atoms are present in the chip?
  - How many atoms of carbon are in a 1.12 carat diamond (1.00 carat = 0.200 g)?

- 7** Calculate the amount, in mole, of the following:
- chlorine molecules and chlorine atoms in 14.2 g of chlorine gas
  - vitamin C molecules,  $C_6H_8O_6$ , in a 2.0 L bottle of orange juice that contains 40 mg of vitamin C per 100 mL orange juice.
- 8** In considering the reserves of oxygen,  $O_2$ , that are available on the Earth, scientists have estimated that each square metre of the surface of the Earth supports  $1.00 \times 10^7$  g of gas above it. If this gas is 20.0% oxygen by mass, how many mole of oxygen molecules are there above each square metre of the Earth?
- 9** Calculate the percentage composition of:
- magnesium hypochlorite
  - saccharin ( $C_7H_5NO_3S$ ).
- 10** Vitamin  $B_{12}$  has a relative molecular mass of 1355.37 and contains fourteen nitrogen atoms per molecule. What is the percentage, by mass, of nitrogen in vitamin  $B_{12}$ ?
- 11** Gaviscone Cool chewable tablets are used to treat indigestion. The label on the box of these tablets shows that each tablet contains:
- 250 mg sodium alginate, 133.5 mg sodium bicarbonate, 80 mg calcium carbonate as the active ingredients, and xylitol, mannitol (E421), polyethylene glycol 20000, aspartame (E951), magnesium stearate, peppermint flavour and colouring (E132).
- a** Calculate the amount, in mole, of calcium carbonate and of sodium hydrogencarbonate in one tablet.
- b** How many mole of calcium ions is in one tablet?
- c** The following warning was on the box:
- Each four tablet dose contains 10.6 mmol of sodium and 3.2 mmol of calcium. If you have been advised a diet restricted in any of these please consult your doctor before taking this product.
- i** Show how the figure of '3.2 mmol of calcium' was calculated from the 80 mg of calcium carbonate in each tablet.
- ii** Sodium alginate is an extract from seaweed. It is composed of long chain molecules similar to carbohydrate chains. The formula of sodium alginate can be represented as  $(C_6H_7NaO_6)_n$ , where n is a very large number.
- From the information that four tablets contain 10.6 mmol of sodium (sodium ions), and assuming that sodium alginate and sodium hydrogencarbonate are the only substances in the tablet containing sodium ions, calculate the mass of sodium (in the form of sodium ions) present in the sodium alginate in each four-tablet dose.**
- 12** Epsom salts (hydrated magnesium sulfate) has a wide variety of uses ranging from treatment of ingrown toenails to correcting magnesium deficiencies in garden soil. If  $MgSO_4 \cdot xH_2O$  is heated to 250°C all the water of hydration is lost. After heating a 2.024 g sample of the hydrate, 0.989 g of anhydrous  $MgSO_4$  remains. What is the value of x in the formula of the hydrated compound?
- 13** The calcium-containing substance in human bone is the complex ionic compound calcium hydroxyapatite,  $[Ca_3(PO_4)_2]_3 \cdot Ca(OH)_2$ . If a 620 g tibia bone contains 69%, by mass, of calcium hydroxyapatite, calculate the mass of calcium in the bone (assume all the calcium is present as calcium hydroxyapatite).
- 14** The following information was shown on the side of a plant fertiliser container:
- Guaranteed Analysis**  
 Total phosphorus (P) — water soluble as mono-ammonium phosphate 4.0%.
- i** Suggest a formula for the compound that has been called 'mono-ammonium phosphate' on the box.  
**ii** What is its correct name?
  - Calculate the percentage, by mass, of phosphorus in 'mono-ammonium phosphate'.
  - The figure of 4% of phosphorus refers to the percentage, by mass, of phosphorus atoms in the fertiliser. What mass of 'mono-ammonium phosphate' is present in the 500 g box of the fertiliser, if this is the only phosphorus-containing compound present?
  - Suggest a reason for why they express the amount of phosphorus in the fertiliser in the way given at the beginning of the question, rather than giving the percentage of the compound 'mono-ammonium phosphate' in the fertiliser product?

The background image shows a massive iceberg floating in a deep blue ocean. The top of the iceberg is white and jagged, while the submerged part below the waterline is a translucent blue. The water is calm with some ripples.

# 7

# Gases, Liquids and solids

## BY THE END OF THIS CHAPTER YOU SHOULD BE ABLE TO:

- use the kinetic theory of matter to explain properties of gases, liquids and solids
- describe the qualitative effect on gases of changes in pressure, volume and temperature
- describe the changes in temperature, potential energy and kinetic energy when a substance undergoes phase changes
- explain the factors that affect the vapour pressure of a liquid
- explain the relationship between vapour pressure and boiling temperature.

## 7.1 Behaviour of gases—the kinetic theory

It is very easy to ignore gases around us. Most are colourless, and for the most part the dominant gases have no taste or odour. Nevertheless, they form an important part of the natural environment. Oxygen, carbon dioxide and nitrogen in the atmosphere are essential for life on Earth. Gases are also used widely in a range of products and appliances. Soft drinks contain dissolved carbon dioxide, light globes contain argon, aerosols often use gaseous hydrocarbons as the propellant, and natural gas is used as a source of heat.



Figure 7.1 Useful gases at a birthday party.

While gases may differ from one another in their chemical reactions, their physical properties are very similar. For example, all gases expand to fill a container, diffuse rapidly, form homogeneous mixtures, can be compressed, and exert a pressure. To explain much of the physical behaviour of gases, scientists have developed the kinetic theory of gases. The word 'kinetic' indicates that it is the constant rapid movement of the particles in the gas phase which is of fundamental importance in determining the physical properties of gases.

The **kinetic theory of gases** is based on the following assumptions:

- Gases consist of tiny particles (atoms in the case of the noble gases [group 18] and molecules for all other gases) moving in rapid, random, straight-line motion until they collide with one another or with the walls of a container.
- Collisions between particles or with the walls of the container are perfectly elastic. There is no change in energy of the particles as a result of these collisions.
- The size of the particles is negligible compared to the size of the container in which they are moving. It can be assumed that each gas particle has mass but no volume. A corollary of this is that the distances between the particles are very large compared to the size of the particles themselves.
- Any attractive or repulsive forces between particles in the gas phase are negligible.
- The average kinetic energy of the particles increases as the temperature of the gas increases. Since the mass of the particle does not alter, and kinetic energy is given by the expression  $KE = \frac{1}{2} mv^2$ , the particles must move faster as the temperature increases. In any sample of a gas at a given temperature, the particles are not all moving at the same velocity. They have a range of velocities, with some moving slower than average and some much faster. The graph in Figure 7.2 shows the distribution of velocities possessed by the particles in a typical gas sample.

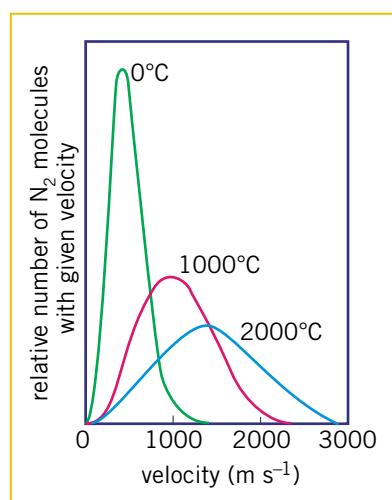


Figure 7.2 The distribution of velocities of the molecules in a sample of nitrogen gas, at different temperatures.

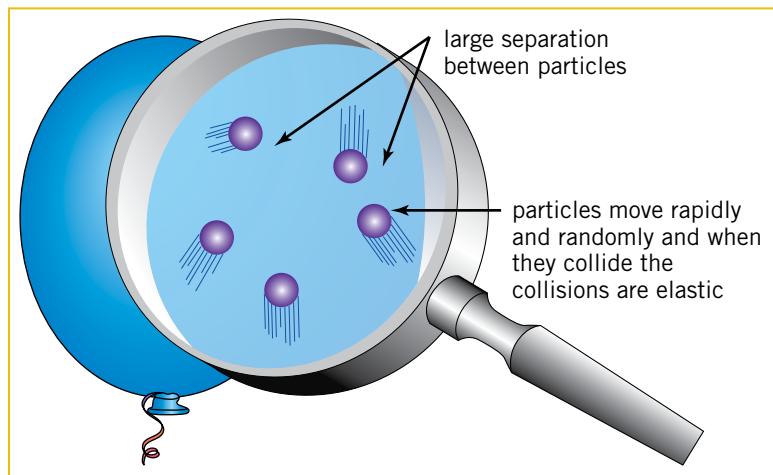


Figure 7.3 Assumptions of the kinetic theory of gases.

The kinetic theory of gases is only a simple model proposed to explain the properties of an ideal gas. The particles in a real gas do have finite volumes and they attract and repel one another. However, the kinetic theory is still a useful model because it can be used to explain observations and predict the results of future experiments involving gases under many experimental conditions.

The **diffusion**, or spreading, of a gas can be explained using the kinetic theory by considering that the particles are in rapid, random, straight-line motion until they collide with one another or with the walls of the containing vessel. The gas particles are free to move in this way because there are no forces of attraction between them to hold them together. When baking bread in the kitchen, the aroma (that is due to particular molecules produced during the baking process) spreads throughout the house. The rapidly moving aroma molecules continue to move in all directions, bouncing off walls and one another, passing through doorways, and ultimately finding their way into much of the house.

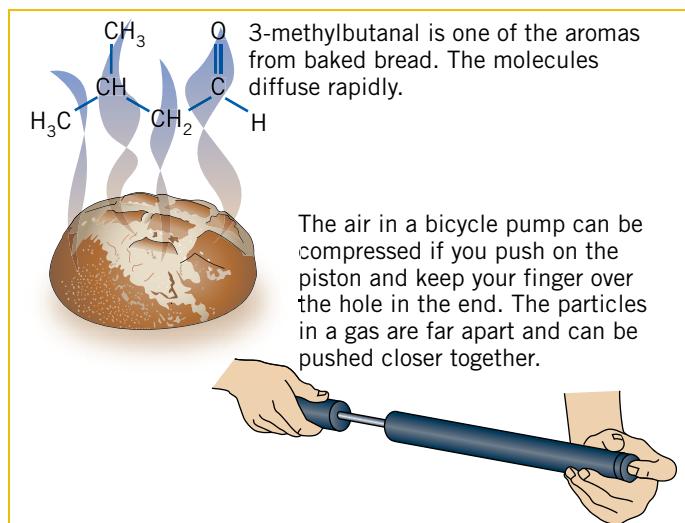


Figure 7.4 Two characteristic properties of gases: they readily diffuse and are highly compressible.

If the volume of the gas particles is negligible compared to the volume of the container occupied by the gas, then most of the gas sample is empty space. As a result, a gas can be **compressed**, or squeezed, into a smaller space, for example, by applying a pressure to the outer walls of a flexible container. In other words, the gas particles can be pushed closer together. If a finger is placed over the end

of a bicycle pump and the piston is pushed down, the volume of gas in the pump can be reduced significantly as a result of the gas particles being squeezed more closely together.

### \* Review exercise 7.1

- 1 List some of the uses of gases shown in the photo in Figure 7.1.
- 2 Someone drops a bottle of perfume in a room. Explain why the perfume can soon be smelt in all parts of the room.
- 3 Air is a homogeneous mixture of approximately 80% nitrogen, 20% oxygen, traces of other gases such as carbon dioxide, and water vapour.
  - a What is meant by the term ‘homogeneous mixture’?
  - b Explain in terms of the kinetic theory why gases form a homogeneous mixture rather than a heterogeneous mixture.
- 4 One of the characteristic physical properties of gases is that they have a variable volume.
  - a What is meant by this statement?
  - b Explain in terms of the kinetic theory why gases have a variable volume.
- 5 The brakes in many cars operate with a fluid in a pipe (brake line) that runs from the brake pedal to the brake mechanism in the wheel. Pressing on the brake pedal exerts a pressure, via the fluid in the brake line, on the brakes to bring them in contact with the wheel. What are the consequences of getting air in the fluid in the brake line during the servicing of a car? Explain your answer in terms of the particles making up the air.

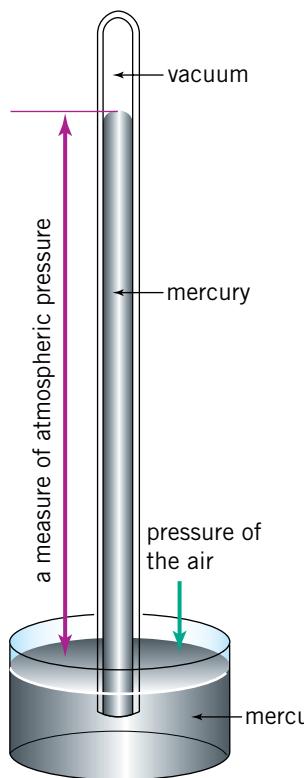
## 7.2 Gas pressure, volume and temperature

### Gas pressure

The kinetic theory can be used to explain why all gases exert a pressure. As the gas particles move around inside a container they collide with the walls and in doing so exert a force on the sides of the container. This force, over a given area of surface, represents the **pressure** of the gas. The tyres of a car maintain their shape or volume because of the pressure that is exerted on the inside walls of the tyre by the trapped gas. Since the particles in a gas are moving very fast (for example, oxygen molecules at 25°C travel in excess of  $480\text{ m s}^{-1}$ , or more than  $1700\text{ km hr}^{-1}$ ), there are many collisions with the walls of the container in a short time interval. The velocities of the gas particles (or more correctly, momentum of the particles) and the frequencies with which they hit the container’s walls, determine the pressure of the gas. For instance, if the velocities of the particles are increased, they will exert a larger force when they hit the walls of the container, therefore the pressure will be greater. Or, if the number of particles in a container is increased, the particles will collide with the container’s walls more frequently, so the pressure will be greater.

### Units of pressure

There are several units that are commonly used in measuring pressure. Historically, the measurement of pressure was based on the height of a mercury column that could be supported by the particular gas pressure (see Figure 7.5).



**Figure 7.5** A simple mercury barometer. The height of the mercury column is a measure of the pressure the air particles are exerting on the mercury surface in the open dish.

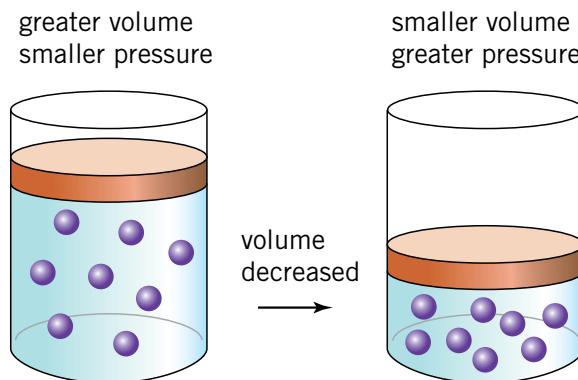
As a result, the unit mm Hg (millimetres of mercury) came into existence. It was found that on average the atmospheric pressure at sea level was 760 mm Hg, which was called one atmosphere. Hence the pressure of one atmosphere is equivalent to a pressure of 760 mm Hg.

The SI unit for pressure is the pascal, Pa. Atmospheric pressures for weather forecasts are measured in hectopascals (1 hPa = 100 Pa), but in chemistry the more common unit is the kilopascal, kPa. The relationship between three pressure units is

$$1 \text{ atmosphere} = 760 \text{ mm Hg} = 101.3 \text{ kPa} (\text{or } 1.013 \times 10^5 \text{ Pa})$$

### Pressure and volume

The pressure of a sample of gas is dependant on its volume and its temperature. If the velocity of the particles or the frequency of collisions is changed, then the gas pressure will be affected. For example, considering a sample of gas in a container at a constant temperature, any change in the volume of the container will change the frequency of collisions between the gas particles and the walls of the container. With a reduction in volume, there will be an increase in the frequency of collisions with the container walls, as the particles do not have as far to travel before striking the walls. Therefore, the pressure in the container would be expected to rise as the volume is decreased. Similarly, if the volume of the container is increased, the frequency of collisions between the gas particles and the container walls will decrease, resulting in a decrease in the gas pressure.



Assuming the temperature and amount of gas remains constant, when the volume is decreased, the particles have less space to move around in, so they will hit the walls more often, leading to a greater pressure

**Figure 7.6** The effect of changing the volume of a sample of gas at constant temperature.

Every breath taken by a person relies on this relationship between pressure and volume of gases. For a person to breathe in, the diaphragm is lowered, allowing the volume of the lungs to increase. This increase in volume lowers the pressure of gas inside the lungs, making it less than atmospheric pressure. As a result, air from the atmosphere rushes into the lung space. To breathe out, the diaphragm moves back up, decreasing the lung volume and increasing the gas pressure in the lungs. As a result, air is expelled from the lungs.



## Pressure and temperature

If a gas in a rigid container (that is, the volume remains constant) is heated or cooled, the pressure exerted by the gas will change. When a gas is heated the average kinetic energy of its particles increases. This means the heated gas particles will be moving faster (and have greater momentum) than the particles of the cooler gas. As a result, the gas particles will collide with the container walls more often and with a larger force, to produce a greater pressure. Sometimes in a situation like the one just described, if the container walls are relatively weak, the increased gas pressure can cause the container to burst. This is why it is very dangerous to leave an aerosol can near a fire or to throw it into the fire. The increase in velocity (and momentum) of the heated gas particles is most likely to result in an explosion of the can.

## Volume and temperature

Once a balloon is blown up and its inlet valve tied, its volume will remain approximately constant providing no gas escapes through the balloon's skin. The air inside the balloon is exerting a pressure on the elastic skin of the balloon, balancing out the pressure exerted by the atmospheric gases on the outside of the balloon skin.

The volume of the balloon will change, however, if the temperature decreases or increases. For example if part of a balloon is plunged into liquid nitrogen (at  $-196^{\circ}\text{C}$ ), the balloon's volume decreases, as shown in Figure 7.7b.



Figure 7.7a Balloon entering liquid nitrogen.



Figure 7.7b Balloon shrinks as it cools in liquid nitrogen.

This observation can be explained in terms of the kinetic theory of gases. As the temperature of a gas is decreased, the average kinetic energy and the average velocities of the particles will decrease. Consequently, the gas particles will collide with the inside of the balloon's skin less often and with a smaller force. The gas pressure inside the balloon will be reduced and as a result the balloon will shrink in size.

It also follows that, at constant pressure, the volume of a fixed amount of gas will increase if the gas is heated. The average velocity of the particles will increase as the gas is heated and so they will collide with the container walls with greater frequency and force. If the pressure is to remain unchanged, the frequency of collisions has to be reduced, and this can only be achieved if the volume is increased, as represented in Figure 7.8.

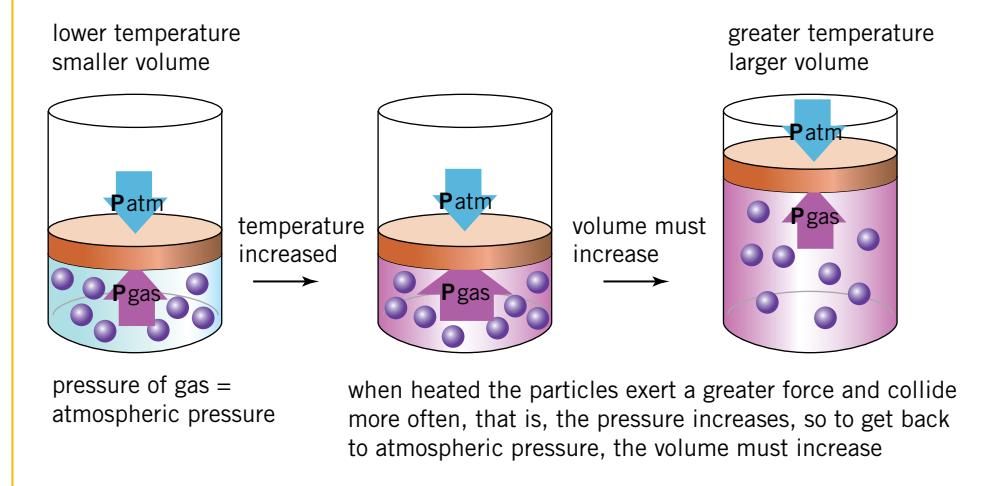


Figure 7.8 The effect of increasing the temperature of a sample of gas, at constant pressure

In nineteenth century France, Jacques Charles studied the effect of changing temperature on a fixed amount of gas held at a constant pressure. Graphs of typical results obtained by Charles are shown in Figure 7.9. From these results, he concluded that there is a linear relationship between the temperature of a fixed mass of gas and its volume, at constant pressure.

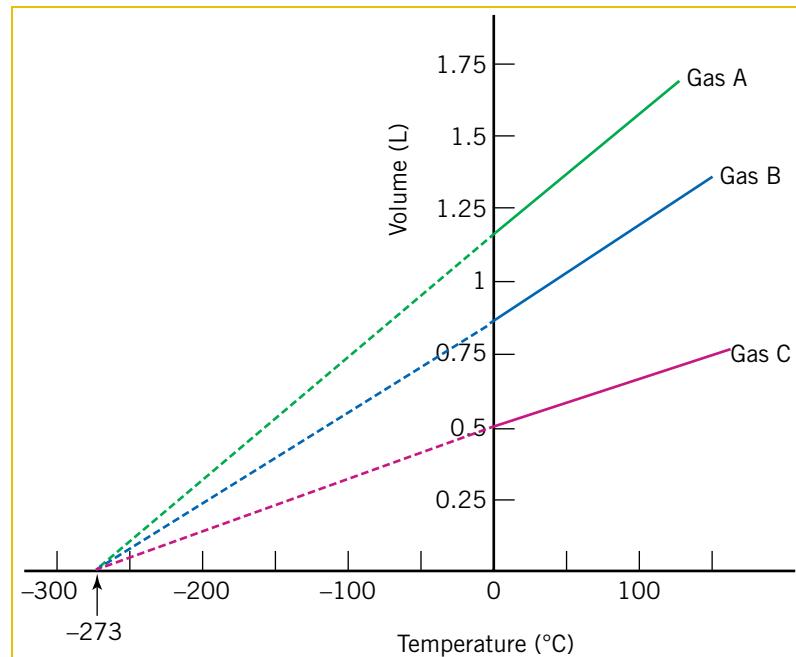


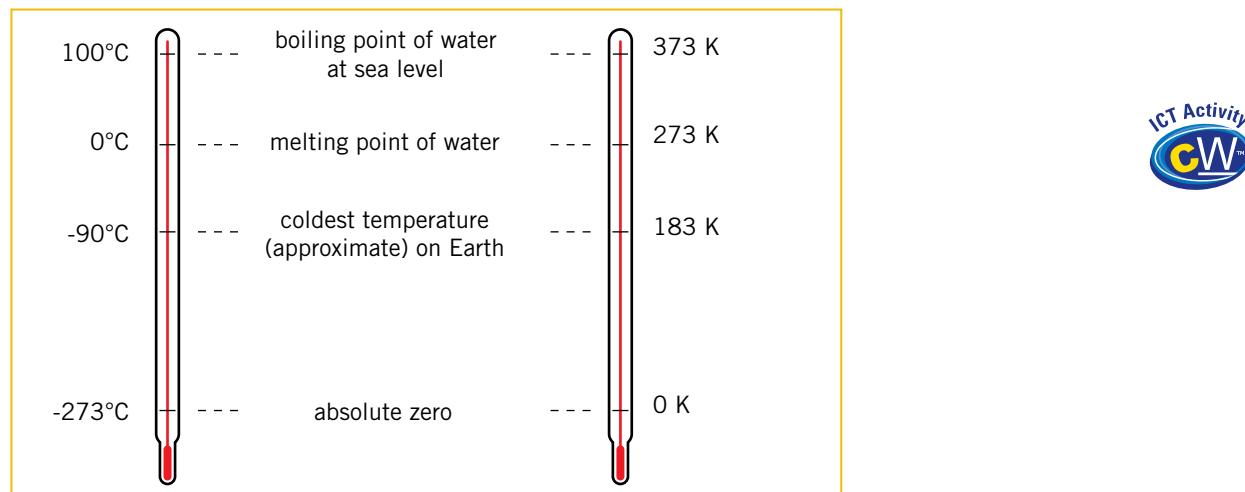
Figure 7.9 Graphs showing how the volumes of three different gases change with temperature, at constant pressure and mass of gas.

When the graphs for different samples of gases are extrapolated back towards the temperature axis, they all meet this axis at  $-273^{\circ}\text{C}$ . It therefore appears that the gases will occupy zero volume at this temperature. In practice, however, all gases condense into liquids before they reach this temperature. Nonetheless, there seems to be a lowest possible temperature that can be reached; a temperature at which, theoretically, all motion of the particles will have stopped. This absolute lowest temperature of  $-273^{\circ}\text{C}$  has been called **absolute zero**.

The lowest possible temperature of  $-273^{\circ}\text{C}$  is used as the starting point of a temperature scale known as the **Kelvin or absolute temperature scale**. On the Kelvin scale 0 K corresponds to  $-273^{\circ}\text{C}$  on the Celsius scale. Also, each unit on the Kelvin scale is equal to  $1^{\circ}\text{C}$ , so the conversion between Celsius temperatures and Kelvin or absolute temperatures is given by:

$$K = ^{\circ}\text{C} + 273$$

A temperature of  $20^{\circ}\text{C}$  is therefore the same as  $20 + 273 = 293$  K, and 200 K is the same as  $200 - 273 = -73^{\circ}\text{C}$ .



**Figure 7.10** Comparison of the Celsius and Kelvin (absolute) temperature scales.

### \* Review exercise 7.2

- 1 Use the kinetic theory to explain why the pressure in vehicle tyres increases on a hot day.
- 2 A helium balloon is set up to measure weather conditions at an altitude of 10 km where the atmospheric pressure is around 24 kPa. After being released at ground level, the volume of the balloon increases as it rises higher in the atmosphere. Explain in terms of the kinetic theory why this occurs.
- 3 Convert the following temperatures:
 

<b>a</b> $1450^{\circ}\text{C}$ to K	<b>c</b> $-150^{\circ}\text{C}$ to K
<b>b</b> 350 K to $^{\circ}\text{C}$	<b>d</b> 10 K to $^{\circ}\text{C}$ .
- 4 Explain why, when baking bread, the small carbon dioxide bubbles trapped in the dough cause the bread to rise during the cooking process.

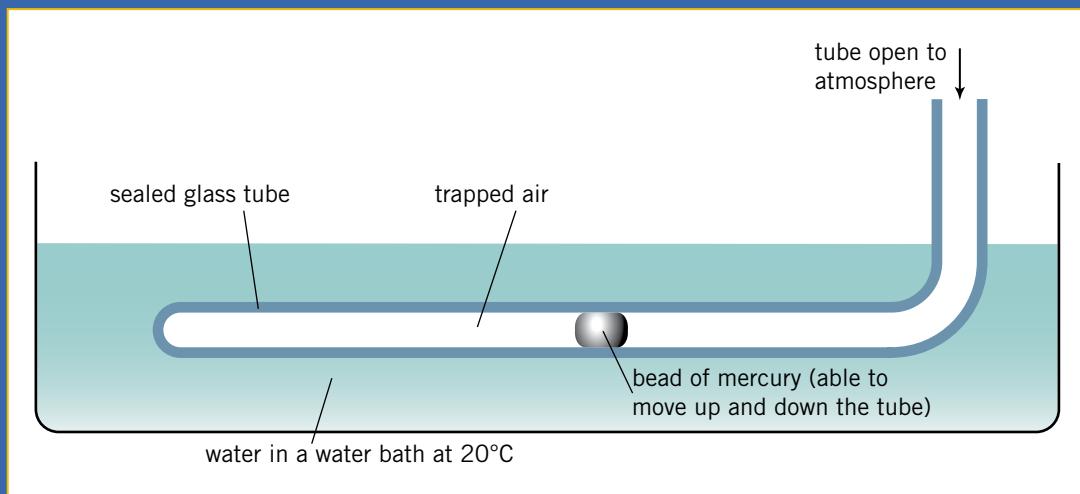
*continued*



**Figure 7.11** A weather balloon for recording temperature, pressure and wind speed at high altitudes.

**Review exercise 7.2 — *continued***

- 5 A small piece of dry ice (solid carbon dioxide), of mass 4 g, was placed in a 2 L rigid bottle and the lid tightly screwed on. The dry ice was allowed to completely sublime. The bottle and its contents were kept at a temperature of 20°C. Three additional rigid bottles, A, B and C, each containing a certain mass of dry ice, were set up in an identical way to the original bottle and kept under the conditions described below. Use the kinetic theory to predict whether the pressure due to gas in each of the three bottles would be greater than, equal to or less than the gas pressure in the original bottle. Explain your reasoning.
- a Bottle A: mass of dry ice 4 g, volume 4 L, held at 20°C
  - b Bottle B: mass of dry ice 4 g, volume 2 L, held at 5°C
  - c Bottle C: mass of dry ice 2 g, volume 2 L, held at 20°C.
- 6 An experiment to investigate the effect of temperature on the volume of a constant mass of gas at constant pressure can be carried out using the equipment shown in Figure 7.12.



**Figure 7.12 Equipment for investigating the effect of temperature on the volume of a sample of gas, at constant pressure.**

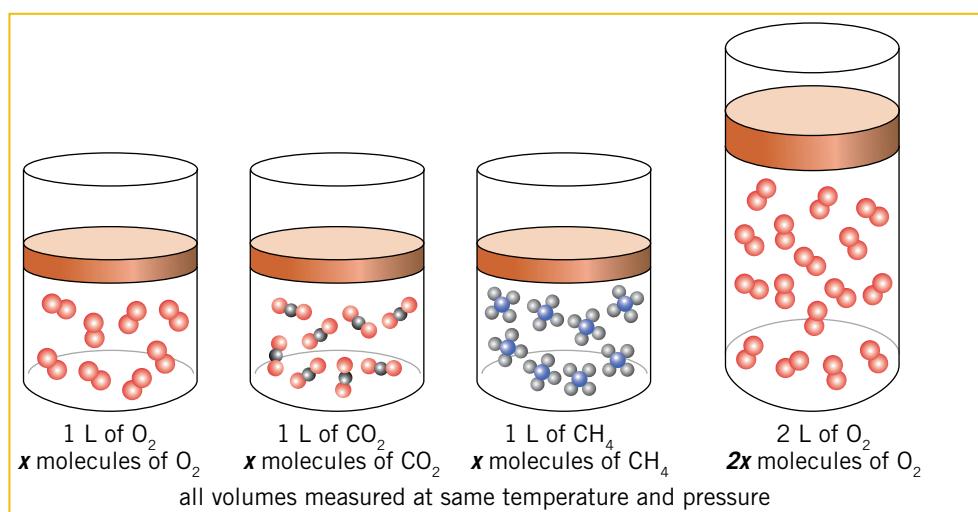
- a If the water at 20°C in the water bath was replaced by boiling water, describe what you would expect to see happen. Explain your prediction in terms of the kinetic theory.
- b If the volume of the trapped gas is measured at different water bath temperatures, this equipment can be used to quantitatively investigate the effect of temperature on the volume of a constant mass of gas at constant pressure. Explain how the mass of gas and the pressure are kept constant using the equipment shown in Figure 7.12.

## 7.3 Volume and the amount of gas

### Avogadro's hypothesis

In the previous section, the effects of pressure and temperature on the volume of a gas were discussed. The volume of a gas also depends on the amount of gas present. Early in the nineteenth century, the Italian scientist Amedeo Avogadro suggested a proposal concerning the relationship between the amount of a gas and its volume. His hypothesis was that 'equal volumes of gases at the same temperature and pressure contain equal numbers of particles'.

It can therefore be concluded that, for example, 1 L of oxygen, O<sub>2</sub>, contains as many molecules as 1 L of carbon dioxide, CO<sub>2</sub>, and as 1 L of methane, CH<sub>4</sub>, assuming all the volumes are measured at the same temperature and pressure. In addition, it means that 2 L of oxygen has twice as many molecules as 1 L of any other gas at the same temperature and pressure.



**Figure 7.13** Equal volumes of different gases, at the same temperature and pressure, contain equal numbers of molecules.

An important inference arising from Avogadro's hypothesis is that the volume occupied by a gas (at constant temperature and pressure) is dependent only on the number of gas particles present. Or in other words, at a particular temperature and pressure, equal numbers of particles of all gases will occupy the same volume. This inference is plausible because, according to the kinetic theory, the volume of each gas particle is assumed to be negligible compared to the distance between the particles.

Mathematically, Avogadro's hypothesis can be represented as:

$$V \propto n \quad (\text{at constant temperature and pressure})$$

That is, the volume (V) occupied by a gas is proportional to the amount in mole (n) of gas present, at constant temperature and pressure. For example, assuming the volumes are measured at the same temperature and pressure, if 1 mole of H<sub>2</sub> occupies a volume of 20 L, then 2 mole of H<sub>2</sub> will occupy 40 L and 0.5 mole of H<sub>2</sub> will occupy 10 L.

The concept of a mole was not established until well after Avogadro's time. However, in honour of Avogadro, the numerical value of one mole,  $6.022 \times 10^{23}$ , is known as the Avogadro constant, N<sub>A</sub>.

A natural extension of Avogadro's hypothesis is that the volume of one mole of all gases at the same temperature and pressure must be identical. This introduces the idea of a molar volume, that is, the volume occupied by one mole of a gas or  $6.022 \times 10^{23}$  gas particles. A standard **molar volume** has been defined as the volume of one mole of an ideal gas at 0°C and 101.3 kPa (also known as standard temperature and pressure or STP). Under STP conditions the value of the molar volume is 22.41 L mol<sup>-1</sup>.

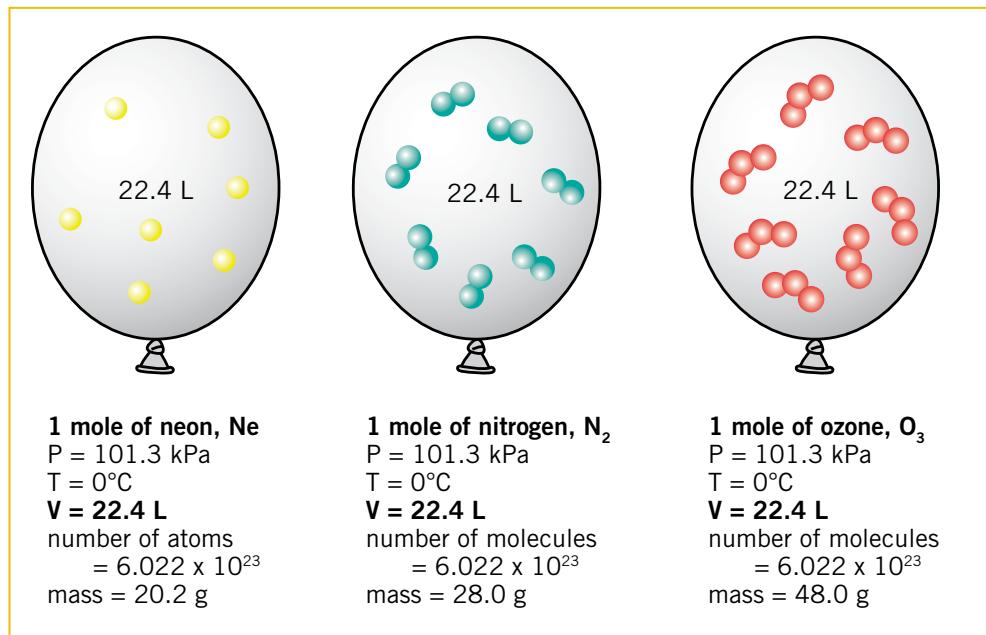


Figure 7.14 Molar volumes of gases at STP.

For gases at STP it is possible to calculate the amount of gas, in mole, from the volume of the gas, by using the following relationship

$$n = \frac{V}{22.41}$$

where V is the volume of the gas in litres at STP, that is, at 0°C and 101.3 kPa pressure.

### \* Review exercise 7.3

- Which of the following gases, at 25°C and 101.3 kPa pressure, would occupy the largest volume?  
0.1 mole of oxygen    10 g of neon     $3.6 \times 10^{22}$  molecules of nitrogen
- Explain Avogadro's hypothesis in terms of the kinetic theory.
- How many mole of gas would be present in each of the following containers?
  - Container A has a volume of 22.4 L and it contains some carbon dioxide at a temperature of 0°C and pressure of 1 atm.
  - Container B has a volume of 22.4 L and it contains some helium at a temperature of 0°C and pressure of 1 atm.

- c Container C has a sample of 11.2 L of nitrogen gas, measured at STP.
- d Container D is filled with 32.1 g of methane, CH<sub>4</sub>.
- 4 Helium atoms are small enough to move or diffuse through the molecules making up the skin of a normal latex party balloon. Explain in terms of the kinetic theory why a latex balloon inflated with helium will 'go flat' over a reasonably short time.

## 7.4 Liquids and solids

The kinetic theory of gases described in Section 7.1 can be extended to explain the behaviour of solids and liquids. In the gaseous state, the particles are widely spaced and exhibit random, straight-line movement. Intermolecular forces are so small they can be ignored. However, in solids and liquids the particles are much closer together and are restricted in their movement. Attractive forces exist between the particles. As a result, the properties of solids and liquids are quite different from those of gases.

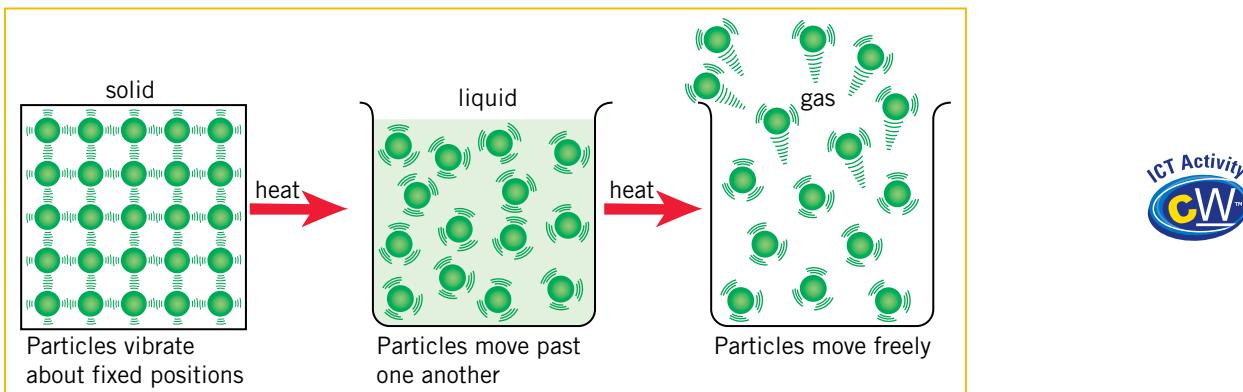


Figure 7.15 Particle arrangements in the three states of matter.

### Liquids

Although the particles are much closer in liquids than in gases, they constantly change their positions. The particles can slip past each other but, because of their close proximity, a particle cannot travel far before colliding with a neighbouring particle. The lack of space between particles is the reason why liquids are virtually incompressible. The fact that the particles of a liquid do not occupy fixed positions, because the attractive forces between the particles are relatively weak, allows the liquid to flow. However, these attractive forces are sufficiently strong to keep the liquid particles together and so give the liquid a definite volume.

### Solids

In solids, the movement of particles is much more restricted than in liquids. The particles in a solid vibrate in fixed positions in the lattice structure. On average, the particles in a solid are closer together than in a liquid, and the attractive forces between the solid's particles are stronger than the forces between the particles in the liquid state. As a result, solids have a definite shape as well as a definite volume.

## Potential energy and kinetic energy

The particles in all solids, liquids and gases possess both **kinetic energy**, or energy due to motion, and **potential energy**, or energy due to position.

The differences in the spacing between the particles of a substance in its solid, liquid and gaseous states correspond to different potential energies. In the solid state, the particles of a particular substance are very close to one another, corresponding to a relatively low potential energy. However, when this substance is in the gaseous state, its particles will be much further apart, corresponding to a much higher potential energy. The potential energy of particles of the substance in the liquid state is somewhat higher than in the solid state but still far less than in the gaseous state.

The increase in the potential energy of the particles going from solid to liquid to gas occurs because energy has been supplied to overcome the attractive intermolecular forces between the particles during the changes in state.

Because they are moving, the particles in solids, liquids and gases possess kinetic energy ( $\frac{1}{2}mv^2$ ). When a substance is heated, the average kinetic energy of its particles increases and they move with greater average velocity. As with a gas, the temperature of a solid and a liquid is related to the average kinetic energy of its particles. When a thermometer is placed in a hot liquid, for example, the liquid's particles collide with the glass of the thermometer bulb resulting in a transfer of kinetic energy to the glass particles. The glass particles in turn transfer kinetic energy to the liquid particles in the thermometer, and this liquid expands. Matching the height of the expanded liquid with a scale mark on the thermometer provides a number which is called the temperature of the liquid. That is, the temperature reading shown on the thermometer is a measure of the average kinetic energy of the particles in the hot liquid.

If the temperatures of several substances are identical then the average kinetic energy of their particles will be the same. For example, the average kinetic energy of the molecules in a glass of water at 20°C will be equal to the average kinetic energy of the atoms in a piece of iron also at 20°C. When comparing substances of different temperatures, the average kinetic energy of the particles will be largest in the substance with highest temperature.

Heat and temperature are often confused. As explained above, **temperature** is a measure of the average kinetic energy of the particles in a substance. **Heat**, or thermal energy, is the energy transferred between objects that are at different temperatures. For example when a saucepan is placed on a hot element on a stove, heat is transferred from the hot element to the cooler saucepan.



## \* Review exercise 7.4

- 1 Summarise, in a table, the characteristic properties of solids, liquids and gases under these headings: Volume, Shape, Compressibility, Diffusion, Ability to flow.
- 2 Explain in terms of the kinetic theory why:
  - a liquids and gases are both known as 'fluids'
  - b the rate of diffusion of liquids is relatively slow, but it increases with an increase in temperature of the liquids.
- 3
  - a Compare the potential energy of water molecules in each of the following:
    - i ice and liquid water at 0°C
    - ii liquid water and steam at 100°C.
  - b Compare the average kinetic energy of particles in each of the following:
    - i water and ethanol both at 20°C
    - ii water at 10°C and ethanol at 60°C.
- 4 The distribution of the velocities of the particles in a sample of gas was described in Section 7.1. Similar distributions occur in solids and liquids.
  - a Sketch a graph showing the distribution of the velocities of the particles in a sample of water.
  - b If the water is heated, how would the graph drawn in part a change?



Figure 7.16 A purple liquid dye diffusing through water.

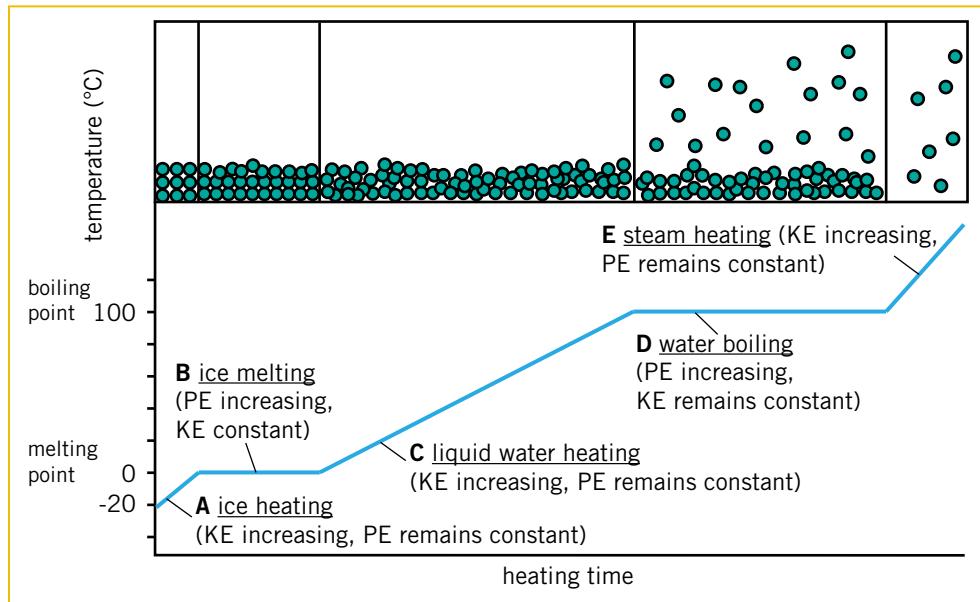
## 7.5 Changes in state

Pure substances undergo changes of state at definite temperatures. For example, ice melts at 0°C and water boils at 100°C at 101.3 kPa pressure. Other pure substances also have definite melting and boiling points that are characteristic of the particular substance.

### Heating curves

Typically, when a solid is heated it will melt to form a liquid. If heating is continued, the liquid will eventually boil to form a gas. The changes in temperature over time that occur during these phase changes can be plotted as a graph. Such a graph is called a **heating curve**.

Figure 7.17 shows a heating curve for water, together with an atomic-level depiction of what is happening at each stage (the water molecules have been represented as single spheres). A certain mass of ice, initially at -20°C, was heated at a constant rate until it melted and then finally until boiling occurred.



**Figure 7.17** Heating curve for water, together with a simplistic particle view of the changes occurring.

What is happening at a macroscopic level and an atomic level during each stage of this heating experiment can be explained as follows:

**Stage A:** The heat energy is causing the ice ( $\text{H}_2\text{O}$ ) molecules to vibrate more. Their kinetic energy is increasing and so the temperature of the ice will rise. Because the  $\text{H}_2\text{O}$  molecules are not significantly changing their positions in the ice lattice, the potential energy of the molecules will remain approximately the same.

**Stage B:** At this stage, the molecules in the ice have become so energetic that they are able to break loose from their lattice positions and so change from solid to liquid. The temperature of the ice/water mixture remains constant during the melting process because the heat energy is being used to disrupt the bonds between the  $\text{H}_2\text{O}$  molecules in the solid ice lattice, and not to increase the kinetic energy of the molecules. That is, the kinetic energy of the molecules remains constant during the change in state, but their potential energy increases as the intermolecular bonds are disrupted and the ice melts to form liquid water. The temperature ( $0^\circ\text{C}$ ) at which the ice melts (shown by a plateau in the graph) is called the melting point.

**Stage C:** All the solid ice has now melted, so the heat energy is again causing the molecules to move around faster. Their kinetic energy is increasing, as is their temperature. However, the potential energy of the molecules is not changing because bonds are not being broken by the added heat energy, and the distance between the molecules is not changing significantly.

**Stage D:** At  $100^\circ\text{C}$ , the liquid water reaches its boiling point and the temperature remains constant as the heat energy is used to break the intermolecular bonds between the  $\text{H}_2\text{O}$  molecules to form steam (gaseous water). During this stage, the potential energy of the molecules increases as they move away from one another in the boiling process. The average kinetic energy of the molecules does not change, so the temperature remains constant until all the molecules have changed from the liquid state to the gas state.

**Stage E:** As the gas continues to be heated, the particles absorb the heat energy, resulting in an increase in their kinetic energy. In other words, the temperature of the gas increases.



Two key points can be made about the changes in potential and kinetic energies of the particles during cooling or heating.

- During a phase change, the temperature of the substance remains constant because the average kinetic energy of its particles does not change, however the potential energy of the particles does alter.
- When a solid or liquid is heated or cooled without a phase change occurring, the temperature of the substance changes since the average kinetic energy of its particles is changing. The average distance between the particles does not significantly alter, so the potential energy is essentially unchanged.

### \* Review exercise 7.5

- 1 Draw the cooling curve that would be expected as mercury is cooled from  $400^{\circ}\text{C}$  to  $-100^{\circ}\text{C}$ . The melting point and boiling point for mercury are  $-39^{\circ}\text{C}$  and  $357^{\circ}\text{C}$  respectively. Label the diagram to show what is happening in each section of the graph.
- 2 Draw a series of diagrams to show what is happening, at the atomic level, during each of the major sections of the graph drawn in question 1.

## 7.6 Evaporation, vapour pressure and boiling

### Evaporation

If water in a cup is left exposed to the atmosphere it eventually evaporates. The water that was present as a liquid has changed to a gas. The process of evaporation is a change, from the liquid to the gaseous state, that occurs at a temperature below the boiling point of the liquid.

The kinetic theory can be used to explain what is happening at the molecular level during evaporation. Because the particles in a sample of a liquid possess a range of kinetic energies, at any particular instant a small fraction of particles will have kinetic energies considerably greater than the average value. If a particle near the surface of the liquid has sufficient kinetic energy, it may be able to escape from the attractive forces of its neighbouring particles and become a gas. Only particles with a sufficiently high kinetic energy will be moving fast enough to escape from the liquid.

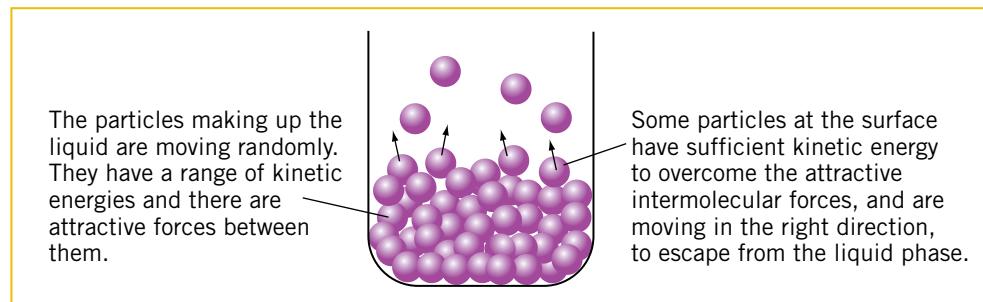


Figure 7.18 Particles escaping from the liquid state during evaporation.

Because the more energetic particles are the ones that tend to escape, this will lower the average kinetic energy of the particles remaining in the liquid. This explains why the temperature of a liquid falls as evaporation takes place.

## Vapour pressure

When a liquid is placed in a container that is then sealed, the amount of liquid will begin to decrease. This happens because the more energetic particles in the liquid are escaping from the surface of the liquid to become a gas. Eventually, however, the amount of liquid present in the container remains constant. As the number of gas particles builds up in the container, the possibility of these gas particles colliding with the liquid's surface and being attracted back into the liquid state (condensing) increases.

Therefore, there are two processes happening at the same time in the closed container. The evaporation, or vaporisation, process for the liquid, that occurs at a constant rate at a given temperature, is taking place. Condensation of the vapour (gas) to reform some of the liquid is also occurring. When the liquid is first put in the container, the rate of this condensation process is zero, but it increases as the number of gas particles formed by evaporation increases. Eventually the rate of evaporation of the liquid equals the rate of condensation of the vapour, that is, the rate at which the particles are escaping from the liquid is equal to the rate at which they are returning to it. When no overall change is occurring in the volume of liquid in the flask, because the two processes are occurring at the same rate, the system is said to be in a state of dynamic equilibrium.

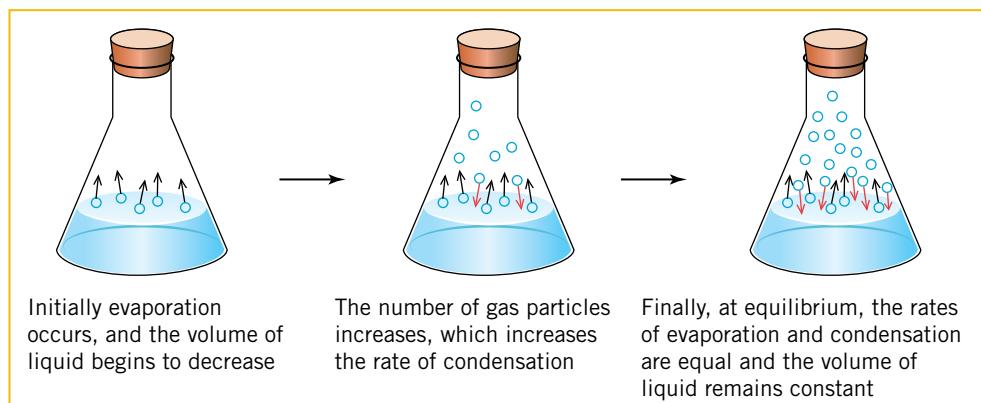


Figure 7.19 Establishing liquid–vapour equilibrium in a closed flask.

The gas particles that evaporate from the liquid exert a pressure due to their collisions with the walls of the container. This pressure of the gas in equilibrium with the liquid in a closed container is called the equilibrium vapour pressure of the liquid, or more commonly, the **vapour pressure** of the liquid. The vapour pressures of some familiar liquids are listed in Table 7.1.

TABLE 7.1 VAPOUR PRESSURES OF SOME FAMILIAR LIQUIDS AT 20°C

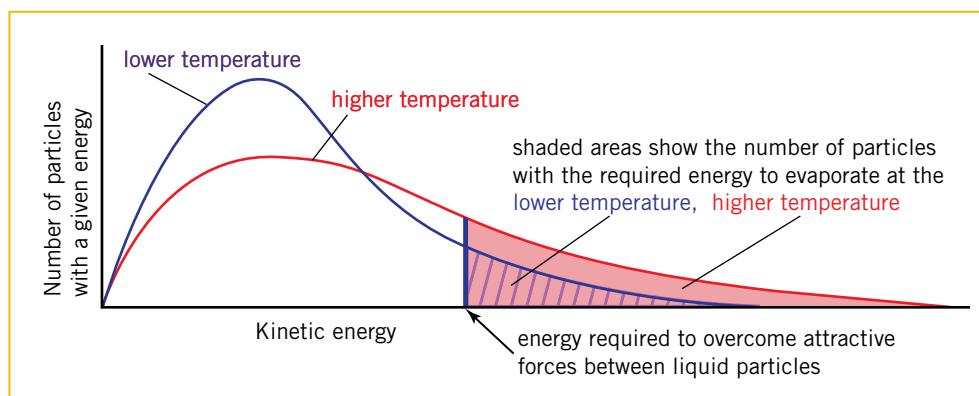
Substance	Vapour pressure (kPa)
Diethyl ether	58.9
Acetone	24.6
Ethanol	5.85
Water	2.34
Mercury	0.000160

As can be seen from the data in Table 7.1, the vapour pressures of different liquids vary widely. Liquids with high vapour pressures, like diethyl ether and acetone, are said to be **volatile liquids**. When in an open container, volatile liquids evaporate rapidly. At a specific temperature, the vapour pressure of a particular liquid is principally determined by the strength of the intermolecular forces between its particles. The stronger these attractive forces, the greater the amount of kinetic energy required by the particles to escape from the liquid to form the gas. Therefore fewer gas particles are produced, leading to a smaller vapour pressure.

The relative strengths of the intermolecular forces of different liquids can be inferred from vapour pressure data. For example, because the pressure of the vapour produced by water is much less than the pressure of the vapour produced by diethyl ether at the same temperature, the water molecules must require much more energy to break away from the liquid than the diethyl ether molecules. It therefore follows that the intermolecular bonds between the water molecules must be stronger than those between the diethyl ether molecules.

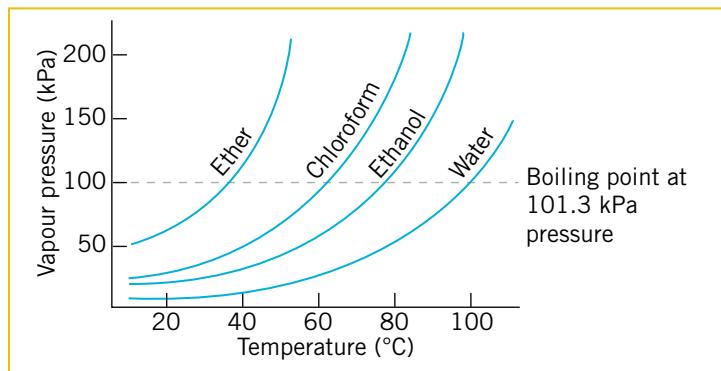
Some solids also produce significant vapour pressures. Naphthalene, which is used in moth balls, and paradichlorobenzene, which is used as a toilet deodorant, have quite high vapour pressures. As a result, they have strong odours and gradually ‘disappear’ over a period of time.

The temperature of the liquid also affects its vapour pressure. As the temperature rises, the vapour pressure of a liquid increases. This occurs because the average kinetic energy of the particles of the liquid increases with increasing temperature, as shown in the graphs in Figure 7.20. As a result, at a higher temperature a greater proportion of the particles will have sufficient kinetic energy to escape from the liquid to produce the vapour.



**Figure 7.20** The effect of temperature on the number of particles with sufficient kinetic energy to evaporate from a liquid.

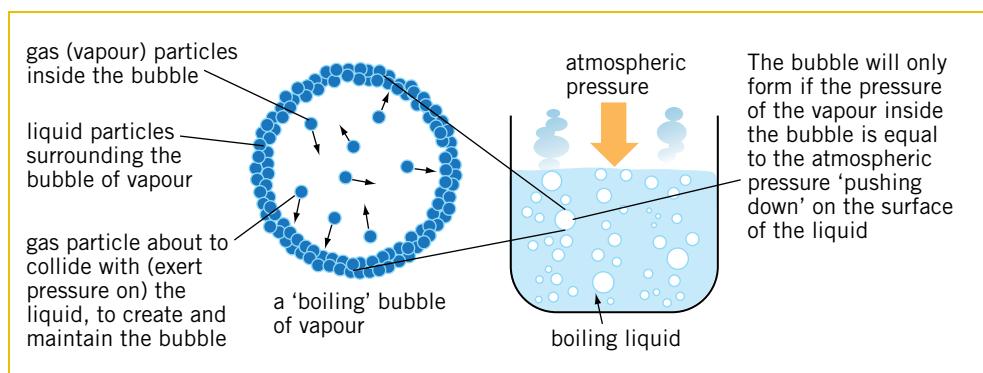
Figure 7.21 shows the variation in vapour pressure of several liquids as a function of temperature. Other liquids show similar increases in vapour pressure as the temperature is increased.



**Figure 7.21** The vapour pressure at some liquids as a function of temperature.

## Boiling

When water is heated to 100°C, at 101.3 kPa pressure, it starts to boil. During boiling, bubbles of steam that rise to the surface are produced within the liquid water. These bubbles of steam can only form in the hot water when the vapour pressure of the water equals the atmospheric pressure of the surroundings. The pressure of the vapour within the 'boiling' bubbles needs to be large enough to stop them from collapsing because of the atmospheric pressure exerted at the liquid's surface. This only occurs at the temperature at which the vapour pressure reaches atmospheric pressure. The process of bubble formation is illustrated in Figure 7.22.



**Figure 7.22** When the vapour pressure of a liquid equals the atmospheric pressure, bubbles of vapour are able to form throughout the liquid, that is, boiling occurs.

At the boiling point of a substance, continuous vaporisation takes place throughout the liquid. This is unlike the evaporation process, where vaporisation only takes place at the surface of the liquid.

It is possible to predict the boiling point of each of the liquids in Figure 7.21 by identifying the temperature at which the vapour pressure equals atmospheric pressure. For example, at an atmospheric pressure of 101.3 kPa, ether has a boiling point of about 35°C and ethanol about 78°C.

As boiling occurs when the vapour pressure of a liquid reaches atmospheric pressure, it follows that any variation in atmospheric pressure will result in a change in boiling point. The lower the atmospheric pressure, the lower the boiling point will be. Under reduced pressure conditions, the liquid will not have to be heated to such a high temperature for its vapour pressure to reach atmospheric pressure. For example, on the peak of Mt Everest, where atmospheric pressure is about 35 kPa, water boils at about 70°C.

## \* Review exercise 7.6

- 1 State the difference between evaporation and boiling in terms of:
  - a the temperature at which they occur
  - b where they occur in a liquid.
- 2 Use the kinetic theory to explain why:
  - a wet clothes dry faster on a hot day than on a cold day
  - b people perspire when they are hot
  - c a puddle of water will 'dry up' slower on a humid day than on a less humid day.
- 3 At 20°C the vapour pressure of water is 2.34 kPa and that of pentane ( $C_5H_{12}$ ) is 55.6 kPa.
  - a Which liquid should have the higher boiling point, at the same atmospheric pressure?
  - b Compare the likely strengths of the intermolecular forces of the two liquids.
- 4 Use Figure 7.21 to predict the:
  - a boiling point of chloroform, at an atmospheric pressure of 101.3 kPa
  - b atmospheric pressure at which ether would boil at 25°C.
- 5 An instruction pamphlet for the use of a pressure cooker for cooking food contained the following information:

*... at 15 psi your food is cooking at 125°C instead of just 100°C. When the heat is turned off and the pressure begins to drop you will sometimes hear the contents begin to boil very rapidly inside the closed pot ...*

  - a In an open saucepan, what is the approximate temperature of boiling water?
  - b Explain why, in a pressure cooker that contains water, the food is cooked at 125°C.
  - c When the heat is turned off, why can rapid boiling sometimes be heard in the closed pot?
- 6 If you like your boiled egg to be cooked for exactly three minutes at sea level (that is, at an atmospheric pressure of 101.3 kPa), why would it take a longer time to cook your 'three minute' egg in boiling water on Mt Everest?



## MAJOR IDEAS

- The kinetic theory of gases explains the physical properties of gases. The main ideas are as follows:
  - the particles are relatively widely spaced
  - the particles move in rapid, straight-line motion
  - collisions between particles are perfectly elastic
  - the forces of attraction between particles are negligible
  - the average kinetic energy of the particles of any gas depends only on the temperature.
- For a constant mass of gas at a constant temperature, its volume decreases as its pressure increases, and vice versa.
- For a constant mass of gas at a constant pressure, as its temperature increases, so does its volume. As its temperature decreases, so does its volume.
- Kelvin temperature (K) = Celsius temperature ( $^{\circ}\text{C}$ ) + 273.
- Avogadro's hypothesis is that equal volumes of gases measured under the same conditions of temperature and pressure contain equal numbers of particles.
- The molar volume of a gas is the volume occupied by a mole of gas. For an ideal gas at STP (273 K [ $0^{\circ}\text{C}$ ] and 101.3 kPa), this is 22.4 L.
- The kinetic theory can be extended to solids and liquids. In solids the particles are closely packed and vibrate about fixed positions. In liquids the particles are fairly closely packed but can move past each other. Intermolecular forces are important in solids and liquids.
- Potential energy is energy due to position. In the gas state the particles of a substance have greater potential energy than in the liquid, which is in turn greater than in the solid state. Kinetic energy is energy due to motion.
- The heating curve for a substance is a plot of the temperature of the substance against heating or cooling time. The temperature remains constant when the substance changes from solid to liquid and when it changes from liquid to gas.
- Evaporation is the change from liquid to gas at a temperature below the boiling point. Evaporation occurs at the surface of a liquid.
- Vapour pressure is the pressure exerted by a vapour in equilibrium with the liquid from which it was derived.
- The vapour pressure of a liquid increases with increasing temperature.
- The larger the intermolecular forces between the molecules of a liquid, the lower its vapour pressure.
- Boiling is the change from liquid to gas at the boiling point. Boiling occurs throughout the liquid.
- The boiling point is the temperature at which the vapour pressure of a liquid equals atmospheric pressure.

## QUESTIONS

- 1 To compare the properties of a sample of a gas and a sample of a liquid, the following experiments were carried out with each of the two samples.

Experiment 1: the sample was transferred from a smaller container to a larger one.

Experiment 2: the sample was placed in a cylinder with a piston and a large force was applied to the piston.

Experiment 3: the sample was heated in an expandable container (assume a change in state did not occur).

- a Describe how the gas and the liquid would differ in their behaviours in each experiment.
- b Explain these differences in terms of the kinetic theory of matter.

- 2 A cylinder with a moveable piston contains some HCl gas, as shown in Figure 7.23.

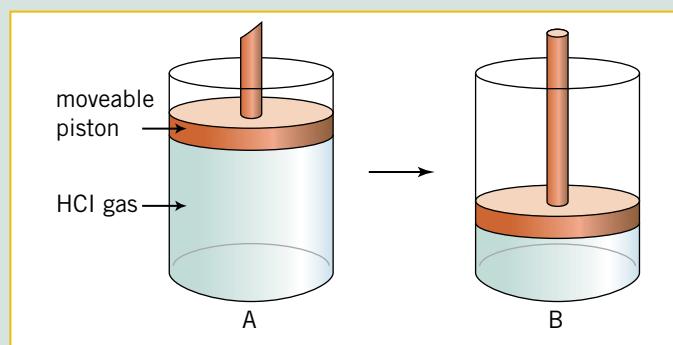


Figure 7.23

Describe three different ways in which the volume of the gas in A can be changed to the volume shown in B. If relevant, state the variables that must be kept constant for your chosen ways.

- 3 a Predict what would happen to the length of the column of mercury in the simple mercury barometer shown in Figure 7.5 if the barometer was moved from a sea-level location to the top of a mountain. Explain your prediction in terms of the kinetic theory of matter.
- b Why was mercury used in the simple barometer shown in Figure 7.5 rather than water?
- 4 Industrial gases are often stored as liquids.
  - a Why is it more convenient to store gases in this way?
  - b What conditions would have to be used to obtain the gas in the liquid state?

- 5 Use the kinetic theory to explain why:
- when most of the air inside a thin-walled can is removed (for example, by a vacuum pump), the can crushes
  - a balloon pushed under water reduces in volume
  - it is not safe to leave a full scuba-diving tank of air in a car parked in the sun
  - if the oven door is opened during the cooking of a cake, the risen cake mixture sometimes sinks or ‘goes flat’
  - 1 mole of  $\text{H}_2$  occupies the same volume as 1 mole of  $\text{N}_2$  at the same temperature and pressure
  - a sealed can partially filled with petrol may begin to bulge in hot weather
  - when most of the air is removed from a can containing some water, the water may begin to boil
  - washing on the clothes line will dry faster on a windy day than on a still day (assuming the temperature is the same on both days).
- 6 At a particular temperature, the average velocity of gaseous helium atoms is approximately  $3.0 \text{ km s}^{-1}$ . What would you expect the approximate average velocity of carbon dioxide molecules to be at the same temperature? (Hint: kinetic energy =  $\frac{1}{2} \text{mv}^2$ )
- 7 Describe how liquids differ in their macroscopic properties from solids.



Figure 7.24 Dry ice subliming.

- 8 Figure 7.24 shows a lump of dry ice (solid  $\text{CO}_2$ ) subliming. Explain what is happening at the molecular level in this photo.

- 9 Describe the changes in kinetic energy and potential energy that occur when a solid is melting at a fixed temperature.

- 10 The density of a material is a measure of the mass of a certain volume of this material. For example, because the density of water at  $25^\circ\text{C}$  is  $1 \text{ g mL}^{-1}$ , 1 mL of water must have a mass of 1 g. The densities of some substances at  $25^\circ\text{C}$  and 101 kPa pressure are given below:

Substance	Aluminium	Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ )	Dry air
Density ( $\text{g mL}^{-1}$ )	2.70	0.78	$1.19 \times 10^{-3}$

- Explain in terms of the kinetic theory why the density of the solid, aluminium, is greater than the density of the liquid, ethanol.
- Would you expect the density of aluminium to be the same, smaller or greater at a temperature of  $100^\circ\text{C}$  than at  $25^\circ\text{C}$ ? Explain your reasoning.
- Propose an explanation for why, at the same temperature and pressure, moist air is less dense than dry air.

- 11 Why is a burn from steam at  $100^\circ\text{C}$  typically more severe than a burn from boiling water at  $100^\circ\text{C}$ ? Include the terms ‘kinetic energy’ and ‘potential energy’ in your answer.
- 12 Dry ice sublimes directly from solid to gas at  $-78^\circ\text{C}$ . Draw a heating curve to show the changes in temperature with time as dry ice is heated from  $-100^\circ\text{C}$  to  $-50^\circ\text{C}$ .
- 13 The boiling points of acetone and acetic acid are respectively  $56^\circ\text{C}$  and  $118^\circ\text{C}$ .
- Which of these two liquids would probably have the stronger intermolecular forces between its molecules?
  - Which is probably the more volatile liquid at room temperature?
  - Which of the two liquids would you expect to have the higher vapour pressure, at the same temperature. Explain your reasoning.
- 14 Explain why, when cooking vegetables in boiling water on a stove, the temperature of the boiling water does not rise above about  $100^\circ\text{C}$  despite the saucepan being continually heated.

- 15** On the planet Mars, the approximate temperature range is 130 K to 293 K and the atmospheric pressure is approximately 1000 Pa.
- Convert the temperature range to °C.
  - What can be concluded about the temperature you would expect water to boil at on Mars (refer to Figure 7.21)?
  - Explain why the boiling point of water on Mars is different to that at normal atmospheric pressure on Earth.
  - NASA's recent Phoenix Mars Lander provided evidence for the existence of frozen water on Mars. One of the Principal Investigators for the Mission commented  
'It must be ice. These little clumps completely disappearing over the course of a few days, that is perfect evidence that it's ice. There had been some question whether the bright material was salt. Salt can't do that.'
- When the solid disappeared, there is no evidence that a liquid formed, so what must have happened to the solid?
  - What other white solid behaves this way?
  - Why can't salt disappear over a couple of days, like the ice did?
- 16** In an experiment, some liquid acetone (boiling point of 56°C) was placed in a closed container at 22°C and atmospheric pressure of 102 kPa. After two minutes the container was very gently heated. At all times during the experiment, some liquid acetone was present in the container. The pressure of the vapour inside the container, measured at various times during the experiment, is shown below:

Time (min)	Pressure (kPa)	Temperature (°C)
0	102	22
0.5	116	22
1.0	129	22
1.5	129	22
2.0	129	22
2.5	138	30
3.0	154	38
3.5	154	38

Explain the variation in the pressure of the vapour during the experiment.

- 17** At about -90°C, the vapour pressure of ethane,  $C_2H_6$ , is 101 kPa. Would you expect ethane to be a gas, liquid or solid at room temperature? Explain your answer.
- 18** Two flasks, X and Y, of equal volume are joined by a closed tap, as shown in Figure 7.25. Several experiments (A–D) were carried out by placing different gases in these two flasks and then opening the tap allowing the gases to mix. For each experiment, describe the contents of each flask and predict whether the pressure in each flask will decrease, increase or stay the same after the tap is opened and the gases have mixed completely. Assume the temperature remains constant.

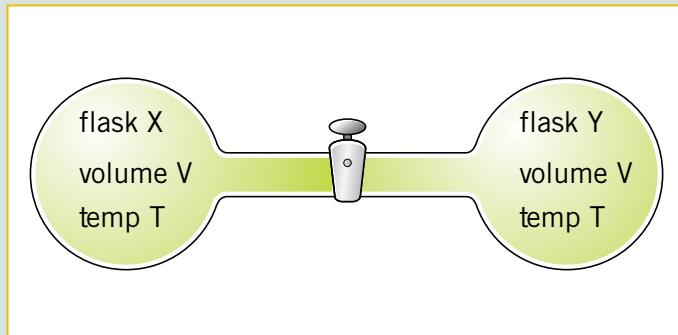


Figure 7.25

	Flask X	Flask Y
Experiment A	$H_2$ at 100 kPa pressure	no gas
Experiment B	$H_2$ at 100 kPa pressure	$N_2$ at 100 kPa pressure
Experiment C	$O_2$ at 100 kPa pressure	$CO_2$ at 300 kPa pressure
Experiment D	0.5 mol of $H_2$	0.5 mol of $N_2$

- 19** Equal masses of oxygen and sulfur dioxide are placed in separate flasks of equal volume at the same temperature. Compare the two gas samples in terms of:
- the numbers of molecules present
  - the gas pressures
  - the average kinetic energies of the molecules
  - the average molecular velocities.

- 20** In the seventeenth century, the Irish scientist Robert Boyle performed a series of experiments in which he investigated how the volume of a fixed mass of gas at a constant temperature changed with external pressure. Some typical values he may have recorded are given below:

Volume (mL)	20.0	15.0	10.0	5.0
Pressure (kPa)	104	138	208	415

- a Explain in terms of the kinetic theory why the pressure of the gas increases as its volume decreases.
- b Plot a graph of volume versus pressure for this data and use it to determine what the pressure of the gas would be if its volume was 25.0 mL.
- c Plot a graph of volume versus  $\frac{1}{\text{pressure}}$ . From this graph what can be inferred about the relationship between the volume and pressure of a gas? (This relationship is called Boyle's Law.)
- d If the temperature was not kept constant during the experiment, for example, if it had increased steadily during the experiment, would the results have been affected? Explain your answer in terms of the kinetic theory.
- e If during the experiment some of the gas had escaped from the vessel containing the gas, how would this have affected the results?
- f Describe, perhaps by drawing a diagram, the equipment set-up that could have been used to obtain data like that given in this question.
- 21** Some gases can be collected by a method called 'displacement of water'. Figure 7.26 shows the equipment that can be used to prepare and collect a sample of oxygen gas by displacement of water.

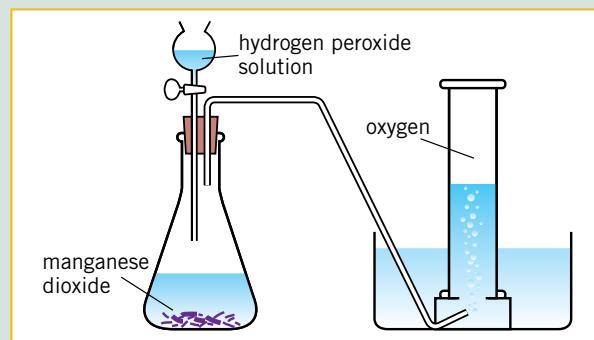


Figure 7.26 Preparation and collection of oxygen.

In this preparation, the hydrogen peroxide decomposes to form the oxygen gas and water when it is added to the manganese dioxide in the flask. The gas moves from the flask, through the delivery tube and then bubbles up through the water to be collected in the gas jar.

- a** Use the kinetic theory to explain why the gas moves out of the conical flask, bubbles up through the water and then finally collects above the water in the gas jar.
- b** For which types of gases would this method of collection not be successful?
- c** Suggest a method that could be used to measure the pressure of the gas inside the gas jar at the completion of the experiment.
- d** The gas collected in the gas jar is not pure oxygen. What other gas will be mixed with the oxygen? Where does this second gas come from?
- 22** **RESEARCH** Investigate the application of the properties of gases, solids and liquids and the kinetic theory of matter to:
- a** scuba diving
- b** the process of freeze-drying.



# 8

# Solutions

**BY THE END OF THIS CHAPTER YOU SHOULD BE ABLE TO:**

- describe a solution as a homogeneous mixture
- explain the difference between unsaturated, saturated and supersaturated solutions
- predict the solubilities of ionic compounds listed in the solubility rules
- determine the concentration of a solution using the measures of  $\text{g L}^{-1}$ ,  $\text{mol L}^{-1}$  and percentage composition
- describe some colligative properties of a solution.

## 8.1 Homogeneous mixtures: solutions

Solutions are defined as homogeneous mixtures. A wide range of artificial and naturally occurring solutions exist, including rainwater, vinegar, stomach acid, brass, sap in plants, wine, petrol, seawater and air. In a homogeneous mixture, all parts of the mixture have the same distribution of components. This means that throughout a sample of a solution, the composition and properties will be constant. In a sample of seawater, for example, the saltiness will be the same at the top, middle and bottom of the sample.



Figure 8.1 Some solutions found in the home.

Simple solutions can be thought of in terms of a **solvent** that ‘does the dissolving’ and a **solute** that ‘is dissolved’. The solvent is usually present in the larger amount and the solute is usually present in the smaller amount. For instance, when sugar is dissolved in water, water is the solvent and sugar is the solute. A sugar in water solution is an example of a solid solute dissolved in a liquid solvent.

A solution does not have to be formed from a solid dissolving in a liquid. Any homogeneous mixture formed from substances in any combination of states is a solution. Vinegar, produced by mixing acetic acid, a liquid, with water is a solution. Carbon dioxide gas dissolved in water to form soda water is also a solution. Air, a mixture of mostly nitrogen and oxygen gases, and brass, a mixture of copper and zinc, are other examples of solutions. Different types of solutions are listed in Table 8.1.

TABLE 8.1 DIFFERENT TYPES OF SOLUTIONS

Type of solution	Examples
Solid in solid	‘silver’ coins (nickel in copper), bronze (tin in copper), stainless steel (carbon and chromium in iron)
Solid in liquid	cordial (sugar in water), seawater (sodium chloride in water)
Liquid in liquid	beer and wine (alcohol in water), vinegar (acetic acid in water), perfumes (liquid fragrant compounds in ethanol)
Gas in liquid	cloudy ammonia (ammonia in water), hydrochloric acid (hydrogen chloride in water), effervescent drinks (carbon dioxide in water)
Gas in gas	air (nitrogen, oxygen, carbon dioxide and other gases)

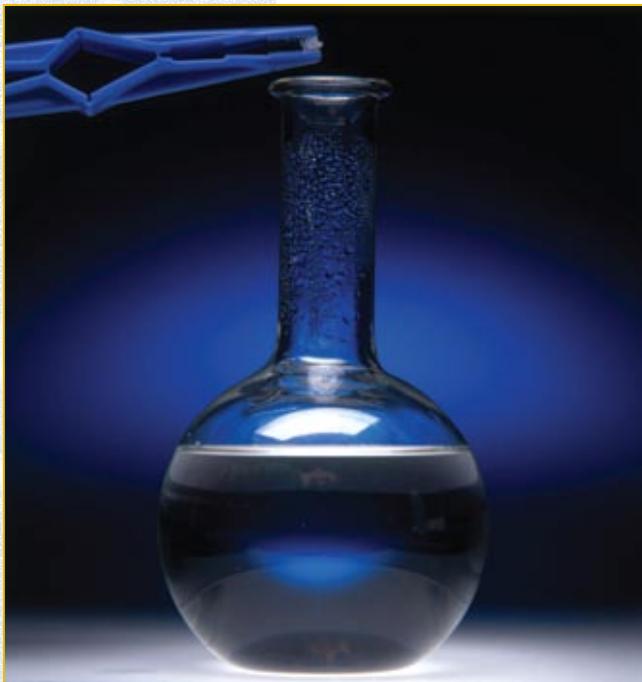


**Figure 8.2** The solution of copper sulfate must be saturated because some solid copper sulfate remains undissolved at the bottom of the test tube.

### Saturated and supersaturated solutions

If sodium chloride is continually added to water, there comes a point at which no more will dissolve. At this point, the solution is said to be 'saturated'. A **saturated solution** is one in which no more solute will dissolve under the existing conditions of temperature and pressure. An **unsaturated solution** is a solution that contains less than the quantity of solute needed to saturate it under the existing conditions.

Under certain conditions it is possible to prepare a solution that contains more dissolved substance than is contained in a saturated solution. For example, a saturated solution of sodium acetate at 50°C contains more dissolved solid than a saturated solution of sodium acetate at 25°C. However, if a saturated solution of sodium acetate is prepared at 50°C, and then the solution is carefully cooled back to 25°C, all the sodium acetate remains dissolved. A **supersaturated solution** is a solution that contains more dissolved solute than a saturated solution could normally hold under the existing set of conditions. Some supersaturated solutions are relatively stable. Toffee is basically a supersaturated solution of sugar in water. It is prepared as a saturated solution at high temperatures and then cooled back to room temperature. Many supersaturated solutions are unstable and the presence of dust or the addition of a small quantity of solid solute can cause the excess solute to crystallise out from solution. This can be seen in Figure 8.3, which shows that when a small crystal of sodium acetate is added to its supersaturated solution, the solid sodium acetate begins to crystallise out of solution.



**Figure 8.3** If a small seed crystal of sodium acetate is added to a supersaturated solution of sodium acetate, sodium acetate crystals are formed until all the excess dissolved solute has crystallised from the solution, leaving a saturated solution.

## \* Review exercise 8.1

- 1 In Chapter 5, it was explained that matter is often classified into four broad categories: elements, compounds, solutions and heterogeneous mixtures. Explain the differences between compounds and solutions in this classification.
- 2 At 25°C the solubility of sodium thiosulfate is 76 g per 100 g water. Decide whether the following solutions at 25°C are unsaturated, saturated or supersaturated:
  - a 152 g of sodium thiosulfate dissolved in 200 g of water
  - b 185 g of sodium thiosulfate dissolved in 250 g of water
  - c 39 g of sodium thiosulfate dissolved in 45 g of water.
- 3 If the solubility of  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  is 41 g per 100 g of water at 25°C, how might it be possible to prepare a supersaturated solution containing 43 g of  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  per 100 g of water?
- 4 A student is given an aqueous solution of a salt and a crystal of the salt. How could the student use this crystal to determine whether the solution is unsaturated, saturated or supersaturated?

## 8.2 Solubilities of different solutes in different solvents

Different substances can exhibit very different solubilities in a particular solvent. Sodium chloride is an example of a substance that is readily soluble in water, while oxygen is less soluble and sand is virtually insoluble. Also, the solubility of a particular substance can be different in different solvents. Olive oil, for example, is insoluble in water but quite soluble in kerosene. One of the factors that affects the solubility of a particular substance is the nature of the solute and the solvent.

### Polar and non-polar substances

Solvents and solutes are often classified as polar or non-polar. Water and sugar are examples of **polar substances** and petrol and oil are examples of **non-polar substances**. Compounds containing  $-\text{OH}$  or  $-\text{NH}-$  groups in their molecules are often polar and compounds whose molecules are mostly composed of carbon and hydrogen atoms tend to be non-polar. Ionic compounds can be regarded as very highly polar substances. Some substances, for example those containing  $-\text{OH}$  groups and carbon and hydrogen atoms, exhibit both polar and non-polar properties. A list of common polar and non-polar substances is shown in Table 8.2. Polar and non-polar substances will be discussed in more detail in Unit 3A.

TABLE 8.2 COMMON POLAR AND NON-POLAR SUBSTANCES

Polar substances	Non-polar substances	Substances which behave as both polar and non-polar
water, $\text{H}_2\text{O}$ glucose, $\text{C}_6\text{H}_{12}\text{O}_6$ sugar (sucrose), $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ hydrogen chloride, $\text{HCl}$ ammonia, $\text{NH}_3$ ionic compounds	natural gas (methane), $\text{CH}_4$ petrol, composed of hydrocarbons e.g. $\text{C}_8\text{H}_{18}$ butter kerosene oil candle wax	ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ acetic acid, $\text{CH}_3\text{COOH}$ acetone, $\text{CH}_3\text{COCH}_3$ soap, e.g. $\text{C}_{16}\text{H}_{33}\text{COO}^-\text{Na}^+$ detergents, e.g. $\text{C}_{20}\text{H}_{41}\text{SO}_3^-\text{Na}^+$



**Figure 8.4** Oil added to water—a mixture of non-polar and polar substances.



## Dissolving polar and non-polar substances

In general, a polar substance will tend to dissolve in a polar solvent, but not in a non-polar solvent. Similarly, a non-polar substance will tend to dissolve in a non-polar solvent but not in a polar solvent. For example, sugar will dissolve in water, but not in cooking oil, and butter will dissolve in cooking oil, but not in water. These solubility generalisations are sometimes expressed as ‘like dissolves like’. Figure 8.4 shows non-polar oil added to polar water. After this mixture has been allowed to settle, a two-layer mixture will form with the less dense oil being the top layer. The two liquids are said to be immiscible because they do not dissolve in one another.

The substances listed in Table 8.2 that have both polar and non-polar characteristics tend to be able to dissolve or be dissolved in both polar and non-polar substances. For example, detergents are used to dissolve grease (a non-polar substance) and they also dissolve in water.

### Solubilities of ionic compounds

The solubilities of ionic compounds in water are a special situation. Many ionic compounds, like sodium chloride, are readily soluble in water, as would be expected considering that ionic compounds are highly polar. However, many ionic compounds, such as iron(III) oxide (rust), are quite insoluble in water. Because ionic compounds are very polar substances, they will not be soluble in non-polar solvents.

Even though the solubilities of ionic compounds in water vary considerably, some broad generalisations can be made, as shown in Table 8.3. The solubility rules summarised in this table are based on the negative ions in the ionic compounds.

**TABLE 8.3 SOLUBILITY RULES FOR IONIC COMPOUNDS IN WATER**

#### Soluble in water

Soluble	Exceptions	
	Insoluble	Slightly soluble
Most chlorides ( $\text{Cl}^-$ )	$\text{AgCl}$	$\text{PbCl}_2$
Most bromides ( $\text{Br}^-$ )	$\text{AgBr}$	$\text{PbBr}_2$
Most iodides ( $\text{I}^-$ )	$\text{Agl}$ , $\text{Pbl}_2$	
All nitrates ( $\text{NO}_3^-$ )	No exceptions	
All acetates (ethanoates)	No exceptions	
Most sulfates ( $\text{SO}_4^{2-}$ )	$\text{SrSO}_4$ , $\text{BaSO}_4$ , $\text{PbSO}_4$	$\text{CaSO}_4$ , $\text{Ag}_2\text{SO}_4$

#### Insoluble in water

Insoluble	Exceptions	
	Soluble	Slightly soluble
Most hydroxides ( $\text{OH}^-$ )	$\text{NaOH}$ , $\text{KOH}$ , $\text{Ba}(\text{OH})_2$	$\text{Ca}(\text{OH})_2$ , $\text{Sr}(\text{OH})_2$
Most carbonates ( $\text{CO}_3^{2-}$ )	$\text{Na}_2\text{CO}_3$ , $\text{K}_2\text{CO}_3$ , $(\text{NH}_4)_2\text{CO}_3$	
Most phosphates ( $\text{PO}_4^{3-}$ )	$\text{Na}_3\text{PO}_4$ , $\text{K}_3\text{PO}_4$ , $(\text{NH}_4)_3\text{PO}_4$	
Most sulfides ( $\text{S}^{2-}$ )	$\text{Na}_2\text{S}$ , $\text{K}_2\text{S}$ , $(\text{NH}_4)_2\text{S}$	

Soluble = more than 0.1 mole dissolves per litre at 25°C

Slightly soluble = between 0.01 and 0.1 mole dissolves per litre at 25°C

Insoluble = less than 0.01 mole dissolves per litre at 25°C.

The solubility rules can be used to predict whether or not a particular ionic substance will be soluble, slightly soluble or insoluble in water. For example, for ionic chlorides, it can be predicted that  $\text{NaCl}$ ,  $\text{CaCl}_2$  and  $\text{AlCl}_3$  are soluble in water but  $\text{AgCl}$  is insoluble. Other examples of solubility predictions are:

- barium sulfate,  $\text{BaSO}_4$ , is insoluble in water
- sodium sulfide,  $\text{Na}_2\text{S}$ , is soluble in water
- copper phosphate,  $\text{Cu}_3(\text{PO}_4)_2$ , is insoluble in water
- potassium hydroxide,  $\text{KOH}$ , is soluble in water.

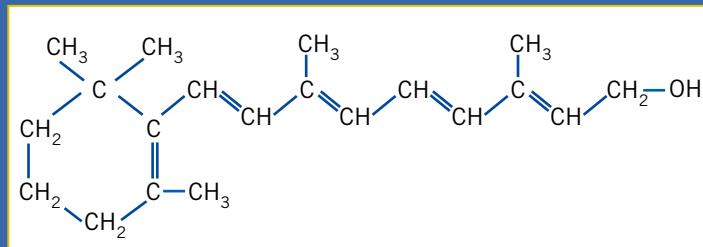
An additional solubility ‘rule’ that is not included in the solubility table given on the previous page is that all ionic compounds containing group 1 metal ions, such as sodium or potassium ions, or ammonium ions are soluble in water. For example, sodium dichromate,  $\text{Na}_2\text{Cr}_2\text{O}_7$ , and ammonium hydrogensulfate,  $\text{NH}_4\text{HSO}_4$ , are soluble in water.

### \* Review exercise 8.2

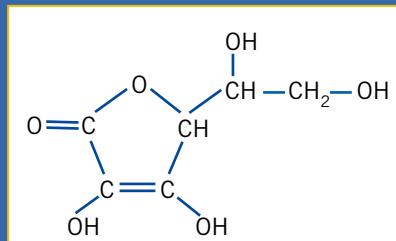
- 1 Compare the likely solubilities of the following substances in water, which is polar, with those in turpentine, which is non-polar.
 

<b>a</b> ammonia, $\text{NH}_3$	<b>e</b> methanol, $\text{CH}_3\text{OH}$
<b>b</b> calcium carbonate, $\text{CaCO}_3$	<b>f</b> copper chloride, $\text{CuCl}_2$
<b>c</b> zinc sulfate, $\text{ZnSO}_4$	<b>g</b> octane, $\text{C}_8\text{H}_{18}$
<b>d</b> methane, $\text{CH}_4$	<b>h</b> magnesium hydroxide, $\text{Mg}(\text{OH})_2$
- 2 Which would be the best liquid, water or kerosene, to remove the following substances? Explain your answers.
  - a** dribbles of lubricating oil on a glass window
  - b** a salt (sodium chloride) deposit on brickwork
- 3 Vitamins B and C are water soluble and excess intakes tend to be excreted in urine. Excess intakes of vitamins A, D, E and K are not excreted but tend to be stored in the body’s fat. Identify which of the following structures represents vitamin A and which represents vitamin C.

Structure a



Structure b



- 4 **a** Describe a method you could use to separate a powdered mixture of potassium chloride, barium sulfate and candlewax. (You may need to refer to Section 5.6 to revisit methods used to separate mixtures.)
   
**b** Explain your chosen method in terms of the properties of the three substances.

## 8.3 The effect of temperature and pressure on solubility

### Temperature

The solubilities of many substances are quite markedly affected by changes in temperature. For most solids dissolved in a liquid, an increase in temperature results in an increase in solubility. Figure 8.5 shows the solubility curves for some ionic substances in water as a function of temperature.

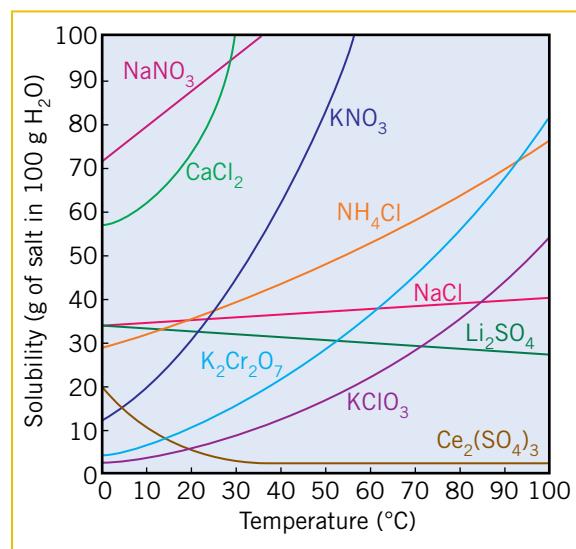


Figure 8.5 The solubility curves for some ionic compounds in water.

The solubilities of gases in liquids decrease with increasing temperature. This explains the bubbles that first appear when water is being heated. These are not bubbles of steam, but air bubbles. Some of the air that was dissolved in the water comes out of solution as the temperature increases. This temperature effect on the solubility of a gas has important environmental implications. If the temperature of the water in rivers, lakes and oceans increases even slightly, then it will contain less dissolved oxygen—possibly not enough oxygen to support aquatic life.

### Pressure

Pressure has little effect on the solubilities of solids and liquids. However, the solubility of a gas in a liquid is directly proportional to the pressure of that gas above the solution. This is the reason for the ‘fizziness’ of soft drinks. The carbon dioxide remains dissolved in the drink while under pressure in the sealed bottle or can. Once the container is opened, the pressure of carbon dioxide above the solution is reduced and some of the dissolved gas bubbles out of solution, as seen in Figure 8.6.



Figure 8.6 Bubbles of gaseous carbon dioxide escaping from the liquid cause the drink to ‘fizz’ out of the can.

### \* Review exercise 8.3

- 1 Use the solubility curves shown in Figure 8.5 to answer the following questions:
  - a Which is more soluble in water at 50°C, ammonium chloride or potassium nitrate?
  - b i What minimum mass of calcium chloride would you need to add to 100 g of water to form a saturated solution at 20°C?  
ii If this saturated solution was then cooled to 5°C, what would you expect to see happen?
  - c What is the maximum amount, in grams, of potassium dichromate that could be dissolved in 200 g of water at 80°C?
- 2 Explain in terms of the kinetic theory why a ‘fizzy drink’ goes flat when the top is taken off the bottle.

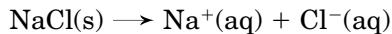
## 8.4 Aqueous solutions

Solutions in which the solute is dissolved in water are called aqueous solutions. During the formation of a solution, a rearrangement of particles occurs. When a solid solute is dissolved in water, the solid crystal structure is broken down and the solute particles mix with the water molecules to form the solution.



### Solutions of ionic compounds

When an ionic solid dissolves in water, the orderly lattice arrangement of positive and negative ions is disrupted and the ions separate from one another and mix with the water molecules. As a result, in a solution of an ionic compound, the ions are not bound together but are moving randomly as separated ions within the solution. For example, when sodium chloride is dissolved in water the ionic lattice breaks up to form separate  $\text{Na}^+$  and  $\text{Cl}^-$  ions which are surrounded by water molecules (see Figure 3.4). The dissolving of sodium chloride in water can be represented as follows.



The process involving the breaking apart of an ionic lattice into separated ions is often called **dissociation**. This means soluble ionic compounds dissociate when mixed with water.

If an ionic solid containing a polyatomic ion, such as  $\text{SO}_4^{2-}$  or  $\text{CO}_3^{2-}$ , dissolves in water, the atoms in the polyatomic ion remain covalently bonded together. When sodium sulfate,  $\text{Na}_2\text{SO}_4$ , is added to water, the ions in the resulting solution are  $\text{Na}^+$  ions and  $\text{SO}_4^{2-}$  ions.

Substances that produce ions in solution are called **electrolytes**. Ionic compounds are labelled as **strong electrolytes** because they completely break up into ions when they dissolve in water. Even an essentially insoluble ionic compound is classified as a strong electrolyte because when added to water, the tiny amount that does dissolve completely breaks up into ions.

## Solutions of covalent molecular substances

In covalent molecular substances, the atoms are strongly bonded together in molecules. When soluble solid molecular substances, such as sugar, dissolve in water, the solute molecules break away from the lattice structure and mix with the water molecules to form the solution shown in Figure 8.7. The dissolving of sugar,  $C_{12}H_{22}O_{11}$ , could be represented as:

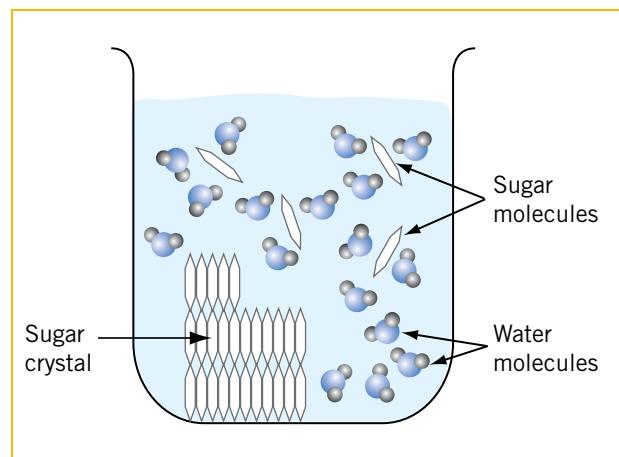
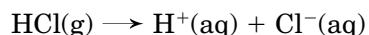


Figure 8.7 A model for sugar dissolving in water.

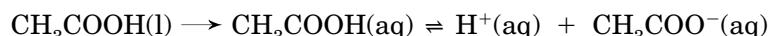
The dissolving process of liquid and gaseous molecular substances in water also involves the substance's molecules mixing with the water molecules to form the solution.

For many molecular substances, their molecules remain intact during the formation of the aqueous solution. These substances are called **non-electrolytes**. The sugar solution, for instance, is made up of only dissolved  $C_{12}H_{22}O_{11}$  molecules and water molecules. However, when some molecular substances are dissolved in water, their molecules form ions. When hydrogen chloride gas, HCl, dissolves in water, all the hydrogen chloride molecules break up to form hydrogen ions and chloride ions in solution.



This process in which a neutral species forms one or more ions is referred to as **ionisation**. In the example above, the neutral HCl molecules have undergone ionisation to form  $H^+$  and  $Cl^-$  ions.

A few of the molecular substances that undergo ionisation in aqueous solution act as strong electrolytes, that is, all the molecules dissolved in the water break up into ions. Examples of these substances include hydrogen chloride, HCl, nitric acid,  $HNO_3$ , and sulfuric acid,  $H_2SO_4$ . However, most molecular substances that ionise in aqueous solution act as **weak electrolytes**, where only some of the dissolved molecules form ions. For example, although liquid acetic acid,  $CH_3COOH$ , is extremely soluble in water, only a small fraction of the dissolved molecules are ionised. Most of the dissolved acid is present in the form of neutral molecules. The behaviour of acetic acid in water can be represented as follows:



The double arrows indicate the reaction does not go to completion. This means the solution contains both the reactant ( $CH_3COOH$ ) and the products ( $H^+$  and  $CH_3COO^-$ ). Other examples of weak electrolytes include ammonia,  $NH_3$ , hydrogen fluoride, HF, and citric acid.

These three different processes that occur when soluble covalent molecular substances are added to water are summarised in Figure 8.8.

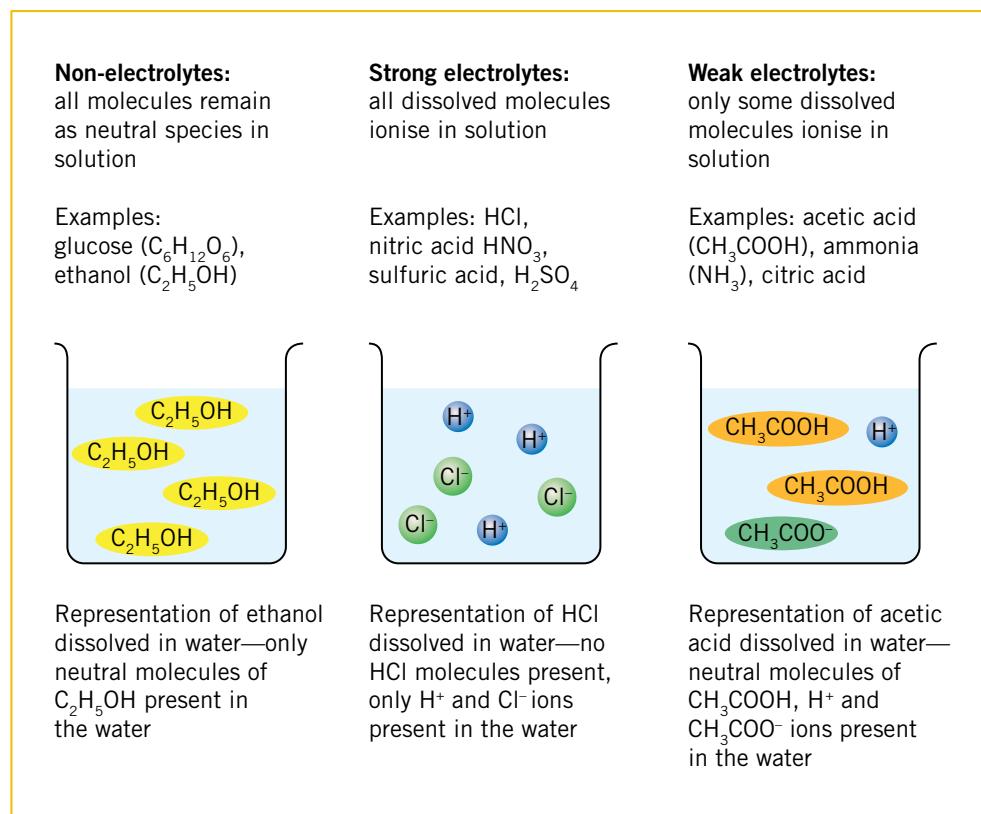


Figure 8.8 Different ways in which molecular substances behave when dissolved in water.

## Conductivity of electrolyte solutions

Evidence for the formation of ions when a substance is dissolved in water is provided by conductivity measurements. Pure water is essentially a non-conductor of electricity, which indicates the presence of very few ions. However, if a soluble strong electrolyte is dissolved in the water, the solution becomes a good conductor of electricity. When a solution such as sodium chloride solution is tested with a conductivity apparatus, like the one shown in Figure 8.9, the light bulb glows brightly. When the electricity is turned on, the  $Na^+$  and  $Cl^-$  ions move through the solution. It is the movement of these ions that is the flow of current in the solution.

In solutions of weak electrolytes such as acetic acid and ammonia, the concentration of ions in the solution is relatively small. As a result, these solutions are poor conductors of electricity. Solutions of non-electrolytes are non-conducting because there are essentially no ions in the solution.

There is also further discussion about conductivities of solutions of electrolytes in Section 8.7.

Figure 8.9 A conductivity apparatus used to determine whether a solution conducts an electric current.



### \* Review exercise 8.4

- 1 Both the ionic compound potassium bromide, KBr, and the molecular compound hydrogen bromide, HBr, are strong electrolytes. However, when they dissolve in water, one compound undergoes ionisation and the other dissociation.
  - a Explain the meaning of the term ‘strong electrolyte’.
  - b Distinguish between the processes of ionisation and dissociation, with reference to the two bromides. Include equations in your answer.
  - c If solutions of each of the two bromides were prepared by adding 1 mole of the compound to 1 L of water, predict the electrical conductivity of these two solutions as high, low or essentially zero.
  - d Silver bromide, AgBr, is also classified as a strong electrolyte, but when 1 mole of this bromide is added to 1 L of water, the resulting mixture is a very poor conductor of electricity. Propose an explanation of this observation.
- 2 Hydrogen ions,  $H^+$ , are very corrosive ions. For example, if a solution of hydrochloric acid, which contains hydrogen ions, is added to lettuce, the lettuce quickly begins to disintegrate. However, a solution of another acid, acetic acid, which also contains hydrogen ions, can be safely added to lettuce, and the ‘dressed’ lettuce eaten. Explain this difference in corrosive properties of the two acid solutions.

## 8.5 Concentrations of solutions

The amount of solute dissolved in a given amount of solution or solvent, called the **concentration**, can be expressed in a variety of ways. Two imprecise but sometimes useful terms used to describe the concentration of a solution are dilute and concentrated. A **dilute solution** is one that contains a small amount of solute in a large volume of solvent. A pinch of sugar in a glassful of water is a dilute, faintly sweet sugar solution. A **concentrated solution** is one in which a large amount of solute is dissolved in a relatively small volume of solvent. An undiluted solution of cordial, which is sickly sweet, is an example of a concentrated solution of sugar.

Chemists often require more accurate measurements of quantities than a ‘pinch of sugar’ or a ‘large volume of solvent’. Quantitative methods of expressing solution concentrations are needed so that the precise quantity of solute in a given volume of solution can be determined.

Three methods of expressing solution concentrations are:

- percentage composition by mass or volume
- gram per litre,  $\text{g L}^{-1}$
- mole per litre,  $\text{mol L}^{-1}$ .



**Figure 8.10** Concentrated (left) and dilute solutions of potassium permanganate. The concentrated solution contains a large number of potassium ions,  $\text{K}^+$ , and permanganate ions,  $\text{MnO}_4^-$ , dispersed in water, but the dilute solution contains fewer ions in the same volume of water.

## Percentage composition of a solution

One of the simplest methods of expressing concentration is based on the percentage composition of the solution. This may be on a mass (weight, w) or volume (v) basis and leads to such notation as 10% w/w, 5% w/v or 15% v/v. The percentage composition of a solution provides information about the mass or volume of a solute dissolved in 100 ‘masses’ or volumes of the solution. The mass or volume of the solution includes the mass or volume of both the solute plus the solvent. For example, a 3% w/w solution of hydrogen peroxide contains 3 g of hydrogen peroxide dissolved in 100 g of solution. That is, 100 g of the hydrogen peroxide solution would contain 3 g of hydrogen peroxide and 97 g of water. Some examples of household solutions and their concentrations are shown in Figure 8.11 and Table 8.4.



Active ingredient: Sodium Hypochlorite 42 g/L (Available Chlorine 4% m/v). At use by date: Available Chlorine 2.0% m/v. Sodium Hydroxide 9 g/L.

Active ingredient: 0.22% w/w Sodium Fluoride.

Figure 8.11 The percentage composition of the active ingredients on the labels of a bottle of White King cleaner and a Colgate toothpaste tube (Note: m/v is the same as w/v.).

TABLE 8.4 CONCENTRATIONS, EXPRESSED AS PERCENTAGE COMPOSITION, OF ACTIVE INGREDIENTS IN SOME HOUSEHOLD SOLUTIONS

Name of household solution	Concentration information shown on label	Meaning of this information
Methylated sprits	96% v/v ethanol	In 100 mL of methylated spirits there is 96 mL of ethanol
Basin, bath and tile cleaner	sodium hydroxide 0.2% w/w, butoxyglycol 6.0% w/w	In 100 g of the cleaner there are 0.2 g of sodium hydroxide and 6.0 g of butoxyglycol
Dettol	chloroxylenol 4.8% w/v	In 100 mL of Dettol there is 4.8 g of chloroxylenol

To calculate the percentage composition of a solution in the different units, the following equations can be used:

$$\text{percentage composition by mass (\% w/w)} = \frac{\text{mass of solute in g}}{\text{mass of solution in g}} \times 100$$

$$\text{percentage composition by volume (\% v/v)} = \frac{\text{volume of solute in mL}}{\text{volume of solution in mL}} \times 100$$

$$\text{percentage composition by mass/volume (\% w/v)} = \frac{\text{mass of solute in g}}{\text{volume of solution in mL}} \times 100$$

### → Example 8.1

A mixture of 60 mL of oil dissolved in enough petrol to make 2.0 L of fuel is used in lawnmower engines. What is the percentage composition by volume of oil in this mixture?

### → Solution

$$\text{volume of solute (oil)} = 60 \text{ mL} \quad \text{volume of solution (fuel)} = 2000 \text{ mL}$$

$$\begin{aligned}\text{percentage composition by volume} &= \frac{\text{volume of solute in mL}}{\text{volume of solution in mL}} \times 100 \\ &= \frac{60}{2000} \times 100 \\ &= \mathbf{3.0\% \text{ v/v}}\end{aligned}$$



### → Example 8.2

What is the percentage composition by mass of a sodium chloride solution that has been prepared by dissolving 25.0 g of NaCl in 485 g of water?

### → Solution

$$\begin{aligned}\text{mass of solution formed} &= 25.0 + 485 \\ &= 510 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{percentage composition by mass (\% w/w)} &= \frac{\text{mass of solute in g}}{\text{mass of solution in g}} \times 100 \\ &= \frac{25.0}{510} \times 100 \\ &= \mathbf{4.90\% \text{ w/w}}\end{aligned}$$

## Gram per litre ( $\text{g L}^{-1}$ )

The concentration of a solution in gram per litre ( $\text{g L}^{-1}$ ) indicates the mass, in gram, of solute dissolved in 1 L of solution. For example, if the concentration of sodium chloride in seawater is  $20 \text{ g L}^{-1}$ , this would mean that in 1 L of seawater there is 20 g of sodium chloride. A formula that can be used to calculate the concentration of a solution in  $\text{g L}^{-1}$  is:

$$\text{concentration of solution in } \text{g L}^{-1} = \frac{\text{mass of solute in g}}{\text{volume of solution in L}}$$

### → Example 8.3

A 300 mL can of lemon-flavoured mineral water contains 5.10 mg of sulfate ions. Calculate the concentration, in  $\text{g L}^{-1}$ , of sulfate ions in the mineral water.

### → Solution

$$\text{concentration of sulfate ions in } \text{g L}^{-1} = \frac{\text{mass of sulfate ions in g}}{\text{volume of mineral water in L}}$$

$$\text{mass of sulfate ions in g} = \frac{5.10}{1000} = 5.10 \times 10^{-3} \text{ g}$$

$$\text{volume of mineral water in L} = \frac{300}{1000} = 3.00 \times 10^{-1} \text{ L}$$

$$\begin{aligned}\text{concentration of sulfate ions in } \text{g L}^{-1} &= \frac{5.10 \times 10^{-3}}{3.00 \times 10^{-1}} \\ &= \mathbf{0.0170 \text{ g L}^{-1}}\end{aligned}$$

## Mole per litre ( $\text{mol L}^{-1}$ )

Concentrations expressed in mole per litre ( $\text{mol L}^{-1}$ ) allow chemists to compare the amount, in mole, of atoms, molecules or ions present in a given volume of solution. For example, a  $0.2 \text{ mol L}^{-1}$  solution of potassium hydroxide contains 0.2 mole of KOH in 1 L of the solution. The concentration, in  $\text{mol L}^{-1}$ , of a solution can be calculated as follows:

$$\text{concentration of solution in mol L}^{-1} = \frac{\text{mole of solute}}{\text{volume of solution in L}}$$

or

$$c = \frac{n}{V}$$

The concentration of a solution in mole per litre is sometimes referred to as the molarity or molar concentration of the solution and is given the symbol M. A  $0.400 \text{ M HCl}$  solution is therefore the same as a  $0.400 \text{ mol L}^{-1}$  HCl solution. (Note: the symbol M was used earlier to represent molar mass. Care should be taken not to confuse the two different uses of the same letter.)

### → Example 8.4

Hydrogen peroxide solution for hair bleaching is sold as solutions containing 5.00 g  $\text{H}_2\text{O}_2$  dissolved in 120 mL of solution. What is the concentration, in  $\text{mol L}^{-1}$ , of this hydrogen peroxide hair bleaching solution?

#### → Solution

$$\text{mole of H}_2\text{O}_2 = \frac{\text{mass of H}_2\text{O}_2}{\text{molar mass of H}_2\text{O}_2}$$
$$\text{molar mass of H}_2\text{O}_2 = (2 \times 1.008) + (2 \times 16.00) = 34.016 \text{ g mol}^{-1}$$
$$\text{mole of H}_2\text{O}_2 = \frac{5.00}{34.016} = 0.1470 \text{ mol}$$
$$\text{concentration of H}_2\text{O}_2 \text{ solution} = \frac{\text{mole of H}_2\text{O}_2}{\text{volume (L) of solution}}$$
$$\text{volume of solution in L} = \frac{120}{1000} = 0.120 \text{ L}$$
$$\text{concentration of H}_2\text{O}_2 \text{ solution} = \frac{0.1470}{0.120} = 1.22 \text{ mol L}^{-1}$$

### → Example 8.5

Phenobarbital,  $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_3$ , is a sedative used to relieve anxiety and for short-term treatment of insomnia. It may be taken as an elixir with 5.00 mL being a dose. If the concentration of the phenobarbital solution is  $0.0170 \text{ mol L}^{-1}$ , what mass of the drug is present in one dose?

#### → Solution

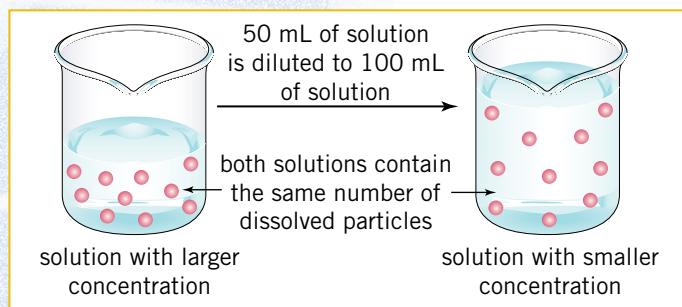
$$c(\text{phenobarbital}) = \frac{n(\text{phenobarbital})}{V}$$
$$\text{volume of solution in L} = \frac{5.00}{1000} = 5.00 \times 10^{-3} \text{ L}$$
$$0.0170 = \frac{n(\text{phenobarbital})}{5.00 \times 10^{-3}}$$
$$n(\text{phenobarbital}) = 0.0170 \times 5.00 \times 10^{-3}$$
$$= 8.50 \times 10^{-5} \text{ mol}$$
$$n(\text{phenobarbital}) = \frac{m(\text{phenobarbital})}{M(\text{phenobarbital})}$$

$$\begin{aligned}
 M(\text{phenobarbital}) &= (12 \times 12.01) + (12 \times 1.008) + (2 \times 14.01) + (3 \times 16.00) \\
 &= 232.236 \text{ g mol}^{-1} \\
 8.50 \times 10^{-5} &= \frac{\text{m(phenobarbital)}}{232.236} \\
 \text{mass of phenobarbital} &= 8.50 \times 10^{-5} \times 232.236 \\
 &= \mathbf{0.0197 \text{ g}}
 \end{aligned}$$

### \* Review exercise 8.5

- 1 How many mole of  $\text{H}_2\text{SO}_4$  is present in 3.20 L of a 35.7% w/w sulfuric acid,  $\text{H}_2\text{SO}_4$ , solution in a car battery? Assume the density of the 35.7% w/w sulfuric acid is 1.28 g  $\text{mL}^{-1}$ .
- 2 A bottle of French cognac is labelled as being 40% v/v alcohol (ethanol). What volume of ethanol would be in a 50 mL ‘shot’ of this drink?
- 3 Oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , is a toxic substance found in rhubarb leaves. Solutions of oxalic acid are used in the dyeing and bleaching industries. What is the concentration, in  $\text{mol L}^{-1}$ , of an oxalic acid solution if 10.2 g of oxalic acid is dissolved in 200 mL of solution?
- 4 The concentration of calcium ions in low-fat milk is  $3.10 \times 10^{-3} \text{ mol L}^{-1}$ . If the recommended daily calcium requirement for teenagers is 1300 mg, what volume of low-fat milk would need to be consumed to supply this amount of calcium?
- 5 The concentration of sodium hypochlorite,  $\text{NaClO}$ , in White Cling hospital-grade disinfectant is 52.5 g  $\text{L}^{-1}$ . What mass of sodium hypochlorite would be required to produce 500 two-litre bottles of this disinfectant?
- 6 If in typical blood serum the concentration of  $\text{NaCl}$  is about  $0.14 \text{ mol L}^{-1}$ , calculate the volume of blood that contains 1.0 mg of  $\text{NaCl}$ .
- 7 A sample of seawater has an average gold content of  $6.00 \times 10^{-3} \text{ mg L}^{-1}$ . Assuming all of the gold is extracted, what volume of seawater is needed to produce 1.00 kg of gold?

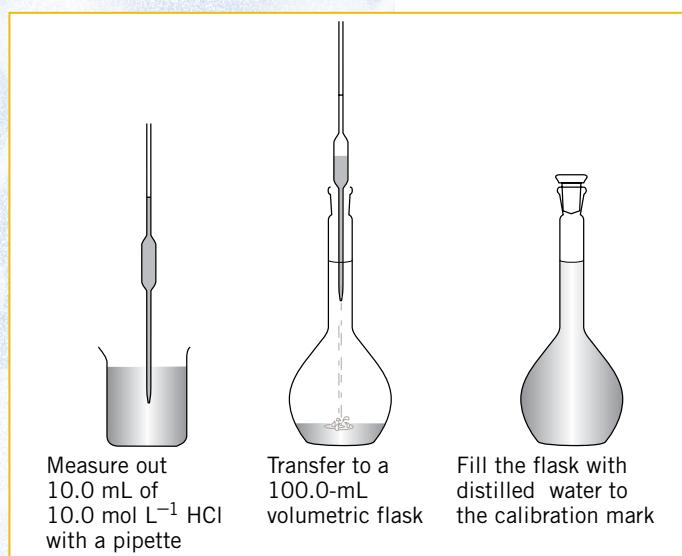
## 8.6 Dilutions



**Figure 8.12** Dilution of a solution—the number of particles remains the same, but the volume increases. The concentration of the first solution will be larger than the concentration of the second solution.



**Figure 8.13** A volumetric flask, showing the calibration mark on the neck.



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 0.1 mol L<sup>-1</sup> sugar solution, the number of molecules of sugar remains unchanged but the volume of the solution they are dissolved in has been increased. This means the sugar molecules are spread further apart during the dilution process, and so the concentration of the sugar solution is decreased. Figure 8.12 illustrates this.

Rather than preparing a dilute solution by weighing out the solute and dissolving it in water, chemists often find it more convenient to prepare the dilute solution from a concentrated solution of the solute. For example, if 10 mol L<sup>-1</sup> HCl solution was available, it would be more convenient to prepare a 1.0 mol L<sup>-1</sup> HCl solution by diluting this concentrated solution rather than trying to weigh out some HCl gas and dissolve it in water.

To prepare a 1.0 mol L<sup>-1</sup> HCl solution from the 10 mol L<sup>-1</sup> solution, a 1:10 dilution is required. If 10 mL of the concentrated solution was diluted to form 100 mL of solution, the diluted solution would have a concentration of 1.0 mol L<sup>-1</sup>.

The usual procedure in a dilution of this sort is illustrated in Figure 8.14. A definite volume of the concentrated solution is measured out with a pipette, and placed into a volumetric flask. Sufficient solvent is then added to the flask to make the solution up to the calibration mark.

When calculating the volume of solution needed to produce a particular volume of a more dilute solution, it is useful to remember that the dilution does not alter the amount, in mole, of solute present. The amount, in mole, of solute is the same before and after the dilution.

Because the amount, in mole, of solute has remained unchanged during the dilution, a formula that is sometimes used to calculate the new concentration of a dilute solution is

$$c_1 V_1 = c_2 V_2$$

where  $c_1$  and  $V_1$  refer to the concentrated solution before dilution and  $c_2$  and  $V_2$  refer to the diluted solution.

This formula is showing that the mole of solute in the volume of concentrated solution (calculated by  $c_1 V_1$ ) equals the mole of solute in the volume of the diluted solution (calculated by  $c_2 V_2$ ).

**Figure 8.14** Preparing a 1.0 mol L<sup>-1</sup> HCl solution by dilution of 10 mol L<sup>-1</sup> HCl.

### → Example 8.6

What volume of  $12.0 \text{ mol L}^{-1}$  HCl is required to prepare 500.0 mL of a  $2.50 \text{ mol L}^{-1}$  solution?

### → Solution

#### Method 1

This method involves calculating the amount, in mole, of HCl required to make the dilute solution, and then using this figure to calculate the volume of the concentrated solution required to 'supply' this amount of HCl.

$$c(\text{dilute HCl}) = \frac{n(\text{HCl in dilute sol})}{V(\text{dilute HCl})}$$

$$\text{volume of dilute HCl in L} = \frac{500}{1000} = 0.500 \text{ L}$$

$$2.50 = \frac{n(\text{HCl in dilute sol})}{0.500}$$

$$n(\text{HCl in dilute sol}) = 2.50 \times 0.500 = 1.25 \text{ mol}$$

$$\text{mol of HCl in the concentrated solution} = \text{mol of HCl in the dilute solution}$$

$$= 1.25 \text{ mol}$$

$$c(\text{conc HCl}) = \frac{n(\text{HCl in conc sol})}{V(\text{conc HCl})}$$

$$12.0 = \frac{1.25}{V(\text{conc HCl})}$$

$$\text{volume of concentrated HCl solution} = \frac{1.25}{12.0} = 0.104 \text{ L}$$

#### Method 2

This method can be used because the mole of HCl in the dilute solution = mole of HCl in the concentrated solution

$$c_1 V_1 = c_2 V_2$$

$$c_1 = 12.0 \text{ mol L}^{-1}, V_1 = ?,$$

$$c_2 = 2.50 \text{ mol L}^{-1}, V_2 = 0.500 \text{ L}$$

$$12.0 \times V_1 = 2.50 \times 0.500$$

$$V_1 = 2.50 \times 0.500 / 12.0 = 0.104 \text{ L}$$



Figure 8.15 A pipette in a flask.

### \* Review exercise 8.6

- 5.00 mL of  $4.50 \text{ mol L}^{-1}$  battery acid ( $\text{H}_2\text{SO}_4$ ) is diluted to 100.0 mL in a volumetric flask. Calculate the concentration of the diluted battery acid.
- 100.0 mL of  $2.00 \text{ mol L}^{-1}$  NaOH is mixed with 80.0 mL of  $2.50 \text{ mol L}^{-1}$  NaOH. Assuming the solution volumes are additive, calculate the NaOH concentration, in  $\text{mol L}^{-1}$ , of the final solution.
- Industrial-grade hydrochloric acid, called muriatic acid, is used to clean brickwork. Its concentration is  $11.7 \text{ mol L}^{-1}$ . Write instructions for diluting the concentrated acid to make 10 litres of  $3.5 \text{ mol L}^{-1}$  HCl for routine use.
- What volume of  $6.00 \text{ mol L}^{-1}$  nitric acid and of water would be required to prepare 500 mL of  $0.100 \text{ mol L}^{-1}$  nitric acid?

## 8.7 Concentrations of ions in solutions

Ionic compounds and some covalent compounds act as strong electrolytes when they dissolve in water. That is, they completely break up into ions in solution. The concentration of these ions in the solution can be calculated from the concentration of the original dissolved substance. For example, if 0.1 mole of  $\text{CaCl}_2$  is added to water to form 1 L of solution, a  $0.1 \text{ mol L}^{-1}$   $\text{CaCl}_2$  solution forms. However, the  $\text{CaCl}_2$  breaks up when it dissolves in water to form  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  ions. For every formula unit of  $\text{CaCl}_2$  dissolved, one  $\text{Ca}^{2+}$  ion and two  $\text{Cl}^-$  ions will be formed. Therefore, the 0.1 mole of  $\text{CaCl}_2$  dissolved will form 0.1 mol of  $\text{Ca}^{2+}$  ions and  $2 \times 0.1 = 0.2$  mole of  $\text{Cl}^-$  ions in the 1 L solution. As a result, the concentration of  $\text{Ca}^{2+}$  in the solution will be  $0.1 \text{ mol L}^{-1}$  and the concentration of  $\text{Cl}^-$  will be  $0.2 \text{ mol L}^{-1}$ , as shown in Figure 8.16.

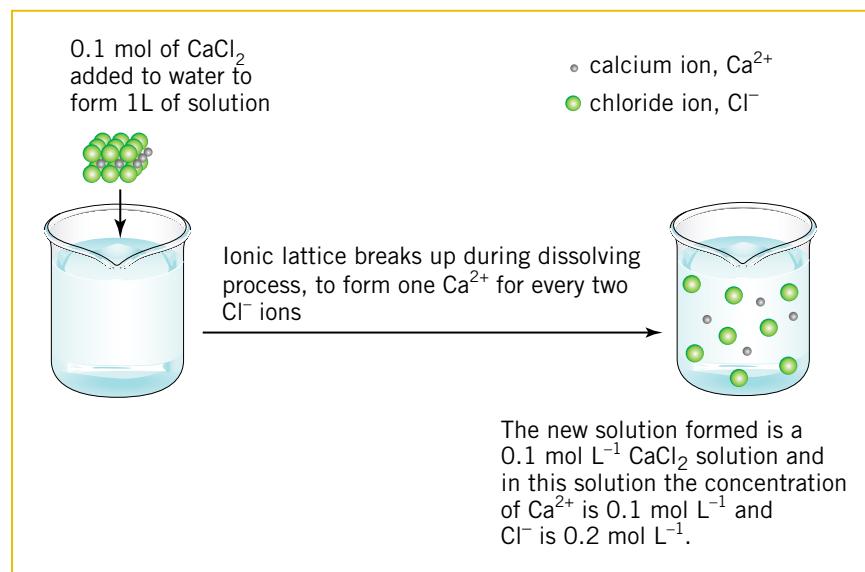


Figure 8.16 Concentration of ions in a  $0.1 \text{ mol L}^{-1}$   $\text{CaCl}_2$  solution.

### → Example 8.7

In 400 mL of a  $0.200 \text{ mol L}^{-1}$   $\text{Na}_2\text{CO}_3$  solution, calculate the concentration of sodium ions.

### → Solution

Because one formula unit of  $\text{Na}_2\text{CO}_3$  breaks up to form two  $\text{Na}^+$  ions and one  $\text{CO}_3^{2-}$  ion, the concentration of  $\text{Na}^+$  in the solution must be  $2 \times 0.200 = 0.400 \text{ mol L}^{-1}$ .

## Electrical conductivities of solutions containing ions

The ability of a solution to conduct electricity is related to the concentration of ions in that solution. For instance, a  $2.0 \text{ mol L}^{-1}$  NaCl solution will be a better conductor of electricity than a  $0.001 \text{ mol L}^{-1}$  NaCl solution (even though both solutions are regarded as good conductors of electricity, compared to the solutions of some other substances). Sodium chloride is a strong electrolyte, so when added to water it completely breaks up into ions. In the  $2.0 \text{ mol L}^{-1}$  solution, the concentration of both the  $\text{Na}^+$  and the  $\text{Cl}^-$  ions will be  $2.0 \text{ mol L}^{-1}$ . But in the  $0.001 \text{ mol L}^{-1}$  NaCl solution, the concentration of these two ions will only be  $0.001 \text{ mol L}^{-1}$ .

In general, solutions of strong electrolytes have high electrical conductivities. Two exceptions to this generalisation are:

- if the solution of the strong electrolyte is extremely dilute, for example a solution prepared by dissolving only a few small crystals of the electrolyte in a large volume of water, its conductivity will be low. In this very dilute solution, even though the strong electrolyte has completely ionised or dissociated, the concentration of ions will be very small
- if the solubility of the strong electrolyte is small, then the conductivity of its solution will be low. All of the dissolved strong electrolyte will break up into ions in the solution, but because only a small amount of it will actually dissolve, the concentration of the ions it produces will be very low. For example, the electrical conductivity of a saturated solution of AgCl (an essentially insoluble compound) is much less than the conductivity of a saturated solution of NaCl.

Solutions of weak electrolytes are poor conductors of electricity, compared to solutions of strong electrolytes. Although many weak electrolytes are often quite soluble in water, only a small percentage of the dissolved molecules are ionised in the solution. For example in a  $0.1 \text{ mol L}^{-1}$   $\text{CH}_3\text{COOH}$  solution, at  $25^\circ\text{C}$ , only about 1.3% of the  $\text{CH}_3\text{COOH}$  molecules have ionised to form  $\text{H}^+$  and  $\text{CH}_3\text{COO}^-$  ions. Consequently, the concentration of ions in solutions of weak electrolytes is always small. A summary of the conductivities of various types of aqueous solutions is given in Table 8.5.

TABLE 8.5 CONDUCTIVITIES OF AQUEOUS ELECTROLYTE SOLUTIONS

Nature of electrolyte	Conductivity of solution
soluble strong electrolyte e.g. NaCl, HCl	high conductivity, conductivity increases with solution concentration for a given electrolyte
insoluble strong electrolyte e.g. AgCl	very low conductivity, conductivity increases with solubility of electrolyte
soluble weak electrolyte e.g. acetic acid, $\text{CH}_3\text{COOH}$	low conductivity, conductivity increases with solution concentration but remains low
soluble non-electrolyte e.g. sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$	non-conducting, conductivity does not change with solution concentration

## \* Review exercise 8.7

- 1 Calculate the amount, in mole, of ammonium ions in 630 mL of a fertiliser solution that contains  $0.554 \text{ mol L}^{-1}$  ammonium sulfate.
- 2 Physiological saline, a solution that corresponds to the approximate concentration of salts in human blood plasma, contains 0.900 g of NaCl in 100 mL of solution. What is the concentration, in  $\text{mol L}^{-1}$ , of sodium ions in this solution?
- 3 A beaker contains 500 mL of a  $0.106 \text{ mol L}^{-1}$  solution of sodium carbonate. 100 mL of acid is added to the beaker and it reacts with 0.0248 mole of the carbonate ions in the sodium carbonate solution. Calculate the concentration, in  $\text{mol L}^{-1}$ , of carbonate ions remaining in the solution after the reaction (assume the solution volumes are additive).
- 4 For each of the following pairs of solutions, select the one with the higher electrical conductivity. Give your reasoning in each case.
  - a  $0.01 \text{ mol L}^{-1}$   $\text{KNO}_3$  solution and  $2.0 \text{ mol L}^{-1}$   $\text{KNO}_3$  solution
  - b  $0.1 \text{ mol L}^{-1}$  NaCl solution and  $0.1 \text{ mol L}^{-1}$   $\text{CH}_3\text{COOH}$  solution
  - c a saturated solution of  $\text{BaSO}_4$  and a saturated solution of  $\text{CuSO}_4$
  - d  $0.1 \text{ mol L}^{-1}$  sugar solution and  $0.1 \text{ mol L}^{-1}$  HCl solution.

## 8.8 Colligative properties of solutions

When a solute dissolves in a solvent, many of the physical properties of the solvent are changed. The degree to which some of these properties change depends on the ratio of the number of particles of solute—not the kind of particles—to the number of particles of solvent in the solution. These properties are referred to as **colligative properties**.

Three such colligative properties are vapour pressure, melting temperature and boiling temperature. Table 8.6 compares these physical properties of pure water to several solutions in water.

**TABLE 8.6 VAPOUR PRESSURE, MELTING POINT AND BOILING POINT FOR PURE WATER AND THREE AQUEOUS SOLUTIONS\***

Liquid or solution	Concentration of solute particles ( $\text{mol L}^{-1}$ )	Vapour pressure at $20^\circ\text{C}$ (kPa)	Melting point ( $^\circ\text{C}$ )	Boiling point ( $^\circ\text{C}$ )
Pure water	—	2.34	0.0	100.0
$1.0 \text{ mol L}^{-1}$ glucose	1.0	2.30	-1.9	100.5
$1.0 \text{ mol L}^{-1}$ NaCl	2.0	2.26	-3.7	101.0
$1.0 \text{ mol L}^{-1}$ $\text{MgCl}_2$	3.0	2.22	-5.6	101.5

\* The values here apply to what are called ideal solutions (similar to ideal gases). In reality, interactions between the solute particles and the solvent particles do modify these values, but at small concentrations of dissolved particles, most solutions behave ideally.

The data in the table shows that the presence of a dissolved solute

- lowers the vapour pressure of the pure solvent
- raises the boiling point above that of the pure solvent
- lowers the freezing point below that of the pure solvent.

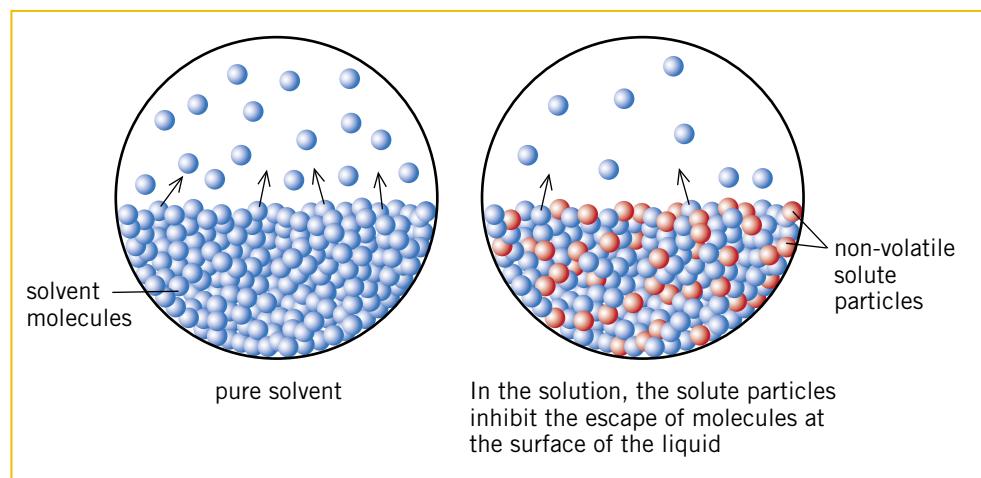
As stated earlier, the extent of the changes in the colligative properties depends on the number of dissolved particles present in the solution. Table 8.6 shows that a  $1.0 \text{ mol L}^{-1}$  solution of glucose produces a boiling temperature elevation of  $0.5^\circ\text{C}$ . However, for a  $1.0 \text{ mol L}^{-1}$  solution of sodium chloride, which contains 2.0 mol of particles ( $\text{Na}^+$  and  $\text{Cl}^-$  ions) in 1 L of solution, the boiling point elevation is  $1.0^\circ\text{C}$ . When there are 3 mole of particles present in 1.0 L of solution ( $\text{Mg}^{2+}$  and  $2\text{Cl}^-$  ions), the boiling point elevation is  $1.5^\circ\text{C}$ , three times that of the glucose solution. Similar trends can be seen in the vapour pressure decrease and boiling temperature depression.



**Figure 8.17** The glycoproteins in the tissue of a naked dragonfish act as an antifreeze. This prevents the naked dragonfish from freezing in Antarctic oceans.

### Vapour pressure lowering

Figure 8.18 illustrates how the presence of dissolved solute particles at the boundary between the solution and the gas phase will interfere with the evaporation of the pure solvent molecules.



**Figure 8.18** Effect of dissolved solute on vapour pressure.

It was noted in Chapter 7 that the vapour pressure of a liquid is due to the particles in the liquid state that have enough kinetic energy to escape from the liquid's surface and move into the gas phase where they exert a pressure. The presence of dissolved solute particles at the surface may prevent some of the particles of solvent, with sufficient energy to leave the liquid, from reaching the surface. Therefore fewer solvent particles are able to move into the gas phase. As a result the vapour pressure of the solution, at that temperature, will be lower than the vapour pressure of the pure solvent. As more solute is dissolved, more solute particles will be present at the surface to interfere with the vaporisation process, and as a consequence the vapour pressure will be decreased more.

### Boiling temperature elevation

In the same way as the dissolved solute lowers the vapour pressure of a liquid, presence of the solute will also raise the boiling point of the solvent. The boiling point was defined earlier as the temperature at which the vapour pressure of the liquid reaches the prevailing atmospheric pressure. If the vapour pressure is lowered by addition of a solute, then the solution will need to be heated to a higher temperature than that required for the pure solvent, in order for the vapour pressure to equal the prevailing atmospheric pressure.

## Freezing temperature depression

The process of freezing involves particles in the liquid state coming together to form a crystal lattice. For water, the particles are molecules that join to one another weakly to form ice. The presence of dissolved solute interferes with this crystallisation process, thus requiring that the temperature of the solution be lowered below the freezing point of the pure solvent in order for freezing to occur.

### \* Review exercise 8.8

- 1 Spreading salt, sodium chloride, on icy roads is observed to melt the ice. Would spreading sugar on these icy roads have the same effect?
- 2 As a solution of salt water slowly freezes it is observed that the freezing point of the remaining liquid falls. Account for this observation.
- 3 Place the following solutions in order of decreasing vapour pressure at 30°C:  
 $2.0 \text{ mol L}^{-1}$  sucrose                     $0.5 \text{ mol L}^{-1}$  calcium chloride  
 $1.0 \text{ mol L}^{-1}$  potassium iodide     $1.0 \text{ mol L}^{-1}$  ammonium sulfate.
- 4 Draw heating curves from  $-15^\circ\text{C}$  to  $120^\circ\text{C}$  for the following:
  - a pure water
  - b  $1 \text{ mol L}^{-1}$  NaCl solution.



**Figure 8.19** A truck spreading salt on an icy road in Chicago, USA.



## MAJOR IDEAS

- A solution is a homogeneous mixture.
- Solutions are classified as
  - saturated—contains as much solute as the amount of solvent can dissolve at a specific temperature
  - unsaturated—contains less solute than is needed to saturate it
  - supersaturated—contains more solute than is needed to saturate it.
- The solubility of a solute in a solvent depends on the nature of the solute and solvent. Polar solvents tend to dissolve polar solutes. Non-polar solvents tend to dissolve non-polar solutes.
- Water tends to dissolve polar solutes and many ionic compounds.
- The solubility of solids in liquids usually increases with increasing temperature.
- The solubility of a gas in a liquid decreases with increasing temperature and with increasing pressure of the gas above the liquid.
- An electrolyte is a substance that, when dissolved in water, produces ions and therefore a conducting solution.
- Substances are classified as:
  - strong electrolytes: substances that are completely ionised in solution
  - weak electrolytes: substances for which only a small fraction of the dissolved molecules are ionised in solution
  - non-electrolytes: substances which do not produce ions when dissolved in solution.
- The conductivity of a solution of an electrolyte depends on the strength of the electrolyte, the solubility of the electrolyte and the concentration of the electrolyte solution.
- Table 8.3 identifies the solubilities of some ionic compounds.
- The percentage composition of a solution provides information about the mass or volume of a solute dissolved in 100 ‘masses’ or volumes of the solution.
- The concentration of a solution in gram per litre ( $\text{g L}^{-1}$ ) indicates the mass, in gram, of solute dissolved in 1 litre of solution.
- The concentration ( $c$ ) of a solution in mole per litre ( $\text{mol L}^{-1}$ ) indicates the amount of solute, in mole, dissolved in 1 litre of solution and it can be calculated using the formula  $c = \frac{n}{V}$ .
- Solutions of non-volatile solutes have lower vapour pressures, lower freezing points and higher boiling points than the pure solvent. The changes in these properties depend on the concentration of solute particles in the solution.

## QUESTIONS

- 1 Explain why the alloy (75% Cu, 25% Ni) used to make the Australian 5c, 10c, 20c and 50c coins can be classified as a solution.
- 2 You are given a bottle containing some small crystals of a white solid and three beakers containing solutions of this solid. One of these solutions is an unsaturated solution, one is a saturated solution and the other is a supersaturated solution.
  - a What is meant by the words ‘unsaturated’, ‘saturated’ and ‘supersaturated’ when referring to solutions?
  - b Describe how you could distinguish between the three solutions in the beakers.
- 3 Sodium thiosulfate-5-water,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , has a solubility of 76 g per 100 g of water at 25°C. Describe how unsaturated, saturated and supersaturated solutions of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  could be prepared.
- 4 After consulting the physical property data given in the table below:
  - a describe a method you could use to obtain a sample of some pure solid malonic acid from a mixture of the three substances listed in the table
  - b briefly explain why your method would be successful.

Substance	Melting point (°C)	Boiling point (°C)	Solubility in water at 20°C (g substance per 100 g of water)	Solubility in water at 80°C (g substance per 100 g of water)
Sulfur	113	445	insoluble	insoluble
Potassium bromide	734	1435	60	90
Malonic acid	136	decomposes at 140	0.8	27

- 5 Waxes are often used to protect items such as furniture, cars and floors. These waxes consist of large molecules containing long chains of carbon and hydrogen atoms, sometimes with several small groups of other atoms attached. Explain why waxing a surface should protect it from water damage.

- 6** An environmental problem known as thermal pollution occurs when large amounts of hot water, resulting from the cooling of products and equipment during industrial processes, are pumped back into lakes and rivers. Explain why the warming of river or lake water could be a threat to aquatic life.
- 7** The solubility of  $\text{KNO}_3$  at  $25^\circ\text{C}$  is quoted as 39 g in 100 g  $\text{H}_2\text{O}$ . Is this the same as saying a saturated solution of  $\text{KNO}_3$  at  $25^\circ\text{C}$  has a concentration of 39 g per 100 g solution?
- 8** Liquid nitric acid,  $\text{HNO}_3$ , is not a conductor of electricity, but when dissolved in water the solution does conduct. Explain this observation.
- 9** The concentration of dissolved oxygen and carbon dioxide gases in seawater at  $25^\circ\text{C}$  are  $206 \mu\text{mol L}^{-1}$  and  $9 \mu\text{mol L}^{-1}$  respectively. Carbon dioxide is around 300 times more soluble in water than oxygen, yet the figures above show that there is around twenty times more oxygen present in seawater at  $25^\circ\text{C}$  than carbon dioxide. Account for this difference.
- 10** Why is turpentine or petrol, rather than water, used to remove oil and grease stains?
- 11** Calculate the mass of sodium hypochlorite required to prepare 375 mL of a bathroom cleaner that contains 1.50% w/v (g/mL) sodium hypochlorite.
- 12** What mass of ethanol is in a 330 mL can of low-alcohol beer that contains 3.80% v/v ethanol? The density of ethanol is  $0.785 \text{ g mL}^{-1}$ .
- 13** In a fully-charged car battery, the concentration of sulfuric acid is approximately  $445 \text{ g L}^{-1}$ .
- If the volume of acid in the battery is 3.80 L, what amount, in mole, of sulfuric acid is present?
  - As well as participating in the reactions that occur in the battery during the discharging (production of electrical energy) and recharging processes, sulfuric acid has another function in a battery.
    - What is this function?
    - Explain why, despite being a covalent molecular compound, sulfuric acid is able to act in this capacity.
- 14** When the contents of a 375 mL can of cool drink were evaporated to dryness, 51.2 g of sugar,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , remained. Calculate the concentration, in  $\text{mol L}^{-1}$ , of sugar in the drink.
- 15** Calculate the mass of ammonia,  $\text{NH}_3$ , in 25.0 mL of a  $0.0185 \text{ mol L}^{-1}$  ammonia solution.
- 16** When the gas hydrogen iodide,  $\text{HI}$ , dissolves in water, it forms a solution with high electrical conductivity. However, a solution formed from hydrogen iodide dissolved in toluene,  $\text{C}_7\text{H}_8$ , does not conduct electricity. What can be inferred from these observations about the behaviour of hydrogen iodide when it dissolves in water and in toluene?
- 17** Two identical 2 L bottles of coke are opened, and half the liquid from one bottle is poured out. The tops are now put back onto the full and the half-filled bottles, and they are placed in the fridge. After several hours, which bottle will contain the more carbonated (fizzy) drink and why?
- 18** Hydrobromic acid,  $\text{HBr}$ , is an example of a strong electrolyte and nitrous acid,  $\text{HNO}_2$ , is an example of a weak electrolyte.
  - What is meant by the terms 'strong electrolyte' and 'weak electrolyte'? Use the two examples to illustrate your answer.
  - Explain how you could use the following properties to distinguish between  $1 \text{ mol L}^{-1}$  solutions of hydrobromic acid and nitrous acid:
    - electrical conductivity
    - colligative properties.
- 19** In a liquid, pressure increases with depth. For example, at a depth of 20 metres the pressure is about 3 atmospheres. One important implication of this for scuba divers is that if they ascend too rapidly to the surface they can suffer from 'the bends'. This occurs when nitrogen gas bubbles out of the blood. Explain why nitrogen would bubble out of the blood during a rapid ascent.
- 20** 'Hard' water contains ions such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Fe}^{3+}$  which cause problems in the pipes used to carry the water, in water storage tanks and when the water is used for washing purposes. Water 'softeners' can be used to remove these ions by replacing them with enough  $\text{Na}^+$  ions to maintain the same number of positive charges in the solution. How many mole of  $\text{Na}^+$  ions would be required to replace the metal ions in 1.00 kL of hard water in which the concentration of the  $\text{Ca}^{2+}$  and  $\text{Fe}^{3+}$  ions are  $0.013 \text{ mol L}^{-1}$  and  $0.0016 \text{ mol L}^{-1}$  respectively.

- 21 Select from the following list of solutions to answer the questions below:

0.1 mol L<sup>-1</sup> NaCl      0.1 mol L<sup>-1</sup> AlCl<sub>3</sub>  
0.1 mol L<sup>-1</sup> HCl      0.1 mol L<sup>-1</sup> glucose  
0.2 mol L<sup>-1</sup> CH<sub>3</sub>COOH

- a Which of the above solutions would you expect to have the lowest boiling point?  
b Which would have the lowest vapour pressure?

- 22 Colligative properties are properties that depend only on the number of particles dissolved—not their identity. For example, the freezing point of a 0.1 mol L<sup>-1</sup> NaBr solution is the same as that of a 0.1 mol L<sup>-1</sup> KCl solution. Which of following solutions would have approximately the same freezing point as these two solutions?

0.2 mol L<sup>-1</sup> NaBr solution  
0.05 mol L<sup>-1</sup> Al(NO<sub>3</sub>)<sub>3</sub> solution  
0.1 mol L<sup>-1</sup> HNO<sub>3</sub> solution  
0.1 mol L<sup>-1</sup> NH<sub>3</sub> solution

- 23 Which solution will evaporate at the slower rate: 0.1 mol L<sup>-1</sup> NaCl or 0.1 mol L<sup>-1</sup> MgCl<sub>2</sub>? Explain why.

- 24 a Using the knowledge that water expands when it freezes, why is it wise to add ethylene glycol, C<sub>2</sub>H<sub>4</sub>(OH)<sub>2</sub>, to your car radiator water before parking your car in an area, such as a mountain top, where the temperature will be below 0°C?  
b Adding ethylene glycol to the radiator water also has an advantage in summer as well. Suggest what this advantage might be.

- 25 Explain why a mixture of sodium chloride and calcium chloride is spread over ice-covered street surfaces in cold countries.

- 26 a Two beakers are set up under a closed container as shown in Figure 8.20. One beaker contains pure water and the other a concentrated NaCl solution. The beakers and their contents were left undisturbed in this set-up for several weeks. Predict and explain what you think might happen to the liquids over this time.

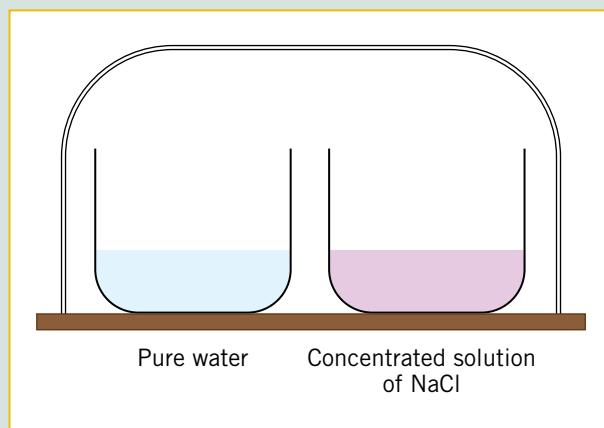


Figure 8.20

- b Years ago, before refrigeration, meat was often salted to prevent it from going rotten. Considering your prediction to the experiment described in part a, suggest how salt acts as a preservative (that is, how it prevents the growth of bacteria on the meat).

- 27 A laboratory assistant is asked to prepare a dilute solution of sulfuric acid from the concentrated acid. What volume of 18 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> is needed to make up 5.0 L of 2.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>?

- 28 Phosphoric acid, H<sub>3</sub>PO<sub>4</sub>, as a dilute solution is thought to be non-toxic and it has a pleasant sour taste. For this reason, phosphoric acid is used in cola drinks like Coca-Cola and Pepsi as a tart flavouring agent. If 10.0 mL of 8.00 mol L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> solution is diluted with 1800 mL of water, calculate the concentration, in mol L<sup>-1</sup>, of the diluted solution. Assume the volumes are additive.

- 29 A gardener prepares a nitrogen-potassium fertiliser solution by dissolving 4.80 g of KNO<sub>3</sub> and 2.70 g of NH<sub>4</sub>NO<sub>3</sub> in enough water to make 15.0 L of solution. Calculate the concentrations, in mol L<sup>-1</sup>, of K<sup>+</sup> ions and NO<sub>3</sub><sup>-</sup> ions in the solution.

- 30 50.0 mL of 2.00 mol L<sup>-1</sup> HCl and 175 mL of 1.34 mol L<sup>-1</sup> HCl solutions are mixed. What is the concentration, in mol L<sup>-1</sup>, of the HCl solution formed?

- 31 Vodka is essentially a solution of ethanol, C<sub>2</sub>H<sub>5</sub>OH, in water. The ‘proof’ of an alcoholic beverage is twice the percentage (v/v) of alcohol in the solution. Consider a bottle of 80-proof vodka. Knowing that the density of pure ethanol is 0.785 g mL<sup>-1</sup>, what is the concentration, in mol L<sup>-1</sup>, of ethanol in the vodka?

- 32 A label from a small carton of spring water is shown in Figure 8.21.



Figure 8.21 Label from spring water container.

- a Calculate the amount, in mole, of each of the ions present in 1 L of the spring water.  
b Does the total charge on the positive ions equal the total charge on the negative ions? If not, propose an explanation to account for the lack of balance.
- 33 A 1 mol L<sup>-1</sup> NaCl solution heated in an open beaker starts to boil at about 101°C. As the boiling continues, the temperature gradually rises until it reaches 103°C. The temperature then remains constant until all the water has boiled away. At the same time as the temperature flattens off, crystals are observed to form in the solution. Explain these observations.

TABLE 8.7

Name	Formula	Description	Density of liquid (g mL <sup>-1</sup> )
Water	H <sub>2</sub> O	colourless liquid	1
Methanol	CH <sub>3</sub> OH	colourless liquid	0.787
1,2-dinitrobenzene	C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub>	yellow solid (non-polar)	—
Iodoethane	C <sub>2</sub> H <sub>5</sub> I	colourless liquid (non-polar)	1.92
Octane	C <sub>8</sub> H <sub>18</sub>	colourless liquid	0.698
Copper sulfate	CuSO <sub>4</sub>	blue solid	—
Barium sulfate	BaSO <sub>4</sub>	white solid	—

34 Layer upon layer

When two polar liquids are mixed, they will dissolve in one another and a single phase mixture will be obtained. The same happens when two non-polar liquids are mixed. When a polar liquid and a non-polar liquid are mixed, they will not dissolve in one another and a two-layer, or two-phase, mixture will be formed, like that shown in Figure 8.22. The less dense liquid will be the top layer.

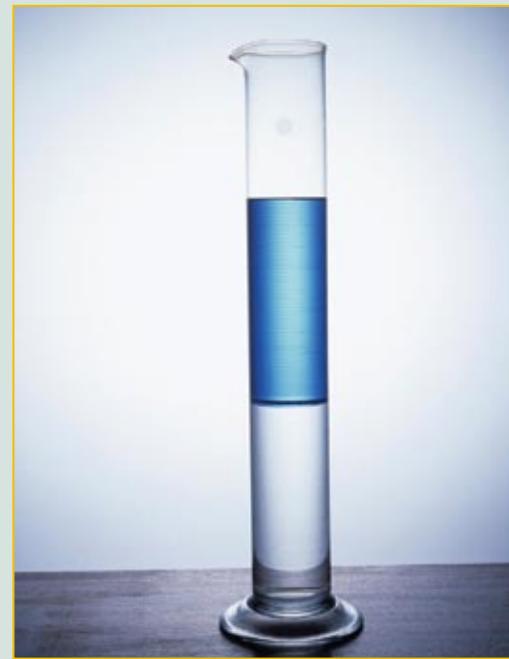


Figure 8.22 A two-phase mixture.

A selection of properties of some polar and non-polar substances are given in Table 8.7.

In a set of experiments, approximately equal volumes of two or three of the substances listed in Table 8.7 are added to a test tube, the test tube is shaken and then left undisturbed, until, if the substances don't mix, the layers separate.

Predict, and show in a diagram, what each of the following mixtures (in **a** and **b**) will look like after they are mixed and allowed to settle. If layers are present, show on your diagram what substances are in the layers.

**a** Mixtures of two substances

- i** water + octane
- ii** water + iodoethane
- iii** water + methanol
- iv** water + small amount of copper sulfate
- v** octane + iodoethane
- vi** octane + small amount of 1,2-dinitrobenzene
- vii** octane + methanol
- viii** octane + small amount of copper sulfate

**b** Mixtures of three substances

- i** water + methanol + iodoethane
- ii** water + octane + small amount of barium sulfate
- iii** water + iodoethane + small amount of 1,2-dinitrobenzene

**c** Suggest what substances may be in the two-phase mixture shown in Figure 8.22.

**d** **RESEARCH** Trying to wash non-polar margarine off a dinner plate with only water, even hot water, will not be very successful. An oily film will be left on the plate. However, if a drop of dishwashing detergent is added to the washing water, the non-polar substance is completely removed from the plate. Briefly explain how detergents interact with water and non-polar substances to make them more soluble in one another.

**e** **RESEARCH** Milk obtained directly from a cow contains liquid fat globules mixed with the rest of the liquid milk. If the milk is left undisturbed, these fat globules collect at the top of the milk, and are called cream. To prevent the cream, or the globules of fat, from separating from the rest of the milk, most of the milk sold in shops today has been homogenised. How is the homogenisation process carried out and what happens to the fat globules during the process to prevent them from separating from the milk?

**f** **RESEARCH** Oil spills in the ocean or in other waterways can cause an environmental disaster.

- i** What damage can be caused to the environment by oil being spilt in the ocean?
- ii** Explain one way in which oil spills are 'cleaned up'.
- iii** Ethanol is thought by some to be a possible fuel of the future. That is, ethanol may one day replace fuels obtained from crude oil. If this is the case and ethanol is shipped in the same way as crude oil is today, what damage, if any, do you think an ethanol spill would cause to the environment?



# 9

# Chemical reactions

**BY THE END OF THIS CHAPTER YOU SHOULD BE ABLE TO:**

- distinguish between physical and chemical changes
- write balanced chemical equations
- apply the law of conservation of mass to chemical reactions
- apply solubility rules to predict the products in a precipitation reaction and write an ionic equation for the reaction
- use the mole ratio shown in a balanced equation to perform calculations involving masses, concentrations and volumes of solutions, and volumes of gases at STP
- apply Gay-Lussac's law to gas volume—volume stoichiometric calculations.

## 9.1 Changes in chemistry

Chemists often use their knowledge of chemistry to change matter into something more useful. Chemists change crude oil into petrol, candle wax, plastics, pharmaceutical drugs and thousands of other products. Consumers of manufactured products make use of chemical reactions, for example, when they chlorinate their swimming pool, bake a cake, use mortar to bond bricks together in housing construction, or clean off the rust stain left by bore water. Changes to matter also occur in the environment. Examples include the evaporation and condensation of water to form clouds, the production of rock from the solidification of lava, the dissolving of salt in water to form seawater, the decomposition of leaves to produce compost, and the reaction of carbon dioxide and water (in the photosynthetic process in a plant's leaves) to form glucose and oxygen.

The changes that matter can undergo are often classified into two categories: physical changes and chemical changes. Changing crude oil into a plastic material, leaves changing into compost, and photosynthesis are all examples of chemical changes. **Chemical changes** are those in which new substances with different compositions and properties are formed.

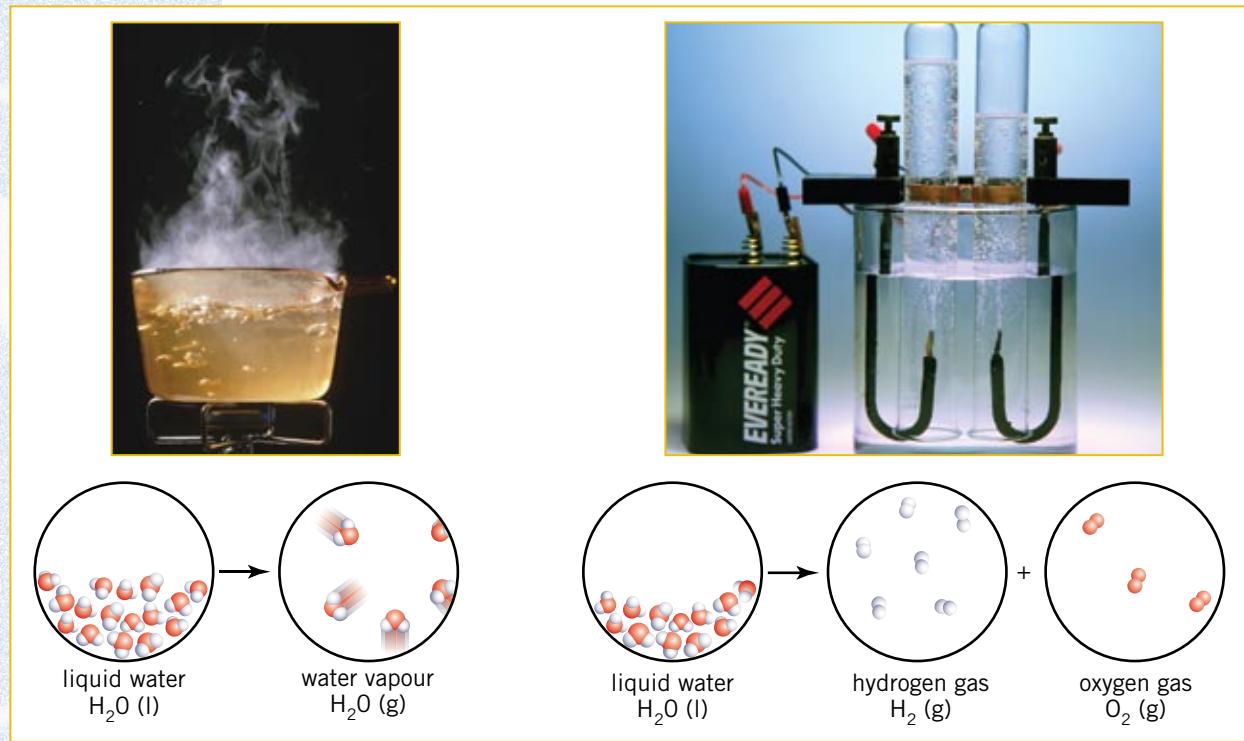
The separation of crude oil into petrol and kerosene, evaporation of water, solidification of lava and dissolving of salt in water are all examples of physical changes. **Physical changes** occur without altering the composition of the particular substance. They are changes in physical properties, such as shape or volume, or changes in state, such as melting or boiling.

Some examples of physical changes and chemical changes water can undergo are given in Table 9.1.

**TABLE 9.1 EXAMPLES OF SOME PHYSICAL AND CHEMICAL CHANGES THAT WATER CAN UNDERGO**

Physical changes
Liquid water boils and turns to steam
When sufficiently cooled, liquid water solidifies as ice
Water vapour, on cooling, condenses to a liquid
Ice melts and changes to a liquid
A blue solution forms when copper sulfate and water are mixed
Chemical changes
When an electric current is passed through water it decomposes to form oxygen and hydrogen
Water and carbon dioxide combine during photosynthesis to produce glucose and oxygen
Chlorine is added to water to produce a solution containing the bleach hypochlorous acid
Carbon dioxide combines with water to produce a dilute solution of carbonic acid

Figure 9.1 shows the boiling of water and the decomposition, by electrolysis, of water at the atomic level. In the physical change from liquid water to steam, the water molecules remain unchanged. They only move further apart. That is, water does not undergo a change in its composition. However, in the electrolysis process, the water molecules are destroyed and two new substances, hydrogen and oxygen, are formed.



**Figure 9.1** Boiling water and electrolysis of water, from an atomic view.

### \* Review exercise 9.1

- 1 Classify the following as chemical or physical changes:
  - a burning natural gas
  - b melting iron
  - c boiling water in a kettle
  - d recharging a mobile phone battery.
- 2 It is more common for the changes around us to be a complex mixture of both physical and chemical changes. Identify examples of both of these types of changes in the following:
  - a eating and digesting breakfast
  - b making a cake
  - c adding calcium hypochlorite (solid ‘chlorine’) to a swimming pool.



## 9.2 Chemical reactions

Paper burning, an egg cooking, autumn leaves changing colour and fireworks exploding are all examples of **chemical reactions**. In a chemical reaction a chemical change occurs and new substances are formed. These new substances have different compositions and properties when compared with the starting materials in the reaction. For example, an orange-coloured solid, commonly called rust, is formed when moist steel wool undergoes a chemical reaction with oxygen in the air.

**Figure 9.2** Rust forms in the reaction between iron, oxygen and water.

When a chemical reaction occurs, one or more of the following is commonly observed:

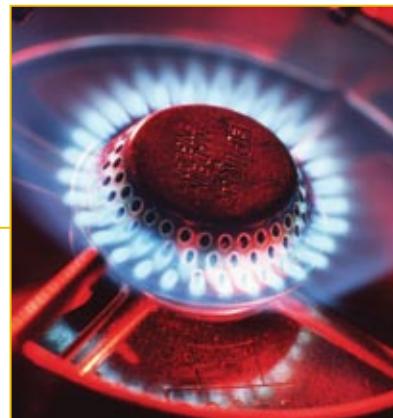
- a colour change; for example, when red meat is cooked, the protein molecules decompose to form brown-coloured products
- the formation of a solid (called a precipitate) in a solution; for example, when carbon dioxide is bubbled through limewater, a white precipitate of calcium carbonate forms
- the production of an odour; for example, lactic acid, which has a pungent smell, forms when milk turns sour
- a significant change in temperature; for example, a large amount of heat is produced when natural gas is burned
- the production of a gas; for example, carbon dioxide is formed when vinegar (acetic acid) is mixed with baking soda (sodium hydrogencarbonate).



a Formation of a precipitate of calcium carbonate when carbon dioxide is bubbled through limewater.



b Carbon dioxide is formed from vinegar and baking soda.



c Burning natural gas (methane).

Figure 9.3 Examples of chemical reactions.

The substances that are combined together in a chemical reaction are called the **reactants** and the new substances formed are called the **products**. For example, when methane in natural gas is burned it reacts with oxygen in the air to form carbon dioxide and water. The reactants in this reaction are methane and oxygen and the products are carbon dioxide and water.

During a chemical reaction the atoms in the reactants are rearranged in the formation of the products. Some or all of the bonds between the atoms in the reactants are disrupted and new bonds are formed to create the products. In this process no atoms are lost or gained. This is consistent with the **law of conservation of mass**, which states that mass is neither destroyed nor created in a chemical reaction. This law can be illustrated by burning a candle in a sealed jar of air. If, for example, the mass of the jar and its contents before the reaction is 210 g, the mass of the jar and products after the reaction will still be 210 g.



## \* Review exercise 9.2

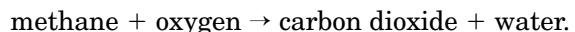
- 1 Which of the following could be classified as chemical reactions?  
**a** combustion of petrol in a car engine      **e** melting of ice-cream  
**b** formation of compost from food scraps      **f** dissolving sugar in water  
**c** evaporation of water      **g** tarnishing of silver  
**d** digestion of food      **h** curdling of milk.
- 2 Name the reactants and products for the following reactions:  
**a** during respiration, glucose reacts with oxygen to form water and carbon dioxide  
**b** carbon monoxide and water are formed when methane is burned in a limited supply of oxygen  
**c** when placed in the mouth, the chemicals in a 'fizzy lolly', sodium hydrogencarbonate and citric acid, react with one another to form carbon dioxide, water and sodium citrate.
- 3 Carbon dioxide and water are formed when octane, a component in petrol, is burned in a car engine. If 29 g of octane reacts exactly with 102 g of oxygen to form 41 g of water, what mass of carbon dioxide must also form?
- 4 When sodium hydrogencarbonate (baking soda) is heated, it decomposes to form sodium carbonate, water and carbon dioxide.  
**a** Some sodium hydrogencarbonate was placed in a container that was sealed and then heated. The sodium hydrogencarbonate decomposed during the heating. Would the mass of the container plus contents be more, less, or the same after the heating compared with before the heating?  
**b** If the experiment in part **a** was repeated, but this time the container was not sealed, would the mass of the container and its contents be more, less, or the same after the heating compared with before the heating? Explain your answer.

## 9.3 Equations for chemical reactions

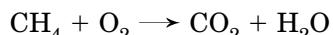
Chemists use equations to represent chemical reactions. A chemical equation shows the reactants on the left-hand side, then an arrow followed by the products on the right-hand side:

reactants → products

For example, the combustion of methane to form carbon dioxide and water can be represented by the following **word equation**:



Chemical formulas can also be used to represent the reactants and the products. The unbalanced equation for the combustion of methane,  $\text{CH}_4$ , would be:



According to the law of conservation of mass, atoms are neither destroyed nor created during a chemical reaction. Consequently, when an equation using formulas is written to correctly represent a chemical reaction, the equation must be **balanced**. This means the number of atoms of each type must be the same on both sides of the arrow. To balance an equation, numbers, called coefficients,



are placed in front of the formulas. For example, the balanced equation for the combustion of methane is:



This equation shows that one molecule of  $\text{CH}_4$  reacts with two molecules of  $\text{O}_2$  to form one molecule of  $\text{CO}_2$  and two molecules of  $\text{H}_2\text{O}$ , as shown in Figure 9.4.

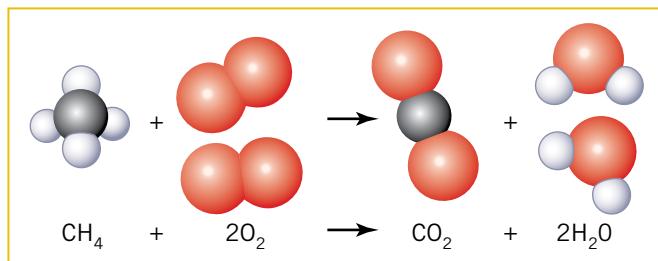


Figure 9.4 Interpreting a balanced chemical reaction.

When writing chemical equations, chemists often indicate the state of each of the reactants and products under the reaction conditions. Gas, liquid and solid are denoted by the symbols (g), (l) and (s) respectively. If a reactant or product is in aqueous solution, the symbol (aq) is used. For example, the above equation can be written as:



This kind of equation is sometimes called a **molecular equation** or overall equation.

The general procedure for writing a balanced equation for a chemical reaction is as follows:

- 1 Write the word equation, showing the names of each of the reactants and products.
- 2 Determine the correct formula and state for each reactant and product and write the unbalanced equation.
- 3 Balance each of the different types of atoms by placing a coefficient in front of the formulas. Do not change any of the actual formulas.
- 4 Make sure that the coefficients are in their lowest possible whole number ratio.

#### → Example 9.1

Write a balanced equation for the reaction between solid aluminium oxide and an aqueous solution of nitric acid to produce water and an aqueous solution of aluminium nitrate.

#### → Solution

**Step 1** Write the word equation:



**Step 2** Write the formulas and states of the reactants and products:

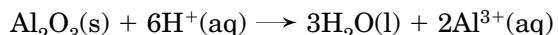


**Step 3** Balance each of the different types of atom:



(the H and O atoms are balanced, making the whole equation balanced)

**Ionic equations** are sometimes written, instead of molecular equations, for reactions involving ions. In an ionic equation, only the ions that actually participate in the reaction are included in the equation. Ionic equations must be balanced in both atoms and charge. For example, the ionic equation for the reaction of aluminium oxide with nitric acid, given in the previous example, is:



Details for writing ionic equations will be given in Chapter 12.

### \* Review exercise 9.3

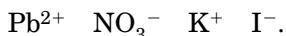
- 1 For each of the following equations, decide whether or not they are balanced correctly. If the equation is not balanced, state which atom or atoms are not balanced.
  - a When octane, a component of petrol, is burnt in a limited supply of air, carbon monoxide and water are formed according to the equation:  
 $\text{C}_8\text{H}_{18}(\text{l}) + 17\text{O}_2(\text{g}) \rightarrow 8\text{CO}(\text{g}) + 9\text{H}_2\text{O}(\text{l})$
  - b The formation of ammonia from nitrogen and hydrogen:  
 $\text{N}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
  - c Copper reacts with nitric acid to produce copper(II) nitrate, water and nitrogen monoxide according to the equation:  
 $3\text{Cu}(\text{s}) + 8\text{HNO}_3(\text{aq}) \rightarrow 3\text{Cu}(\text{NO}_3)_2(\text{aq}) + 2\text{NO}(\text{g}) + 4\text{H}_2\text{O}(\text{l})$
- 2 Balance the following equations:
  - a  $\text{Mg}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{MgO}(\text{s})$
  - b  $\text{S}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g})$
  - c  $\text{Mg}(\text{s}) + \text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2(\text{g})$
  - d  $\text{H}_2(\text{g}) + \text{Fe}_2\text{O}_3(\text{s}) \rightarrow \text{Fe}(\text{s}) + \text{H}_2\text{O}(\text{g})$
  - e  $\text{KClO}_3(\text{s}) \rightarrow \text{KCl}(\text{s}) + \text{O}_2(\text{g})$
  - f  $\text{Al}_2(\text{CO}_3)_3(\text{s}) + \text{HCl}(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{AlCl}_3(\text{aq})$
  - g  $\text{C}_2\text{H}_6(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
  - h  $\text{Cu}(\text{s}) + \text{HNO}_3(\text{aq}) \rightarrow \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{Cu}(\text{NO}_3)_2(\text{aq})$
  - i  $\text{KNO}_3(\text{s}) + \text{C}(\text{s}) + \text{S}(\text{s}) \rightarrow \text{K}_2\text{CO}_3(\text{s}) + \text{K}_2\text{S}(\text{s}) + \text{CO}_2(\text{g}) + \text{CO}(\text{g}) + \text{N}_2(\text{g})$ .
- 3 Write balanced chemical equations for the following reactions.
  - a When sodium is added to water, the products formed are a solution of sodium hydroxide,  $\text{NaOH}$ , and hydrogen gas.
  - b Butane,  $\text{C}_4\text{H}_{10}$ , burns, that is reacts with oxygen, to form carbon dioxide and water.
  - c An aqueous solution of hydrogen peroxide,  $\text{H}_2\text{O}_2$ , decomposes to form oxygen gas and water.
  - d Solid zinc sulfide reacts with oxygen gas to form solid zinc oxide and sulfur dioxide gas.
  - e Sulfur dioxide, water and a solution of aluminium sulfate are formed when an aqueous solution of sulfuric acid is added to solid aluminium sulfite.

## 9.4 Precipitation reactions

In order to make sense of the huge array of known chemical reactions, chemists often classify reactions based on how they proceed. Four different classes of reactions will be discussed in this textbook: precipitation, combustion, acid-base, and oxidation-reduction.

A **precipitation reaction** is said to have occurred 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. For example, when a colourless solution of lead nitrate is mixed with a colourless solution of potassium iodide, a yellow precipitate of lead iodide is formed, as shown in the photo of the first page of this chapter.

To understand what has happened in this reaction, it is necessary to identify the ions present in the reactant solutions. In the lead nitrate solution there are lead ions,  $\text{Pb}^{2+}$ , and nitrate ions,  $\text{NO}_3^-$ , and in the potassium iodide solution there are potassium ions,  $\text{K}^+$ , and iodide ions,  $\text{I}^-$ , as shown in Figure 9.6. In both of these solutions, all the ions are moving around independently. When one solution is added to the other, the mixture formed will contain the ions:



As these ions move around in the solution, they will collide with one another. When positively charged lead ions collide with negatively charged iodide ions, they attract one another to form insoluble lead iodide, which is the yellow precipitate. The potassium ions and nitrate ions will also collide with one another, but they just bounce apart again to remain dissolved in the solution. This occurs because potassium nitrate is soluble in water.



Figure 9.5 Precipitates of copper(II) hydroxide, iron(II) hydroxide and cobalt(II) hydroxide.

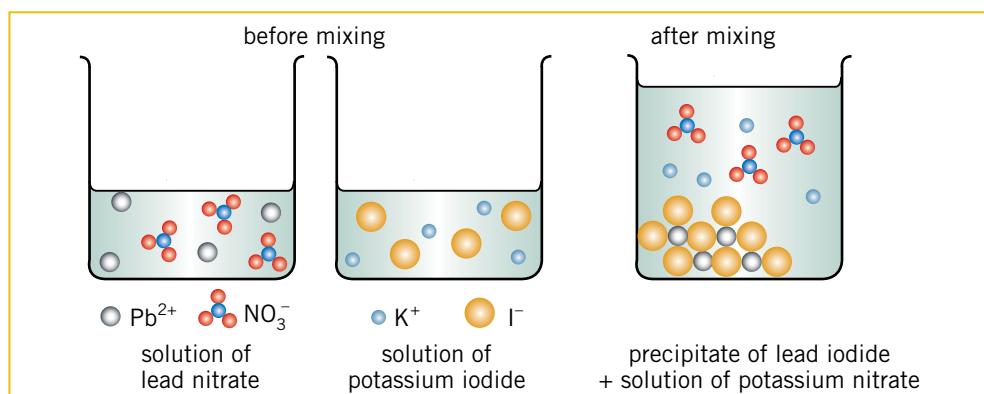
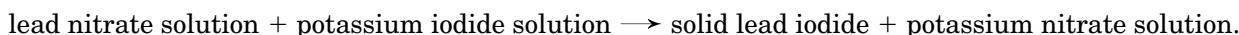
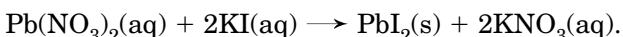


Figure 9.6 The ions present both before and after mixing solutions of lead nitrate and potassium iodide (the sizes of the ions are greatly exaggerated and they are not shown in the correct proportional numbers).

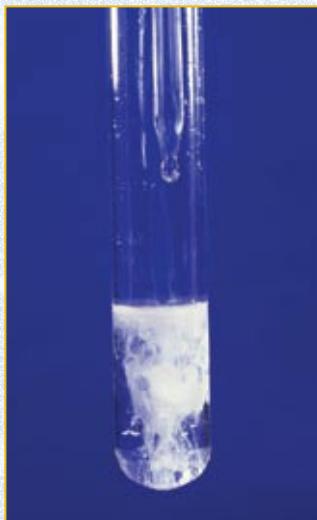
The reaction can be summarised as:



An alternative representation is in the form of a balanced overall equation:

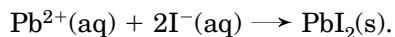


When the lead nitrate and potassium iodide solutions are mixed, the only new substance actually formed is solid lead iodide. The potassium ions and nitrate ions are not involved in the reaction. They were dissolved in the solution before the reaction and are still dissolved in the solution after the reaction. The only

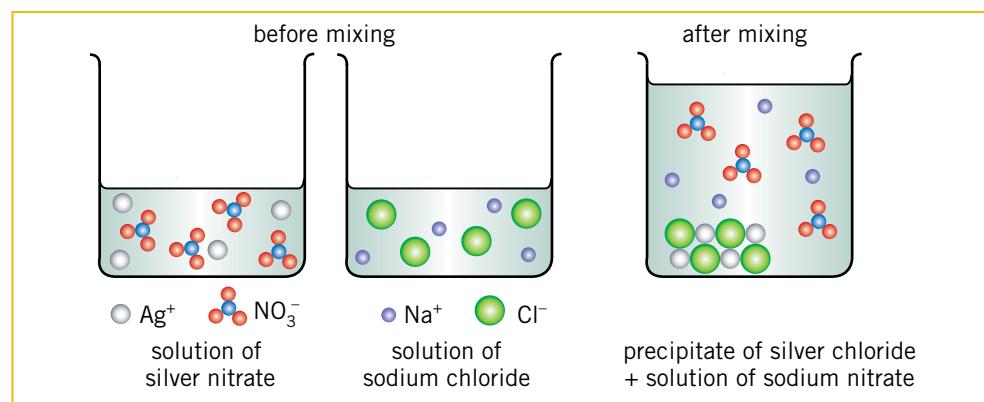


**Figure 9.7** The white precipitate of silver chloride is formed when colourless solutions of silver nitrate and sodium chloride are mixed. The sodium and nitrate ions remain dissolved in the colourless solution.

only change that has occurred when the two solutions are mixed is that the lead ions have joined up with the iodide ions to form a precipitate of lead iodide. Chemists sometimes write a simplified version of the balanced equation written on the previous page to show only the ions involved in the reaction, rather than showing all the particles present in the reaction mixture. This simplified equation is called an ionic equation and it includes only the species that have undergone a change during the reaction. For the reaction of a solution of lead nitrate with a solution of potassium iodide, the balanced ionic equation is:



A second example of a precipitation reaction is one that occurs when a solution of silver nitrate is mixed with a solution of sodium chloride. In this reaction, a white precipitate of silver chloride is formed, and the nitrate ions and sodium ions remain in solution, as shown in Figure 9.7. What is happening during this reaction at the atomic level is represented in Figure 9.8.

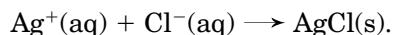


**Figure 9.8** The reaction of solutions of silver nitrate and sodium chloride, represented at the atomic level.

The formation of the precipitate of silver chloride during the reaction between solutions of silver nitrate and sodium chloride can be represented by the overall equation:



or by the ionic equation:



For precipitation reactions, the ionic equation just shows the formation of the precipitate. The other ions that remain unchanged and in solution are not included in the equation.

### Predicting products in precipitation reactions

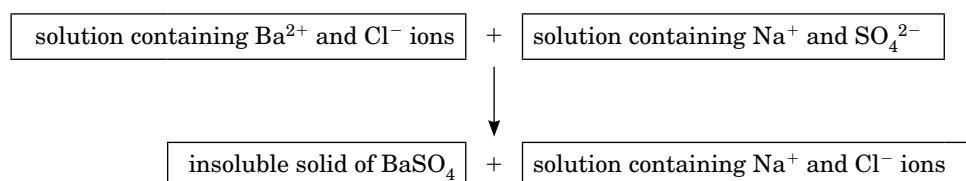
Using the solubility table (see Table 8.3), the precipitate formed in a precipitation reaction can be predicted. When the two solutions of ionic compounds are mixed, there will be four different types of ions present in the mixture. A precipitate will be formed if one of the positive ions and one of the negative ions can combine to form an insoluble compound. For example, if a solution of barium chloride is mixed with a solution of sodium sulfate the four ions present in the mixture prior to the reaction are:



The two possible new compounds, disregarding the original reactants, that could result from the combination of these four ions are  $\text{BaSO}_4$  and  $\text{NaCl}$ .



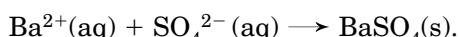
One of these compounds,  $\text{BaSO}_4$ , is insoluble in water, and so will form as a precipitate. The other compound,  $\text{NaCl}$ , is soluble in water and will remain dissolved in the solution. This reaction can be summarised as follows:



The overall equation for this reaction is:



The ionic equation, showing only the species that have been changed during the reaction, is:



A precipitation reaction does not always occur when two solutions of ionic compounds are mixed. For example, when a solution of sodium chloride is added to a solution of magnesium nitrate, the four ions present after mixing are  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$  and  $\text{NO}_3^-$ . None of these ions will combine to form an insoluble solid because the two possible ion combinations,  $\text{NaNO}_3$  and  $\text{MgCl}_2$ , are both soluble in water. As a consequence, no precipitation reaction occurs.

### → Example 9.2

Name and give the formula of any precipitate formed when the following solutions are mixed:

- a a solution of sodium phosphate and a solution of calcium nitrate
- b a solution of zinc sulfate and a solution of potassium carbonate
- c a solution of magnesium chloride and a solution of copper nitrate.

### → Solution

- a The ions present in the reaction mixture are:



The two new possible compounds that could form are:  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{NaNO}_3$ .

$\text{NaNO}_3$  is soluble and so will remain dissolved in the solution.

$\text{Ca}_3(\text{PO}_4)_2$  is insoluble.

The precipitate will therefore be **calcium phosphate**,  $\text{Ca}_3(\text{PO}_4)_2$ .

- b The ions present in the reaction mixture are:



The two new possible compounds that could form are:  $\text{ZnCO}_3$  and  $\text{K}_2\text{SO}_4$ .

$\text{K}_2\text{SO}_4$  is soluble and so will remain dissolved in the solution.

$\text{ZnCO}_3$  is insoluble.

The precipitate will therefore be **zinc carbonate**,  $\text{ZnCO}_3$ .

*continued*

c The ions in the solution are:



The two new possible compounds that could form are:  $\text{CuCl}_2$  and  $\text{Mg}(\text{NO}_3)_2$ .

$\text{CuCl}_2$  and  $\text{Mg}(\text{NO}_3)_2$  are both soluble and so will remain dissolved in the solution.

That is, **no precipitate** will form when the two solutions are mixed.

### Colour of a precipitate



Figure 9.9 Solutions (from left) of calcium nitrate, cobalt nitrate, nickel nitrate, copper nitrate and zinc nitrate.

The colour of an ionic compound is usually determined by the colour of the ions of which it is composed. For instance, in most compounds the copper ion is blue and the nitrate ion is colourless, so copper nitrate will probably be a blue colour. Table 9.2 shows the colours of some common ions in solution. In most cases, these colours will be the same when the ions are part of a solid ionic compound, such as, a precipitate. If a solid is composed of two ions that are shown as colourless in the table, the colour of the solid is usually referred to as white.

TABLE 9.2 COLOURS OF COMMON IONS IN AQUEOUS SOLUTION

Cation	Colour	Cation	Colour	Anion	Colour
$\text{Al}^{3+}$	colourless	$\text{Mg}^{2+}$	colourless	$\text{Cl}^-$	colourless
$\text{NH}_4^+$	colourless	$\text{Mn}^{2+}$	very pale pink	$\text{Br}^-$	colourless
$\text{Ba}^{2+}$	colourless	$\text{Hg}_2^{2+}$	colourless	$\text{I}^-$	colourless
$\text{Cd}^{2+}$	colourless	$\text{Hg}^{2+}$	colourless	$\text{NO}_3^-$	colourless
$\text{Ca}^{2+}$	colourless	$\text{Ni}^{2+}$	green	$\text{SO}_4^{2-}$	colourless
$\text{Cr}^{3+}$	deep green	$\text{K}^+$	colourless	$\text{OH}^-$	colourless
$\text{Co}^{2+}$	pink	$\text{Ag}^+$	colourless	$\text{CO}_3^{2-}$	colourless
$\text{Cu}^{2+}$	blue	$\text{Na}^+$	colourless	$\text{PO}_4^{3-}$	colourless
$\text{Fe}^{2+}$	pale green	$\text{Sr}^{2+}$	colourless	$\text{S}^{2-}$	colourless
$\text{Fe}^{3+}$	brown	$\text{Sn}^{2+}$	colourless		
$\text{Pb}^{2+}$	colourless	$\text{Zn}^{2+}$	colourless		

Using this information, the following precipitate colours can be predicted:

silver chloride	white
chromium phosphate	deep green
aluminium sulfide	white
iron(III) hydroxide	brown
nickel carbonate	green

While predictions of colours using Table 9.2 will work for most situations, there are exceptions. The yellow colour of lead(II) iodide has already been mentioned. Application of the information in the table would suggest that the solid should be white.

### → Example 9.3

Write ionic equations for the following reactions. Also, give the observations for each reaction.

- a A solution of sodium sulfate is added to a solution of lead nitrate.
- b Solutions of potassium iodide and zinc sulfate are mixed.
- c A solution of nickel sulfate is mixed with a solution of sodium phosphate.

### → Solution

- a The ions present in the reaction mixture are:  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Pb}^{2+}$ ,  $\text{NO}_3^-$ .

The two new possible compounds that could form are:  $\text{NaNO}_3$  and  $\text{PbSO}_4$

$\text{NaNO}_3$  is soluble and will remain dissolved in the solution.

$\text{PbSO}_4$  is insoluble and will form a precipitate.

The ionic equation shows only the formation of the precipitate. The  $\text{Na}^+$  and  $\text{NO}_3^-$  ions are not included in the equations because they remain 'unchanged' during the reaction, that is, they are in solution both before and after the reaction.

The balanced ionic equation is therefore



**Observation:** the colourless solutions react to form a white precipitate.

- b The ions present in the reaction mixture are:  $\text{K}^+$ ,  $\text{I}^-$ ,  $\text{Zn}^{2+}$ ,  $\text{SO}_4^{2-}$ .

The two new possible compounds that could form are:  $\text{K}_2\text{SO}_4$  and  $\text{ZnI}_2$ .

Both these compounds are soluble in water. That is, no **observable reaction** will occur (and no equation can be written).

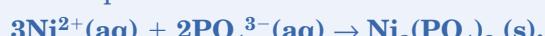
- c The ions present in the reaction mixture are:  $\text{Ni}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{PO}_4^{3-}$ .

The two new possible compounds that could form are:  $\text{Ni}_3(\text{PO}_4)_2$  and  $\text{Na}_2\text{SO}_4$ .

$\text{Ni}_3(\text{PO}_4)_2$  is insoluble and will form a precipitate.

$\text{Na}_2\text{SO}_4$  is soluble and will remain dissolved in the solution.

The balanced ionic equation is



**Observation:** the green solution and the colourless solution react to form a green precipitate.



**Figure 9.10** Precipitate of lead sulfate formed by mixing solutions of sulfuric acid and lead nitrate.

### \* Review exercise 9.4

- 1 Give the formula and colour of the precipitate you would expect to form when each of the following pairs of solutions are mixed. If no precipitate forms, write 'no precipitate'.
  - a potassium sulfate solution and barium nitrate solution
  - b potassium carbonate solution and nickel chloride solution
  - c zinc chloride solution and magnesium sulfate solution
  - d sodium hydroxide solution and copper chloride solution
  - e sodium phosphate solution and cobalt bromide solution.

*continued*

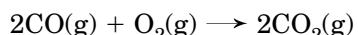
### Review exercise 9.4 — *continued*

- 2 Write ionic equations for the reactions that may occur when the following solutions are mixed. Also, give the observations for each.
  - a copper nitrate solution is added to a solution of potassium hydroxide.
  - b potassium bromide solution is added to a solution of silver nitrate.
  - c  $\text{Li}_3\text{PO}_4(\text{aq})$  is added to  $\text{FeCl}_3(\text{aq})$
  - d  $\text{NaCl}(\text{aq})$  is mixed with  $\text{CuSO}_4(\text{aq})$
  - e  $\text{AgNO}_3(\text{aq})$  is added to  $\text{K}_2\text{S}(\text{aq})$ .
- 3 Give examples of two solutions that could be mixed together to form each of the following as a precipitate in a reaction.
  - a  $\text{Ca}_3(\text{PO}_4)_2$
  - b  $\text{ZnS}$
- 4 Identify substances A and B from the following descriptions:
  - a Substance A is a nitrate of  $\text{Pb}^{2+}$ ,  $\text{K}^+$  or  $\text{Al}^{3+}$ . When a solution of A is mixed with a solution of potassium sulfate, a white precipitate forms.
  - b Substance B is a bromide of  $\text{Ni}^{2+}$ ,  $\text{Mg}^{2+}$  or  $\text{K}^+$ . When a solution of B is mixed with a solution of sodium carbonate, a white precipitate forms.

## 9.5 The mole and chemical equations

Chemists are often confronted with questions such as ‘what mass of carbon dioxide will form from the combustion of  $10^6$  kg of natural gas?’ or ‘what mass of sulfur will be required to form 100 tonnes of sulfuric acid,  $\text{H}_2\text{SO}_4$ ?’. Information necessary to answer these questions is contained in the balanced equation for the relevant reaction. The area of study associated with the quantities of materials consumed and produced in a chemical reaction is called **stoichiometry**.

A balanced chemical equation not only represents the ratio in which atoms, molecules and ions react and are formed, but it also shows the mole ratio in which the substances react and are formed. For example, the balanced equation for the reaction of carbon monoxide with oxygen to form carbon dioxide is:



From the coefficients in this equation, the following statements can be made:

- 2 molecules of CO will react with 1 molecule of  $\text{O}_2$  to form 2 molecules of  $\text{CO}_2$
- or 4 molecules of CO will react with 2 molecules of  $\text{O}_2$  to form 4 molecules of  $\text{CO}_2$
- or 100 molecules of CO will react with 50 molecules of  $\text{O}_2$  to form 100 molecules of  $\text{CO}_2$
- or  $2 \times 6.022 \times 10^{23}$  molecules of CO will react with  $6.022 \times 10^{23}$  molecules of  $\text{O}_2$  to form  $2 \times 6.022 \times 10^{23}$  molecules of  $\text{CO}_2$
- or 2 mole of CO will react with 1 mole of  $\text{O}_2$  to form 2 mole of  $\text{CO}_2$ .

That is, the coefficients in a balanced equation show the ratio, in mole, of reactants and products in a reaction. It therefore follows that the amount, in mole, of one substance involved in a reaction can be calculated from the amount, in mole, of a

second substance involved in the same reaction, providing the balanced chemical equation is known.

→ **Example 9.4**

The balanced equation for the combustion of methane is:



- How many mole of oxygen would be required to react with 0.300 mol of methane?
- How many mole of methane would be required to form 14.8 mol of water?

→ **Solution**

- From the balanced equation:

1 mol of  $\text{CH}_4$  will react with 2 mol of  $\text{O}_2$

so 0.300 mol of  $\text{CH}_4$  will react with  $2 \times 0.300 = 0.600$  mol of  $\text{O}_2$

- From the balanced equation:

2 mol of  $\text{H}_2\text{O}$  will form from 1 mol of  $\text{CH}_4$

that is 1 mol of  $\text{H}_2\text{O}$  will form  $\frac{1}{2}$  mol of  $\text{CH}_4$

so 14.8 mol of  $\text{H}_2\text{O}$  will form  $\frac{1}{2} \times 14.8 = 7.40$  mol of  $\text{CH}_4$

→ **Example 9.5**

When iron(III) oxide is heated strongly with carbon monoxide, they react to form iron and carbon dioxide. How many mole of iron would form from the reaction of 295 mol of carbon monoxide with iron(III) oxide?

→ **Solution**

A balanced equation for the reaction must first be written:



From this equation:

3 mol of CO will form 2 mol of Fe

that is, 1 mol of CO will form  $\frac{2}{3}$  mol of Fe

so 295 mol of CO will form  $\frac{2}{3} \times 295 = 197$  mol of Fe

✳ **Review exercise 9.5**

- Vinegar should not be used to clean marble tiles or benchtops because the acetic acid in the vinegar reacts with the marble ( $\text{CaCO}_3$ ) according to the equation:



- Calculate the amount in mole of acetic acid required to react with 0.813 mol of marble.
  - How many mole of carbon dioxide would form from the reaction of 1.66 mol of acetic acid with marble?
- Consider the reaction for the combustion of propane used in barbecues:



- How many mole of  $\text{H}_2\text{O}$  is produced when 3.84 mol of propane is burned?
- How many mole of propane would be required to produce 71.4 mol of carbon dioxide?
- If 0.893 mol of oxygen is consumed, how many mole of water will be produced?

*continued*

### Review exercise 9.5 — *continued*

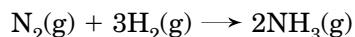
- 3 A solution of calcium chloride contains 0.0528 mol of calcium ions,  $\text{Ca}^{2+}$ . If sufficient sodium phosphate solution for reaction with all the calcium ions is added to the calcium chloride solution, how many mole of calcium phosphate would precipitate?
- 4 In the photosynthesis process carried out in the leaves of plants, glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) and oxygen are produced from carbon dioxide and water. Calculate the amount, in mole, of carbon dioxide required to produce 0.718 mol of glucose.

## 9.6 Mass–mass stoichiometric calculations

A chemical equation can be used to determine the masses of the reactants and products involved in a reaction since there is a relationship between the mass and the amount, in mole, of each substance. This relationship can be expressed in the following way:

$$\text{amount of the substance in mole}(n) = \frac{\text{mass of the substance (m)}}{\text{molar mass of the substance (M)}}$$

For example, in the reaction between nitrogen and hydrogen to produce ammonia:



this balanced equation shows that

1 mol of  $\text{N}_2$  would react with 3 mol of  $\text{H}_2$  to form 2 mol of  $\text{NH}_3$ .

However, it also shows that

28 g of  $\text{N}_2$  would react with  $3 \times 2 = 6$  g of  $\text{H}_2$  to form  $2 \times 17 = 34$  g of  $\text{NH}_3$ , where the values 28, 2 and 17, in  $\text{g mol}^{-1}$ , are the molar masses of  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  respectively.

As with the mole problems discussed in Chapter 6, a flowchart, shown in Figure 9.11, can be used to determine the steps involved in simple mass–mass stoichiometric calculations.

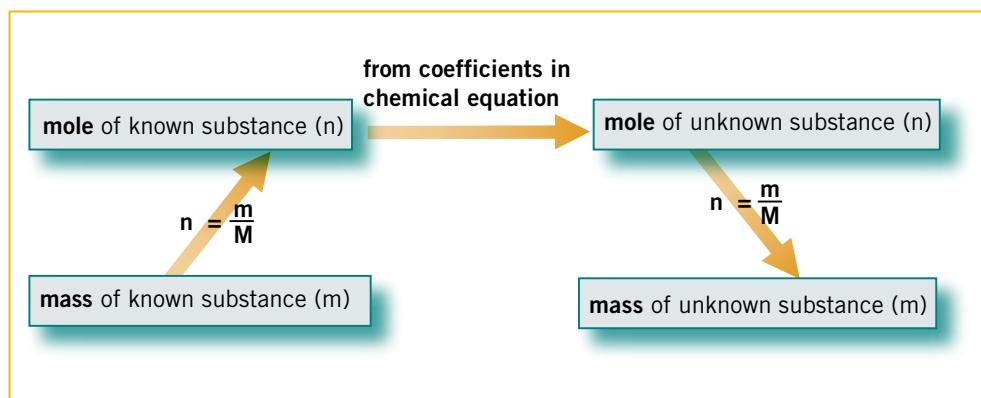


Figure 9.11 Flowchart for mass–mass stoichiometric calculations.

### → Example 9.6

Silicon is produced for the electronics industry by the following reaction:

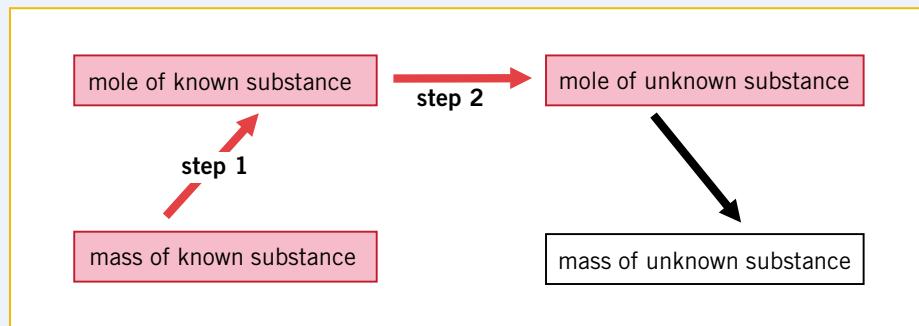


How many mole of carbon is required to form 382 g of silicon?

### → Solution

This is a two-step problem:

mass of Si → mole of Si → mole of C



$$\begin{aligned}\text{Step 1} \quad \text{mole of Si} &= \frac{\text{mass of Si}}{\text{molar mass of Si}} \\ &= \frac{382}{28.09} = 13.60 \text{ mol}\end{aligned}$$



**Step 2** From the balanced equation:

$$\begin{aligned}1 \text{ mol of Si would form from } 2 \text{ mol of C} \\ \text{so} \quad 13.60 \text{ mol of Si would form from } 2 \times 13.60 = \mathbf{27.2 \text{ mol of C}}$$

### → Example 9.7

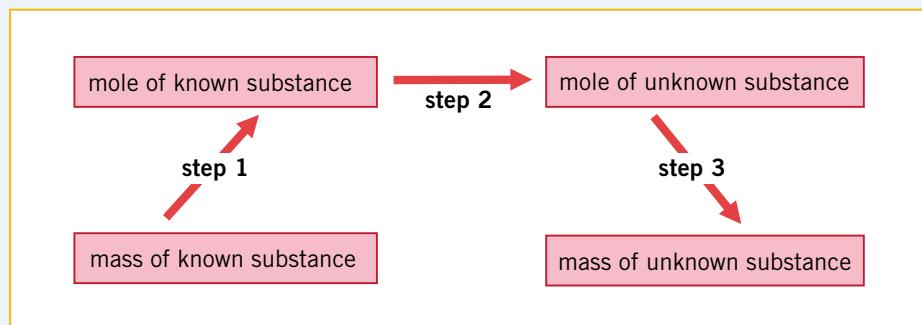
When aluminium is heated strongly with chlorine gas, a reaction occurs to form aluminium chloride. What mass of chlorine would be required to react with 25.8 g of aluminium?

### → Solution

This problem involves three calculation steps. Also, a balanced equation for the reaction must be written.

The three calculation steps are:

mass of Al → mole of Al → mole of  $\text{Cl}_2$  → mass of  $\text{Cl}_2$



*continued*

The balanced equation for the reaction is



**Step 1** mole of Al =  $\frac{\text{mass of Al}}{\text{molar mass of Al}}$   
=  $\frac{25.8}{26.98} = 0.9563 \text{ mol}$

**Step 2** From the balanced equation:

2 mol of Al will react with 3 mol of Cl<sub>2</sub>  
that is, 1 mol of Al will react with  $\frac{3}{2}$  mol of Cl<sub>2</sub>  
so 0.9563 mol of Al will react with  $\frac{3}{2} \times 0.9563 = 1.434$  mol of Cl<sub>2</sub>

**Step 3** mole of Cl<sub>2</sub> =  $\frac{\text{mass of Cl}_2}{\text{molar mass of Cl}_2}$   
molar mass of Cl<sub>2</sub> =  $2 \times 35.45 = 70.90 \text{ g mol}^{-1}$   
 $1.434 = \frac{\text{mass of Cl}_2}{70.90}$   
mass of Cl<sub>2</sub> =  $1.434 \times 70.90 = 102 \text{ g}$

### \* Review exercise 9.6

- 1 Octane, C<sub>8</sub>H<sub>18</sub>, is one of the hydrocarbons in petrol. When octane burns it reacts with oxygen to form carbon dioxide and water.
  - a Write a balanced equation for the reaction.
  - b How many mole of carbon dioxide would be formed from the combustion of 0.827 mol of octane?
  - c What mass of water will form together with 0.600 mol of carbon dioxide during the combustion of octane?
- 2 Oxygen gas can be prepared in the laboratory by strongly heating a sample of potassium chlorate.



- a What mass of oxygen would form from the decomposition of 15.4 g of potassium chlorate?
  - b If the potassium chlorate was heated in a test tube, propose a way in which you could collect the oxygen gas formed in the reaction. In your answer, include a labelled diagram of the equipment you would use.
- 3 Calcium carbonate is used as a polishing agent in some toothpastes. To determine the percentage of calcium carbonate in toothpaste, 10.4 g of the toothpaste was reacted with hydrochloric acid. The following reaction occurred:



- a If 3.57 g of carbon dioxide was formed in this reaction:
    - i what mass of calcium carbonate was present in the 10.4 g of toothpaste?
    - ii what is the percentage, by mass, of calcium carbonate in the toothpaste?
  - b What assumption was made in these calculations about the reaction of the acid with the toothpaste?

- 4 The airbags that are now common in cars contain the explosive sodium azide,  $\text{NaN}_3$ . This compound decomposes, during the collision, to form sodium and gaseous nitrogen. (A further reaction involving the sodium also occurs.)
- Write a balanced equation for the decomposition reaction of sodium azide.
  - What mass of nitrogen would be formed from the decomposition of 205 g of sodium azide?
  - If at  $25^\circ\text{C}$  and 101.3 kPa pressure, 1 mole of nitrogen occupies a volume of 24.5 L, what volume of nitrogen, at this temperature and pressure, would you expect to form from the 205 g of sodium azide?

## 9.7 Solution stoichiometry

Calculations based on balanced chemical equations can also be extended to those involving chemicals in solutions. The flowchart given in Figure 9.11 can be expanded to include the formula that relates the concentration of a solution to the mole of solute dissolved in the solution and the volume of the solution (Figure 9.12):

$$\text{concentration (mol L}^{-1}\text{)} = \frac{\text{mole of solute}}{\text{volume of solution (in L)}}$$

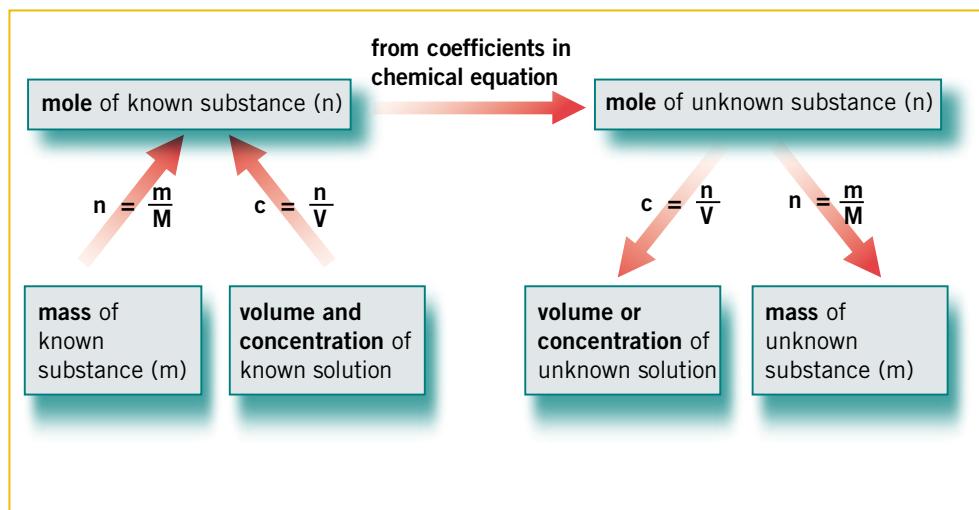


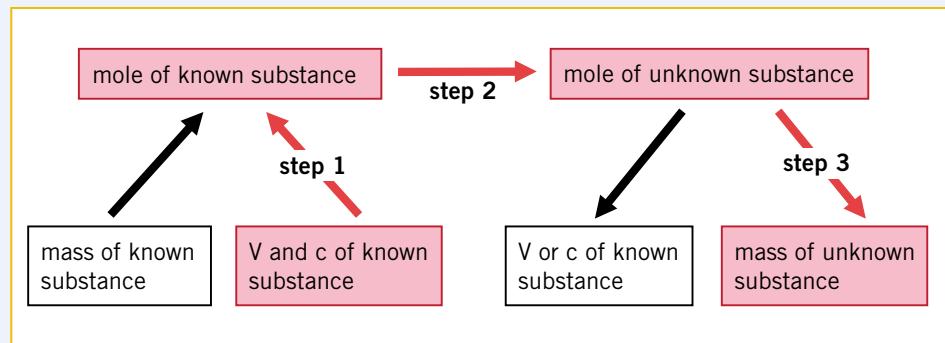
Figure 9.12 Stoichiometric mole chart including solution calculations.

→ Example 9.8

What mass of calcium phosphate will precipitate if 128 mL of 0.170 mol L<sup>-1</sup> sodium phosphate solution is added to an excess of calcium nitrate solution?

→ Solution

This problem involves three major calculation steps, even though the first step in a stoichiometric calculation must always be to write a balanced equation for the reaction:



(The term 'an excess of calcium nitrate solution' means that there is more than enough calcium nitrate to react with the sodium phosphate. There will be some calcium nitrate left over after the reaction.)



**Step 1a**  $c \text{ (of } \text{Na}_3\text{PO}_4 \text{ solution)} = \frac{n(\text{Na}_3\text{PO}_4)}{V(\text{Na}_3\text{PO}_4 \text{ solution})}$

$$V(\text{Na}_3\text{PO}_4 \text{ solution}) = \frac{128}{1000} = 0.128 \text{ L}$$

$$0.170 = \frac{n(\text{Na}_3\text{PO}_4)}{0.128}$$

$$n(\text{Na}_3\text{PO}_4) = 0.170 \times 0.128 = 0.02176 \text{ mol}$$

**Step 1b** Because the balanced equation shows the reactant to be  $\text{PO}_4^{3-}$ , not  $\text{Na}_3\text{PO}_4$ , it is necessary to calculate the mole of  $\text{PO}_4^{3-}$  involved in the reaction, from the mole of  $\text{Na}_3\text{PO}_4$ :

1 mol of  $\text{Na}_3\text{PO}_4$  contains 1 mol of  $\text{PO}_4^{3-}$

so 0.02176 mol of  $\text{Na}_3\text{PO}_4$  contains 0.02176 mol of  $\text{PO}_4^{3-}$

**Step 2** From the balanced equation:

2 mol of  $\text{PO}_4^{3-}$  will form 1 mol of  $\text{Ca}_3(\text{PO}_4)_2$

or 1 mol of  $\text{PO}_4^{3-}$  will form  $\frac{1}{2}$  mol of  $\text{Ca}_3(\text{PO}_4)_2$

so 0.02176 mol of  $\text{PO}_4^{3-}$  will form  $\frac{1}{2} \times 0.02176 = 0.01088$  mol of  $\text{Ca}_3(\text{PO}_4)_2$

**Step 3**  $n(\text{Ca}_3(\text{PO}_4)_2) = \frac{m(\text{Ca}_3(\text{PO}_4)_2)}{M(\text{Ca}_3(\text{PO}_4)_2)}$        $M(\text{Ca}_3(\text{PO}_4)_2) = 310.18 \text{ g mol}^{-1}$

$$0.01088 = \frac{m(\text{Ca}_3(\text{PO}_4)_2)}{310.18}$$

$$m(\text{Ca}_3(\text{PO}_4)_2) = 0.01088 \times 310.18 = 3.37 \text{ g}$$

### \* Review exercise 9.7

- 1 What volume of  $0.200 \text{ mol L}^{-1}$  silver nitrate solution is required to produce 3.24 g of silver sulfide from the complete reaction with excess potassium sulfide solution?
- 2
  - a What volume of  $0.100 \text{ mol L}^{-1}$  sodium sulfate solution is required to precipitate all the barium ions out of 125.0 mL of a  $0.0300 \text{ mol L}^{-1}$  solution of barium chloride?
  - b What mass of barium sulfate would be obtained in part a assuming all the barium ions in solution were precipitated as barium sulfate?
- 3 To determine the amount of acetic acid,  $\text{CH}_3\text{COOH}$ , in a particular brand of vinegar, the vinegar was reacted with a certain mass of sodium carbonate dissolved in water:



It was found that 29.34 mL of the vinegar was required to react exactly with 0.278 g of sodium carbonate dissolved in water. What is the concentration, in  $\text{mol L}^{-1}$ , of acetic acid in the vinegar?

## 9.8 Gases and stoichiometry

### Mass–gas volume calculations

In Chapter 7, the relationship between the amount, in mole, of a gas and its volume measured at  $0^\circ\text{C}$  and  $101.3 \text{ kPa}$  pressure (STP conditions) was discussed. Under most laboratory conditions, according to Avogadro's hypothesis, equal amounts, in mole, of all gases occupy the same volume at the same temperature and pressure. For instance, the volume occupied by 1 mole of all gases at STP is very close to 22.41 L. Using this information, the volume, at STP, of any amount of a gas can be determined. A formula often used for this calculation is

$$\text{mole of gas} = \frac{\text{volume of gas at STP (L)}}{22.41} \quad (\text{or } n = \frac{V}{22.41})$$

This relationship between the volume and amount, in mole, of a gas can be used in stoichiometric problems where the volume, at STP, of a gaseous reactant or product is given or is to be determined. A mole flowchart, including the mole–volume formula, is shown in Figure 9.13.

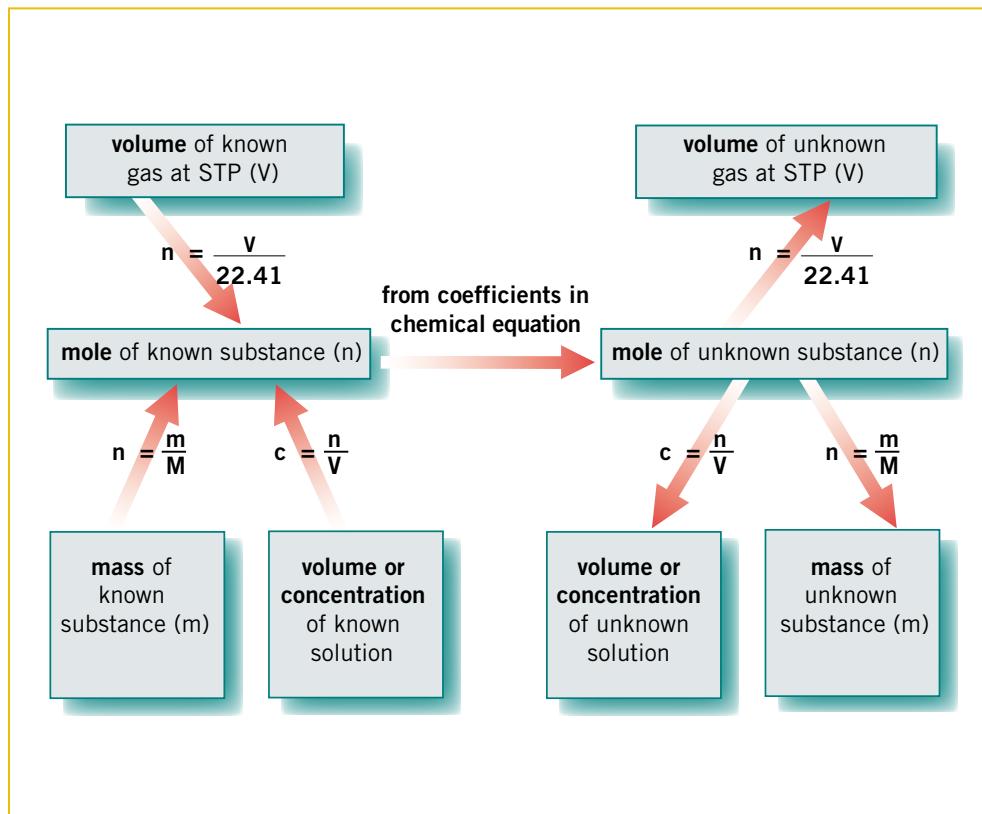


Figure 9.13 Stoichiometric mole chart including mass, solution and gas calculations.

#### → Example 9.9

Carbon dioxide can be removed from air by bubbling it through a solution of sodium hydroxide. The equation for the reaction that occurs is:



What mass of NaOH, dissolved in the solution, would be required to remove 0.800 L, measured at STP, of carbon dioxide from a sample of air?

#### → Solution

The three major calculation steps are:

volume at STP of  $\text{CO}_2(\text{g}) \rightarrow$  mole of  $\text{CO}_2 \rightarrow$  mole of  $\text{OH}^-$  (or NaOH)  $\rightarrow$  mass of NaOH

$$\text{Step 1 } n(\text{CO}_2) = \frac{V(\text{CO}_2)}{22.41} = \frac{0.800}{22.41} = 0.03570 \text{ mol}$$

**Step 2** From balanced equation:

1 mol  $\text{CO}_2$  reacts with 2 mol  $\text{OH}^-$

so  $0.03570 \text{ mol CO}_2$  reacts with  $2 \times 0.03570 = 0.07140 \text{ mol OH}^-$

**Step 3** 0.07140 mol of  $\text{OH}^-$  was formed from 0.07140 mol of NaOH

$$n(\text{NaOH}) = \frac{m(\text{NaOH})}{M(\text{NaOH})} \quad M(\text{NaOH}) = 39.998 \text{ g mol}^{-1}$$

$$0.07140 = \frac{m(\text{NaOH})}{39.998}$$

$$m(\text{NaOH}) = 0.07140 \times 39.998 = 2.86 \text{ g}$$

## Gas volume–volume calculations

Stoichiometric calculations involving only the volumes of gases, at the same temperature and pressures, can also be performed.

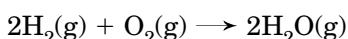
At a given temperature and pressure, such as STP, the volume of any gas is proportional to the amount, in mole, of this gas. For example, this relationship is expressed in the formula

$$n = \frac{V}{22.41} \text{ when the gas volume is measured at STP.}$$

Therefore the balancing coefficients in a chemical equation, that give the mole ratio of substances involved in a reaction, must also give the volume ratio of any gases involved in a reaction. For this to be true, the gas volumes must be measured at the same temperature and pressure. This idea was first proposed by a French chemist, Joseph Gay-Lussac in the early nineteenth century. Gay-Lussac's law can be stated as

'The volumes of different gases involved in a reaction, if measured at the same temperature and pressure, are in the same ratio as the coefficients in a balanced equation.'

For example, the equation for the reaction of hydrogen with oxygen to form gaseous water is



It would therefore be expected that, assuming the volumes for each reaction mixture are measured at the same temperature and pressure:

- 2 L of  $\text{H}_2(\text{g})$  will react with 1 L of  $\text{O}_2(\text{g})$  to form 2 L of  $\text{H}_2\text{O}(\text{g})$   
or
- 1 L of  $\text{H}_2(\text{g})$  will react with 0.5 L of  $\text{O}_2(\text{g})$  to form 1 L of  $\text{H}_2\text{O}(\text{g})$   
or
- 0.50 L of  $\text{H}_2(\text{g})$  will react with 0.25 L of  $\text{O}_2(\text{g})$  to form 0.50 L of  $\text{H}_2\text{O}(\text{g})$

It is important to note that Gay-Lussac's law only applies to gases, so when a reaction involves both gases and solids, gases and liquids or gases and solutions, it is not possible to apply the same simplifying volume ratios to the substances that are not gases.

### → Example 9.10

What volume of carbon dioxide and of steam are obtained from the complete combustion of 3 L of methane (assume all volumes are measured at the same temperature and pressure)?

### → Solution

The balanced equation for the reaction is



$\text{CO}_2$ : from the balanced equation:

1 volume of  $\text{CH}_4$  will form 1 volume of  $\text{CO}_2$   
so 3 L of  $\text{CH}_4$  will form **3 L of  $\text{CO}_2$**

$\text{H}_2\text{O}$ : from the balanced equation:

1 volume of  $\text{CH}_4$  will form 2 volumes of  $\text{H}_2\text{O}(\text{g})$   
so 3 L of  $\text{CH}_4$  will form  **$2 \times 3 = 6 \text{ L of } \text{H}_2\text{O}(\text{g})$**



### → Example 9.11

With careful heating, ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , decomposes to produce dinitrogen monoxide,  $\text{N}_2\text{O}$ , and steam. What volume of dinitrogen monoxide can be obtained together with 3.4 L of steam?

### → Solution

The balanced overall equation for the reaction is



From the balanced equation:

2 volumes of  $\text{H}_2\text{O}$  will form with 1 volume of  $\text{N}_2\text{O}$

or 1 volume of  $\text{H}_2\text{O}$  will form with  $\frac{1}{2}$  volume of  $\text{N}_2\text{O}$

so, 3.4 L of  $\text{H}_2\text{O}$  will form with  $\frac{1}{2} \times 3.4 = 1.7 \text{ L of } \text{N}_2\text{O}$

(Note that it would not be possible to complete any calculations associated with the amount of ammonium nitrate from the given information as it is a solid and not a gas.)

### \* Review exercise 9.8

- 1 Zinc has some important uses, including the galvanising of iron, in dry cells and in alloys such as brass. Zinc is extracted from zinc sulfide ores, with Australia being one of the largest producers of this metal. The extraction of zinc from its sulfide ores involves several stages, the first being the reaction



- Sulfur dioxide is one of the main contributors to air pollution, and its production during the extraction of zinc must be carefully controlled. What volume, in litres, of  $\text{SO}_2$  at STP would be produced from 2.00 tonne of zinc sulfide?

- 2 A zinc–copper alloy behaves in its chemical reaction with sulfuric acid as a mixture of copper and zinc, that is, the zinc reacts with the acid, but the copper does not. 6.00 g of a particular zinc–copper alloy reacts with excess dilute sulfuric acid giving 1.12 L, measured at STP, of hydrogen. Calculate the mass of copper in the alloy.



- 3 9.00 L of hydrogen reacts with chlorine to give hydrogen chloride gas



Assuming all the volumes are measured at the same pressure and temperature:

- what volume of hydrogen chloride is formed in the reaction?
- what volume of chlorine reacts with the hydrogen?

## MAJOR IDEAS

- Chemical changes involve the formation of new substances while physical changes do not alter the composition of the material undergoing the change.
- On the molecular level chemical change involves the rearrangement of the atoms in the reactants.
- Chemical reactions can involve changes such as gas production, solid formation, colour changes, etc.
- Chemical reactions can be summarised in the form of a balanced chemical equation.
- Atoms are conserved in a chemical reaction.
- Precipitation reactions occur when two or more solutions are mixed and an insoluble solid is formed.
- A table of solubilities can be used to predict whether a precipitation reaction is likely to take place.
- Ionic equations, showing the ions that react to form the insoluble substance, are written for precipitation reactions.
- The balancing coefficients in a balanced equation show the mole ratio of the substances involved in the reaction.
- The mole is the unifying concept that enables the calculation of masses of substances, volumes and concentrations of solutions, and volumes of gases at STP involved in reactions (see Figure 9.13).
- Gay-Lussac's law states that the volumes of different gases involved in a reaction, if measured at the same temperature and pressure, are in the same ratio as the coefficients in the balanced equation.

## QUESTIONS

- Write balanced chemical equations for the following reactions:
  - When ammonia gas reacts with oxygen at 1000°C, the products formed are nitrogen monoxide gas, NO, and water vapour.
  - In the production of wine, glucose,  $C_6H_{12}O_6$ , in the grapes is converted to ethanol,  $C_2H_5OH$ , and carbon dioxide,  $CO_2$ , by yeast.
  - When the explosive TNT (trinitrotoluene),  $C_7H_5(NO_2)_3$ , decomposes, it forms carbon monoxide, water, nitrogen and carbon.
- Write ionic equations for any precipitation reactions that may occur when the following pairs of solutions are mixed. Also, give the observations for the reactions.
  - solution of sodium carbonate + solution of nickel chloride
  - solution of zinc nitrate + solution of potassium phosphate

- solution of potassium chloride + solution of copper nitrate.
- Name two solutions that could be mixed to give the following observations.
  - When a colourless solution is mixed with a blue solution, a blue precipitate forms.
  - A brown precipitate forms when a colourless solution is mixed with an orange-brown solution.
- a** A solution is known to contain either sodium sulfate or sodium chloride. Describe an experiment you could carry out to show which of these salts is present in the solution. Explain your reasoning, including any relevant ionic equations.  
**b** You are given unlabelled samples of three colourless solutions and one blue solution and told that these solutions are barium chloride, copper chloride, magnesium chloride and potassium chloride. Describe experiments you could carry out to determine the identity of each of the unlabelled solutions. Include details of the expected results and relevant ionic equations.
- In an experiment to identify three unknown solutions, A, B and C, the following results were obtained when they were tested with the three known solutions of sodium chloride, sodium sulfate and silver nitrate:

	Solution A	Solution B	Solution C
NaCl(aq)	no precipitate	no precipitate	white precipitate
Na <sub>2</sub> SO <sub>4</sub> (aq)	white precipitate	no precipitate	white precipitate
AgNO <sub>3</sub> (aq)	no precipitate	white precipitate	no precipitate

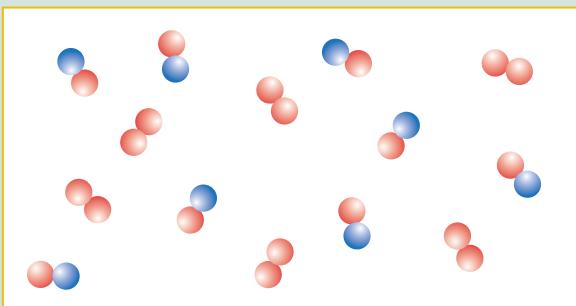
One of the unknown solutions is lead nitrate, another is barium nitrate and the third is potassium bromide.

Use the results given above to determine the identities of A, B and C.

- A large iron nail is left outside to rust.
  - Assuming all the rust remains stuck on the nail, will the mass of the rusted nail be the same, more or less than the mass of the unrusted nail? Explain your reasoning.
  - If the rust is brushed off the nail, will the mass of the cleaned nail be the same, less or more than the mass of the original unrusted nail? Explain your answer.

- 7 The brown colour of photochemical smog often seen over cities is due to the presence of nitrogen dioxide. This brown-coloured gas is formed in the reaction of nitrogen monoxide, NO, with oxygen. (The nitrogen monoxide is produced from the oxidation of nitrogen in vehicle engines.)

The box below shows some molecules of nitrogen monoxide and oxygen. Assuming these molecules react as completely as possible, draw the molecules that would be present after the reaction.



- 8 A rocket propellant system consists of oxygen difluoride ( $\text{OF}_2$ ), as an oxidant, and kerosene as the fuel. If the kerosene burns according to the equation:



how many mole of gas, in total, would be formed from the reaction of 425 mole of oxygen difluoride with kerosene?

- 9 During a marathon race, a runner drinks an aqueous solution containing 5.00% by mass of glucose. Glucose reacts with oxygen in the body cells to release energy according to the equation:



If the runner consumes  $1.00 \times 10^3 \text{ g}$  (approximately 1 L) of the glucose solution during the marathon, calculate the mass of oxygen required to react with the glucose consumed.

- 10 Sodium hydrogencarbonate and magnesium hydroxide are both used in antacids. Antacids are pharmaceutical preparations used to combat excess acidity in the stomach of someone suffering from indigestion. Sodium hydrogencarbonate reacts with the hydrochloric acid (HCl) in the stomach to form carbon dioxide, water and a solution of sodium chloride. Magnesium hydroxide reacts with the acid (HCl) to form water and a solution of magnesium chloride. Which is the more effective antacid per gram, sodium hydrogencarbonate or magnesium hydroxide?

- 11 Kerosene is used as a fuel in jet engines and home heaters. It is composed of a mixture of long chain hydrocarbons.

- a Assuming a typical molecule in kerosene has the formula of  $\text{C}_{16}\text{H}_{34}$ , write a balanced equation for the combustion of  $\text{C}_{16}\text{H}_{34}$  in which carbon dioxide and water are formed.  
b What mass of carbon dioxide would be formed from the combustion reaction of  $1.0 \times 10^2 \text{ L}$  of  $\text{C}_{16}\text{H}_{34}$ , assuming the density of  $\text{C}_{16}\text{H}_{34}$  is  $0.82 \text{ g mL}^{-1}$ ?

- 12 Sulfur dioxide is used in industry on a vast scale, and so its method of production is important. One commonly used method involves a two-step process:  
Step 1: Iron(III) sulfide is subjected to moist combustion to yield sulfur:



Step 2: The sulfur obtained from Step 1 is then burned to form sulfur dioxide:



- a How many mole of sulfur would be formed from the reaction of 1.00 tonne of iron(III) sulfide?  
b What mass of sulfur dioxide would be produced from the sulfur formed in part a?

- 13 Lead(II) sulfate can be obtained from the reaction of 465 mL of  $0.238 \text{ mol L}^{-1}$  lead(II) nitrate solution with excess  $1.0 \text{ mol L}^{-1}$  sodium sulfate solution.

- a Write the ionic equation for the reaction.  
b Determine the amount, in mole, of lead nitrate in 465 mL of  $0.238 \text{ mol L}^{-1}$  lead nitrate solution.  
c What amount, in mole, of lead sulfate, would be produced in the reaction?  
d What mass of lead sulfate is formed?  
e To avoid the use of excess sodium sulfate solution, what volume of the  $1.0 \text{ mol L}^{-1}$  solution would be required for complete reaction?

- 14 A 5.00 mL sample of commercial vinegar (a dilute solution of acetic acid) completely reacted with 24.50 mL of  $0.157 \text{ mol L}^{-1}$  sodium hydroxide solution. Calculate the acetic acid concentration, in  $\text{mol L}^{-1}$ , of the vinegar.



- 15 2.00 L of a solution of hydrochloric acid is found to produce 4.76 L of hydrogen at STP when reacted with excess magnesium. What is the concentration, in  $\text{mol L}^{-1}$ , of the hydrochloric acid?



- 16** In the production of nitric acid, one stage involves the catalytic oxidation of ammonia at 900°C,  

$$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g}).$$
- a** What volume of the gas nitrogen monoxide (NO) will be produced by the complete oxidation of 4.00 L of ammonia?
- b** What volume of oxygen is required to react with 23.0 L of ammonia?  
 (All temperatures and pressures constant.)
- 17** Vinegar is the recommended treatment for the hard water deposits that form in kettles and electric jugs. Assuming the deposit is only calcium carbonate, what volume of vinegar (4.0% acetic acid by mass, and assuming the density of vinegar is 1.0 g mL<sup>-1</sup>) is required to remove a build-up of 0.56 g of calcium carbonate in an electric jug?
- $$\text{CaCO}_3(\text{s}) + 2\text{CH}_3\text{COOH}(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{CH}_3\text{COO}^-(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$$
- 18** A small piece of marble (calcium carbonate), which is insoluble in water, has a mass of 1.50 g. It is placed in a solution containing 1.26 g of nitric acid, HNO<sub>3</sub>. What mass of the marble will remain after the reaction has ceased?
- $$\text{HNO}_3(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$$
- $$\text{CaCO}_3(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$$
- 19** 2.00 g of a mixture of chalk (CaCO<sub>3</sub>) and sand, when treated with excess dilute hydrochloric acid, yielded 0.436 g of carbon dioxide. What is the percentage by mass of chalk in the mixture?
- $$\text{CaCO}_3(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}).$$
- 20** Physical and chemical changes are experienced in many places in the home. During physical changes, the covalent bonds within the particles are not disturbed, but the bonds between the particles often are. However, during a chemical change, covalent bonds between atoms within the particles are broken, atoms are rearranged and new bonds are formed. Descriptions of some chemical and physical changes are:

**A** *Using baking powder as the rising (leavening) agent when making a cake*

Baking powder contains sodium hydrogen-carbonate and potassium hydrogentartrate, KHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>, in dry form. No reaction occurs in the dry powder, but when water is added for cooking, the two chemicals dissolve and a reaction occurs to release carbon dioxide gas that is trapped in the flour mixture. Once heated, the trapped bubbles of gas expand, causing the cake to rise. Water and a mixture of sodium

tartrate and potassium tartrate are also formed in the reaction.

**B** *Boiling water to make a cup of tea*

Steam is formed when water is boiled.

**C** *Using a dry cell to power a torch*

When a dry cell is producing electrical energy, electrons flow through a wire from one part of the cell, where zinc reacts, to another part where manganese(IV) oxide and an aqueous paste of ammonium chloride react. The products formed are zinc chloride, ammonia dissolved in the aqueous paste, manganese(III) oxide and water.

**D** *Rusting of a steel spade in the garden*

In the presence of water and oxygen from the air, iron will slowly form rust. Rust is hydrated iron(III) oxide, which is often represented by the formula Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O.

**E** *Using vinegar to clean a kettle*

With consistent use a build-up of calcium carbonate often occurs in kettles. If vinegar, an aqueous solution of acetic acid, is added to the kettle, it reacts with the calcium carbonate to form water, carbon dioxide, and a solution of calcium acetate.

**F** *Dissolving salt in swimming pool water*

Sodium chloride, which is added regularly to the swimming pool water, dissolves and acts as a source of chloride ions for the chlorination process described next.

**G** *Chlorinating a salt water swimming pool*

In a small electrolysis cell, the sodium and chloride ions in the pool water react with dissolved oxygen and water to form chlorine and a solution of sodium hydroxide. The chlorine then reacts further with water to form a dilute solution containing hypochlorous acid, HOCl, and hydrochloric acid. The hypochlorous acid acts as the principal disinfecting agent.

**H** *Burning a candle*

Candle wax is mainly a mixture of alkanes. For the purpose of this question, it will be assumed that candle wax is composed of only one alkane, C<sub>25</sub>H<sub>52</sub>. When candle wax reaches its ignition temperature, it undergoes an exothermic reaction with oxygen to form carbon dioxide and water.

For each of the changes A–H:

- a** identify it as a chemical or physical change; justify your choice
- b** write a balanced equation for each change, including the state symbols
- c** identify what type or types of bonds have been disrupted during each change.

# 10

# Energy changes in reactions

## BY THE END OF THIS CHAPTER YOU SHOULD BE ABLE TO:

- relate bond breaking and forming to the energy changes in chemical reactions
- apply the law of conservation of energy to chemical reactions
- define the enthalpy of a system
- explain temperature changes in exothermic and endothermic reactions
- draw energy (enthalpy) diagrams for exothermic and endothermic reactions
- identify the essential components of a thermochemical equation.

Society is mostly powered by energy produced from the combustion (burning) reactions of fossil fuels such as petrol, coal and natural gas. Energy from fossil fuels is used to heat homes, cook food, make a vehicle move or an aeroplane fly, and to generate electricity. Fossil fuels account for about 90% of the world's primary energy needs, with petroleum (40%), coal (24%) and natural gas (22%) being the leading players. In Western Australia, coal provides for almost 70% of the state's energy needs.

During the burning process, the fossil fuel reacts with oxygen from the air. In this reaction, some of the potential energy stored in the fossil fuel and the oxygen is converted to heat energy. This heat energy is released to the surroundings, causing an increase in temperature. Combustion is an exothermic process.

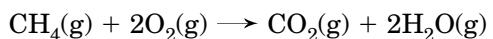
The exothermic nature of these combustion reactions can be illustrated by the following examples. When methane burns in a domestic oven or in a Bunsen burner, temperatures of approximately 300°C are obtained. Burning petrol in a car engine can result in an increase in temperature of up to about 500°C. In a fossil-fuel power station, temperatures of approximately 1500°C are reached during the burning of black coal.



**Figure 10.1** Firecrackers exploding. Another example of an exothermic reaction.

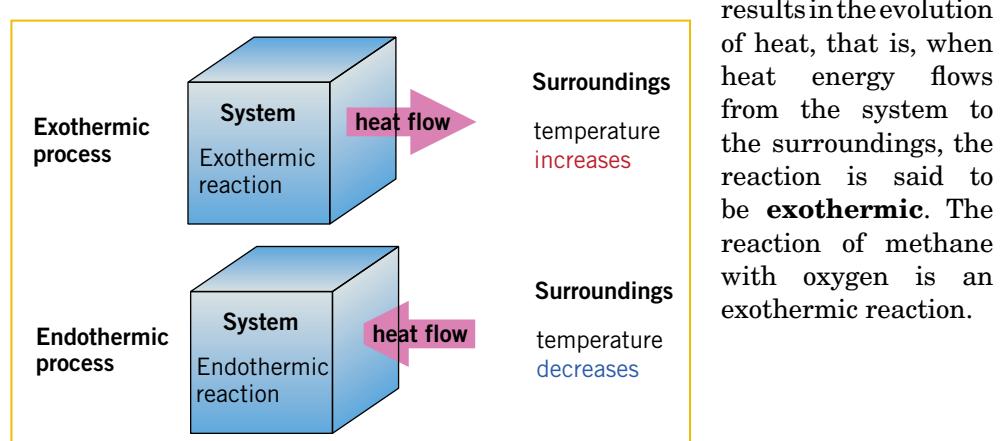
## 10.1 Exothermic and endothermic reactions

All chemical reactions involve energy changes, resulting in energy being gained or lost by the reactants. To keep track of these energy changes during a chemical reaction, it is convenient to distinguish between the system (the collection of atoms, molecules or ions involved in the reaction) and the surroundings (everything outside the system). For example, when a gas heater in the room is turned on, natural gas (methane) burns according to the following equation, with the production of heat energy.



The reactants, CH<sub>4</sub> and O<sub>2</sub>, and the products, CO<sub>2</sub> and H<sub>2</sub>O, of this reaction are referred to as the system. The air, furniture, people and other things in the room, are referred to as the surroundings.

The energy changes that occur during chemical reactions usually result in heat energy flowing to or from the chemical system. For example, as described in the combustion reaction in the previous paragraph, heat energy is produced when methane reacts with oxygen. This heat energy flows from the system to the surroundings and the temperature of the surroundings increases. When a reaction



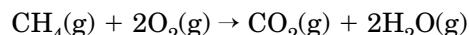
**Figure 10.2** Exothermic and endothermic reactions.

When ammonium nitrate dissolves in water, the temperature of the water decreases. In this example, heat energy flows from the surroundings (the water) to the system (the dissolving solid). This type of reaction results in a decrease in temperature of the surroundings and is called an **endothermic reaction**.

The **law of conservation of energy** states that energy cannot be created or destroyed but it can be converted from one form to another. So, for an exothermic reaction, where does the energy released as heat come from? The answer to this question is based on the understanding that all substances have stored chemical energy, or chemical potential energy, due to the attractive and repulsive forces between the particles (components) making up the substances. For example, there are attractive and repulsive forces between the electrons and nuclei of atoms and between the atoms, ions or molecules of the substances.

The particles of different substances are held together by bonds of varying strengths, hence every substance will probably possess a unique amount of potential energy. It therefore follows that in a chemical reaction, the products formed will most likely have different potential energies to the reactants.

The relative potential energies of the reactants and products involved in a reaction can be represented in an energy diagram. The combustion reaction of methane:



is represented by the energy diagram shown in Figure 10.3.

For this exothermic reaction, the diagram shows that the total potential energy of the products is less than the total potential energy of the reactants. Some of the chemical potential energy stored in the reactants is converted into heat energy during the exothermic reaction. This heat energy is released to the surroundings. As a result, the temperature of the surroundings will increase.

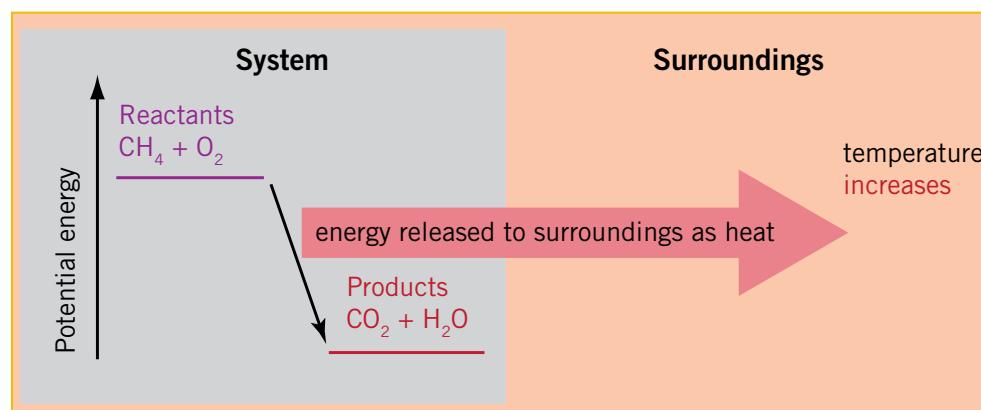


Figure 10.3 Relative energies of reactants and products in an exothermic reaction.

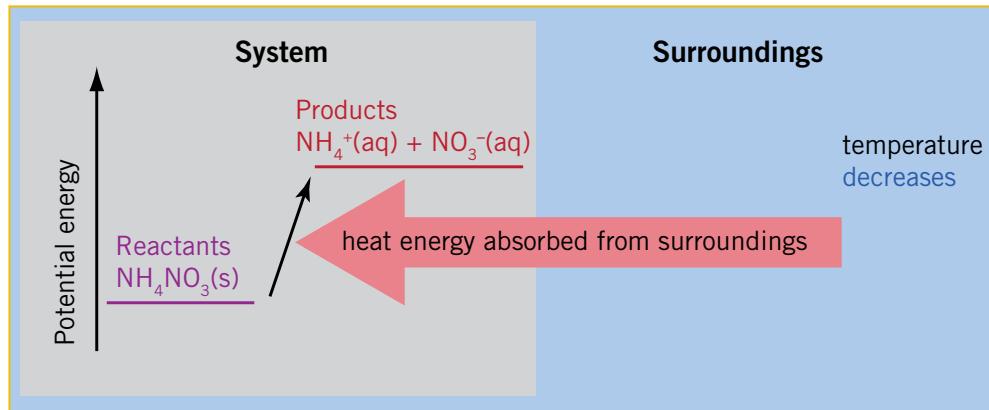
The dissolving of ammonium nitrate in water is an example of an endothermic process:



The potential energy of solid ammonium nitrate is less than the total potential energy of the dissolved ammonium and nitrate ions, as shown in Figure 10.4.

During endothermic reactions, heat energy absorbed from the surroundings is converted into potential energy stored in the products. The products therefore have more potential energy than the reactants. Also, because heat energy has been absorbed from the surroundings, the temperature of the surroundings decreases.



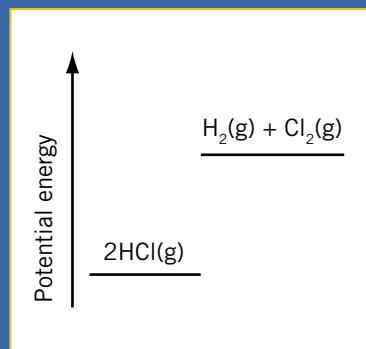


**Figure 10.4** Relative energies of reactants and products in an endothermic reaction.

### \* Review exercise 10.1

- The energy diagram shown on the right is for the decomposition of hydrogen chloride:  $2\text{HCl(g)} \rightarrow \text{H}_2\text{(g)} + \text{Cl}_2\text{(g)}$ .
  - Is this reaction exothermic or endothermic?
  - Is heat energy released to or absorbed from the surroundings during this reaction?
  - Sketch an energy diagram for the reverse process, that is:  $\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{HCl(g)}$
  - Is the reverse reaction exothermic or endothermic?
  - Will this reverse reaction cause an increase or decrease in the temperature of the surroundings?
- Complete the gaps in the two paragraphs, selecting from the words given below.

released	absorbed	increases	decreases
kinetic	potential	greater	less
produced			



For an **endothermic reaction**, the potential energy of the reactants is ..... than the potential energy of the products in the reacting system. Heat energy is ..... from the surroundings and changed to ..... energy by the system. The temperature of the surroundings therefore .....

For an **exothermic reaction**, the potential energy of the reactants is ..... than the potential energy of the products in the reacting system. Heat energy is ..... by the system, and ..... to the surroundings. The temperature of the surroundings therefore .....

- Sketch energy diagrams showing the relative potential energies of the 'reactants' and 'products' for the following two physical changes
  - When a few pellets of sodium hydroxide were dissolved in some water in a test tube, the temperature of the water changed from  $15^\circ\text{C}$  to  $30^\circ\text{C}$ .
  - The evaporation of water.

## 10.2 Heat of reaction and enthalpy

The amount of heat released or absorbed during a chemical reaction is often called the **heat of reaction**. For reactions undertaken at constant pressure, which is true for most reactions carried out in the laboratory, chemists also usually refer to the amount of heat released or absorbed during a reaction as the **enthalpy change** of the reaction. The enthalpy change of a reaction is given the symbol  $\Delta H$ , where ‘ $\Delta$ ’, delta, represents ‘change in’ and  $H$  is the symbol for enthalpy. It is beyond the scope of this course to give an explanation of what enthalpy actually is, but under conditions of constant pressure, enthalpy and the energy stored (potential energy) in a particular substance are very closely related.

It is not possible to determine the absolute enthalpy of a substance, but the change in enthalpy can be determined from the measurement of the temperature change that accompanies a chemical reaction (see question 13, page 246, for a simple example of this type of calculation). The relationship between the heat of reaction, or enthalpy change,  $\Delta H$ , and the enthalpies of the reactants and products is

$$\Delta H = \text{enthalpy of products} - \text{enthalpy of reactants}.$$

In an exothermic reaction the enthalpy of the reactants is larger than the enthalpy of the products. That is, there is a decrease in the enthalpy of the system during an exothermic reaction, and as a result a corresponding amount of heat energy is released to the surroundings. Consequently, the temperature of the surroundings will increase. Since the enthalpy change of a reaction is defined as the difference between the enthalpy of the products and the enthalpy of the reactants,  $\Delta H$  for exothermic reactions has a negative sign. This information is summarised in Figure 10.5.

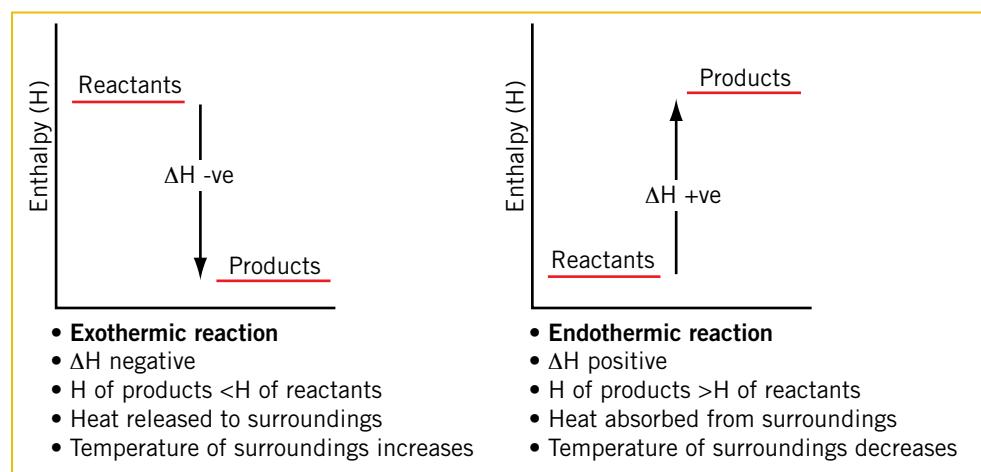


Figure 10.5 Summary of an exothermic reaction and an endothermic reaction.

The reactants have a smaller enthalpy than the products in an endothermic reaction. This enthalpy increase in the system is achieved through the loss of heat energy from the surroundings. As a result, the temperature of the surroundings decreases in an endothermic reaction. Because the products have a larger enthalpy than the reactants, the values of  $\Delta H$  for endothermic reactions are positive.

When a  $\Delta H$  value for a reaction is quoted, it is accompanied by an equation, indicating the amount, in mole, of reactants that need to react to evolve or absorb the quoted amount of heat. For example, the equation



shows that 184 kJ of heat energy are released to the surroundings when 1 mole of gaseous H<sub>2</sub> reacts with 1 mole of gaseous Cl<sub>2</sub> to form 2 mole of gaseous HCl. The value of ΔH is negative, which means the reaction is exothermic.

An example of an endothermic reaction is the decomposition of water:



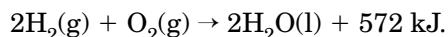
This equation shows that when 2 mole of liquid H<sub>2</sub>O is decomposed to form 2 mole of gaseous H<sub>2</sub> and 1 mole of gaseous O<sub>2</sub>, 572 kJ of heat energy is absorbed from the surroundings.

A balanced chemical equation that also includes the value and sign of ΔH is sometimes called a thermochemical equation. If a thermochemical equation is written in the reverse direction, then the ΔH value will have the opposite sign. For example, the combustion of hydrogen to form liquid water can be represented by the following thermochemical equation:



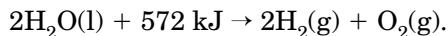
This reaction is shown as an exothermic reaction because it is the reverse of the decomposition of liquid water, which is an endothermic reaction.

In some situations it is convenient to think of the quantity of heat involved in a reaction as a reactant or a product and include it in the equation. For example, the equation given in the previous paragraph, which shows that when 2 mole of gaseous H<sub>2</sub> reacts with 1 mole of gaseous O<sub>2</sub> to form 2 mole of liquid H<sub>2</sub>O, 572 kJ of heat is also produced, could be written as



That is, the heat produced can be thought of as a product of this reaction.

For an endothermic reaction, the heat absorbed can be thought of as a reactant. For example, the equation for the endothermic decomposition of 2 mole of liquid H<sub>2</sub>O can be written as



Information contained in a thermochemical equation can be used to calculate the amount of heat released or absorbed in a chemical reaction, or it can be used to determine the amount of substance required to release or absorb a certain amount of heat.

### → Example 10.1

The thermochemical equation for respiration is



What mass of carbon dioxide is produced when  $1.50 \times 10^3$  kJ of heat energy is released to the surroundings during respiration?

### → Solution

**Step 1:** Find mol of CO<sub>2</sub> from amount of heat released

From the balanced equation:

2803 kJ of heat energy is released when 6 mol of CO<sub>2</sub> forms

1 kJ of heat energy is released when  $\frac{6}{2803}$  mol of CO<sub>2</sub> forms

so  $1.50 \times 10^3$  kJ of heat energy is released when

$$\frac{6}{2803} \times 1.50 \times 10^3 = 3.211 \text{ mol of CO}_2 \text{ forms}$$

*continued*



**Step 2: Find mass of CO<sub>2</sub>**

$$n(\text{CO}_2) = \frac{m(\text{CO}_2)}{M(\text{CO}_2)}$$

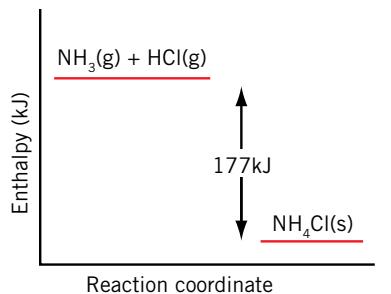
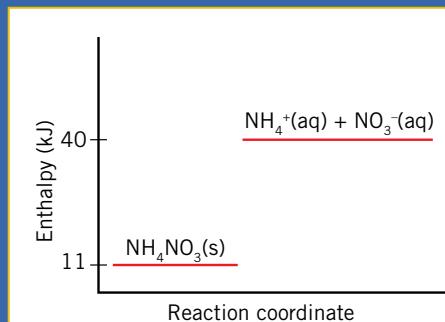
$$M(\text{CO}_2) = 12.01 + (2 \times 16.00) = 44.01 \text{ g mol}^{-1}$$

$$3.211 = \frac{m(\text{CO}_2)}{44.01}$$

$$m(\text{CO}_2) = 3.211 \times 44.01 = 141 \text{ g}$$

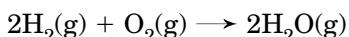
**\* Review exercise 10.2**

- 1 The enthalpy changes that occur during two reactions are shown in the diagrams. For each reaction:
- write the balanced chemical equation
  - determine the ΔH value
  - state whether the reaction is exothermic or endothermic
  - state whether the reaction will result in an increase or decrease in temperature of the surroundings.
- 2 Draw diagrams like those shown in question 1 to show the enthalpy changes that occur for the following reactions:
- the production of ammonia, which is used to manufacture fertilisers:  
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g}); \Delta H = -92 \text{ kJ}$
  - the formation of a solution of potassium nitrate:  
 $\text{KNO}_3(\text{s}) \rightarrow \text{K}^+(\text{aq}) + \text{NO}_3^-(\text{aq}); \Delta H = +37 \text{ kJ}$ .
- 3 The condensation of water vapour is represented by the following thermochemical equation:
- $$\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}); \Delta H = -44 \text{ kJ}$$
- Will the temperature of the surroundings increase or decrease during this phase change?
  - Which has the higher enthalpy, water vapour or liquid water?
  - What is the ΔH value, including the sign, for the phase change shown in the equation  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$ ?
  - i How much heat energy will be released to or absorbed from the surroundings when 10.0 g of water vapour condenses to form liquid water?  
ii Will this heat energy be released to or absorbed from the surroundings?
- 4 Methanol, CH<sub>3</sub>OH, is a possible fuel alternative to petrol. When methanol undergoes combustion, 1 mole of it produces 726 kJ of heat energy.
- Write a balanced thermochemical equation for the combustion reaction of methanol, assuming the products formed are carbon dioxide and liquid water.
  - Calculate the mass of methanol required to produce, on combustion, 535 kJ of heat energy.



## 10.3 Breaking and forming bonds during a reaction

The release or absorption of energy by a chemical reaction may also be rationalised in terms of the breaking and forming of bonds that occur during the reaction. In almost all reactions, bonds within or between the atoms, molecules or ions present in the reactants must be broken, and new bonds formed in the products. During the combustion reaction of hydrogen, to form water,



the covalent bonds between the hydrogen atoms in the  $\text{H}_2$  molecules and between the oxygen atoms in the  $\text{O}_2$  molecules must be broken, and new covalent bonds between hydrogen and oxygen atoms must be formed, to produce the  $\text{H}_2\text{O}$  molecules, as shown in Figure 10.6.

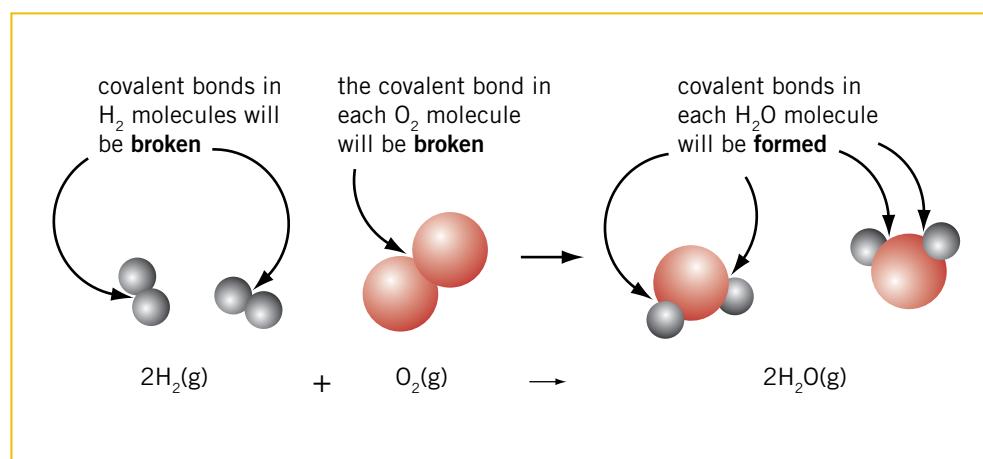
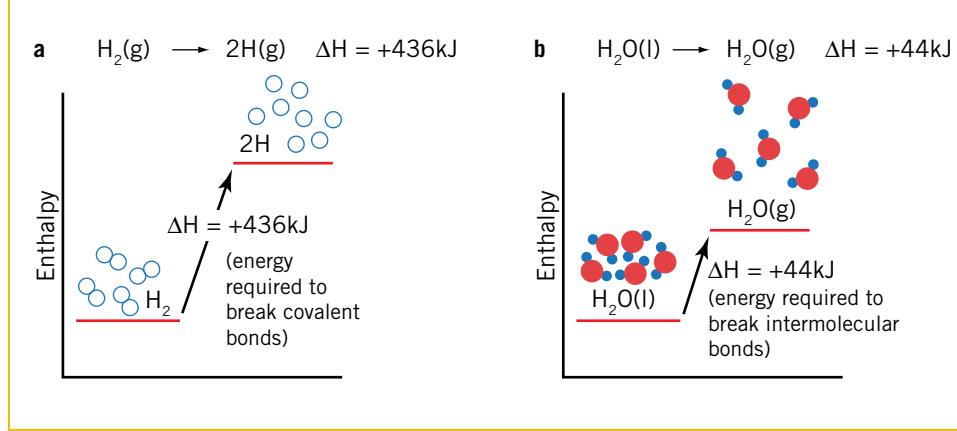


Figure 10.6 Hydrogen and oxygen molecules reacting to form water.

Bonds are attractive forces that hold atoms, ions and molecules together. The different types of bonds such as ionic bonds, covalent bonds, metallic bonds and intermolecular bonds were discussed in earlier chapters. Energy is required to break bonds of any kind, to enable the particles to overcome the attractive forces holding them together. The breaking of bonds is therefore an endothermic process, with the energy required to break the bonds between the particles being stored, as potential energy, in the separated particles. As a result, the separated particles have more potential energy than the bonded particles. For example, if hydrogen molecules are heated to a sufficiently high temperature, the covalent bond between the two atoms in each molecule can be broken to form the separated atoms:

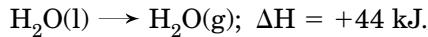


The equation shows that 436 kJ of energy is required to break the covalent bonds between the pairs of atoms in 1 mole of  $\text{H}_2$  molecules. The enthalpy diagram for this reaction is shown in Figure 10.7a.



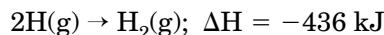
**Figure 10.7 Enthalpy diagrams for bond-breaking reactions. Bond breaking is an endothermic process.**

Another example of a bond-breaking process is the boiling of water:

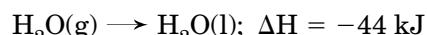


In this endothermic process, heat energy is absorbed from the surroundings, resulting in the weak intermolecular bonds between the liquid water molecules being broken. The molecules of gaseous water possess more potential energy than the molecules of water in the liquid state, as shown in Fig 10.7b. (This energy change was also discussed in Chapter 7).

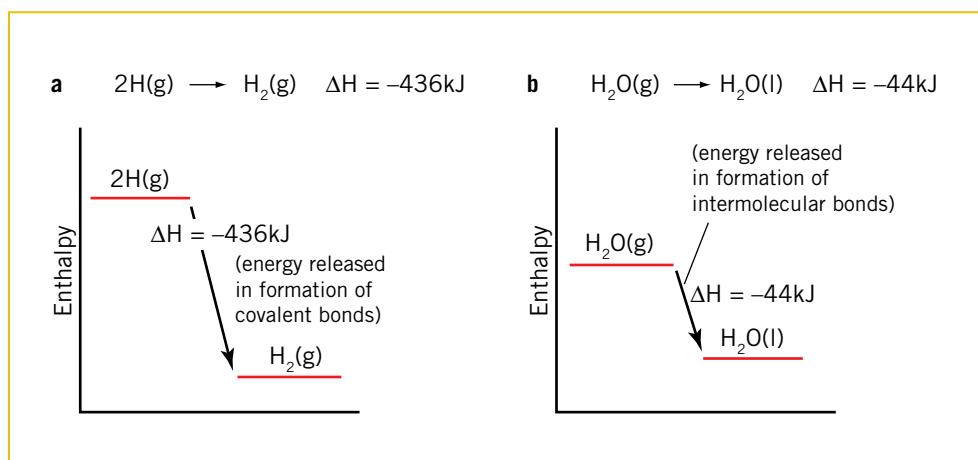
If the breaking of bonds requires energy, then the reverse process, the forming of bonds, must release energy. In other words, the forming of bonds is an exothermic process. For example, the formation of hydrogen molecules from hydrogen atoms, and the condensation of water vapour to form liquid water are both exothermic processes and result in potential energy being converted into heat energy:



and



The enthalpy diagrams for these reactions are given in Figure 10.8.

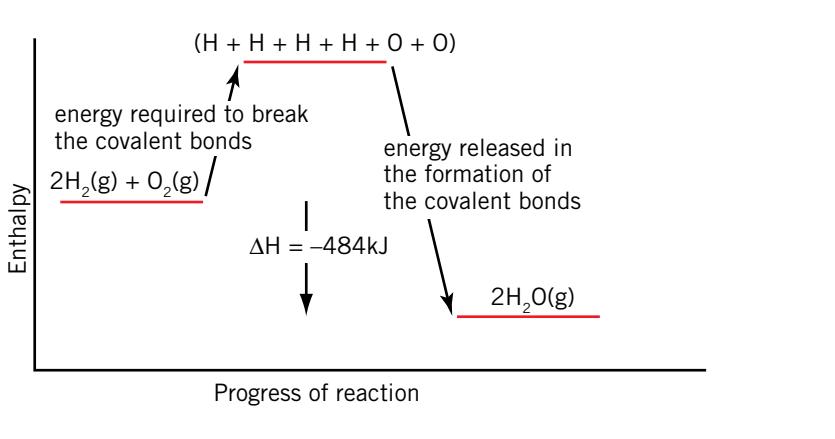


**Figure 10.8 Enthalpy diagrams for bond-forming reactions. Bond forming is an exothermic process.**

As mentioned previously, most reactions involve both bond breaking and bond forming. If the energy required to break the bonds is less than the energy released in the formation of the new bonds, then the overall reaction will be exothermic and energy will be released to the surroundings. As shown in Figure 10.9, for the exothermic reaction

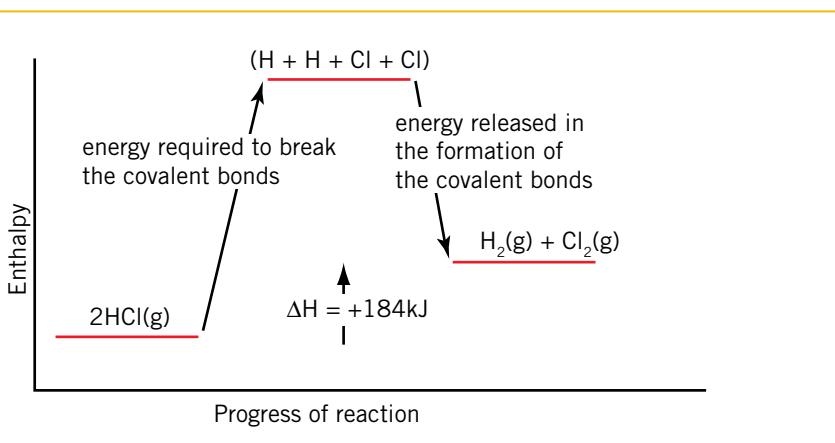
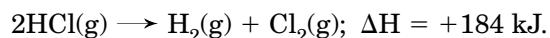


the energy required to break the covalent bonds in the hydrogen molecules and the oxygen molecules is less than the energy released when new covalent bonds form between the hydrogen and oxygen atoms to produce water:



**Figure 10.9** Enthalpy diagram for an exothermic reaction showing that less energy is required to break bonds, compared to the energy released in forming bonds.

For an endothermic reaction, the energy required to break the bonds of the reactants is greater than the energy released when the new bonds in the products are formed. These ideas are expressed in Figure 10.10 for the reaction

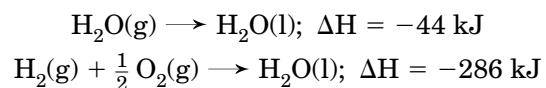


**Figure 10.10.** Enthalpy diagram for an endothermic reaction showing that more energy is required to break bonds, compared to the energy released in forming bonds.

Information concerning the relative strengths of the bonds in reactants and products can be inferred from the knowledge of whether or not a reaction is endothermic or exothermic. These inferences are based on the assumptions that the stronger the bond, the more energy it will take to break it, and the amount of energy required to break a bond is equivalent to the amount of energy released when the same bond is formed. For example, in the decomposition of HCl molecules represented in Figure 10.10, more energy was required to break the covalent bonds in the HCl molecules than was released when the new covalent bonds between the H atoms and between the Cl atoms formed. From this information, it can be inferred that the covalent bonds in HCl molecules are possibly stronger than the covalent bonds in H<sub>2</sub> and Cl<sub>2</sub> molecules.

### ΔH and physical and chemical changes

From experimental data, it is found that often the enthalpy changes associated with **physical changes**, such as changes in state and dissolving, are much smaller than those associated with **chemical changes**. For example, the enthalpy changes involved in the formation of liquid water from water vapour and from hydrogen and oxygen are given below:



The formation of liquid water from water vapour is a physical change (condensation). It releases much less energy than the chemical change process in which liquid water is formed in the chemical reaction of hydrogen with oxygen.

A possible reason why physical processes involve smaller enthalpy changes than chemical processes is that the bonds broken and formed in the physical processes are often weaker than the bonds broken and formed in the chemical processes. For example, the intermolecular bonds formed in the condensation of water vapour are much weaker than the covalent bonds broken and formed in the formation of water from hydrogen and oxygen.

### \* Review exercise 10.3

- 1 Compare the potential energies of:
  - a a chlorine molecule, Cl<sub>2</sub>, and two separate chlorine atoms
  - b 1 mole of solid sulfur and 1 mole of liquid sulfur.
- 2 When fluorine, F<sub>2</sub>, and hydrogen, H<sub>2</sub>, react to form hydrogen fluoride, HF, the energy required to break the bonds in the F<sub>2</sub> and H<sub>2</sub> molecules is less than the energy released in the formation of the bonds in the HF molecules.
  - a Draw an enthalpy diagram for the reaction (like that in Figure 10.10) showing the relative energies required for bond breaking and bond formation.
  - b Is this reaction exothermic or endothermic?
  - c Is heat energy absorbed from or released to the surroundings during this reaction?
  - d Which would you predict to have the stronger covalent bonds, HF molecules or H<sub>2</sub> together with F<sub>2</sub> molecules?

## 10.4 Examples of enthalpy changes

### Examples of exothermic and endothermic processes

It is usually not possible to decide just by inspecting a chemical equation whether or not it is an exothermic or endothermic reaction. However, some general statements concerning the identification of some reactions as exothermic or endothermic can be made, as given in Table 10.1.

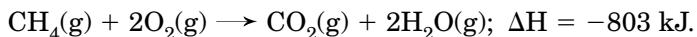
**TABLE 10.1 SOME EXAMPLES OF EXOTHERMIC AND ENDOTHERMIC REACTIONS**

Exothermic reactions/ processes	<ul style="list-style-type: none"><li>• combustion (burning) reactions such as the burning of carbon or hydrocarbons e.g. <math>\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})</math></li><li>• reactions in which single atoms bond together e.g. <math>2\text{Cl}(\text{g}) \rightarrow \text{Cl}_2(\text{g})</math></li><li>• reactions in which an electron is gained by a positive ion e.g. <math>\text{Na}^+(\text{g}) + \text{e}^- \rightarrow \text{Na}(\text{g})</math></li><li>• the changes in state from gas to liquid (condensation) and liquid to solid (solidification)</li><li>• respiration i.e. <math>\text{C}_6\text{H}_{12}\text{O}_6(\text{aq}) + 6\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})</math></li></ul>
Endothermic reactions/ processes	<ul style="list-style-type: none"><li>• reactions in which a molecule is ‘broken up’ to form single atoms e.g. <math>\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g})</math></li><li>• reactions in which an atom or ion loses an electron e.g. <math>\text{Na}(\text{g}) \rightarrow \text{Na}^+(\text{g}) + \text{e}^-</math></li><li>• the changes in state from solid to liquid (melting), liquid to gas (vaporisation) and solid to gas (sublimation)</li><li>• photosynthesis i.e. <math>6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{aq}) + 6\text{O}_2(\text{g})</math></li></ul>

### Important types of enthalpy changes

Three enthalpy changes that are frequently referred to and have special names and definitions are:

**Heat of combustion:** the enthalpy change obtained when a fixed amount of a substance reacts with oxygen in a combustion reaction. For example, the heat of combustion of methane is  $-803 \text{ kJ}$  per mole of methane, as shown in the equation:



**Heat of fusion:** the enthalpy change that occurs during the melting of 1 mole of a solid at its melting point. For example, the heat of fusion of sodium chloride is  $28 \text{ kJ}$ , that is



The melting (or fusion) of a solid is an endothermic process. As explained in Chapter 7, when a solid is melting, heat energy is absorbed from the surroundings. This energy is ‘used’ in disrupting the attractive forces between the solid’s particles, resulting in these particles moving further apart to form the liquid. As a consequence, during the melting process the potential energy of the particles, or the system, increases.

**Heat of vaporisation:** the enthalpy change that occurs during the vaporisation of 1 mole of a liquid at its boiling point. For example, the heat of vaporisation of ethanol is  $43.3 \text{ kJ}$ , that is



As with melting, vaporisation is an endothermic process. The flow of heat energy from the surroundings results in the breaking of bonds between the liquid's particles as the liquid vaporises. The vapour, or gas, therefore has more potential energy than the liquid, with the particles in the gaseous state being further apart than in the liquid state. When a gas condenses to form a liquid, the potential energy 'stored' in the gas is converted into heat energy which is released to the surroundings. That is, the condensation process is exothermic.

### \* Review exercise 10.4

- 1 For each of the following processes:
  - i State whether the process is exothermic or endothermic.
  - ii Identify whether the reactants or products have the higher enthalpy.
  - iii Indicate whether heat energy would be absorbed from or released to the surroundings.
    - a melting wax
    - b condensation of steam
    - c combustion of petrol
    - d  $\text{S(s)} + \text{O}_2\text{(g)} \rightarrow \text{SO}_2\text{(g)}$
    - e  $2\text{NO}_2\text{(g)} \rightarrow 2\text{NO(g)} + \text{O}_2\text{(g)}$
    - f  $\text{I}_2\text{(s)} \rightarrow \text{I}_2\text{(g)}$
    - g  $6\text{CO}_2\text{(g)} + 6\text{H}_2\text{O(l)} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6\text{(aq)} + 6\text{O}_2\text{(g)}$
    - h  $\text{Ca(g)} \rightarrow \text{Ca}^{2+}\text{(g)} + 2\text{e}^-$
    - i  $2\text{N(g)} \rightarrow \text{N}_2\text{(g)}$
- 2 a If the heat of combustion of ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ , is  $-1367 \text{ kJ}$  per mole of ethanol, how much heat energy is produced when  $125 \text{ g}$  of ethanol undergoes combustion?  
 b If the heat of vaporisation of ethanol is  $43 \text{ kJ mol}^{-1}$ , how much heat energy is released when  $20.0 \text{ g}$  of ethanol vapour condenses?
- 3 The heats of fusion and vaporisation of substances are related to the strengths of the forces between their particles. Table 10.2 contains the heats of fusion and vaporisation of some familiar substances.

**TABLE 10.2 HEATS OF FUSION AND VAPORISATION OF SOME COMMON SUBSTANCES**

Substance	Heat of fusion ( $\text{kJ mol}^{-1}$ )	Heat of vaporisation ( $\text{kJ mol}^{-1}$ )
Methane, $\text{CH}_4$	1	8
Water	6	44
Sodium chloride	28	207
Carbon (graphite)	105	611

- a Explain the differences in the heat of vaporisation data for methane, sodium chloride and graphite in terms of the bonding between the particles in the three substances.
- b After considering the data shown in Table 10.2, would you expect the boiling point of methane to be higher or lower than the boiling point of water? Explain your reasoning.

- c Give the  $\Delta H$  values, including the sign, for the following processes:
- $\text{Na}^+(\text{l}) + \text{Cl}^-(\text{l}) \rightarrow \text{NaCl}(\text{s})$
  - $\text{CH}_4(\text{g}) \rightarrow \text{CH}_4(\text{l})$
  - $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{g})$ , (the sublimation of graphite).
- d Propose an explanation for why the heat of vaporisation is larger than the heat of fusion for each substance.

## 10.5 Energy in society

As explained at the beginning of this chapter, modern society is dependent on the energy produced by the exothermic combustion reactions of fossil fuels. Be it coal, petrol, natural gas or diesel oil, their use in keeping vehicles running, generating electricity, heating homes, cooking foods, or acting as heat sources for industry is vital to everyday life. However, with the ready availability of fossil fuels rapidly diminishing together with the pollution these fuels create, there is a continual search for new renewable and cleaner fuels.

A fuel can be broadly defined as a substance that releases energy when it reacts, usually with oxygen. Obviously the more heat generated per gram or mole of fuel, the more desirable the fuel. Fuels are compared by their fuel value which is a measure of the amount of energy produced when 1 g of the fuel undergoes combustion. Table 10.3 shows the fuel values of some common fuels.

TABLE 10.3 FUEL VALUES OF THE COMMON FUELS

Fuel	Natural gas	Petrol	Coal	Wood (pine)	Hydrogen
Fuel value, $\text{kJ g}^{-1}$	49	48	32	18	142

The fuel values are expressed as  $\text{kJ g}^{-1}$  rather than  $\text{kJ mol}^{-1}$  because most of the fuels are mixtures and not pure substances.

Apart from combustion reactions, there are also other useful exothermic reactions, for example, doctors sometimes recommend the use of heat packs to increase blood flow to muscle injuries. Two forms of heat pack exist, one of which is reversible and the other a single use product.

The reversible heat pack makes use of the fact that sodium acetate readily forms a supersaturated solution on heating. This solution is stable so long as there is no suitable surface on which the crystals of sodium acetate can form. The plastic container of the heat pack does not provide such a surface. However, inside the container are several discs that, when flexed or bent, provide a surface for the crystallisation. Once one crystal has formed, the bulk of the sodium acetate starts to crystallise in an exothermic reaction.



Carefully warming the pack after the sodium acetate has crystallised (for example, in a microwave oven) will cause the crystals to once again dissolve to form a supersaturated solution.

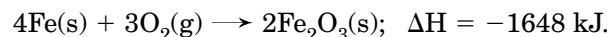


**Figure 10.11** A disposable instant cold compress pack.



**Figure 10.12** The energy content label on a breakfast cereal packet.

The non-reversible heat pack uses the fact that the rusting of iron is exothermic. The heat pack consists of an outer wrapper covering a cloth or paper bag with many small holes in it. This inner bag contains a mixture of iron powder, salt, charcoal and sawdust all dampened with water. Removing the outer bag and shaking the inner one exposes the iron to oxygen in the air, promoting the exothermic reaction to produce iron oxide:



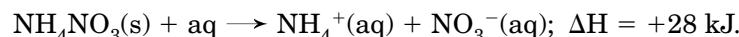
This is a highly exothermic reaction, but the rate is low and so the heat energy is given off over several hours.

Endothermic reactions also have their uses. Evaporative coolers make use of the endothermic vaporisation of liquid water:

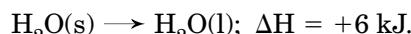


During evaporation, as the higher-energy molecules escape from the surface of the liquid the temperature of the remaining water drops. In an evaporative cooler, water is allowed to trickle across a large surface area of material. A fan then blows air across this material, removing the water vapour which results in cooling the liquid even more. The colder water absorbs energy from the air that is blowing across it, producing a flow of cooler air from the front of the cooler.

Cold packs may be recommended for pain or injury—to reduce swelling and the leaking of fluid into the area of the injury or to numb the pain. In the past, ice packs have contained a solid such as ammonium nitrate in a bag, surrounded by water. When the bag is broken, the ammonium nitrate dissolves in an endothermic reaction

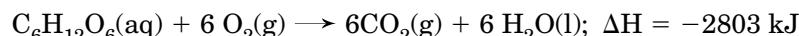


As ammonium nitrate is also a powerful explosive, it is less likely to be found in cold packs today. The simplest cold pack is ice placed inside a plastic bag. The melting of ice is also an endothermic reaction:



## Energy and life

The respiration process, involving the reaction between glucose and oxygen, is an example of an exothermic process. The complex set of biochemical reactions necessary to keep cells alive is driven by the energy produced by the oxidation of glucose to carbon dioxide and water.



Photosynthesis involves the reverse of this reaction and takes place in the chloroplasts, found in the cells of green plants. This is a complex set of reactions that combines carbon dioxide and water to ultimately produce glucose and oxygen. This endothermic process is driven by the energy of sunlight.

## Energy and food

Food is a source of the nutrients necessary for the synthesis of a variety of molecules that are essential for life. In addition, foods provide the molecules that produce the energy for warmth and that drive the complex chemistry of life.

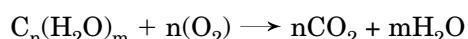
A certain amount of energy is needed simply to ‘stay alive’. While this varies, depending on factors such as stress and age, the value is around 90 kJ per kg of body mass per day for a person at rest and who has not eaten in the last 12 hours. With greater activity the rate at which energy is used increases. For example, reading this text requires about 7 kJ of energy per minute (learning it might take a little more energy!).

The major sources of energy in food come from fats, carbohydrates and proteins. Fats provide around  $38 \text{ kJ g}^{-1}$  while carbohydrate and protein each supply around  $17 \text{ kJ g}^{-1}$ . The breakfast cereal shown in Figure 10.12 quotes the protein, fat and carbohydrate figures for one serve (30 g) as

protein	2.3 g
total fat	<0.1 g
total carbohydrate	25.1 g

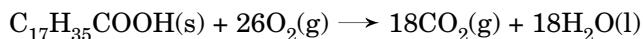
Using the energy values above, this corresponds to a total energy per serve of  $((2.3 \times 17) + (25.1 \times 17)) = 466 \text{ kJ}$ , which is very close to the value of 475 kJ per serve given on the label. These energy values per gram or per serve are usually calculated from reactions that involve the complete combustion of the food in excess oxygen (see question 3 in Review exercise 10.5).

Carbohydrates are generally derived from simple sugars such as glucose, so the energy produced in combustion or in respiration comes from reactions with equations that can be represented as



In this equation,  $\text{C}_n(\text{H}_2\text{O})_m$  is a general formula for a carbohydrate. For example, glucose with the formula  $\text{C}_6\text{H}_{12}\text{O}_6$  or  $\text{C}_6(\text{H}_2\text{O})_6$  is a simple carbohydrate.

Fats are more like hydrocarbons (compounds that contain only carbon and hydrogen) in their structure and do not have as much combined oxygen in the molecule. As a result, more oxygen is required for the combustion reaction, and more energy is given out as both the carbon and the hydrogen atoms in the fat molecules have to be oxidised. For example, stearic acid,  $\text{C}_{17}\text{H}_{35}\text{COOH}$ , is one of the molecules that might be formed from a sample of fat. The combustion reaction for stearic acid is



## \* Review exercise 10.5

- 1 A particular batch of grapes contains 3.9% glucose by mass. What mass of grapes would you need to consume to provide 110 kJ of energy? (Assume that all of the glucose in the grapes is converted immediately to energy).
- 2
  - a Compare the amounts of heat released in the combustion reactions of 1 mole of hydrogen, 1 mole of natural gas (methane) and 1 mole of petrol (assume petrol is composed of octane,  $C_8H_{18}$ ).
  - b Comment on and compare the advantages and disadvantages of using hydrogen, natural gas and petrol as fuels.
- 3 A food chemist is asked to determine the energy content of a particular brand of biscuit. Several biscuits are dried in an oven for several hours. A 2.45 g sample of the dried biscuits is placed in an instrument called a bomb calorimeter, filled with excess oxygen and placed in a water bath. The temperature of the bath is recorded as a steady  $22.58^\circ\text{C}$ .  
The biscuit and oxygen mixture in the calorimeter is ignited and the temperature of the water bath observed to rise from  $22.58^\circ\text{C}$  to  $23.35^\circ\text{C}$ .  
It is found that it takes 4055 kJ of energy to change the temperature of the bomb calorimeter and its water bath by  $1^\circ\text{C}$ .
  - a What is the energy content of the biscuits in  $\text{kJ g}^{-1}$ ?
  - b Biscuits such as these may not release this amount of energy when consumed by a human. Explain why this might be the case.



## MAJOR IDEAS

- All chemical reactions involve an energy change although overall energy is conserved.
- The change in enthalpy is a measure of the change in the chemical potential energy during a reaction.
- Exothermic reactions involve a flow of heat energy to the surroundings, which get hotter.
- Endothermic reactions involve a flow of heat energy from the surroundings, which get colder.
- Energy (enthalpy) diagrams can be used to depict exothermic and endothermic reactions.
- The heat of reaction,  $\Delta H$ , is a measure of the energy change for a reaction and has both a magnitude and a sign.
- $\Delta H$  is defined as  $H_{\text{products}} - H_{\text{reactants}}$ .
- A thermochemical equation includes the balanced equation, the states of all the reactants and products, and the heat of reaction.
- Any change to the coefficients in the equation or to the states of the chemicals involved will be reflected in changes to the magnitude and/or sign of  $\Delta H$ .
- Chemical reactions involve the breaking and forming of bonds.
- Bond breaking requires energy and bond forming releases energy.
- The difference in the energies of the bond-breaking and bond-formation processes of a reaction determines whether a reaction is exothermic or endothermic.
- The heat produced or absorbed in the reaction of a particular amount of reactant (or product) can be determined from the thermochemical equation of the reaction.

## QUESTIONS

- 1 Account for the fact that all chemical reactions involve an energy change.
- 2 Outline the differences between an exothermic and endothermic reaction in terms of energy flow, systems and surroundings.
- 3 For each of the following, state whether the process is endothermic or exothermic, indicate which has the higher enthalpy, the reactants or the products, and state whether heat energy flows to or from the surroundings.
  - a burning diesel fuel in a car

b turning water into steam to run a power station

c eating sherbet lollies (citric acid and sodium hydrogencarbonate), which produces a cool fizzing sensation in the mouth

d water vapour condensing from the atmosphere to form clouds.

- 4 Draw and label an enthalpy diagram, showing the relative enthalpies of the reactants and products for the following reactions:



- 5 Both hydrogen and methane are used as gaseous fuels. Their combustion reactions are given below:



Which of these two fuels would produce the larger amount of heat per gram of fuel?

- 6 When methane,  $\text{CH}_4$ , burns in the presence of oxygen, carbon dioxide and water are produced.

a Identify the bonds that break and form in this reaction.

b Compare the amount of energy required to break the bonds in the reactants with the amount of energy released during the formation of the bonds in the products.

- 7 Account for the data in the following table in terms of the nature of the bonds present in the solids.

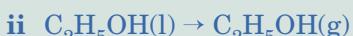
Substance	Molar heat of fusion ( $\text{kJ mol}^{-1}$ )
$\text{H}_2\text{O}$	6
Al	11
NaF	33
Si	50

- 8 When bonds are being broken and formed in a chemical reaction, is this change taking place in the system or the surroundings? Explain your answer.

9 Yeasts gain their energy by converting glucose into alcohol according to the following equation:



Brewers then distill the alcohol from the mixture as represented by the following equation:



a Are reactions i and ii exothermic or endothermic?

b Which of these reactions is likely to involve the larger energy change? Why?

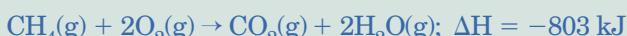
10 For each of the following reactions, choose its relevant characteristics from those given in the box below:

- A results in an increase in temperature of the surroundings
- B results in a decrease in temperature of the surroundings
- C is an exothermic reaction
- D is an endothermic reaction
- E energy is absorbed by the system
- F energy is released by the system
- G heat energy is released to the surroundings
- H heat energy is absorbed from the surroundings
- I  $\Delta H$  has a positive value
- J  $\Delta H$  has a negative value
- K enthalpy of reactants > enthalpy of products
- L enthalpy of products > enthalpy of reactants



- a burning coal (C) to form carbon dioxide
- b sublimation of diamond (C)
- c  $3\text{C}(\text{s}) + 4\text{H}_2(\text{g}) \rightarrow \text{C}_3\text{H}_8(\text{g}) + 104 \text{ kJ}$
- d  $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g}); \Delta H = +131 \text{ kJ}$

11 The thermochemical equation for the combustion of natural gas is



- a How much energy is released during the complete combustion of 56.0 g of methane?

b What mass of oxygen would be taken from the atmosphere during the release of 2250 kJ of energy?

12 The fuel often used for barbecues is LPG (liquefied petroleum gas), which is a mixture of 95% (by mass) propane,  $\text{C}_3\text{H}_8$ , and 5% butane,  $\text{C}_4\text{H}_{10}$ . LPG is also the autogas that can be used in cars that have been converted to run on gas. The heat of combustion for propane is  $-2219 \text{ kJ}$  per mole propane and for butane  $-2877 \text{ kJ}$  per mole butane. If a portable gas cylinder used for a barbecue contains 88 g of LPG, how much heat will be produced in the combustion of this gas?

13 A calorimeter is a device used to measure the heat released during a reaction. A simple calorimeter is shown in Figure 10.13.

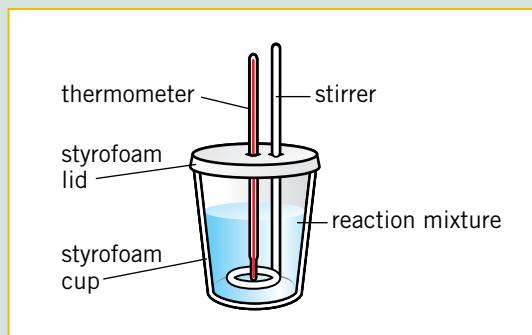


Figure 10.13 A simple calorimeter.

To determine the enthalpy change for the reaction  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$ , 50.0 mL of 1.0 mol  $\text{L}^{-1}$  HCl at 20°C and 50.0 mL of 1.0 mol  $\text{L}^{-1}$  NaOH at 20°C were mixed in the calorimeter. The temperature was found to increase to 26.8°C. Calculate the  $\Delta H$  value for the reaction given above by answering the following questions:

- a What was the temperature change due to the reaction?
- b The specific heat capacity of water is  $4.18 \text{ J } ^\circ\text{C}^{-1}\text{g}^{-1}$ . This means that 4.18 J of energy is required to raise the temperature of 1 g of water by 1°C. Assuming there is 100 g of water in the calorimeter, how much heat energy was released during the reaction?
- c How many mole of HCl, and hence  $\text{H}^+$ , participated in the reaction?
- d Using your answers to parts b and c, how much heat energy was released when 1 mol of  $\text{H}^+$  reacted with  $\text{OH}^-$ ?

- e Write the thermochemical equation for the reaction of  $\text{H}^+$  with  $\text{OH}^-$  ions in aqueous solution.
- f Explain why the cup and lid of the calorimeter are made of styrofoam rather than another material.
- 14 For the chemical reaction
- $$\text{NH}_3(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}); \Delta H = -53 \text{ kJ}$$
- a What amount of heat is evolved when 100 mL of 0.10 mol L<sup>-1</sup> ammonia solution is added to 100 mL of 0.10 mol L<sup>-1</sup> hydrochloric acid in a beaker?
- b If it takes 4.18 J to change the temperature of 1.00 g of this solution by 1.00°C, determine the temperature change that would accompany this reaction. Assume 1 mL of the solution has a mass of 1 g.
- c Why would this temperature change not be observed in this experiment?
- 15 The energy content of various foods is usually expressed in kJ per gram, kJ per 100 g or kJ per serve (with the amount in a serve specified).
- A student investigating the energy content of a brazil nut cleans the surface of the nut and cuts the end to make it look like the wick on a candle. The mass of the nut is determined as 4.15 g. She then places the nut under a metal can containing 300 g of water that is initially at a temperature of 20.23°C. The nut is ignited with a match and allowed to burn just below the base of the metal can.
- The water in the can is stirred continuously and after about five minutes the burning nut is extinguished. The water in the can is kept stirred and the highest temperature reached is recorded. The student obtains the following data.
- |                                      |         |
|--------------------------------------|---------|
| Final mass of brazil nut             | 3.97 g  |
| Highest temperature reached by water | 23.13°C |
- a Assuming that it takes 4.18 J to change the temperature of 1.00 g of water by 1.00°C, calculate the energy content of a brazil nut in kJ per g from this data.
- b Why is the energy content of foodstuffs not expressed in  $\text{kJ mol}^{-1}$ ?
- c The actual value of the energy content of a brazil nut is 30.1 kJ per g. What aspects of the experimental design need to be modified in order to achieve a value closer to the actual value?
- d **RESEARCH** The determination of the energy content of foodstuffs is often carried out using a bomb calorimeter. How does a bomb calorimeter work and how does it address the limitations that you hinted at in your answer to part c?
- e While you are reading this question your body is using about 7 kJ of energy per minute. Using the actual value for the energy content of a brazil nut, how many minutes of reading will a serving of 10 g of brazil nuts support?
- f The time you have determined in part e is only an approximation. Is the value of this time too high, or too low? Explain your answer.
- 16 Biologists sometimes refer to adenosine triphosphate, ATP, as a molecule with a 'high energy bond', justifying their statement with the fact that the hydrolysis (reaction with water) of ATP to give adenosine diphosphate (ADP) and a phosphate group is exothermic. Some biologists may go on to state, 'energy is released when the high energy bond in ATP breaks'. Explain the error in this statement.
- 17 A particular chemical reaction is represented by the equation
- $$\text{B} + \text{D} \rightarrow \text{E}; \Delta H \text{ negative}$$
- The reaction actually involves two steps that can be represented as
- $$\text{B} + \text{D} \rightarrow \text{Q}; \Delta H \text{ positive}$$
- followed by  $\text{Q} \rightarrow \text{E}; \Delta H \text{ negative}$
- What would the energy profile diagram for this reaction look like?



# 11 Reaction rates

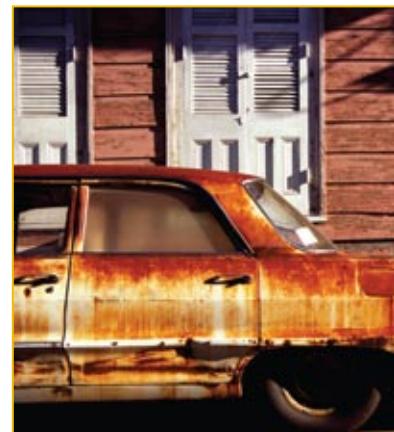
**BY THE END OF THIS CHAPTER YOU SHOULD BE ABLE TO:**

- draw energy profile diagrams that include activation energy barriers and label the activated complex
- define rate of reaction
- explain the factors influencing reaction rates in terms of the collision theory
- explain the effect of catalysts on the reaction rate.

If you place a burning match on a sample of wheat, the grain may splutter and burn, but there is no evidence of a particularly fast reaction. If the same sample of wheat is ground into fine flour and blown into a flame, the mixture ignites with explosive violence. Indeed, there are recorded instances of such explosions in wheat silos in Australia when a stray spark has ignited the dust as wheat was poured into the silo. A mixture of natural gas and air will do nothing until a match is applied, at which time a rapid exothermic reaction takes place. Glucose and oxygen will not react in a beaker, even when the glucose is warmed to 40°C. However, in every living cell of our body glucose combines rapidly with oxygen to provide the energy for cell function.

Each of the examples in the previous paragraph is associated with the question 'How fast is a chemical reaction?' This is a particularly important question both commercially and biologically. It is also an important question to be asked, and resolved, when dealing with everyday chemistry in the home. How can the rate at which food 'goes off' in the kitchen be slowed down? How long will it take for a fibreglass patch placed on a surfboard to set? When can a person get back into the swimming pool after treating it with 'chlorine'? How long does a builder have to wait for the concrete footings to set before building a brick wall on it?

To answer questions such as these, an understanding is needed of the requirements for a chemical reaction to occur, and the factors that affect the rates of these reactions.



**Figure 11.1** The rusting of iron is an example of a relatively slow reaction.



**Figure 11.2** Petrol exploding after a car accident. The reaction of petrol with oxygen occurs at a fast reaction rate at a high temperature.

## 11.1 Measuring reaction rates

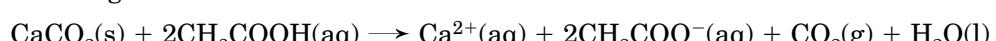
When a burning match is put near some petrol, an almost instantaneous reaction occurs to produce an often dangerous fire. However, if a piece of iron is left exposed to the atmosphere it may take months or years to be completely converted to rust. These two reactions are said to have different reaction rates, with the combustion of petrol occurring at a much faster rate than the rusting of iron.

In general, the rate at which a reaction occurs can be quantitatively determined in one of the following ways:

- measuring the rate at which a reactant disappears. For example, determining how rapidly a piece of magnesium disappears when placed in an acid solution
- measuring the rate at which a product is formed. For example, determining how rapidly hydrogen gas is formed in the reaction of an acid with magnesium.

That is, the rate of a reaction can be quantitatively expressed by measuring the change in the amount of a reactant or product over a period of time.

If marble chips (calcium carbonate), are added to vinegar (acetic acid), the following reaction occurs:



Some changes which take place during this reaction are:

- the mass of  $\text{CaCO}_3(\text{s})$  decreases
- the concentration of  $\text{CH}_3\text{COOH}(\text{aq})$  decreases
- the amount of  $\text{Ca}(\text{CH}_3\text{COO})_2(\text{aq})$  increases
- the volume or mass of  $\text{CO}_2(\text{g})$  produced increases.



**Figure 11.3** Reaction of a marble chip with vinegar.



**Figure 11.4** The equipment set up that could be used to study the rate of a reaction. The flask contains calcium carbonate and an acid.

The rate of this reaction can be determined by measuring any of these changes over known time intervals. For example, if a flask containing a known mass of calcium carbonate and vinegar was placed on a balance, as shown in Figure 11.4, and its mass measured over a series of time intervals, the average rate of reaction during various time intervals could be determined using the expression

$$\text{average reaction rate during the time interval} = \frac{\text{mass of CO}_2 \text{ produced in time interval}}{\text{time interval}}$$

Alternatively, if the mass of calcium carbonate consumed had been measured during the reaction, the following expression could be used as a measure of the average reaction rate over a specific time interval:

$$\text{average reaction rate during the time interval} = \frac{\text{mass of CaCO}_3 \text{ consumed in time interval}}{\text{time interval}}$$

#### → Example 11.1

An experiment studying the rate of the reaction between calcium carbonate and vinegar was carried out using the equipment set-up shown in Figure 11.4. The following results were obtained:

Time (s)	0	30	60	90	120
Mass of CO <sub>2</sub> formed (g)	0	0.99	1.29	1.52	1.65

Calculate the average rate of the reaction:

- a during the first 30 seconds
- b in the 90 to 120-second time interval

#### → Solution

- a During the first 30 seconds, 0.99 g of CO<sub>2</sub> formed, so

$$\text{average reaction rate during first 30 seconds} = \frac{0.99}{30} = \mathbf{0.033 \text{ g of CO}_2 \text{ s}^{-1}}$$

- b During the 90 to 120-second time interval:

$$\begin{aligned} \text{mass of CO}_2 \text{ formed} &= 1.65 - 1.52 = 0.13 \text{ g} \\ \text{time interval} &= 120 - 90 = 30 \text{ seconds} \end{aligned}$$

average reaction rate during 90 to 120 s time interval

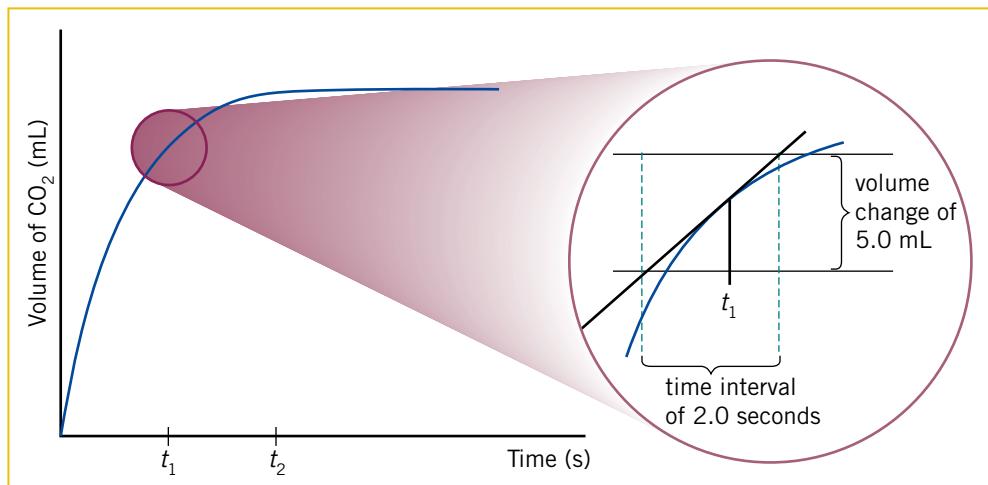
$$= \frac{0.13}{30} = \mathbf{0.0043 \text{ g of CO}_2 \text{ s}^{-1}}$$

A graph can also be drawn to represent the change in the rate of a reaction as the reaction proceeds. If this graph shows the amount of reactant or product on the vertical axis and the time on the horizontal axis, then the slope (gradient) of the graph at a particular time is a measure of the reaction rate at that time. The steeper the slope of the graph, the faster the reaction rate.

For the reaction of vinegar with calcium carbonate, if the volume of carbon dioxide formed at various times during the reaction is measured, a typical graph would be like that shown in Figure 11.5.

The rate of this reaction is quickest at the beginning of the reaction, as shown by the steepness of the slope of the graph. However, as the reaction proceeds, the rate decreases, until at time  $t_2$ , it is complete. At this point, one of the reactants will have been consumed completely.

A graph like the one given in Figure 11.5 can also be used to calculate the rate at any given instant during the reaction, that is, the instantaneous rate. This is done by determining the slope of the tangent to the curve at the particular time.



**Figure 11.5** Graph showing the volume of carbon dioxide formed versus time during a reaction of vinegar and calcium carbonate.

A section of the graph has been expanded to show how the instantaneous rate at time  $t_1$  might possibly be calculated. The tangent to the curve at time  $t_1$  has been drawn and then its gradient ( $\frac{\text{rise}}{\text{run}}$ ) determined. In this example the instantaneous rate of reaction at time  $t_1$  is  $\frac{5.0}{2.0} = 2.5 \text{ mL s}^{-1}$ .

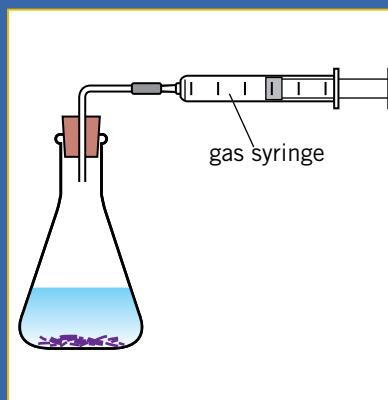
### \* Review exercise 11.1

- 1 When hydrochloric acid is added to magnesium, the following reaction occurs:

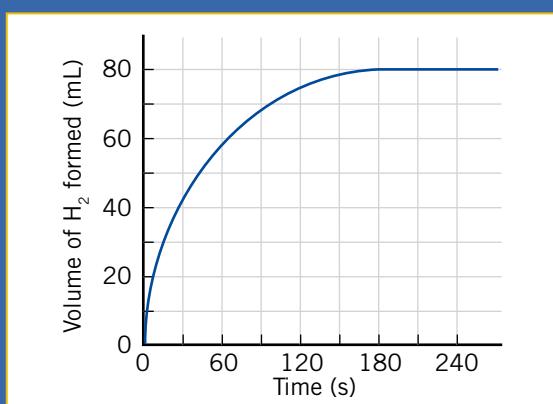


In an experiment designed to investigate the rate of this reaction, a 5 cm strip of magnesium ribbon was put into a conical flask together with an excess of  $0.5 \text{ mol L}^{-1}$  hydrochloric acid. A gas syringe was then quickly attached to the flask, as shown in Figure 11.6. The volume of hydrogen produced in the reaction was measured every 30 seconds. The graph below shows the results obtained for this experiment.

- a Describe how the rate of reaction changes qualitatively during the 240 seconds shown on the graph.
  - b What was the average rate of reaction during the 30 to 60 second time interval?
  - c What was the instantaneous rate of reaction 90 seconds after the beginning of the reaction?
- 2 When sulfuric acid is added to zinc, hydrogen gas and a solution of zinc sulfate are produced.
- a Write an equation for the reaction.
  - b Describe two ways that could be used to follow the rate of the reaction.



**Figure 11.6**

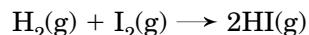


## 11.2 What happens in chemical reactions

### The collision theory

To better understand why different reactions occur at different rates and how these rates can be altered, chemists have proposed the collision theory. While a chemical equation provides information about the substances reacting and the products formed, the collision theory explains what happens during the reaction, at the molecular level.

The reaction between hydrogen and iodine provides an insight into the three requirements, according to the collision theory, for a chemical reaction to occur:



The first, and perhaps obvious requirement is that the two reacting molecules must collide. However, it is not enough for the molecules just to collide for a reaction to occur. The collision between the reactant particles must occur with enough energy to disrupt the bonds in the reactant particles, if a reaction is to result. This minimum energy that must be possessed by the colliding particles, if they are to react, is called the activation energy. Without this minimum energy the molecules will collide and rebound unchanged.

Finally, for many reactions the actual orientation of the collision, that is, the way the particles collide with one another, will influence how fast the reaction proceeds. Figure 11.7 shows the difference between favourable and unfavourable collisions for the reaction between hydrogen molecules and iodine molecules.

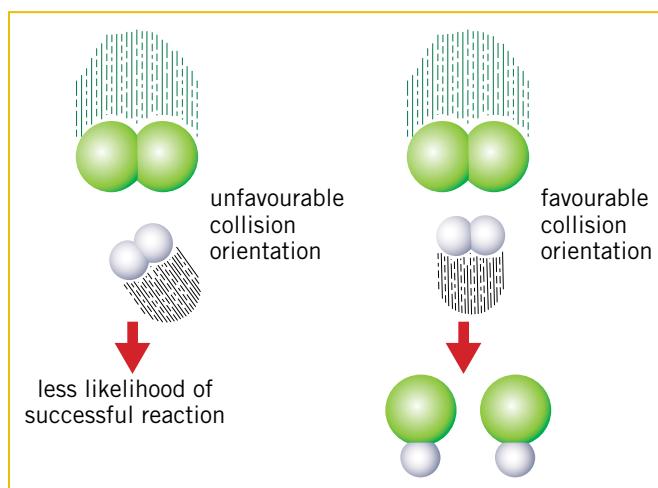


Figure 11.7 Effect of collision orientation on the likelihood of a reaction occurring.

In summary, according to the **collision theory**, the requirements that must be met before a chemical reaction will occur are:

- the reacting particles must collide
- they must collide with a specific minimum amount of energy, called the activation energy
- the particles must collide with a favourable orientation.

## Energy and rate—energy profile diagrams

Energy profile diagrams can be used to show the potential energy changes during the course of a chemical reaction. Figure 11.8. shows a typical energy profile diagram for an exothermic reaction.

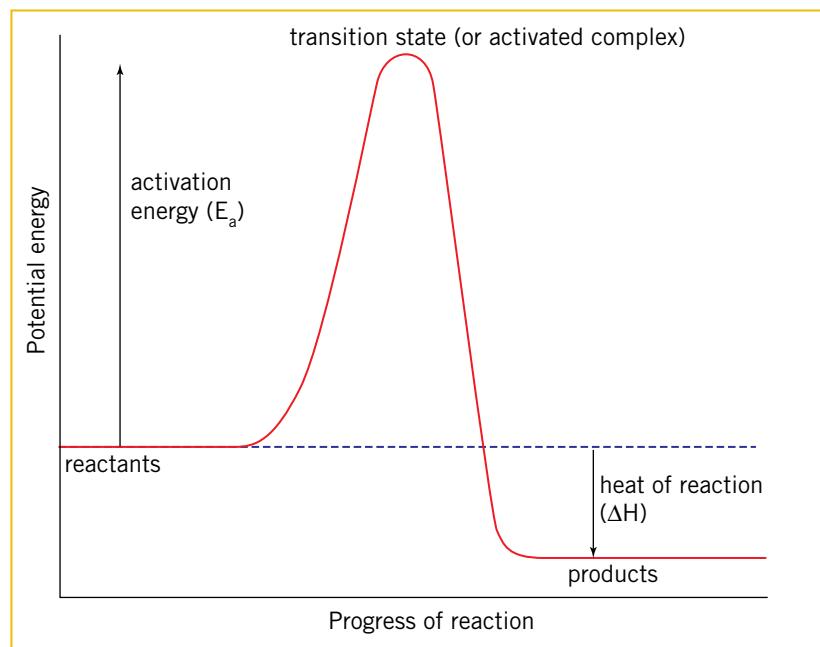
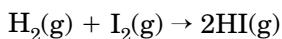


Figure 11.8 A typical energy profile diagram for an exothermic reaction.

This energy profile of a reaction introduces the idea that as the reactant molecules collide some of their kinetic energy is transformed into potential energy. That is, initially the potential energy of the reacting system increases. The change in potential energy occurs because of the breaking of bonds and rearrangement of atoms taking place in the colliding molecules. If enough energy is available in the collision, known as the **activation energy**,  $E_a$ , then the activated complex or transition state is reached. The **transition state** represents the stage of maximum potential energy in the reaction. Bond breaking and bond forming are occurring at this stage. The transition state or activated complex is an arrangement of atoms that is unstable and exists only for the briefest instant before the reaction moves to completion as new bonds form to produce the products.

As shown on the energy profile diagram in Figure 11.8, the energy difference between the reactants and products represents the heat of reaction, that is,  $\Delta H$  for the reaction. The energy difference between the reactants and the transition state represents the activation energy,  $E_a$ , for the forward reaction.

The energy profile diagram for the endothermic reaction



is shown in Figure 11.9. A molecular representation of the reaction is also shown.

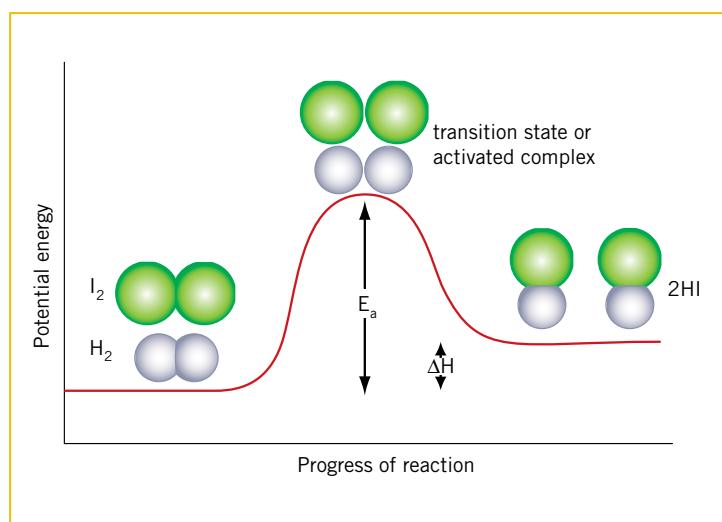
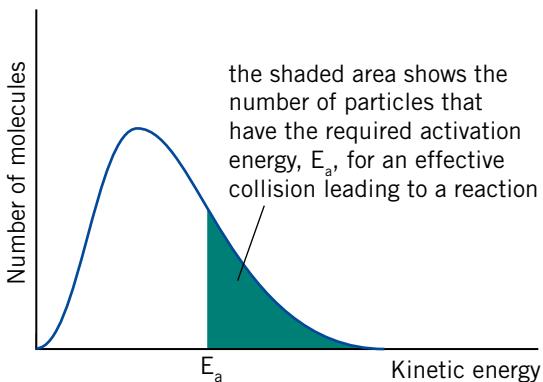


Figure 11.9 Energy profile diagram for the endothermic reaction  $H_2(g) + I_2(g) \rightarrow 2HI(g)$ .

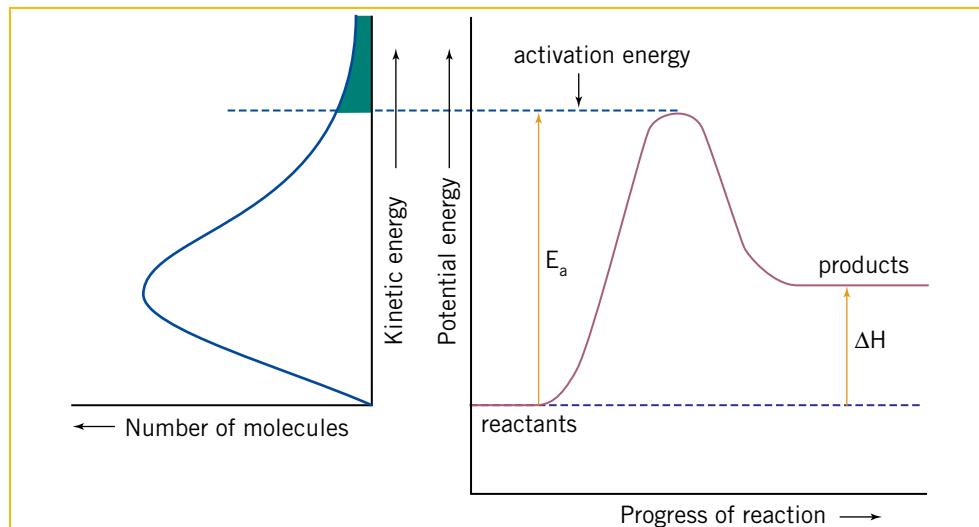


**Figure 11.10 Distribution of kinetic energies of the molecules in a substance at a particular temperature.**

It might be expected that if one molecule in a reaction system has sufficient kinetic energy to react, then all the molecules would have that energy. In fact, the molecules of a particular substance at any given temperature have a range of kinetic energies. The individual molecules have a distribution of kinetic energies like that shown in Figure 11.10.

If the activation energy for a reaction is  $E_a$ , then, as shown in the diagram, the number of molecules that will have the equivalent of or more than this activation energy is shown in the shaded area. In the mixture of reacting substances at the temperature represented in Figure 11.10, many of the collisions will not be effective, as they will involve molecules whose kinetic energy is less than the required activation energy for a successful reaction.

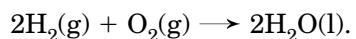
Another way of depicting this minimum energy requirement for a reaction to occur is to draw the energy profile diagram alongside the distribution of kinetic energies, as shown in Figure 11.11

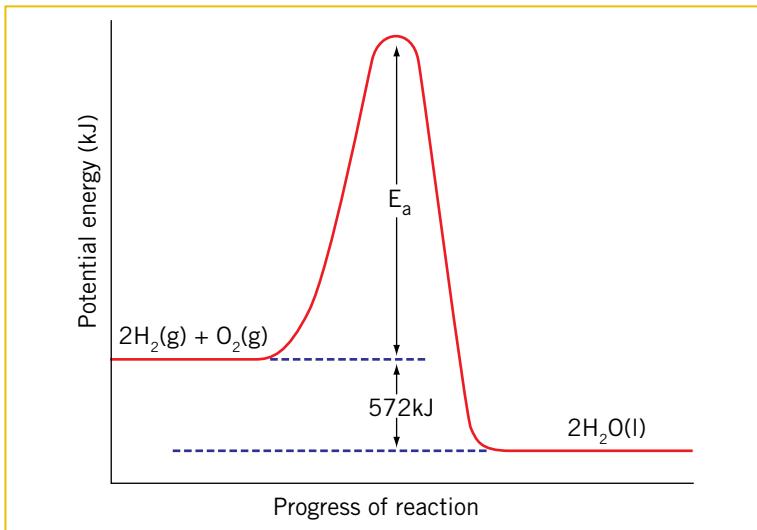


**Figure 11.11 Reaction rate depends on how many molecules have the activation energy necessary for a reaction.**

All chemical reactions have a specific activation energy. For reactions that occur rapidly at room temperature, the activation energy is low, while it is high for reactions that are slow or do not occur readily at room temperature. The magnitude of the activation energy does not provide any information about whether the reaction will be endothermic or exothermic. For example, there are highly exothermic reactions, such as the reaction between hydrogen and oxygen, that have a very large activation energy, and others, such as the reaction of potassium with water, that have low activation energies.

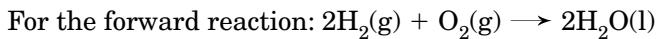
An energy profile diagram for a particular reaction also provides information about its reverse reaction. For example, Figure 11.12 shows the energy profile diagram for the reaction of hydrogen with oxygen to produce liquid water



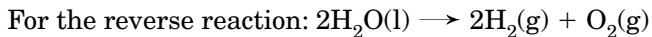


**Figure 11.12** Energy profile diagram for the reaction  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$ .

From this diagram, the following data about both the forward and reverse reactions can be inferred:



- the reaction is exothermic
- the heat of reaction,  $\Delta\text{H}$ , is  $-572 \text{ kJ}$
- the activation energy, is  $E_a \text{ kJ}$



- the reaction is endothermic
- the heat of reaction,  $\Delta\text{H}$ , is  $+572 \text{ kJ}$
- the activation energy, is  $(E_a + 572) \text{ kJ}$

### \* Review exercise 11.2

- 1 a Draw an energy profile diagram for the reaction



given that the enthalpy change is  $+200 \text{ kJ}$  and the activation energy is  $210 \text{ kJ}$ .

- b What is the enthalpy change and the activation energy for the reverse reaction



- 2 Explain why a reaction does not always occur when two reactant molecules collide.

- 3 Draw energy profile diagrams, showing the relative potential energies of the reactants and products and the transition state, for the following reactions. Briefly explain the shapes of these diagrams for each reaction.

- a A spontaneous reaction occurs when potassium is added to water, producing hydrogen and a solution of potassium hydroxide. Considerable heat is released during the reaction.
- b A piece of magnesium needs to be strongly heated in a Bunsen flame before it will burn with a bright light to produce magnesium oxide.

## 11.3 Factors that affect reaction rates

Knowing how fast a reaction occurs can be important. For instance, knowing how quickly blood clots or how quickly a medicine takes to act can make a difference between whether a patient lives or dies. Being aware of how long it takes for mortar to set between bricks or how long concrete needs to rest for the chemical reactions to produce a stable structure for further building work is important for the construction industry. The rates of these processes tend to depend on the same variables, most of which chemists are often able to manipulate to control the rate of the reaction they are interested in. Variables, or factors, that can affect rates of reactions are:

- the nature of the reactants
- concentration (or pressure for reactions of gases)
- temperature
- surface area
- presence of a catalyst.

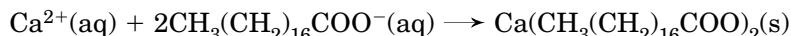
### The nature of the reactants

The type of reactants involved in a chemical reaction can influence how fast it will occur. However, accurate predictions about the rate of a particular reaction are very difficult to make by just considering the reactants involved. While experimental measurement is the only sure way to determine the rate of a chemical reaction, there are some broad generalisations that can be made about the effect of the type of reactants on reaction rates.

Natural gas (methane) combines with oxygen in air, during the combustion process, according to the following equation.



At room temperature, the rate of this reaction is virtually zero. If natural gas is allowed to mix with air at room temperature none of the methane will react with the oxygen. In contrast to this, the white scum that forms when soap is added to water supplies in much of Western Australia, does so very quickly. This water, which is often called hard water, contains calcium ions that undergo a precipitation reaction with soap:



The stearate ion,  $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-$ , is one of the main components in many soaps. (The stearate ion is represented as  $\text{St}^-$  in Figure 11.13.)

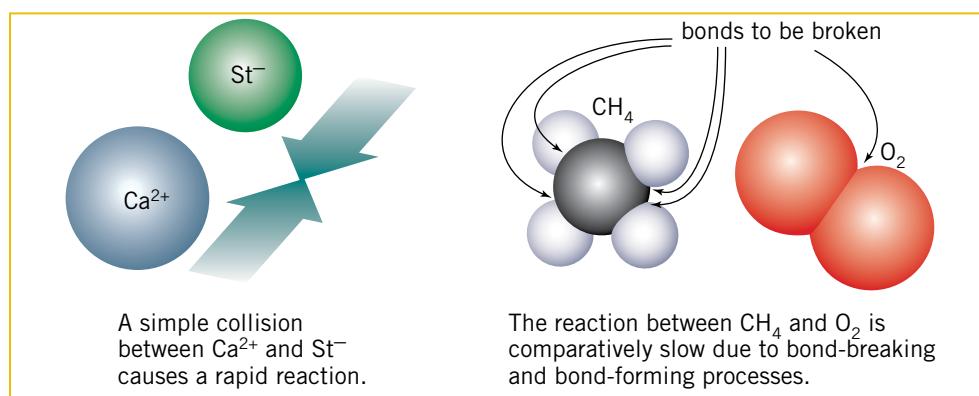


Figure 11.13 Comparison of reactions involving molecules with those involving ions.

Reactions involving molecular substances with covalent bond-breaking and covalent bond-forming requirements, such as that between methane and oxygen, are likely to be slower than those involving the simple combination of oppositely charged ions. In the reactions involving molecules, the collisions must have enough energy to overcome the activation energy barrier, and there may also be a particular requirement for a favourable collision orientation. The combination of ions that form an insoluble solid usually only require collision for the electrostatic attraction to keep the ions together. There is likely to be no significant energy requirement, other than a collision.

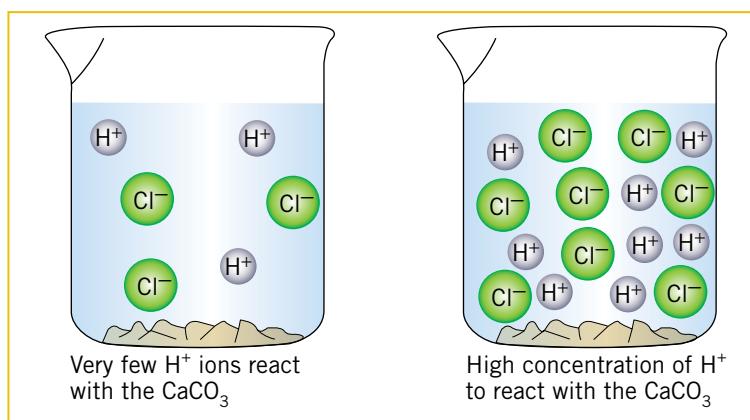
Between the very fast and the very slow reactions there are a range of reactions about which few predictions can be made with respect to their rate.

### The concentrations of the reactants

After a brick wall has been constructed using mortar to bind the layers of bricks together, a white residue, composed mainly of calcium carbonate, often remains on the wall. In order to remove this white solid from the wall, the builders use hydrochloric acid, HCl. The solid calcium carbonate reacts with hydrochloric acid to produce a solution containing calcium ions and chloride ions (which can be washed away) and evolving carbon dioxide.



If dilute acid is used the reaction is slow. However, if the acid is made more concentrated the reaction rate speeds up. Generally, builders wearing rubber gloves, boots, other safety clothing and safety spectacles, use concentrated hydrochloric acid (about  $10 \text{ mol L}^{-1}$ ) to rapidly remove the coating of carbonate from the wall. Figure 11.14 shows the effect of using more concentrated acid on the rate of reaction.

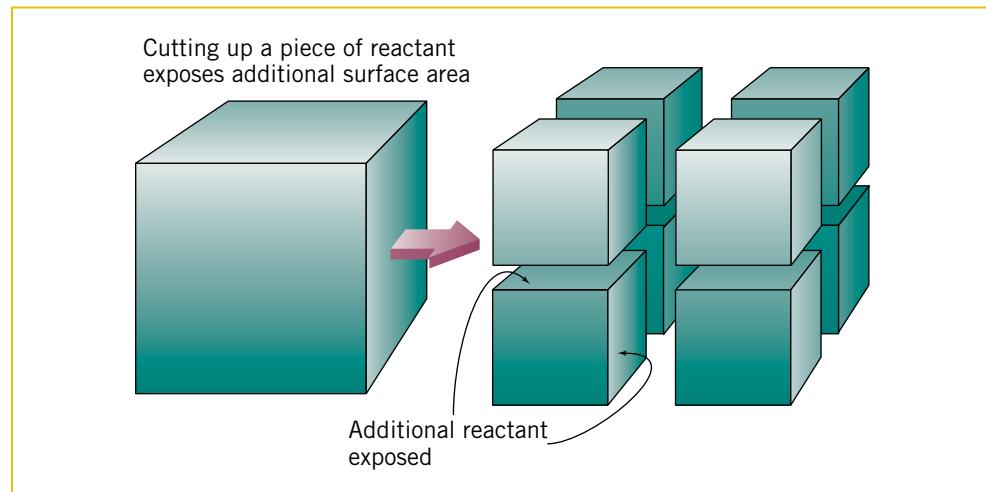


**Fig 11.14 Reaction between calcium carbonate and acid at low and high concentrations.**

In the more concentrated solution of hydrochloric acid there are more hydrogen ions (one of the reactants) in a particular volume, compared to the dilute solution. As a result, there will be an increase in the number of collisions between the reactant particles. Hence there is a greater chance that collisions with enough energy, and the favoured orientation, will occur, resulting in an increase in the reaction rate for the concentrated acid.

## The state of sub-division of the reactants

In heterogeneous systems where the reactants are in different states, for example, a solid and a solution, or a solid and a gas, the reaction rate can be affected by the state of sub-division of the solid or liquid. For example, a log of wood cut into smaller pieces burns far more rapidly than if it were in one piece. The effect of cutting the log into pieces is to expose more of the wood to the air and consequently increasing the number of collisions, and hence the rate of reaction, between the molecules in the wood and the oxygen molecules. This is illustrated in Figure 11.15.



**Figure 11.15** When a solid (or liquid) is broken up into smaller pieces, its surface area is increased. This will allow an increase in the collision rate between the reacting particles, and possibly an increase in the reaction rate.



**Figure 11.16** Both beakers contain equal amounts of acid and calcium carbonate, but the beaker on the left contains the calcium carbonate as a powder and the one on the right as large chunks. The reaction rate is much quicker for the powdered reactant that has the greater surface area.

Figure 11.16 shows two beakers containing hydrochloric acid of equal concentration and equal masses of calcium carbonate. But in the beaker on the right, the calcium carbonate is in large chunks and in the other beaker it is in a powdered form. A much more vigorous reaction takes place at the larger surface area of the powdered reactant because of the greater rate of collision between the reactant particles.

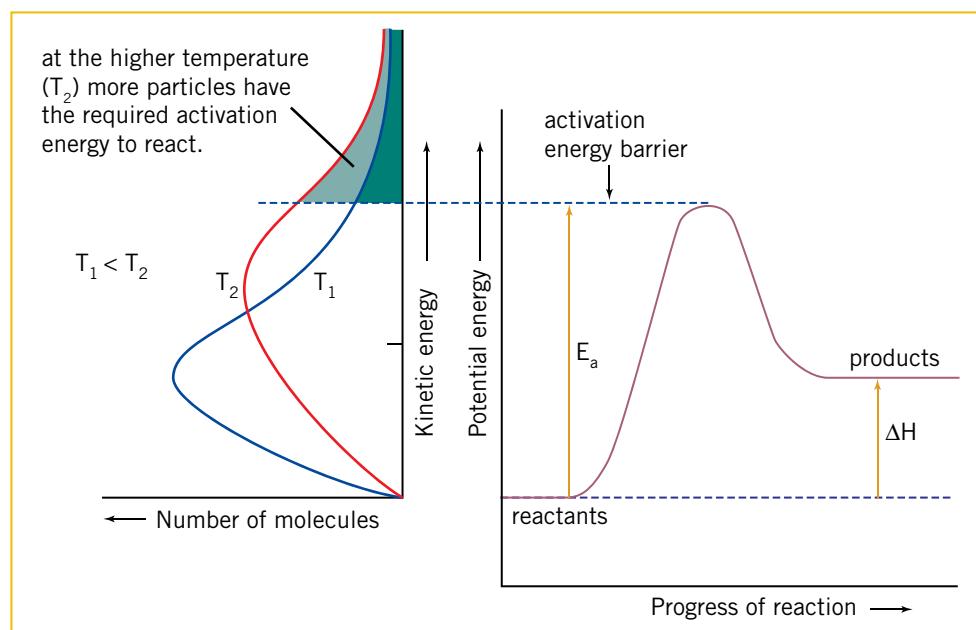
### Temperature

Two-part epoxy glues such as Araldite strongly bond two surfaces together when a hardener reacts with the adhesive. Araldite, like most glues, sets more quickly in hot weather than in cold weather. At the higher temperature there is more likelihood of collisions, between the hardener and adhesive particles, that have the activation energy required for a reaction to occur.

The spoiling of foodstuffs such as milk and meat is mainly due to chemical reactions carried out by bacteria. By storing these foods in a refrigerator it is possible to slow down the rate of spoiling by reducing the number of particles with sufficient energy to overcome the activation energy barrier when they collide.

The rate of a reaction is approximately doubled for every  $10^{\circ}\text{C}$  increase in temperature. At a higher temperature the average kinetic energy of the particles increases. As such, the number of particles with energy greater than the required activation energy,  $E_a$ , for a particular reaction, increases significantly. In Figure 11.17 the kinetic energy distribution of particles at two different temperatures, when matched against the energy profile diagram, shows that at the higher temperature many more particles will have the required activation energy for a reaction to occur.

In addition, because the particles are moving faster, there will be a greater number of collisions at the higher temperature. The main reason, however, for the increase in reaction rate is because of the effect of the increase in temperature on the distribution of the kinetic energies of the reactant particles.



**Figure 11.17** Effect of an increase in temperature on the number of particles having the required activation energy for a reaction to occur.

## Catalysts

Modern household laundry cleaners are expected to clean clothes and remove stains at the lowest possible temperature. Increasing the concentration of detergent in the wash water would increase the rate of the cleaning process, but would also add more detergent to the environment, perhaps creating long-term problems. High temperatures are not favoured because of the energy costs and the effect that the more forceful conditions might have on delicate clothing. Manufacturers have therefore chosen to add enzymes (biological catalysts) that speed up the reaction involving the detergent and the dirt, grease or stain.

A **catalyst** is a substance that provides an alternative reaction pathway, with a lower activation energy, for a particular reaction (see Figure 11.18). In addition, the catalyst is unchanged at the end of the reaction and so can be used over and over again and in small amounts, to speed up the reaction. There is little doubt that the catalyst takes part in the reaction, either in the reaction itself or by providing a surface upon which the reaction can more readily take place. However, during some stage of the reaction sequence the catalyst is regenerated.

The catalyst affects the rate by providing a lower activation energy barrier. It therefore follows that more particles will have the required activation energy to react. That is, more collisions between the reactant particles will result in a reaction and the reaction rate will be increased. In some cases the catalyst may promote a more favourable collision orientation by providing a surface on which the reacting particles are brought into the ideal contact geometry.

Manganese dioxide,  $\text{MnO}_2$ , acts as a catalyst to increase the rate of decomposition of hydrogen peroxide,  $\text{H}_2\text{O}_2$ . In the absence of a catalyst, hydrogen peroxide decomposes into oxygen and water at a very slow rate.

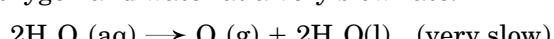


Figure 11.19 The hydrogen peroxide reacts more vigorously when the catalyst is added.

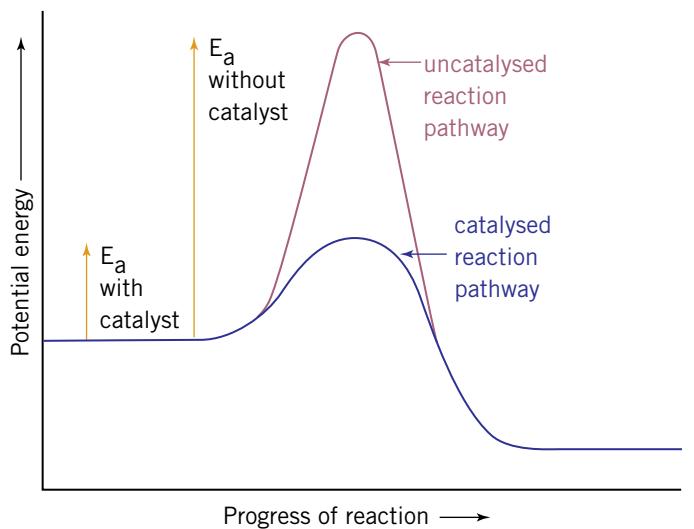
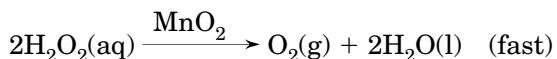


Figure 11.18 A catalyst provides an alternative reaction pathway with a lower activation energy.



The addition of a small amount of manganese dioxide causes the hydrogen peroxide solution to bubble vigorously due to the rapid production of gaseous oxygen. The mass of manganese dioxide is the same before and after the reaction, showing that the catalyst is not consumed.

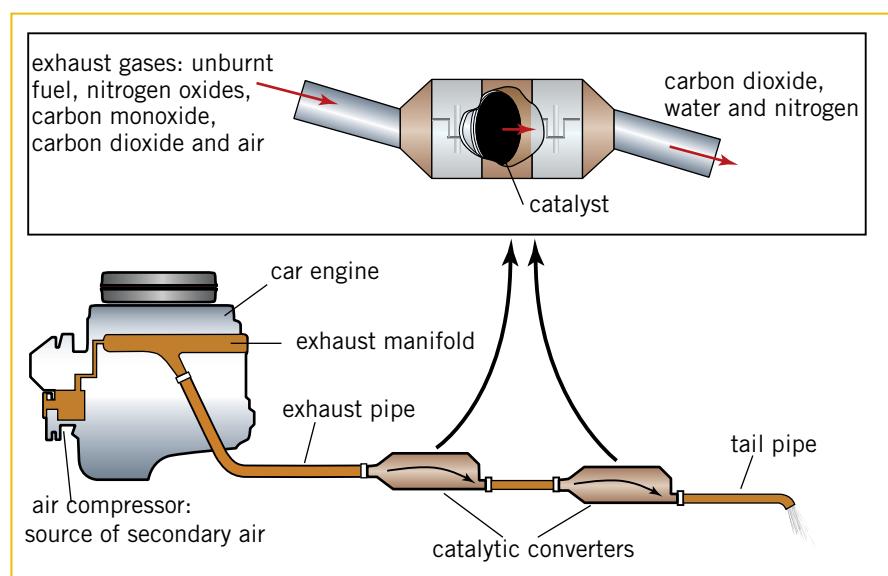


Notice that in this equation, the catalyst is written above the arrow to show that although it is not consumed, it plays an essential role in the reaction.

### Catalytic converters in cars

First developed by Kathleen Taylor in 1975 while working at General Motors, the catalytic converter has become part of all automobile exhaust systems today. In Australia, it has been part of all cars produced since 1986.

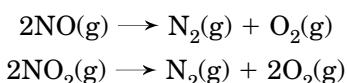
The catalytic converter is located between the engine and the tail pipe. It consists of a very porous ceramic structure with a thin coating of a platinum, rhodium or palladium catalyst. The whole structure is built in a manner that will increase the surface area of catalyst exposed to the exhaust gases.



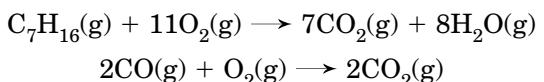
**Figure 11.20** Arrangement of two catalytic converters to remove nitrogen oxides, unburned hydrocarbons and carbon monoxide from motor vehicle exhausts.

There are two catalytic reactions involved in dealing with the complex mixture of polluting gases that comes from the combustion of petrol in the engine. The gas mixture coming from the engine includes unburned hydrocarbons, oxides of nitrogen and carbon monoxide, major polluting gases.

In the first catalytic converter the oxides of nitrogen are reduced to elemental nitrogen and oxygen



The exhaust gases then pass into the second catalytic converter which oxidises the unburned hydrocarbons, such as heptane,  $C_7H_{16}$ , to carbon dioxide and water, as well as converting carbon monoxide to carbon dioxide. These reactions also use, in part, the oxygen that has been produced in the first converter.



### \* Review exercise 11.3

- 1 Which of the following reactions are likely to be rapid at room temperature?
  - a  $Pb^{2+}(aq) + CO_3^{2-}(aq) \rightarrow PbCO_3(s)$
  - b  $2C(s) + O_2(g) \rightarrow 2CO(g)$
  - c  $C_6H_{12}(l) + Cl_2(g) \rightarrow C_6H_{11}Cl(l) + HCl(g)$
  - d  $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
- 2 The rate of the reaction between  $H_2(g)$  and  $I_2(g)$  to form  $HI(g)$  is found to decrease when the volume of the system is increased. Explain this observation.
- 3
  - a Draw and label an energy profile diagram for the reaction of glucose with oxygen to produce carbon dioxide and water.
  - b In a simple fashion, show how an enzyme catalyst in a cell would change the profile.
  - c Explain why this change should result in an increase in the reaction rate.
- 4 When a substance has its temperature increased the average kinetic energy of the molecules increases. What property of the molecules changes in order for this increase in energy to occur?
- 5 Why are many metal catalysts used in the form of fine wire mesh?
- 6 Explain the following observations:
  - a although wheat is usually slow to burn, wheat silos have been known to explode
  - b food products are often stored in refrigerators
  - c liquid hydrogen, used as a fuel to propel the space shuttle, is reacted with pure liquid oxygen rather than air.
- 7 In the manufacture of ammonia, hydrogen and nitrogen gases are reacted according to the following equation:



Under standard conditions of temperature and pressure the rate of this reaction is very slow. Suggest three ways in which the rate of the reaction might be increased. Justify your suggestions in terms of the collision theory.



## MAJOR IDEAS

- Reaction rate is a measure of the change in some measurable amount of reactant or product as a function of time.
- Rates can be measured from graphs of changes in some quantity against time, by determining the gradient of the graph at a particular time.
- Collision theory establishes the three requirements for a chemical reaction—collisions, sufficient energy of collision (enough energy to overcome the activation energy barrier), and a favourable collision orientation.
- Energy profile diagrams provide information about the activation energy and the heat of reaction for a chemical reaction.
- The peak of the energy profile curve represents the activated complex or transition state.
- At any temperature the particles in a substance have a range of kinetic energies.
- Not all particles in a reaction mixture will have enough energy to overcome the activation energy barrier.
- Chemical reactions are reversible and the back reaction also has an activation energy.
- Five factors that influence rate are—nature of reactants, concentration or pressure, temperature, state of subdivision and catalysts.
- The effect of each of these factors can be explained in terms of collision theory.
- Catalysts are substances that provide an alternative reaction pathway with a lower activation energy and are not consumed in the reaction.

## QUESTIONS

- The rate of reaction of vinegar with marble chips is expressed in the graph shown in Figure 11.5. Explain why the rate of the reaction decreases as the reaction proceeds.
- Using the collision theory, explain the following:
  - a large piece of wood burns slower than smaller pieces of wood
  - food cooks quicker in almost boiling oil than in boiling water
  - 10 mol L<sup>-1</sup> hydrochloric acid used for brick cleaning is much more dangerous than the 1 mol L<sup>-1</sup> hydrochloric acid used in the laboratory
  - coal dust in a coal mine is an explosion hazard.

3 Sulfur dioxide combines with oxygen to form sulfur trioxide. The reaction liberates 200 kJ of heat for every two mole of sulfur dioxide consumed. The activation energy for this reaction is 225 kJ.

- Write an equation for the reaction of sulfur dioxide with oxygen to give sulfur trioxide.
  - Give the value (including the sign) of  $\Delta H$  for the equation you have written.
  - Draw an energy profile diagram for the reaction. Your sketch should show the relative energies of the reactants and the products, and should identify  $\Delta H$  and the activation energy.
  - This reaction is catalysed by vanadium pentoxide. On the same diagram draw the energy profile you would expect for the catalysed reaction, taking care to indicate how the catalyst affects the activation energy and  $\Delta H$ .
- 4 The following questions refer to Figure 11.21.
- What is the activation energy for the reaction  $H_2(g) + I_2(g) \rightarrow 2HI(g)$ ?
  - Is the reaction referred to in a exothermic or endothermic?
  - Where is the transition state on the diagram?
  - What is the heat of reaction for the reaction  $H_2(g) + I_2(g) \rightarrow 2HI(g)$ ?
  - What is the activation energy for the reaction  $2HI(g) \rightarrow H_2(g) + I_2(g)$ ?
  - What is the heat of reaction for the reaction  $2HI(g) \rightarrow H_2(g) + I_2(g)$ ?

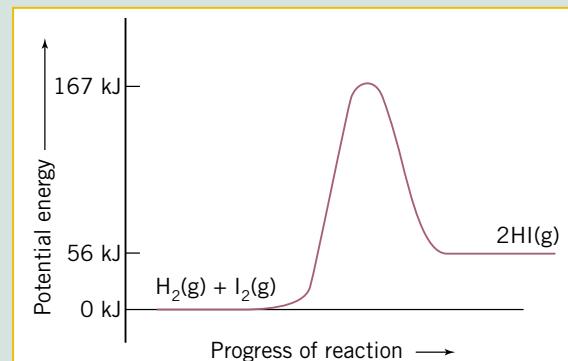


Figure 11.21

- 5 A solution of hydrogen peroxide was decomposed in the presence of manganese dioxide, according to the equation  $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ .

Three experiments were performed using a fixed mass of catalyst but with:

- 50 mL of  $2.0 \text{ mol L}^{-1}$  hydrogen peroxide solution
- 100 mL of  $1.0 \text{ mol L}^{-1}$  hydrogen peroxide solution
- 100 mL of  $2.0 \text{ mol L}^{-1}$  hydrogen peroxide solution.

The volume of oxygen produced against time was recorded as shown in Figure 11.22.

Which of the curves relate to the solutions i, ii and iii?

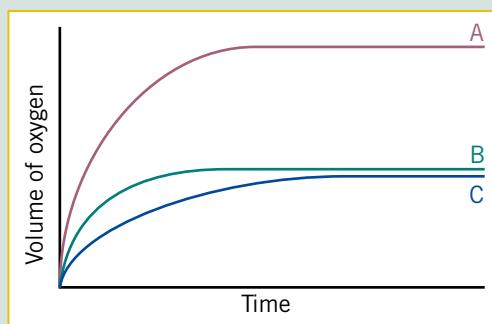


Figure 11.22

- 6 Rates of reaction increase with increasing temperature. Many of the chemical reactions that take place in the body are particularly complex and need a range of enzymes to speed up the reactions. Why then does body temperature remain at around  $37^\circ\text{C}$  when the reactions would go even faster at a higher body temperature?

- 7 A 6% solution of hydrogen peroxide is often kept in the medicine cupboard as a mild bleach. It is capable of acting as a sterilising agent on some wounds. The hydrogen peroxide is stored in a dark bottle because it breaks down to water and oxygen in the presence of sunlight. A friend comments that the sunlight must be a catalyst for the decomposition of the hydrogen peroxide. Explain why this statement is not correct. How would you explain the effect of sunlight to your friend?

- 8 a When an apple is freshly cut the white interior slowly goes brown. Provide an explanation for this in terms of reaction rates and collision theory.  
b Why is it that vegetables are often cut up into smaller pieces prior to cooking?

- 9 About 20 g of marble chips (calcium carbonate) were placed in an open flask together with 100 mL of  $2 \text{ mol L}^{-1}$  hydrochloric acid (similar to that shown in Figure 11.4). The flask and contents were weighed at the moment of addition of the acid and then again at 30-second intervals. The results obtained were plotted on the graph shown in Figure 11.23.

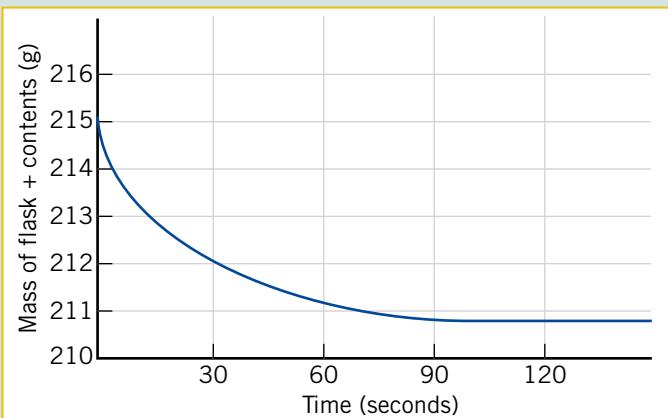


Figure 11.23

- Write the equation for the reaction between marble chips and hydrochloric acid solution, in which a solution of calcium chloride, carbon dioxide and water are formed.
- What mass of carbon dioxide was formed in the first 60 seconds? What mass of marble has reacted in this time?
- A loose plug of cotton wool was placed in the neck of the flask at the beginning of the reaction, prior to the initial weighing. What was the purpose of the cotton wool?
- Calculate the average rate of reaction, as mass of carbon dioxide per second, during the time interval between 30 seconds and 60 seconds.
- Was the reaction rate greater, smaller or the same, at the time of 15 seconds compared with the time of 60 seconds? How would you explain this observation?
- Why was there no decrease in the mass of flask and contents after 90 seconds?
- Sketch qualitatively the shape of the curve you would expect for the graph of concentration of hydrochloric acid against time for this experiment.

- 10 Some explanations, A–E, based on the collision theory, are given below:

#### EXPLANATION A

When strong covalent bonds are broken, the reaction has a higher activation energy and so is slower.

#### EXPLANATION B

An increase in temperature increases the number of particles having the energy to overcome the activation energy barrier. Thus, more collisions will be successful, resulting in a greater reaction rate.

#### EXPLANATION C

When concentration or gas pressure increases, so too will the rate of collisions, and hence the reaction rate.

#### EXPLANATION D

A catalyst provides an alternative pathway with a lower activation energy. Hence, more particles will collide having the required (lower) activation energy to react.

#### EXPLANATION E

An increase in state of subdivision increases the rate of collision between reactants, and hence reaction rate.

Choose the correct explanations for the following observations.

- a For the reaction  $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$ , if the pressure is increased (by decreasing the volume), then the rate of reaction increases.
- b To start a fire, small pieces of wood are used rather than logs of wood.
- c The reaction  $2\text{Ag}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{AgCl}(\text{s})$  occurs much slower than the reaction  
 $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$ .
- d Concentrated hydrochloric acid is more dangerous than  $0.1 \text{ mol L}^{-1}$  hydrochloric acid.
- e Milk goes sour more quickly if it is left out of the refrigerator.
- f Hydrogen peroxide decomposes very slowly according to the equation  
 $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$ .

However, if a small amount of animal liver is added to the hydrogen peroxide, it decomposes very rapidly.

- 11 When magnesium reacts with sulfuric acid,  $\text{H}_2\text{SO}_4$ , the products formed are hydrogen gas and a solution of magnesium sulfate. The two diagrams in Figure 11.24 provide graphs of the volume of hydrogen collected against time in the reaction of magnesium with a fixed volume of sulfuric acid.

Diagram 1

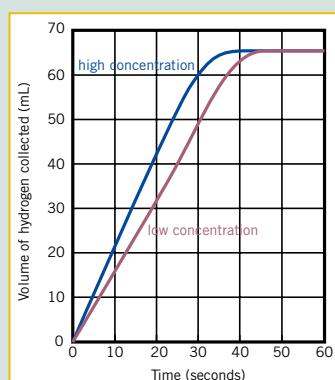


Diagram 2

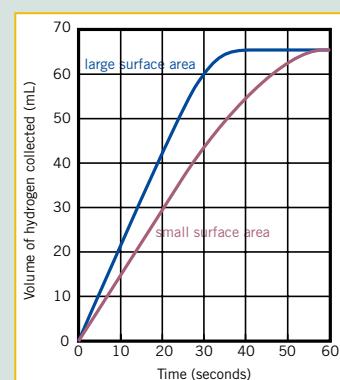


Figure 11.24

Diagram 1 shows the effect of changing the concentration of the acid on the reaction with a fixed amount of magnesium, while Diagram 2 shows the difference between using magnesium fragments and magnesium powder.

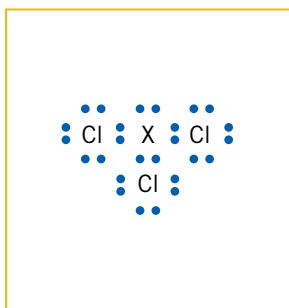
- a Why do the curves flatten out?
- b Using the collision theory, explain the differences between the blue and red curves in each of Diagram 1 and 2.
- c From the information supplied, is the acid or the magnesium present in excess? How do you know?
- d The experiment is repeated twice more using the experimental conditions corresponding to those used for the blue curve (high concentration) in Diagram 1, except in one experiment the temperature was increased and in the other a catalyst was used. Draw a graph to show how the increase in temperature would be expected to change the volume of hydrogen versus time graph, compared to the graph for the original mixture. Draw a second graph showing the changes expected when a catalyst is used.

- 12 RESEARCH Investigate the way in which enzymes are used in the dairy industry to make yoghurt and cheese.

## Unit 2A Review Questions

### \*PART A: MULTIPLE-CHOICE QUESTIONS

1 The electron dot diagram of a compound formed between an element X and chlorine is shown below.



What would be the expected formula of the compound formed between X and barium?

- A  $\text{BaX}$
- B  $\text{BaX}_2$
- C  $\text{Ba}_2\text{X}_3$
- D  $\text{Ba}_3\text{X}_2$

2 The mass number of atom Y is 27. Y forms a cation with a charge of +3. If the number of neutrons in the cation is 14, what is the number of electrons in the cation?

- A 10
- B 13
- C 14
- D 17

3 Which of the following aqueous solutions has the greatest number of ions in 1.00 L?

- A  $2 \text{ mol L}^{-1}$  hydrochloric acid
- B  $2 \text{ mol L}^{-1}$  sodium hydroxide
- C  $3 \text{ mol L}^{-1}$  acetic acid
- D  $2 \text{ mol L}^{-1}$  copper chloride

4 The electron configuration of the elements X and Y are 2, 8, 8, 2 and 2, 8, 7 respectively. Elements X and Y react to form the compound Q. Which of the following statements about Q is NOT correct?

- A The most likely formula of Q is  $\text{XY}_2$ .
- B Q is formed in a reaction that involves the transfer of electrons from one atom to another.
- C Q is a liquid at room temperature.
- D Q conducts electricity in the liquid state.

5 Which of the following statements about catalysts are true?

- i Catalysts change the rate of a chemical reaction.
  - ii Catalysts increase the final amount of product produced in the reaction.
  - iii A catalyst provides an alternative reaction pathway for the reaction.
  - iv Catalysts change the activation energy of the reaction.
- A (i), (ii) and (iii) only
  - B (i), (ii) and (iv) only
  - C (i), (ii), (iii) and (iv)
  - D (i), (iii) and (iv) only

6 Magnesium combines with oxygen according to the equation



Which one of the following statements concerning this reaction is true?

- A The reaction is endothermic.
- B The temperature of the surroundings will decrease during the reaction.
- C The enthalpy of the product will be less than the enthalpy of the reactants.
- D The energy required to break the bonds in magnesium and oxygen is greater than the energy released in the forming of the bonds in magnesium oxide.

7 What causes the pressure of a gas to decrease when the volume of a given amount of gas is increased at constant temperature?

- A There are fewer molecules present in the new volume.
- B The molecules are moving more slowly in the large volume.
- C The molecules have further to travel and so will slow down and not hit the walls with as great a force.
- D Because of the larger surface area the molecules will be hitting the surface less often.

8 Which one of the following statements is correct?

- A Equal masses of argon and oxygen have the same volume at STP.
- B Equal volumes of oxygen and nitrogen contain the same number of molecules at STP.
- C Equal masses of argon and nitrogen contain the same number of molecules.
- D Equal volumes of neon and oxygen contain the same number of atoms at STP.

**9** What mass of silver chloride will form when 50.0 mL of 0.0200 mol L<sup>-1</sup> silver nitrate solution is added to a solution of sodium chloride? Assume the sodium chloride is in excess.

- A** 0.001 g **B** 0.108 g **C** 0.143 g **D** 0.179 g

**10** What is the main reason why molten CaCl<sub>2</sub> conducts an electric current while solid CaCl<sub>2</sub> does not?

- A** Solid CaCl<sub>2</sub> is a molecular compound.
- B** Solid CaCl<sub>2</sub> forms a metallic lattice compound.
- C** The ions in molten CaCl<sub>2</sub> are mobile, but in solid CaCl<sub>2</sub> they are not.
- D** Ca and Cl atoms in the solid become ionised when the solid melts.

**11** Which of the following best explains why a mixture of petrol and air in the petrol tank of a car does not react at room temperature to form carbon dioxide and water?

- A** The reaction is exothermic and therefore the mixture must be heated for reaction to occur.
- B** The energy of collisions of the reactant particles is not sufficient to provide the required activation energy.
- C** The activation energy barrier is not high enough for a successful reaction to take place.
- D** The enthalpy of the products is too high for any significant reaction to take place at room temperature.

**12** Under the same conditions of temperature and pressure two identical samples of magnesium are placed in open vessels. Excess 1.0 mol L<sup>-1</sup> sulfuric acid is added to one, and excess 0.1 mol L<sup>-1</sup> sulfuric acid is added to the other. Hydrogen gas and a solution of magnesium sulfate are formed in the reactions. Which of the following is the same for the two reaction mixtures?

- A** The overall mass lost from the vessels.
- B** The rate at which magnesium is consumed in the first 5 seconds of the reaction.
- C** The time it takes for the reaction to be completed.
- D** The rate of formation of hydrogen during the first 5 seconds of the reaction.

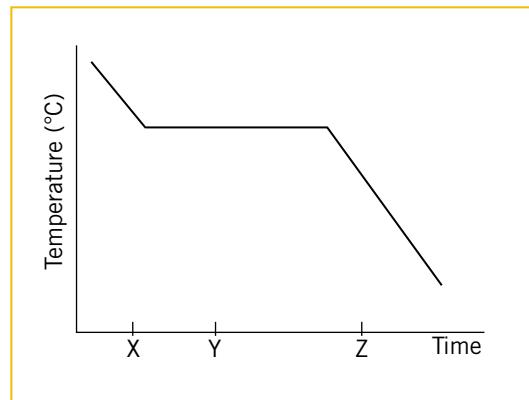
**13** Which of the following is the best description of a saturated solution?

- A** It is the solution that forms when a solid is dissolved in a solvent at room temperature.
- B** It is the mass of solute dissolved in 100 g of water.
- C** It contains as much solute as the amount of solvent can dissolve at a given temperature.
- D** It is the amount of solute that is dissolved in 100 g of solution.

**14** Which of the following will have the lowest vapour pressure at 25°C?

- A** Pure water
- B** A solution of 0.1 mol L<sup>-1</sup> sucrose in water
- C** A solution of 0.1 mol L<sup>-1</sup> sodium bromide in water
- D** a solution of 0.1 mol L<sup>-1</sup> calcium nitrate in water

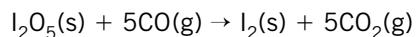
**15** The following graph shows a cooling curve for a liquid that is cooled by immersing the test tube containing the melted compound in a bath of water.



Which one of the following gives the correct states of the substance at X, Y and Z?

- | <b>X</b>        | <b>Y</b>         | <b>Z</b>         |
|-----------------|------------------|------------------|
| <b>A</b> gas    | liquid           | solid            |
| <b>B</b> liquid | solid            | solid            |
| <b>C</b> liquid | solid and liquid | solid            |
| <b>D</b> liquid | liquid           | solid and liquid |

**16** I<sub>2</sub>O<sub>5</sub> can be used to detect the presence of carbon monoxide, according to the equation



What mass of I<sub>2</sub>O<sub>5</sub> would be required to react with 7.00 × 10<sup>-2</sup> g of carbon monoxide?

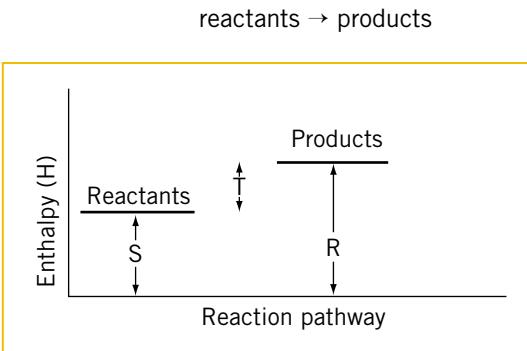
- A** 0.167 g **B** 0.334 g **C** 3.34 g **D** 1.67 g

**17** Polonium is extremely dangerous because of its intense radioactivity. Amounts greater than 4 × 10<sup>-12</sup> g cannot be tolerated in the human body. (A<sub>r</sub>(Po) = 210.)

The number of atoms contained in 4 × 10<sup>-12</sup> g of polonium is:

- A**  $\frac{4 \times 10^{-12}}{210}$
- B**  $4 \times 10^{-12} \times 6.02 \times 10^{23}$
- C**  $\frac{4 \times 10^{-12}}{6.02 \times 10^{23}}$
- D**  $\frac{4 \times 10^{-12}}{210} \times 6.02 \times 10^{23}$

- 18** The following graph represents the enthalpy ( $H$ ) changes that occur in the reaction



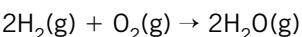
Which of the following represents the  $\Delta H$  of the reaction?

- A** S    **B** T    **C** R    **D** S + T

- 19** Which one of the following is correct for the reaction in Q 18?

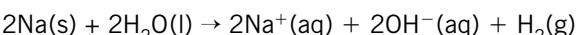
	Type of reaction	Sign of $\Delta H$	Change in temperature of surroundings due to the reaction
A	endothermic	negative	increase in temperature
B	endothermic	positive	decrease in temperature
C	exothermic	negative	increase in temperature
D	exothermic	positive	decrease in temperature

- 20** How many litres of oxygen are required to react completely with 2.40 L of hydrogen to form water? (Assume all volumes are measured at the same temperature and pressure.)



- A** 1.20 L    **B** 0.600 L    **C** 2.40 L    **D** 4.80 L

- 21** What volume of hydrogen would form at STP when 2.0 g of sodium is added to an excess of water?



- A** 0.043 L    **B** 0.97 L    **C** 1.0 L    **D** 3.9 L

- 22** A solution of potassium sulfate is added to a solution of lead nitrate. The correct ionic equation for this reaction is

- A**  $\text{SO}_4^{2-}(\text{aq}) + \text{Pb}^{2+}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s})$   
**B**  $\text{K}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \rightarrow \text{KNO}_3(\text{s})$   
**C**  $\text{K}_2\text{SO}_4(\text{aq}) + \text{Pb}(\text{NO}_3)_2(\text{aq}) \rightarrow 2\text{KNO}_3(\text{aq}) + \text{PbSO}_4(\text{s})$   
**D** no reaction occurs

- 23** What mass of NaOH is contained in 100 mL of 5.0 mol  $\text{L}^{-1}$  NaOH solution?

- A** 10 g    **B** 20 g    **C** 40 g    **D** 80 g

- 24** In Mexico City, water normally boils at 93°C. This is because

- A** the water in Mexico City is not very pure.  
**B** the city is situated at a high altitude.  
**C** the boiling point of water varies with the temperature of the surroundings.  
**D** the city is in a depression that is slightly below sea level.

- 25** Consider the following three oxides: potassium oxide, carbon dioxide and silicon dioxide. In which of the following lists are the oxides listed in order of increasing melting point?

- A** potassium oxide, carbon dioxide, silicon dioxide  
**B** silicon dioxide, potassium oxide, carbon dioxide  
**C** carbon dioxide, silicon dioxide, potassium oxide  
**D** carbon dioxide, potassium oxide, silicon dioxide

## \*PART B: COMPREHENSION QUESTIONS

### Context 1: Building chemistry

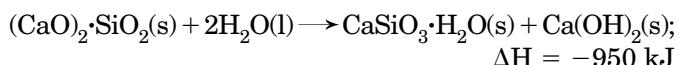
A great deal of chemistry is involved in the construction of a house. Some of it, like the curing or hardening of concrete, is extremely complex.

Most houses start with a concrete foundation. Concrete is very strong under compression—in other words, once hardened it will hold very large loads placed on top of it. It is not as strong when subjected to bending forces, however, so it is generally reinforced with iron mesh, placed near the base of the concrete slab.

Cement, one of the components of concrete, is made from calcium carbonate, silicon dioxide (sand), aluminium oxide, iron oxide and magnesium oxide. Heating this complex mixture of minerals results in a set of reactions that converts the calcium carbonate to calcium oxide, and then causes the mixture of oxides and silica to form various calcium silicates, aluminates, and aluminoferrates.

When cement, sand and stone (called aggregate) are combined with water, concrete is formed. The water reacts with the cement in a chemical reaction called hydration, and it is this hydration reaction that causes the concrete to eventually harden. One of the equations

taking place in the setting concrete is the hydration of dicalcium silicate. The reaction is much more complex but can be simply represented in an equation similar to that below.



The calcium silicate hydrate and calcium hydroxide precipitate as fine particles between the large stone and finer sand grains acting as a type of ‘glue’ to bind the whole mass together. The concrete then slowly hardens over 7–28 days as these hydration reactions continue to bind the mixture of materials together. The setting of concrete therefore does not involve the evaporation of the water in the mixture, but rather the formation of hydrates and calcium hydroxide. The mass of the hardened concrete is not much different from that of the original concrete and water at the beginning of construction.

As brick walls are constructed on the concrete base, the mortar that holds the bricks together is a mixture of cement, sand and water. The same process of hydrate formation, this time binding the grains of sand to the material in the brick, takes place when mortar sets. Bricks may need to be cut to size and this is accomplished using saws that have their blades tipped with a diamond surface in order to cut through the tough brickwork.

Plumbing work involves the use of plastic pipes (often imbedded in the concrete) to take wastewater away from the house and copper pipes to bring water into the house. Plastics such as PVC (polyvinyl chloride) are made from long chains of carbon atoms, with the chains tangling together to give the plastic extra strength, but at the same time capable of being moulded into various shapes.

Windows and doors are often constructed from aluminium, which does not corrode as readily as some other metals, despite it being more reactive than iron. The aluminium forms a thin layer of oxide that does not allow any more air to penetrate to the reactive metal beneath. In some cases the aluminium surface is chemically modified in a process called anodising.

Once the walls are in place the electrical wiring, and perhaps the wiring for various ‘smart technologies’, is put in place. Generally, this wiring is made from copper surrounded by a layer of flexible plastic.

Timber is often used to form the roof frame of the house, and metal brackets and nails are then used to join the timber together. Finally, the roof itself is placed on the house. In many cases, the roofing material chosen is a metal such as aluminium or iron.

Using the information from the previous section, answer the following questions.

**1** Where are metals used in the construction of a house and how does the bonding in these metals together with their related properties allow them to be used for particular construction purposes?

**2 a** Describe the nature of the bonding present in the following components of concrete:

- i silica ( $SiO_2$ )
- ii calcium carbonate
- iii water
- iv hydrated calcium silicate,  $CaSiO_3 \cdot H_2O$ .

**b** Draw electron dot diagrams for (ii) and (iii).

**3** Assuming plastic is made from long chains of carbon atoms also bonded to hydrogen and other elements such as chlorine and oxygen, explain why it can be used for water pipes as well as for covering the metal wires in electrical circuits.

**4** Limestone blocks and paving bricks are also cut to size with diamond-tipped blades. What is the nature of the bonding in diamond and why is it suited to this purpose?

**5** Cement is made by heating a mixture of calcium carbonate (limestone) and clay. During the heating, the limestone decomposes and gives off carbon dioxide.

In one particular cement-manufacturing plant, 100 tonnes of limestone is mixed with clay in order to make a batch of cement. Write the equation for the decomposition of limestone and determine the mass of calcium oxide that would be produced in this reaction.

**6 a** Using the equation for the hydration of dicalcium silicate as a guide, write a simple equation for the hydration of tricalcium silicate,  $(CaO)_3 \cdot SiO_2$ .

**b** Is this reaction exothermic or endothermic? Justify your answer.

**c** How would the magnitude of  $\Delta H$  for your equation compare to that for the hydration of dicalcium silicate? Explain your answer.

**7** Concrete is described as a heterogeneous mixture. What is meant by this expression?

## Context 2: Some garden chemistry

Nitrogen is essential for plant growth. The element is found combined with carbon, hydrogen, oxygen and several other elements in proteins, deoxyribonucleic acid (DNA) and other biologically active compounds. Almost 80% of the atmosphere is elemental nitrogen, N<sub>2</sub>, but this is not very reactive. For most plants, the nitrogen must enter the plant by other means.

One such process involves the conversion of atmospheric nitrogen into nitrogen dioxide. This takes place in thunderstorms at the high temperatures produced by lightning, as well as in fires. The nitrogen dioxide can react further with water and oxygen to produce a solution of nitric acid, HNO<sub>3</sub>. The solution of nitric acid contains free nitrate ions that are capable of being taken into the plant cells via the root system.

Carbon and oxygen are also essential for plant growth and are taken into the plant during the process of photosynthesis. In this reaction, carbon dioxide from the atmosphere combines with water from the soil, in the presence of chlorophyll, to form glucose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, and oxygen gas. Glucose is then used to provide food for the plant and to form the more complex structural compounds in plants, such as starch and cellulose.

Two other elements required in reasonably large quantities for good growth in plants are phosphorus and potassium. These two elements, together with nitrogen, are often referred to as macronutrients. Often there is not enough of these macronutrients present in soil so artificial fertilisers are used to provide these key elements for plant growth.

Using this information answer the following questions.

- 1 a** Why is atmospheric nitrogen not able to be taken directly into the plant cell?
  - b** Draw the electron dot diagram of the nitrogen molecule.
  - c** Write a balanced equation for the reaction of nitrogen with oxygen to form nitrogen dioxide.
  - d** Draw a labelled energy profile diagram for this reaction showing whether the reaction is exothermic or endothermic and indicating whether the activation energy barrier is large or small. Explain your answer.
  - e** Explain why the reaction is faster at high temperature.
- 2 a** In the presence of air and water, nitrogen dioxide forms a solution of nitric acid.
    - i** Draw the electron dot diagram of nitric acid.
    - ii** Nitric acid forms the nitrate ion in water. Draw the electron dot diagram of the nitrate ion.

**iii** Explain why nitrogen in the form of the nitrate ion is more readily taken into plants than atmospheric nitrogen.

- b** The commercial production of nitrogen-containing fertilisers begins with the reaction between atmospheric nitrogen and hydrogen to produce ammonia, NH<sub>3</sub>.
  - i** Write a balanced equation for this reaction.
  - ii** Draw the electron dot diagram for the ammonia molecule.
  - iii** Describe the conditions that you would recommend for the fastest possible reaction between hydrogen and nitrogen.
  - iv** This reaction is exothermic. Draw a fully labelled energy profile diagram for the reaction.

- 3 a** Using the work in the previous chapters as a guide, what single classification can be given to the two reactants and two products involved in the photosynthesis reaction?
  - b** Write a balanced equation for photosynthesis.
  - c** The four substances involved in this reaction can be further subdivided into two groups. What is the name given to each of these groups?
  - d** Would you expect the photosynthesis reaction to be exothermic or endothermic? Explain your answer and draw a labelled energy profile diagram for the reaction.
- 4 a** A soluble fertiliser is required to provide all the macronutrients for plant growth. Which of the following combinations would produce a soluble fertiliser? Justify your answer and explain why you rejected the others.
  - i** calcium nitrate and potassium phosphate
  - ii** sodium phosphate and potassium nitrate
  - iii** ammonium phosphate and potassium chloride
  - iv** potassium phosphate and sodium carbonate
  - v** zinc phosphate and potassium nitrate.
- b** The amount of nitrogen, phosphorus and potassium in a brand of fertiliser is often expressed as an NPK ratio, where the numbers in the ratio are the percentage, by mass, of each of the elements in the mixture. Thus a fertiliser with an NPK ratio of 19:4:3 has 19% nitrogen by mass together with 4% of phosphorus and 3% of potassium by mass. For each of the fertiliser mixtures you have chosen as possible combinations in part **a**, determine the NPK ratio if equal masses of the individual salts were chosen for the mixture.

### Context 3: Bread baking, self-raising flour and popcorn

The baking of bread or a cake and the popping of popcorn in a microwave oven all have one thing in common: the material at the end seems to take up more space than at the beginning.

The chemistry and physics of bread baking is still being argued, though there are some aspects that are generally agreed. Flour, water, yeast and a small amount of salt are mixed to make bread. The mixture is repeatedly folded, rolled and pulled in a process called 'kneading' until it has gained a semi-gelatinous state known as dough.

Biological catalysts called enzymes in the yeast break down the starch in the flour to glucose,  $C_6H_{12}O_6$ , and then other yeast enzymes catalyse the breakdown of glucose into ethanol,  $C_2H_5OH$ , and carbon dioxide. These reactions are taking place during the kneading process, as are other reactions involving the flour and water that cause some of the protein in the flour to form an elastic substance called gluten. This gluten stretches and traps some of the carbon dioxide produced in the bread in the form of gas bubbles. The other flavours and the aroma of fresh bread arise from other reactions between the enzymes in yeast and the complex mixture of chemicals present in flour.

During the baking process the carbon dioxide trapped in the elastic gluten pores expands and produces the characteristic holes that are found inside bread. One explanation for this suggests that the tough, elastic gluten behaves like small balloons filled with a gas that expands when heated. Another explanation proposes that the gluten does not physically hold back the trapped carbon dioxide, but that the moist region around the trapped carbon dioxide bubble is already saturated with dissolved carbon dioxide and the gas molecules are therefore unable to pass through the dough and out of the bread by simple diffusion.

Leavening is the name given to any method in which carbon dioxide is added to a flour/water mixture. In bread the leavening agent is biological, but in cakes the agent is chemical. Sometimes, recipes call for the addition of baking soda to the cake mixture. Baking soda is sodium hydrogencarbonate,  $NaHCO_3$ , which decomposes to sodium carbonate, carbon dioxide and water when heated to around  $50^\circ C$ .

Self-raising flour usually contains baking powder. This is a mixture of baking soda and one or more acids. As a mixture of solids, the basic sodium hydrogencarbonate and acids do not react. In the presence of added water, however, the acid combines with the sodium

hydrogencarbonate to produce carbon dioxide gas. Baking powder can be either single acting, containing only one acidic substance, or double acting, with two acids present. The acidic substance present in the single-acting baking powder is often a salt such as calcium dihydrogenphosphate,  $Ca(H_2PO_4)_2$ , which combines with the sodium hydrogencarbonate at low temperature, in the presence of water, to produce carbon dioxide. The carbon dioxide produced in this reaction causes the dough mixture to start rising as the ingredients are added. The double-acting baking powder also contains an acid that works at higher temperatures to produce more carbon dioxide during the cooking process.

In the commercial manufacture of biscuits and cookies, the leavening agent is often ammonium hydrogencarbonate,  $NH_4HCO_3$ , which decomposes when heated to  $60^\circ C$ . Again, one of the products of the decomposition is carbon dioxide, which contributes to the rising of the biscuit dough during cooking.

Popcorn is a cereal grain, like wheat, comprising starch, protein, fat, minerals and water. These ingredients are held within a tough casing called a pericarp. In popcorn this pericarp is particularly tough and when the grain is heated, or placed in a microwave oven, the water inside the casing turns to steam and the pressure builds up high enough to cause the casing to explode. During the explosion the starch and protein inside the grain expand and fold outward to produce the white solid of popped corn.

Recent research into the reason why some popcorn does not 'pop' has revealed that the failures are due to defects in the pericarp, allowing the water vapour to vent from inside the grain before the pressure builds up sufficiently for the violent popping reaction. The corn is more likely to pop where the grain produces a pericarp that has a highly ordered crystalline arrangement of the cellulose molecules. Further work is now underway to breed those popcorn grains that have the ideal arrangement of cellulose in the casing.

- 1 a** Bread dough rises without the bread being heated. Explain this observation in terms of the kinetic molecular theory.
- b** Use the kinetic molecular theory to explain the popping of popcorn.
  
- 2 a** Write the equation for the conversion of glucose into ethanol and carbon dioxide during the kneading of bread dough.
- b** Draw an electron dot diagram of the ethanol molecule.

- c Ethanol is produced in the fermentation of beer and wine. From your knowledge of the properties of substances like ethanol, explain why it is that it is not possible to become intoxicated by eating baked bread.
- d One suggestion for the rising of bread dough was based on gas being trapped inside a thin protein membrane. The other suggestion proposed that the carbon dioxide gas simply could not move out of the bubble in which it was trapped. Explain, in terms of the behaviour of matter studied in earlier chapters, why each of these suggestions might lead to the formation of larger bubbles of trapped gas in the bread dough.
- 3 a** Write the equation for the thermal decomposition of sodium hydrogencarbonate.
- b** A particular recipe calls for the addition of 2.0 g of baking soda to a particular cake recipe. What mass of carbon dioxide would be produced if the decomposition of the baking soda was complete?
- c** At the temperature of the cooking process 10.0 g of carbon dioxide occupies a volume of around 6.5 litres. What would be the approximate volume of the carbon dioxide produced in the reaction in **b**?
- d** What is the nature of the bonding present in baking soda?
- e** Why is it that the action of baking powder begins only when water is present in a mixture being prepared for baking a cake?
- 4 a** Write an equation for the decomposition of ammonium hydrogencarbonate. What is an advantage of this reaction?
- b** Draw the electron dot diagram of ammonium hydrogencarbonate.
- c** When ammonium hydrogencarbonate is used as a leavening agent for baking a cake there is an unpleasant taste and smell associated with the cake. Why might this not be the case when it is used as the leavening agent in baking biscuits?
- 5** The best popcorn is claimed to have a pericarp made up of ‘highly ordered crystalline arrangements of cellulose’. Explain why such an arrangement might contribute to the superiority of this popcorn.

#### Context 4: Aspects of swimming pool chemistry

The presence of calcium ions in swimming pools can create problems. Calcium hardness in the pool water is a measure of the amount of dissolved calcium ions in a certain volume of the water. In concrete pools low calcium hardness results in calcium ions being removed from the pool walls, causing the wall to form small holes or pits in which algal growth can take place. If the calcium hardness is high then it is possible that scale will form on the pool surrounds and the water will become cloudy. Where tiles are used on the swimming pool walls, the grout that is used contains a mixture of calcium silicate and calcium sulfate.

Chlorination of household swimming pools may involve adding ‘liquid chlorine’, which is actually a 10–15% solution of sodium hypochlorite,  $\text{NaOCl}$ . Alternatively, granulated calcium hypochlorite can be added as ‘solid chlorine’. More recently, lithium hypochlorite has been introduced as a preferred chlorinating agent in hot tubs or spas.

‘Stabilised chlorine’ tablets contain the chlorine in a form that is released slowly and does not undergo photolysis as readily as the chlorinating agents that produce the hypochlorite ion,  $\text{OCl}^-$ , directly. In the photolysis reaction the hypochlorite ion is converted to chloride and oxygen gas in the presence of ultraviolet radiation in sunlight.

When chlorine gas,  $\text{Cl}_2$ , is dissolved in water only one of the chlorine atoms in the original molecule is converted to the hypochlorite ion (the reaction of chlorine with water produces a 1:1 mole mixture of hydrogen chloride and hypochlorous acid). The hypochlorite ion (or better, hypochlorous acid) attacks the cell walls of micro organisms and bacteria, destroying the enzymes inside the cell that are responsible for various key metabolic reactions. In normal swimming pool operation it is also important to maintain the concentration of hydrogen ions ( $\text{H}^+(\text{aq})$ ) at a sufficiently high level to form enough hypochlorous acid to ensure the destruction of harmful micro organisms.

One commercial form of ‘stabilised chlorine’ is known as trichloro-s-triazinetrione and is claimed to have 90% available chlorine. The percentage of available chlorine in a pool chlorinating agent is based on a value of 100 for chlorine gas,  $\text{Cl}_2$ , even though it is only one of the chlorine atoms that becomes active in killing the micro organisms. To determine the percentage of available chlorine in a pool chemical it is necessary to know the formula of the compound, as the value is determined using the relationship

$$\% \text{ available chlorine in agent} = 2 \times \frac{\text{mass of chlorine atoms as } \text{OCl}^- \text{ in 1 mol of agent}}{\text{molar mass of agent}} \times 100.$$

The factor of 2 in the equation above is based on the fact that  $\text{Cl}_2$  is defined as 100% available chlorine. However, only one mole of  $\text{HOCl}$  is produced when one mole of chlorine gas is dissolved in water. Hence the value for the expression

$$\frac{\text{mass of chlorine atoms as } \text{OCl}^- \text{ in 1 mol of agent}}{\text{molar mass of agent}}$$

$$= \frac{35.45}{70.90} \times 100 = 50 \text{ for } \text{Cl}_2.$$

To give the defined value of 100, the factor of 2 must be included in the calculation.

As a result of this definition, values in excess of 100% available chlorine are possible.

Using the information, answer the following questions.

**1** Draw electron dot diagrams for

- a Chlorine gas
- b Hypochlorous acid,  $\text{HOCl}$
- c Calcium hypochlorite.

- 2** a Assuming that calcium sulfate is one of the materials in the grout used on swimming pool tiles, write the equation for the dissolving process of calcium sulfate in water.
- b If it is possible for chemical reactions to go forward and backward, explain why adding more calcium ions to a swimming pool might prevent the formation of the small holes or pits in the surface of the grout.
- c A neighbour with a fibreglass swimming pool has read an article about the need to maintain a calcium balance in swimming pools to prevent the walls from being eaten away and asks you whether he needs to check on the amount of calcium ion in his pool. What advice do you provide? Explain the chemistry behind this advice.
- d High levels of calcium hardness can produce cloudy swimming pool water. When carbon dioxide dissolves in water, it forms carbonic acid,  $\text{H}_2\text{CO}_3$ . Use this information to suggest what is happening to produce the cloudiness.

**3** Under normal circumstances ‘solid chlorine’ is added in the form of tablets of compressed chlorinating agent. However, the build up of organic matter in the pool over time requires the addition of large amounts of chlorine that need to be readily available to react with the organic matter. This is known as shock treatment.

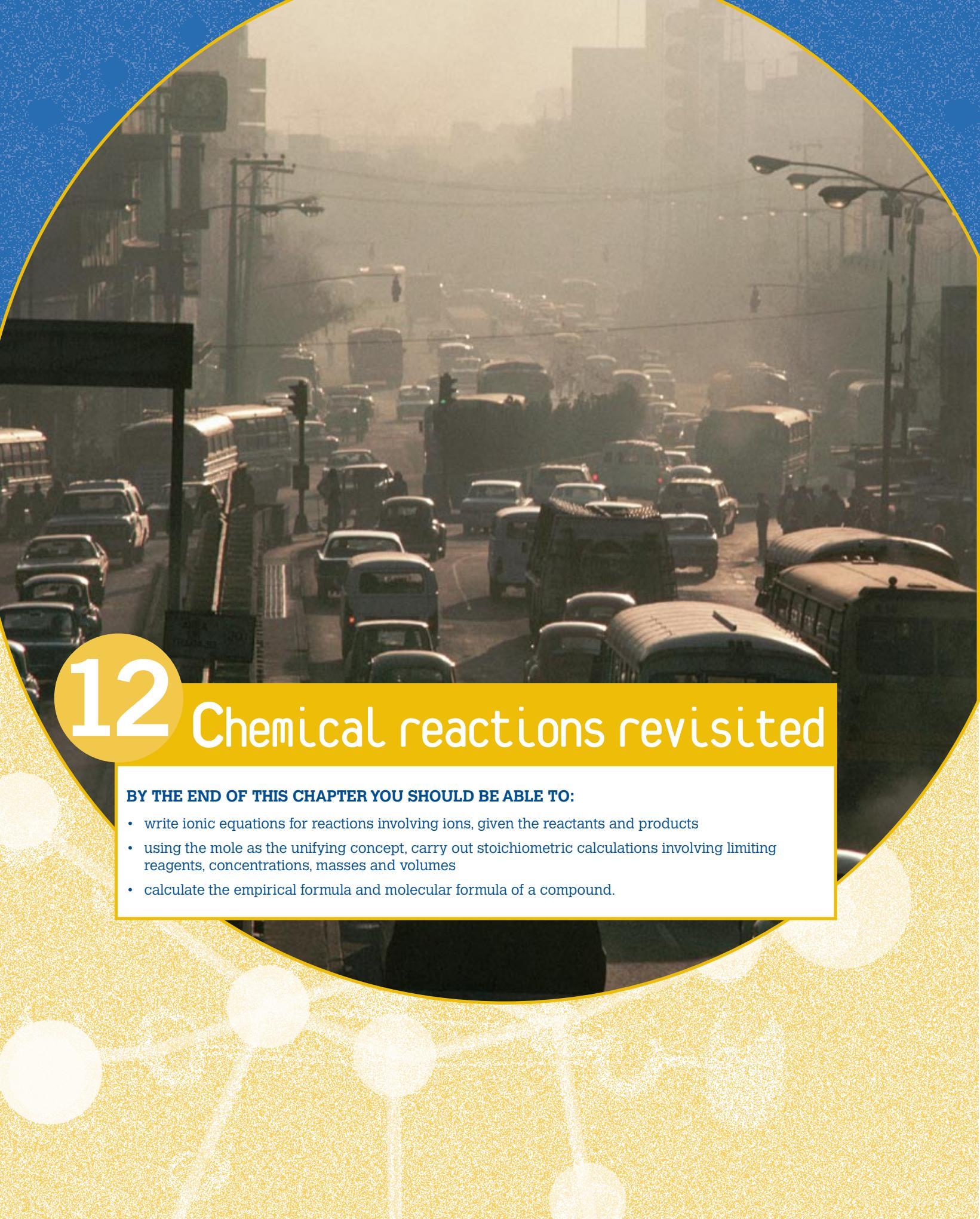
- a What is the advantage of using compressed tablets of solid ‘chlorine’ for normal operation of a swimming pool?
  - b In what form would you supply the chlorine for shock treating a swimming pool? Explain.
- 4** a Write an equation for the decomposition of hypochlorite ion under the influence of ultraviolet light.
- b Is this reaction exothermic or endothermic? Explain how you arrived at this answer.
- c Draw an energy profile diagram for this photolysis reaction.
- 5** a Household bleach is a solution of sodium hypochlorite in water. The bleach is sold as a 5% solution by mass. Determine the % available chlorine in household bleach.
- b Commercial solid chlorine tablets are generally 70% by mass of calcium hypochlorite. Determine the % available chlorine in a tablet of solid pool chlorine.

# 12

# Chemical reactions revisited

**BY THE END OF THIS CHAPTER YOU SHOULD BE ABLE TO:**

- write ionic equations for reactions involving ions, given the reactants and products
- using the mole as the unifying concept, carry out stoichiometric calculations involving limiting reagents, concentrations, masses and volumes
- calculate the empirical formula and molecular formula of a compound.



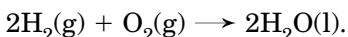
*"What in the world isn't chemistry?"*

car bumper sticker

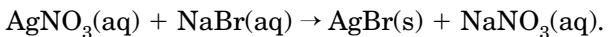
Chemistry is the science of the materials in our natural and built environment. Consequently, chemistry is pivotal to the development, sustainable use and appropriate management of our built and natural world. Whether it be issues associated with health, nutrition, agricultural development, mineral resources, manufacturing industries, energy production, or local and global environment, chemists today are working to develop and broaden our understanding of these and other areas through research on the structure, and physical and chemical properties of matter.

## 12.1 Writing ionic equations

A balanced chemical equation is used by chemists to summarise key information about a chemical reaction. It shows the composition of the reacting substances and the products they form, as well as the relative amounts of these substances involved in the reaction. The use of molecular equations to represent chemical reactions was explained in Chapter 9. In a molecular equation, the substances present in the reaction mixture are shown as neutral formulas. For example, the molecular or overall equation for the reaction of hydrogen with oxygen to form water is



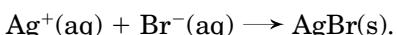
However, for reactions involving ions, a molecular equation can be misleading because often it appears that some substances are products of the reaction, when in reality these substances remain unchanged during the reaction. For example, the molecular (or overall) equation for the precipitation reaction that occurs between solutions of silver nitrate and sodium bromide is



From this equation it seems that two products form, silver bromide and sodium nitrate. The sodium nitrate is present at the completion of the reaction as sodium ions and nitrate ions dissolved in the solution. Before the reaction, these two ions were also dissolved in a solution. That is, the dissolved sodium and nitrate ions have remained unchanged during the reaction, and so sodium nitrate is not an actual product. The solid silver bromide is, however, a 'true' product because it was not present before the reaction. The silver ions and bromide ions originally dissolved in the solution have reacted to form the solid silver bromide.

A more accurate way of representing reactions such as the one just described, would be to use an ionic equation. An **ionic equation** shows only the atoms, molecules and ions undergoing a chemical change during the reaction. The ions that take no part in the chemical reaction, although they are present in the reaction mixture, are not shown in an ionic equation. These ions are called **spectator ions**.

The ionic equation for the precipitation reaction that occurs between the solutions of silver nitrate and sodium bromide is



The sodium and nitrate ions act as spectator ions.

Ionic equations are also used for a much broader range of reactions than just the formation of precipitates, although they are predominantly used for reactions that take place in water. Writing ionic equations for this wider array of reactions



**Figure 12.1** Silver bromide formed from the reaction of solutions of silver nitrate and sodium bromide.

requires knowledge of how substances exist in water. This is because in an ionic equation the formulas of the substances are written so that they best represent how the substances actually exist in the aqueous reaction mixture.

As described previously in Chapter 8, for substances that dissolve in water three classifications are possible:

- **Strong electrolytes:** substances that exist completely as ions in solution. Ionic compounds and the covalent molecular compounds that are strong acids ( $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$ ) are regarded as strong electrolytes.
- **Weak electrolytes:** substances that only partially ionise in solution. Only a small proportion of the molecules in the dissolved sample undergo ionisation. Examples of weak electrolytes include the covalent molecular substances that act as weak acids and bases, such as acetic acid,  $\text{CH}_3\text{COOH}$ , and ammonia,  $\text{NH}_3$ .
- **Non-electrolytes:** substances that dissolve in water but do not produce ions. These include a range of covalent molecular substances such as glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , and ethanol,  $\text{C}_2\text{H}_5\text{OH}$ .

The following set of ‘rules’ can be applied when writing ionic equations:

- Solutions of strong electrolytes are written as dissolved or ‘separated’ ions, for example, a solution of  $\text{NaCl}$  is written as  $\text{Na}^+(\text{aq})$  and  $\text{Cl}^-(\text{aq})$ ; dilute  $\text{HNO}_3$  is written as  $\text{H}^+(\text{aq})$  and  $\text{NO}_3^-(\text{aq})$ .
- Weak electrolytes in solution are written in the neutral molecular form, for example,  $\text{CH}_3\text{COOH}(\text{aq})$  and  $\text{NH}_3(\text{aq})$ .
- Non-electrolytes in solution are written in the neutral molecular form, for example,  $\text{C}_6\text{H}_{12}\text{O}_6(\text{aq})$  and  $\text{CH}_3\text{CH}_2\text{OH}(\text{aq})$ .
- Insoluble or solid substances are written as the full or neutral formula, for example,  $\text{CaCO}_3(\text{s})$  and  $\text{AgCl}(\text{s})$ .
- Gases are written in the neutral molecular form, for example,  $\text{NH}_3(\text{g})$  and  $\text{H}_2(\text{g})$ .
- Metals are written as their neutral formula, for example,  $\text{Fe}(\text{s})$  and  $\text{Cu}(\text{s})$ .
- Spectator ions (ions that remain unchanged in solution throughout the reaction) are not included in an ionic equation.
- Equations must be balanced in atoms and electric charge.

How the formulas of some common substances are shown in ionic equations is summarised in Table 12.1.

**TABLE 12.1 SUMMARY OF CHEMICAL FORMULAS USED WHEN WRITING IONIC EQUATIONS FOR REACTIONS IN AQUEOUS SOLUTIONS.**

Written as ‘separated’ ions	<ul style="list-style-type: none"><li>• solutions of ionic compounds: e.g. potassium nitrate solution, <math>\text{K}^+(\text{aq}) + \text{NO}_3^-(\text{aq})</math></li><li>• solutions of strong acids: hydrochloric acid (<math>\text{HCl}</math>), <math>\text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})</math> nitric acid (<math>\text{HNO}_3</math>), <math>\text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq})</math> sulfuric acid (<math>\text{H}_2\text{SO}_4</math>), <math>\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})</math> (or <math>\text{HSO}_4^- (\text{aq})</math>)</li></ul>
Written as neutral formulas	<ul style="list-style-type: none"><li>• insoluble ionic compounds: e.g. silver chloride, <math>\text{AgCl}(\text{s})</math></li><li>• solid ionic compounds: e.g. solid sodium carbonate, <math>\text{Na}_2\text{CO}_3(\text{s})</math></li><li>• metals: e.g. zinc, <math>\text{Zn}(\text{s})</math>; magnesium, <math>\text{Mg}(\text{s})</math></li><li>• water: <math>\text{H}_2\text{O}(\text{l})</math></li><li>• gases: e.g. carbon dioxide, <math>\text{CO}_2(\text{g})</math>; hydrogen, <math>\text{H}_2(\text{g})</math>; oxygen, <math>\text{O}_2(\text{g})</math>; hydrogen sulphide, <math>\text{H}_2\text{S}(\text{g})</math>; sulfur dioxide, <math>\text{SO}_2(\text{g})</math></li><li>• solutions of molecular weak acids: e.g. acetic acid, <math>\text{CH}_3\text{COOH}(\text{aq})</math></li><li>• solutions of molecular weak bases: e.g. ammonia, <math>\text{NH}_3(\text{aq})</math></li></ul>

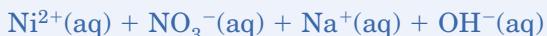
### → Example 12.1

Write the ionic equation for the reaction that takes place when a nickel nitrate solution and a sodium hydroxide solution are mixed.

#### → Solution

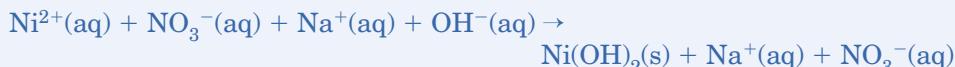
**Step 1:** Write the formulas of the reactants in their ‘correct form’:

Since both ionic compounds are present as solutions, the formulas should be written as separated ions, that is



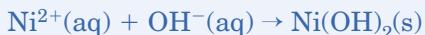
**Step 2:** Determine the products and write their formulas in the ‘correct form’:

This is a precipitation reaction. The two possible products are nickel hydroxide and sodium nitrate. Nickel hydroxide is insoluble in water (according to the solubility table given on page 178), and so will form as a precipitate (a solid), but sodium nitrate is soluble in water, so the sodium ions and nitrate ions will remain in solution. The nickel hydroxide is a solid and it is written as the neutral formula, but the sodium ions and nitrate ions are written as ‘separated’ ions:



**Step 3:** Cancel out any spectator ions (unchanged ions) in the equation:

The sodium ions and nitrate ions remain dissolved in the aqueous solution during the reaction so they are spectator ions (that is, their formulas are identical on both sides of the equation). The equation (unbalanced) becomes:



**Step 4:** Balance the equation in atoms and charge:



### → Example 12.2

Write the ionic equation for the reaction of solid sodium carbonate with dilute hydrochloric acid. The products formed in this reaction are carbon dioxide, water and a solution of sodium chloride.

#### → Solution

**Step 1:** Write the formulas of the reactants in their ‘correct form’:

Sodium carbonate is added as a solid so its ‘full’ neutral formula will be written. Hydrochloric acid is a strong electrolyte (a strong acid), consisting of  $\text{H}^+(\text{aq})$  and  $\text{Cl}^-(\text{aq})$ .



**Step 2:** Determine the products and write their formulas in the ‘correct form’:

The products have been given in the question. Carbon dioxide and water are both written as neutral formulas, and the solution of sodium chloride is written as individual ions:



**Step 3:** Cancel out any spectator ions:

The chloride ions remain unchanged during the reaction; they are the spectator ions. The unbalanced ionic equation is therefore:



**Step 4:** Balance the equation in atoms and charge:



**Figure 12.2** Reaction of nickel nitrate solution with sodium hydroxide solution.



Figure 12.3 Magnesium reacting with acetic acid.

→ Example 12.3

Write the ionic equation for the reaction of acetic acid with magnesium. The products in this reaction are hydrogen gas and a solution of magnesium acetate.

→ Solution

**Step 1:** Reactants:

acetic acid—a weak acid, written as a neutral formula,  $\text{CH}_3\text{COOH}(\text{aq})$   
magnesium—a metal, written as a neutral formula,  $\text{Mg}(\text{s})$



**Step 2:** Products:

hydrogen—written as a neutral formula,  $\text{H}_2(\text{g})$

solution of magnesium acetate—written as individual ions,



**Step 3:** Cancel spectator ions: there are no spectator ions.

**Step 4:** Balance equation in charge and atoms:

Ionic equation:



### Describing observations for reactions

Sometimes in assessments, the question asks for the observations for a particular reaction to be given. To answer this type of question, first the ionic equation should be written and then any changes that occur during the reaction should be described. In this description, the reactants and products are not identified by their chemical names, instead mention of their relevant properties is made. Where appropriate, some of the observations that could be described are:

- the colour and odour of any gas produced
- the change in colour of the reaction solution
- the colour of an insoluble substance produced
- the disappearance or appearance of a smell during the reaction
- whether or not a solid dissolves or is produced during the reaction
- the change in appearance of the reactants
- an increase or decrease in temperature during the reaction.

The colours of some ions in solution were given in Table 9.2. It is inferred that solids containing these ions will be of the same colour as that given in this table. The colours and distinctive odours of some additional substances (not including ionic substances) often involved in reactions in solutions are given in Table 12.2.

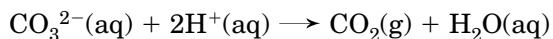
**TABLE 12.2 COLOURS AND DISTINCTIVE ODOURS OF SOME SUBSTANCES (NOT INCLUDING IONIC SUBSTANCES) INVOLVED IN REACTIONS IN SOLUTIONS.**

	Names of substance	Formula (as shown in an ionic equation)	Description
Gases	ammonia	$\text{NH}_3(\text{g})$ or (aq)	colourless gas with pungent odour, colourless as a solution
	carbon dioxide	$\text{CO}_2(\text{g})$	colourless, odourless gas
	chlorine	$\text{Cl}_2(\text{g})$	yellow gas with choking odour
	hydrogen	$\text{H}_2(\text{g})$	colourless, odourless gas
	hydrogen chloride	$\text{HCl}(\text{g})$	colourless gas with choking odour
	hydrogen sulfide	$\text{H}_2\text{S}(\text{g})$	colourless gas with rotten-egg odour
	nitrogen	$\text{N}_2(\text{g})$	colourless, odourless gas
	nitrogen dioxide	$\text{NO}_2(\text{g})$	brown gas with pungent odour
	oxygen	$\text{O}_2(\text{g})$	colourless, odourless gas
	sulfur dioxide	$\text{SO}_2(\text{g})$	colourless gas with pungent odour
Liquids	acetic acid	$\text{CH}_3\text{COOH}(\text{l})$ or (aq)	colourless liquid, colourless solution, vinegar odour
	bromine	$\text{Br}_2(\text{l})$ or (aq)	dark red liquid, orange solution
	ethanol	$\text{C}_2\text{H}_5\text{OH}(\text{l})$	colourless liquid, sweet odour
Solids	iodine	$\text{I}_2(\text{s})$	dark-coloured solid
	sulfur	$\text{S}(\text{s})$ or $\text{S}_8(\text{s})$	yellow solid
	copper	$\text{Cu}(\text{s})$	shiny, orange solid
	gold	$\text{Au}(\text{s})$	shiny, yellow solid
	other metals	e.g. $\text{Mg}(\text{s})$ , $\text{Zn}(\text{s})$	grey solids (perhaps shiny)
Aqueous solutions	hydrochloric acid	$\text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$	colourless liquid
	nitric acid	$\text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$	colourless liquid
	phosphoric acid	$\text{H}_3\text{PO}_4(\text{aq})$	colourless liquid
	sulfuric acid	$2\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$	colourless liquid



**Figure 12.4 Chlorine, bromine and iodine. (Bromine has a low boiling point, so it appears mostly as a gas in this photo.)**

For reactions in aqueous solutions, the formation of water is not referred to in the observations. In most reactions, only a very small amount of water will be formed, compared to the volume of water already present in the aqueous solutions. As a result, no observable change will actually occur during the reaction due to the formation of the water. For example, for the reaction between the solutions of sodium carbonate and hydrochloric acid:

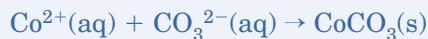


a satisfactory observation would be ‘a colourless odourless gas forms’. That is, no comment is made about the fact that a colourless liquid (water) forms. If a little more detail is required in the observation, then a comment like ‘the reaction mixture remains as a colourless solution’ could be added to the description of the formation of the gas.

#### → Example 12.4

Give the observations for the following reactions:

- a When solutions of cobalt nitrate and sodium carbonate are mixed the following reaction occurs:



- b The following reaction occurs when concentrated nitric acid is poured onto small pieces of copper:



- c If a warm solution of hydrochloric acid is added to zinc, the following reaction occurs:



- d When an excess of sodium hydroxide is added to some acetic acid, the equation that describes the reaction is:



#### → Solution

For some of these answers, an explanation has been given, as well as the observation. However, an explanation **should not** be given as part of the answer to an observation question in an assessment (unless the question asks for an explanation).

- a Cobalt ions are pink in colour, and carbonate ions are colourless, so cobalt carbonate will be a pink solid.

**Observation:** The pink and the colourless solutions mix to form a pink precipitate (or solid).

- b As the copper metal reacts, it would change from a solid to an ion dissolved in the solution. This is normally expressed in an observation as ‘the orange solid dissolved to form ...’

**Observation:** The shiny orange solid dissolves in the colourless liquid to form a brown gas with a pungent odour, and a blue solution.

- c **Observation:** The grey solid dissolves in the colourless liquid to form a colourless, odourless gas and a colourless solution remains.

- d Acetic acid has an odour, but the acetate ions,  $\text{CH}_3\text{COO}^-$ , do not.

**Observation:** When the two colourless solutions are mixed, the vinegar smell disappears and a colourless solution remains.



Figure 12.5 The reaction of copper with concentrated nitric acid.

## \* Review exercise 12.1

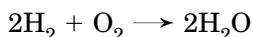
- 1 Write ionic equations for the following reactions. Also, give observations for each. You may need to revise the prediction of products in a precipitation reaction (see Section 9.4) for several of these reactions.
- A solution of chromium chloride is mixed with a solution of potassium phosphate.
  - When dilute nitric acid is added to a solution of sodium hydrogencarbonate, the products formed are carbon dioxide, water and a solution of sodium nitrate.
  - Solutions of potassium hydroxide and copper nitrate are mixed.
  - Lead nitrate solution is added to hydrochloric acid solution.
  - Limewater is used to test for carbon dioxide. In this test, carbon dioxide is bubbled through a solution of calcium hydroxide (limewater) to form calcium carbonate and water.
  - Silver and a solution of copper nitrate are formed when a solution of silver nitrate is added to copper.
  - A vigorous reaction occurs if some potassium is added to water. The products formed are hydrogen and a solution of potassium hydroxide.



Figure 12.6 The reaction between a few drops of water and a lump of potassium.

## 12.2 Limiting reagents

For a reaction, it is possible to calculate the amounts of reactants consumed and products formed from the balanced chemical equation. As explained in Chapter 9, the coefficients in a balanced chemical equation show the relative amounts, in mole, of reactants and products involved in the particular reaction. For example, the equation for the reaction between hydrogen and oxygen to form water:

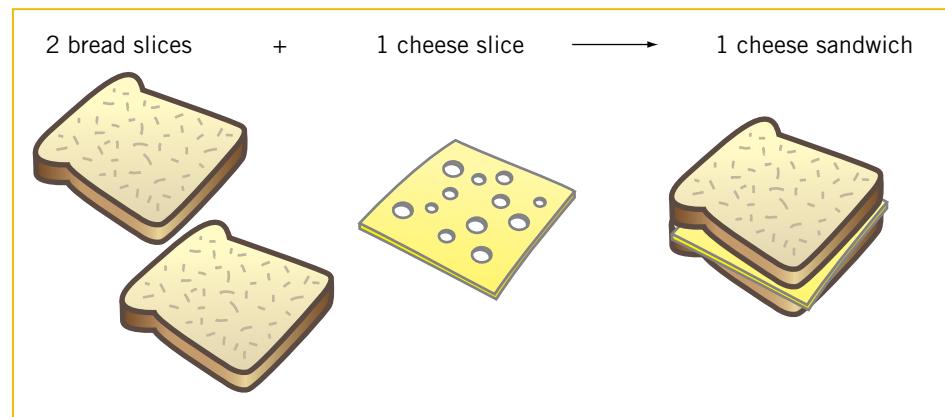


shows that for every 2 mole of hydrogen, 1 mole of oxygen will be required to react with it, and 2 mole of water will be produced. These relative amounts or mole ratio of the reactants and products shown in the balanced equation are often called the stoichiometric ratio or stoichiometric amounts of substances involved in the reaction.

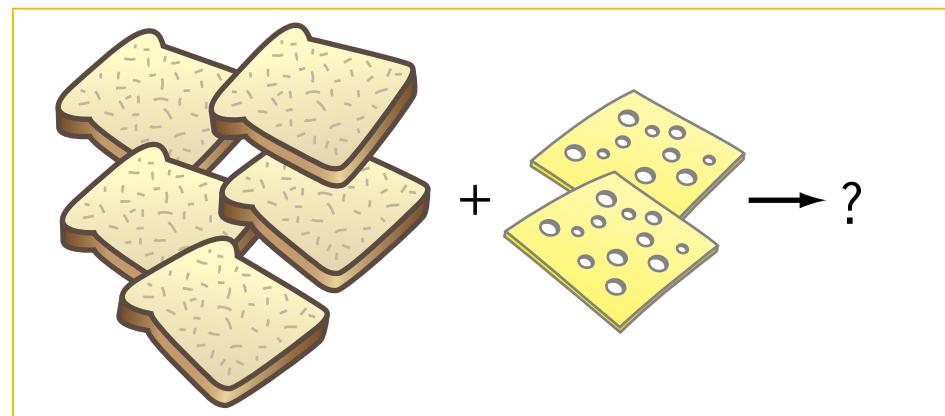
In many reactions, the reactants are not mixed together in the exact mole ratio, or stoichiometric amounts, shown in the balanced equation. For instance, if 2 mole of hydrogen and 4 mole of oxygen are mixed together for the production of water, the two reactants are not present in the stoichiometric ratio (2:1) given in the equation. In this example, the 2 mole of hydrogen will only react with 1 mole of oxygen. That is, too much oxygen is present and  $4 - 1 = 3$  mole of it will remain at the completion of the reaction. When two reactants are present in non-stoichiometric quantities, one substance is said to be in excess, and the other is called the limiting reagent. In the reaction just described, the oxygen is the excess reagent and the hydrogen is the limiting reagent.



To clarify the understanding of excess and limiting reagents, it may be useful to introduce a familiar analogy — making cheese sandwiches. Each cheese sandwich is made by putting 1 slice of cheese between 2 slices of bread. That is,

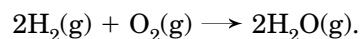


Suppose 5 slices of bread and 2 slices of cheese are available for making the sandwiches. How many cheese sandwiches can be made?



The answer is fairly obvious—two sandwiches can be made and there will be one slice of bread left over. In this problem, the bread is said to be in excess, that is, it is the excess ‘reagent’. The cheese slices limit the number of sandwiches that can be made, so the cheese slices are the limiting ‘reagent’.

The same idea explained in the cheese sandwich example applies to chemical reactions. For a problem such as ‘How many mole of water can be formed from a mixture of 4 mole of hydrogen and 3 mole of oxygen?’, the reactant that will not be completely consumed or used up during the reaction is called the **excess reagent** and the reactant that will be completely consumed is the **limiting reagent**. The amount of product formed in such a problem is determined by the amount of limiting reagent present in the reaction mixture, not the amount of excess reactant. To illustrate this concept further, some examples of the number of water molecules formed from varying reaction mixtures of hydrogen and oxygen molecules are shown in Figure 12.7. These hydrogen and oxygen molecules react according to the equation



During this reaction, every 2 hydrogen molecules will react with 1 oxygen molecule. That is, they will react in a 2:1 ratio.

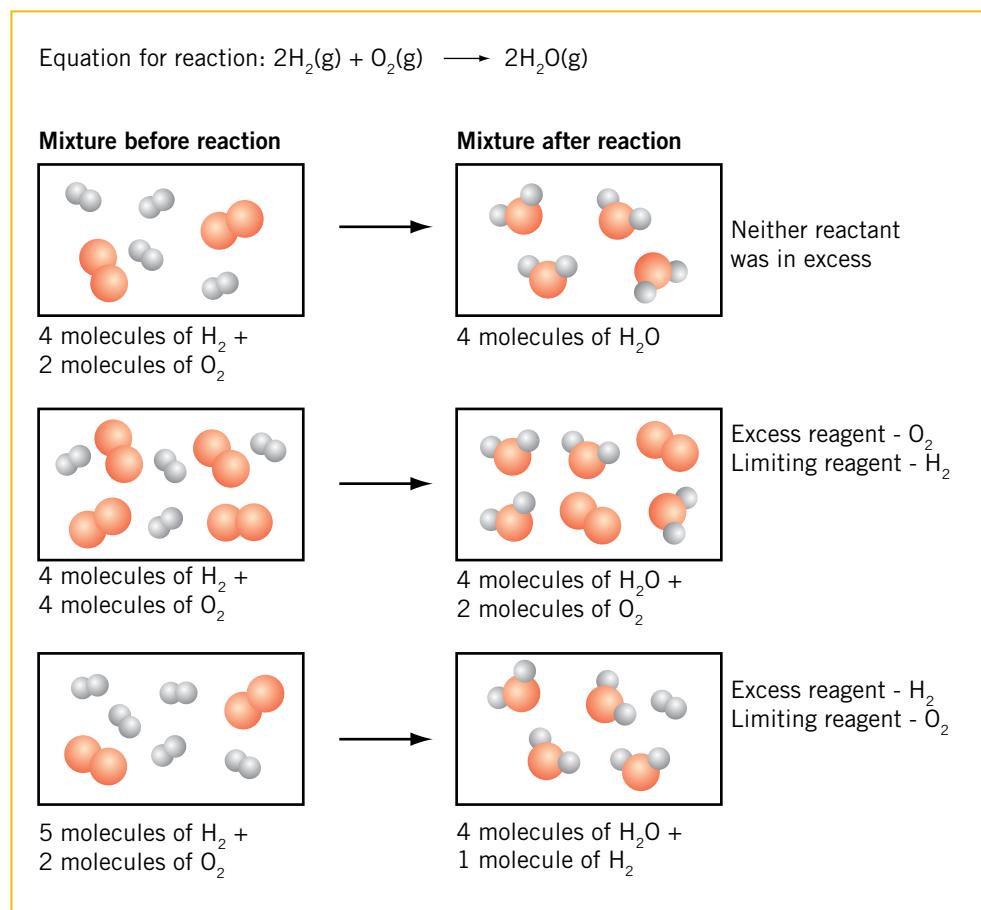
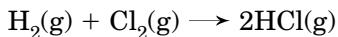


Figure 12.7 Limiting reagent examples for the reaction  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$ .

In limiting reagent problems, the quantities of at least two reactants are given, so the first step is to determine which reactant is the limiting reagent. To determine the amount of product formed, the calculation is then carried out using the amount of limiting reagent in a similar way to the stoichiometric problems described in Chapter 9.

Table 12.3 shows examples in which different amounts, in mole, of hydrogen and chlorine are reacted to form hydrogen chloride, according to the equation



The amount, in mole, of HCl formed and of the excess reagent left over after the reaction, are calculated as follows:

- the amount of HCl formed is calculated from the amount of limiting reagent present in the reaction mixture.
- the amount of excess reagent remaining after the reaction is calculated by subtracting the amount of this reactant that reacts from the original amount of it present, that is, (original amount present – amount reacted).

**TABLE 12.3 LIMITING AND EXCESS REAGENTS IN THE REACTION OF H<sub>2</sub> WITH Cl<sub>2</sub> ACCORDING TO THE EQUATION H<sub>2</sub>(g) + Cl<sub>2</sub>(g) → 2HCl(g)**

Mole of H <sub>2</sub>	Mole of Cl <sub>2</sub>	Limiting reagent	Excess reagent	Mole of HCl produced	Mole of excess reagent remaining after reaction
1.0	1.0	—	—	2 × 1.0 = 2.0	—
1.0	2.0	H <sub>2</sub>	Cl <sub>2</sub>	2 × 1.0 = 2.0	Cl <sub>2</sub> : 2.0 – 1.0 = 1.0
3.0	1.0	Cl <sub>2</sub>	H <sub>2</sub>	2 × 1.0 = 2.0	H <sub>2</sub> : 3.0 – 1.0 = 2.0
4.0	7.0	H <sub>2</sub>	Cl <sub>2</sub>	2 × 4.0 = 8.0	Cl <sub>2</sub> : 7.0 – 4.0 = 3.0
6.0	3.0	Cl <sub>2</sub>	H <sub>2</sub>	2 × 3.0 = 6.0	H <sub>2</sub> : 6.0 – 3.0 = 3.0

In the examples above, involving the reaction of hydrogen with chlorine, it was reasonably easy to determine which reactant was the limiting reagent because of the simple 1:1 stoichiometric ratio of the reactants. In many problems, however, it is not always obvious which one of the reactants is the limiting reagent. Several different methods can be used to determine the limiting reagent. These methods are explained in the solution to Example 12.5 below.

#### → Example 12.5

A mixture of 4 mole of hydrogen and 3 mole of oxygen react to form water, according to the equation:



Which of the two reactants is the limiting reagent in this reaction?

#### → Solution

##### Method 1

One method used to determine the limiting reagent involves choosing one of the reactants and calculating how much of the second reactant is required to react with it. This required amount is then compared with that actually present in the original mixture of reactants.

The first step in answering the example could therefore be to calculate the amount, in mole, of O<sub>2</sub> required to react with 4 mole of H<sub>2</sub>:

From the balanced equation 2 mole of H<sub>2</sub> will react with 1 mole of O<sub>2</sub>

or                    1 mole of H<sub>2</sub> will react with  $\frac{1}{2}$  mole of O<sub>2</sub>

so                    4 mole of H<sub>2</sub> will react with  $\frac{1}{2} \times 4 = 2$  mole of O<sub>2</sub>

However, the reaction mixture contains 3 mole of O<sub>2</sub>, that is, there is too much O<sub>2</sub> in the mixture to react with the 4 mole of H<sub>2</sub>. O<sub>2</sub> must therefore be in excess, and H<sub>2</sub> is the limiting reagent.

##### Method 2

A related method sometimes used to determine which reactant is the limiting reagent is to compare the mole ratio of the reactants given in the balanced equation (stoichiometric ratio) with the mole ratio of reactants actually present in the reaction mixture (actual ratio).

For the mixture of 4 mole of H<sub>2</sub> and 3 mole of O<sub>2</sub>, given in this example

- from the balanced equation: stoichiometric ratio =  $\frac{2 \text{ mol H}_2}{1 \text{ mol O}_2} = 2$
- from the actual amounts of reactants: actual ratio =  $\frac{4 \text{ mol H}_2}{3 \text{ mol O}_2} = 1.33$



Because the actual ratio is less than the stoichiometric ratio, the **H<sub>2</sub> is the limiting reagent** (the actual ratio is smaller than it should be because the bottom line of the fraction is too large, that is, there is too much O<sub>2</sub> to react with the H<sub>2</sub>, so O<sub>2</sub> is in excess and H<sub>2</sub> must be the limiting reagent).

If the actual ratio had been greater than 2, then H<sub>2</sub> would have been the excess reagent, and O<sub>2</sub> the limiting reagent.

### Method 3

A third method involves calculating the amount in mole of product formed from each reactant, assuming an excess of the other reactants. Whichever reactant ‘yields’ the smaller amount of product is the limiting reagent.

For the example:

4 mole of H<sub>2</sub> could produce 4 mole of H<sub>2</sub>O

or            3 mole of O<sub>2</sub> could produce  $2 \times 3 = 6$  mole of H<sub>2</sub>O

The H<sub>2</sub> produces the smaller amount of H<sub>2</sub>O, so it **must be the limiting reagent**.

#### → Example 12.6

If 4.18 mole of aluminium is burnt with 5.92 mole of chlorine to form aluminium chloride, which reactant is the limiting reagent?



#### → Solution

To solve this problem, the answer to the following question must be determined:

If 4.18 mole of Al reacts, how many mole of Cl<sub>2</sub> will react with it?

From the balanced equation    2 mole of Al will react with 3 mole of Cl<sub>2</sub>

or                          1 mole of Al will react with  $\frac{3}{2}$  mole of Cl<sub>2</sub>

so    4.18 mole of Al will react with  $\frac{3}{2} \times 4.18 = 6.27$  mole of Cl<sub>2</sub>

However, the mixture contains only 5.92 mole of Cl<sub>2</sub>, that is, there is not enough Cl<sub>2</sub> in the mixture to react with all the Al. So, not all the Al will be able to react, which means the Al must be in excess. Therefore, **Cl<sub>2</sub> is the limiting reagent**.

### Mass–mass limiting reagent problems

In many limiting reagent problems, the amount of each reactant is given as a mass not as mole, so the first step in these problems is to calculate the amount in mole of each reactant, from its mass and molar mass. The stoichiometric ratio expressed by the coefficients in a balanced equation is a mole ratio, not a mass ratio, and it can only be used in a calculation if the amount of reactant is also in mole. The major steps in mass–mass limiting reagent problems are therefore:

**Step 1**—write a balanced equation for the reaction

**Step 2**—calculate the mole of each reactant from its known mass (and molar mass), using the formula

$$\text{mole of substance} = \frac{\text{mass of substance}}{\text{molar mass of substance}} \quad \text{or } n = \frac{m}{M}$$

**Step 3**—calculate the limiting reagent, using the stoichiometric ratio shown in the balanced equation

**Step 4**—from the mole of limiting reagent, calculate the mole of product formed (using the stoichiometric ratio shown in the balanced equation)

**Step 5**—calculate the mass of product from the mole of product.

→ **Example 12.7**

Silicon carbide is an important ceramic material that is made by heating a mixture of sand (silicon dioxide) with powdered carbon at a very high temperature. Carbon monoxide is also formed.



Calculate the mass of carbon monoxide formed when 102 g of silicon dioxide is reacted with 98.3 g of carbon according to the above equation.

→ **Solution**

**Step 1:** The equation is  $\text{SiO}_2(\text{s}) + 3\text{C}(\text{s}) \rightarrow \text{SiC}(\text{s}) + 2\text{CO}(\text{g})$

**Step 2:**  $n(\text{SiO}_2) = \frac{m(\text{SiO}_2)}{M(\text{SiO}_2)}$   $M(\text{SiO}_2) = 28.09 + (2 \times 16.00) = 60.09 \text{ g mol}^{-1}$

$$n(\text{SiO}_2) = \frac{102}{60.09} = 1.697 \text{ mol}$$

$$n(\text{C}) = \frac{m(\text{C})}{M(\text{C})} \quad M(\text{C}) = 12.01 \text{ g mol}^{-1}$$

$$n(\text{C}) = \frac{98.3}{12.01} = 8.185 \text{ mol}$$

**Step 3:**

If 1.697 mole of  $\text{SiO}_2$  reacts, how many mole of C will it react with?

From the balanced equation 1 mole of  $\text{SiO}_2$  will react with 3 mole of C

so 1.697 mole of  $\text{SiO}_2$  will react with  $3 \times 1.697 = 5.091$  mole of C

However, the mixture contains 8.185 mole of C, that is, there is too much C in the mixture to react with 1.697 mole of  $\text{SiO}_2$ . C must therefore be in excess and  $\text{SiO}_2$  is the limiting reagent.

**Step 4:**

$\text{SiO}_2$  is the limiting reagent, so the amount of CO formed will be calculated from the amount of  $\text{SiO}_2$  reacted:

From the balanced equation 1 mole of  $\text{SiO}_2$  will form 2 mole of CO

so 1.697 mole of  $\text{SiO}_2$  will form  $2 \times 1.697 = 3.394$  mole of CO

**Step 5:**

$$n(\text{CO}) = \frac{m(\text{CO})}{M(\text{CO})} \quad M(\text{CO}) = 12.01 + 16.00 = 28.01 \text{ g mol}^{-1}$$

$$3.394 = \frac{m(\text{CO})}{28.01}$$

$$\text{mass of CO} = 3.394 \times 28.01 = 95.1 \text{ g}$$

At times, a limiting reagent problem will require the amount of the excess reagent remaining after the reaction to be calculated. The steps in this type of problem are similar to those described for the previous example except the amount of excess reagent consumed in the reaction is calculated. This amount is then subtracted from the amount of the excess reactant in the mixture before the reaction occurred. The major steps are therefore:

**Step 1**—write a balanced equation for the reaction

**Step 2**—calculate the mole of each reactant from their known mass

**Step 3**—calculate the limiting reagent, using the stoichiometric ratio shown in the balanced equation

**Step 4**—from the mole of limiting reagent, calculate the mole of excess reagent consumed in the reaction (using the stoichiometric ratio shown in the balanced equation)

**Step 5**—for the excess reagent, subtract the mole consumed from the mole originally present, to determine the mole of excess reagent remaining after the reaction

**Step 6**—if required by the question, calculate the mass of excess reagent remaining after the reaction

→ **Example 12.8**

Sulfur dioxide reacts with oxygen according to the equation



What mass of the excess reagent will remain after the reaction of a mixture of 75.0 g of sulfur dioxide and 50.0 g of oxygen?

→ **Solution**

**Step 1:** The equation is  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$ .

$$\text{Step 2: } n(\text{SO}_2) = \frac{m(\text{SO}_2)}{M(\text{SO}_2)} \quad M(\text{SO}_2) = 32.06 + (2 \times 16.00) = 64.06 \text{ g mol}^{-1}$$

$$n(\text{SO}_2) = \frac{75.0}{64.06} = 1.171 \text{ mol}$$

$$n(\text{O}_2) = \frac{m(\text{O}_2)}{M(\text{O}_2)} \quad M(\text{O}_2) = 2 \times 16.00 = 32.00 \text{ g mol}^{-1}$$

$$n(\text{O}_2) = \frac{50.0}{32.00} = 1.562 \text{ mol}$$

**Step 3:**

If 1.171 mole of  $\text{SO}_2$  reacts, how many mole of  $\text{O}_2$  will it react with?

From the balanced equation    2 mole of  $\text{SO}_2$  will react with 1 mole of  $\text{O}_2$

or                                1 mole of  $\text{SO}_2$  will react with  $\frac{1}{2}$  mole of  $\text{O}_2$

so    1.171 mole of  $\text{SO}_2$  will react with  $\frac{1}{2} \times 1.171 = 0.5855$  mole of  $\text{O}_2$

However, the mixture contains 1.562 mole of  $\text{O}_2$ , that is, there is too much  $\text{O}_2$  in the mixture to react with all the  $\text{SO}_2$ .  $\text{O}_2$  must therefore be **in excess** and  $\text{SO}_2$  is the **limiting reagent**.

**Step 4:**

From step 3, it was determined that

1.171 mole of  $\text{SO}_2$  will react with 0.5855 mole of  $\text{O}_2$

**Step 5:**

1.562 mole of  $\text{O}_2$  was originally present before the reaction, and 0.5855 mole of this reacted with the  $\text{SO}_2$

mole of  $\text{O}_2$  remaining after the reaction =  $1.562 - 0.5855 = 0.9765 \text{ mol}$

**Step 6:**

$$n(\text{O}_2) = \frac{m(\text{O}_2)}{M(\text{O}_2)} \quad M(\text{O}_2) = 32.00 \text{ g mol}^{-1}$$

$$0.9765 = \frac{m(\text{O}_2)}{32.00}$$

$$\text{mass of } \text{O}_2 \text{ remaining} = 0.9765 \times 32.00 = 31.2 \text{ g}$$

Limiting reagent calculations involving the concentrations and volumes of solutions can also be undertaken using the same basic ideas described for the ‘mass–mass’ problems. As detailed in Chapter 8, the relationship between the amount in mole of a substance dissolved in a solution and the volume and concentration, in mol L<sup>-1</sup>, of the solution is expressed in the formula

$$\text{concentration of the solution, in mol L}^{-1} = \frac{\text{mole of substance dissolved}}{\text{volume of solution in L}}$$

### \* Review exercise 12.2

- 1 When an electric spark is passed through a mixture of hydrogen and oxygen, these two substances react to form gaseous water:



Five different mixtures, A–E, of hydrogen and oxygen were prepared, and each mixture was sparked causing a reaction to occur. For each of these mixtures listed in the Table 12.4, fill in the gaps by determining which reactant is limiting and which is in excess, how many mole of water would form in the reaction and how many mole of the excess reagent would remain unreacted after the reaction.

TABLE 12.4

Experiment	Mole of H <sub>2</sub>	Mole of O <sub>2</sub>	Limiting reagent	Excess reagent	Mole of H <sub>2</sub> O produced	Mole of excess reagent remaining after reaction
A	2.0	1.0				
B	2.0	2.0				
C	3.0	1.0				
D	4.0	4.0				
E	7.0	3.0				

- 2 Baking powder causes cakes to rise as a result of the reaction between cream of tartar (potassium hydrogentartrate, KHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>) and baking soda (sodium hydrogencarbonate). These substances react according to the equation



What mass of carbon dioxide would be formed from a mixture of 8.00 g of cream of tartar and 5.50 g of baking soda?

- 3 Boron nitride is a compound that behaves in a similar fashion to carbon. This is not surprising given that it is made from a one-to-one combination of the atoms of each of the elements on either side of carbon in the periodic table. In simple terms, the formation of boron nitride can be represented by the equation



What mass of boron nitride, BN, can be obtained from the reaction between 25.0 g of boric oxide, B<sub>2</sub>O<sub>3</sub>, and 15.0 g of ammonia?

- 4 When hydrochloric acid is added to magnesium carbonate, the reaction produces a solution of magnesium chloride, carbon dioxide and water. If hydrochloric acid containing 1.46 g of hydrogen chloride is added to 1.70 g of magnesium carbonate, determine the following:
- the limiting reagent
  - the mass of magnesium chloride produced
  - the volume of carbon dioxide produced at STP.
- 5 What mass of barium sulfate is produced when 100.0 mL of a  $0.100 \text{ mol L}^{-1}$  solution of barium chloride is mixed with 100.0 mL of a  $0.100 \text{ mol L}^{-1}$  solution of iron(III) sulfate?
- 6 100 mL of  $0.100 \text{ mol L}^{-1}$  KCl is added to 30.0 mL of  $0.200 \text{ mol L}^{-1}$   $\text{AgNO}_3$  to form a precipitate of  $\text{AgCl}$ .
- Calculate the amount, in mole, of chloride ions remaining in the solution after the reaction.
  - Calculate the concentration, in  $\text{mol L}^{-1}$ , of chloride ions in the solution after the reaction.

## 12.3 Stoichiometric problems involving percentages

The mole is the unifying concept in stoichiometric calculations. This significance of the mole concept is emphasised in the mole calculation flowchart introduced earlier in Chapters 6 and 9. Figure 12.8 shows this flowchart.

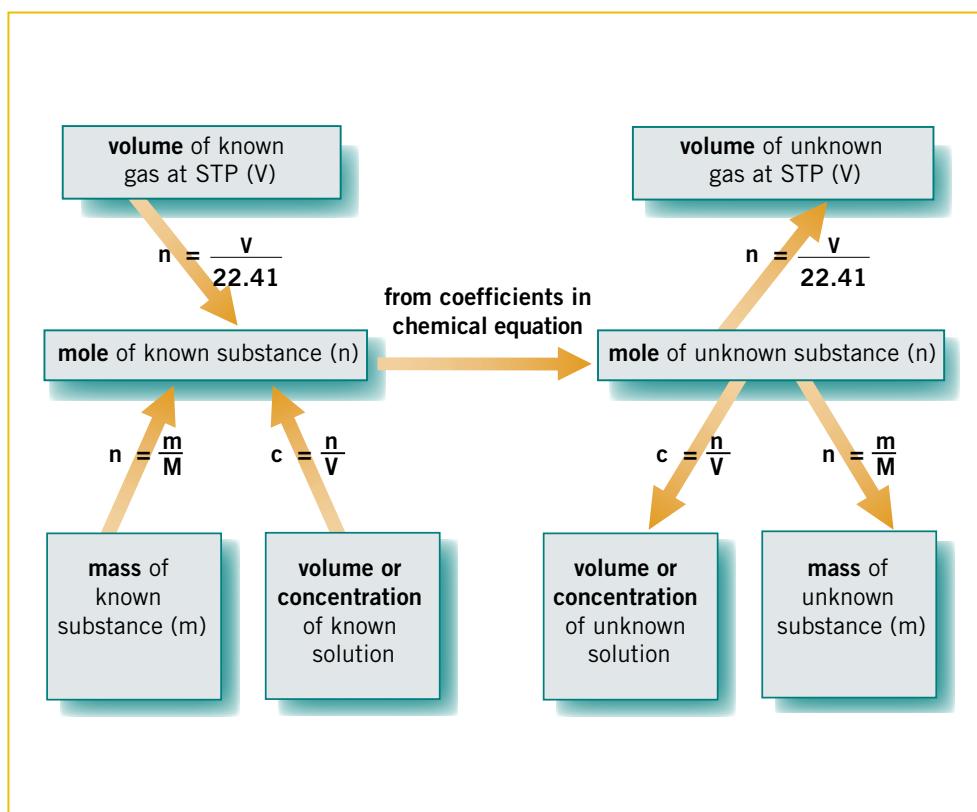


Figure 12.8 Stoichiometric mole chart including mass, solution and gas calculations.

The steps involved in many simple stoichiometric calculations, and the order in which they need to be carried out, are summarised in this flowchart. However, sometimes the solution of the particular stoichiometric problem requires one or more extra steps to be carried out either before or after the steps shown in the flowchart. For example, a question like Example 12.9 below, may ask for the percentage purity of a particular impure substance to be calculated. To answer this question, the first steps are shown in the flowchart, but an extra final step, the calculation of the percentage purity, is not shown in the chart.

In chemistry, the word ‘percent’ has the same meaning as in mathematics, namely, percent means ‘parts in 100’. For example, if a sample of limestone is 89% calcium carbonate, by mass, then there will be 89 g of calcium carbonate in 100 g of limestone, or  $\frac{89}{100}$ ths of limestone is calcium carbonate. This figure, often called the percentage purity of the impure material, can be calculated using the formula

$$\text{percentage purity of an impure substance} = \frac{\text{mass of pure substance in the sample}}{\text{mass of the sample of impure substance}} \times 100$$

#### → Example 12.9

Aluminium reacts with iron oxide according to the equation



24.0 g of an impure sample of aluminium was reacted with iron oxide, and 45.7 g of iron was formed. Calculate the percentage purity of the sample of impure aluminium.

#### → Solution

This is a four-step problem:

mass of iron → mole of iron → mole of Al → mass of Al → percentage purity of Al sample

$$\begin{aligned}\text{Step 1: } n(\text{Fe}) &= \frac{m(\text{Fe})}{M(\text{Fe})} \\ &= \frac{45.7}{55.85} = 0.8183 \text{ mol of Fe}\end{aligned}$$

**Step 2:** from balanced chemical equation:

9 mol of Fe are formed from 8 mol of Al

or 1 mol of Fe is formed from  $\frac{8}{9}$  mol of Al

so 0.8183 mol of Fe is formed from  $\frac{8}{9} \times 0.8183 = 0.7274$  mol of Al

$$\begin{aligned}\text{Step 3: } n(\text{Al}) &= \frac{m(\text{Al})}{M(\text{Al})} \\ 0.7274 &= \frac{m(\text{Al})}{26.98}\end{aligned}$$

mass of pure Al =  $0.7274 \times 26.98 = 19.63$  g

$$\begin{aligned}\text{Step 4: percentage purity of the Al sample} &= \frac{\text{mass of pure Al}}{\text{mass of impure sample}} \times 100 \\ &= \frac{19.63}{24.0} \times 100 = 81.8\%\end{aligned}$$

#### → Example 12.10

A 2.07 g sample of brass, used to make bolts and screws, was reacted with 0.729 mol L<sup>-1</sup> hydrochloric acid. The brass is an alloy composed of 64.8% copper and 35.2% zinc. Assuming only the zinc reacts with the acid, what volume of the hydrochloric acid is required to react with the sample of brass?



### → Solution

There are four major steps in this problem:

mass of brass → mass of Zn → mole of Zn → mole of H<sup>+</sup> (or HCl) → volume of hydrochloric acid

**Step 1:** If the brass is composed of 35.2% of zinc then

$$\text{mass of Zn} = 35.2\% \text{ of } 2.07 = \frac{35.2}{100} \times 2.07 = 0.7286 \text{ g}$$

$$\text{Step 2: } n(\text{Zn}) = \frac{m(\text{Zn})}{M(\text{Zn})} = \frac{0.7286}{65.38} = 0.01114 \text{ mol}$$

**Step 3:** From balanced equation: 1 mol Zn reacts with 2 mol H<sup>+</sup>

i.e. 0.01114 mol Zn reacts with  $2 \times 0.01114 = 0.02228$  mol H<sup>+</sup>

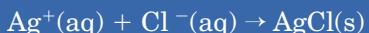
**Step 4:** 0.02228 mol of H<sup>+</sup> was formed from 0.02228 mol of HCl

$$c(\text{HCl}) = \frac{n(\text{HCl})}{V(\text{HCl})} \quad 0.729 = \frac{0.02228}{V(\text{HCl})}$$

$$\text{volume of HCl solution} = \frac{0.02228}{0.729} = \mathbf{0.0306 \text{ L}}$$

### \* Review exercise 12.3

- 1 Calculate the volume of 0.200 mol L<sup>-1</sup> AgNO<sub>3</sub> solution required to precipitate the chloride ion from a sample of rock salt weighing 0.585 g and containing 96.0% by mass of NaCl.



- 2 A student analysed a floor-cleaner solution containing ammonia by reacting 12.5 g of the solution with 0.162 mol L<sup>-1</sup> hydrochloric acid solution. 38.2 mL of the acid solution was required for a complete reaction. Calculate the percentage, by mass, of ammonia in the floor-cleaner solution.



- 3 1.66 g of a mixture of potassium chloride and potassium carbonate required 37.2 mL of 0.152 mol L<sup>-1</sup> hydrochloric acid for complete reaction. Calculate the percentage, by mass, of potassium carbonate in the mixture.



(KCl does not react with hydrochloric acid.)

## 12.4 Empirical formula

The empirical formula of a compound gives the simplest whole number ratio of the atoms present in the compound. Examples of empirical formulas include Al<sub>2</sub>O<sub>3</sub>, NH<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and CH<sub>2</sub>O. However, formulas such as H<sub>2</sub>O<sub>2</sub> and C<sub>4</sub>H<sub>8</sub> are not empirical formulas.

Empirical formulas can be determined experimentally by measuring the masses of elements combined in the compound, or from the percentage composition of the compound. The whole number mole ratio of the elements present, which can be calculated from mass data, is equivalent to the whole number ratio of the atoms present in the compound. Specifically to calculate the empirical formula of a compound, it is necessary to determine the whole number mole ratio of the atoms present in the compound.

→ **Example 12.11**

Urea is the principal end product of nitrogen metabolism in most mammals. It is transported in the blood to the kidneys, where it is filtered out to form urine. The concentration of urea in urine is about 60 to 70 times greater than that in blood. A particular sample of urea contains 1.121 g N, 0.161 g H, 0.480 g C and 0.640 g O. What is the empirical formula of urea?

→ **Solution**

	N	H	C	O
Mass	1.121 g	0.161 g	0.480 g	0.640 g
Mole	<u>1.121</u> 14.01 = 0.08001	<u>0.161</u> 1.008 = 0.1597	<u>0.480</u> 12.01 = 0.03997	<u>0.640</u> 16.00 = 0.04000
Divide by smallest number	= $\frac{0.08001}{0.03997}$ = 2.002	= $\frac{0.1597}{0.03997}$ = 3.995	= $\frac{0.03997}{0.03997}$ = 1	= $\frac{0.04000}{0.03997}$ = 1.001
Round off to whole numbers	= 2	= 4	= 1	= 1

The empirical formula is therefore  $\text{N}_2\text{H}_4\text{CO}$ .

(Note that in the final step of this type of calculation, a particular number should only be rounded to a whole number if it is within 0.1 of a whole number. If one or more of the numbers is not within 0.1 of a whole number, then it will be necessary to multiply all the numbers by a factor that will convert all of them to within 0.1 of a whole number.)

→ **Example 12.12**

Borax, a white, crystalline solid, has a wide variety of uses ranging from its use as a fire retardant to its use in pesticides. If the percentage composition of borax is 12.06% Na, 11.34% B, 71.32% O and 5.286% H, calculate its empirical formula.

→ **Solution**

The percentage composition figures can be thought of as the mass of each of the elements present in 100 g of the compound. That is, 100 g of borax contains 12.06 g of Na, 11.34 g of B, 71.32 g of O and 5.286 g of H.

	Na	B	O	H
Mass	12.06 g	11.34 g	71.32 g	5.286 g
Mole	<u>12.06</u> 22.99 = 0.5246	<u>11.34</u> 10.81 = 1.049	<u>71.32</u> 16.00 = 4.458	<u>5.286</u> 1.008 = 5.244
Divide by smallest number	= $\frac{0.5246}{0.5246}$ = 1	= $\frac{1.049}{0.5246}$ = 2.000	= $\frac{4.458}{0.5246}$ = 8.498	= $\frac{5.244}{0.5246}$ = 9.996
Multiply all numbers by 2	= 2	= 4.000	= 17.00	= 19.99
Round off to whole numbers	= 2	= 4	= 17	= 20

The empirical formula is therefore  $\text{Na}_2\text{B}_4\text{O}_{17}\text{H}_{20}$ .

(Borax is actually sodium borate-10-water,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ .)

### \* Review exercise 12.4

- 1 Nicotine is a toxic addictive substance found in tobacco. Calculate its empirical formula if a sample of nicotine contains 74.0 mg of C, 8.63 mg of H and 17.2 mg of N.
- 2 Cholesterol is a lipid found in the membranes of all cells. It is present in the highest concentration in the liver, brain and spinal cord in the human body. If cholesterol contains 83.87% C and 11.99% H, with the remainder being oxygen, what is its empirical formula?
- 3 A chloride of mercury can be reduced to mercury by reacting it with hypophosphorous acid. Thirty or so years ago, this reaction was used in school laboratories to determine the empirical formula of the chloride of mercury. In one such experiment a certain mass of the mercury chloride was placed in an evaporating basin together with an aqueous solution of hypophosphorous acid. The mixture was heated until no further reaction occurred. The aqueous solution was carefully poured out of the basin leaving behind the mercury. After careful washing and drying, the mercury in the evaporating basin was weighed. The data obtained in the experiment is given below:

mass of empty evaporating basin 65.239 g

mass of evaporating basin + mercury chloride 73.578 g

mass of evaporating basin + mercury 71.357 g

a Calculate the empirical formula of the chloride of mercury from this data.

b Why is this experiment no longer carried out in school laboratories?

## 12.5 Molecular formula

A pure substance consisting of molecules is represented by a molecular formula. The molecular formula specifies the exact number of each type of atom in each molecule of the substance. For some molecular compounds the empirical formula and the molecular formula are the same, but for others, the molecular formula will be a whole-number multiple of the empirical formula. For example, the molecular formula of butane is  $C_4H_{10}$  but its empirical formula is  $C_2H_5$ . However, for methane its molecular formula of  $CH_4$  is also its empirical formula.

The empirical formulas and molecular formulas of some common substances are given in Table 12.5.

The molecular formula of a compound can be determined from the empirical formula, if the relative molecular mass of the compound is known. The relative molecular mass is numerically equivalent to the molar mass of the compound, which can be determined experimentally. The molecular formula is a whole number multiple of the empirical formula.

**TABLE 12.5 THE EMPIRICAL FORMULAS AND MOLECULAR FORMULAS OF SOME COMPOUNDS**

Substance	Molecular formula	Empirical formula
water	H <sub>2</sub> O	H <sub>2</sub> O
hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	HO
ethane	C <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub>
ethene	C <sub>2</sub> H <sub>4</sub>	CH <sub>2</sub>
butene	C <sub>4</sub> H <sub>8</sub>	CH <sub>2</sub>
ammonia	NH <sub>3</sub>	NH <sub>3</sub>
glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	CH <sub>2</sub> O
potassium chloride	*	KCl
sodium carbonate	*	Na <sub>2</sub> CO <sub>3</sub>
aluminium nitrate	*	Al(NO <sub>3</sub> ) <sub>3</sub>

\* Does not occur as discrete molecules.

→ **Example 12.13**

If a compound has an empirical formula of CH and a relative molecular mass of approximately 78, what is its molecular formula?

→ **Solution**

The molecular formula will be (CH)<sub>n</sub> where n is a whole number.

That is,  $(12.01 + 1.008) \times n = 78$

$$13.018 \times n = 78$$

$$n = \frac{78}{13.018} = 5.99 \approx 6$$

The molecular formula is (CH)<sub>6</sub> or C<sub>6</sub>H<sub>6</sub>.

→ **Example 12.14**

Caffeine, a stimulant found in coffee, chocolate and tea, has a percentage composition of 49.48% carbon, 5.15% hydrogen, 28.87% nitrogen and 16.49% oxygen. If 0.00173 mol of caffeine has a mass of 0.334 g, what is its molecular formula?

→ **Solution**

There are three major steps involved in this question.

**Step 1:** determine the empirical formula of caffeine

**Step 2:** determine the relative molecular mass of caffeine

**Step 3:** using this relative molecular mass, find the molecular formula

**Step 1**

	C	H	N	O
Mass	49.48 g	5.15 g	28.87 g	16.49 g
Mole	49.48	5.15	28.87	16.49
	12.01	1.008	14.01	16.00
	= 4.120	= 5.109	= 2.061	= 1.031
Divide by smallest number	= $\frac{4.120}{1.031}$	= $\frac{5.109}{1.031}$	= $\frac{2.061}{1.031}$	= $\frac{1.031}{1.031}$
	= 3.996	= 4.955	= 1.999	= 1
Round off to whole numbers	= 4	= 5	= 2	= 1

The empirical formula of caffeine is C<sub>4</sub>H<sub>5</sub>N<sub>2</sub>O.

**Step 2**

$$\text{mole (caffeine)} = \frac{\text{mass (caffeine)}}{\text{molar mass (caffeine)}}$$

$$0.00173 = \frac{0.334}{\text{molar mass (caffeine)}}$$

$$\text{molar mass (caffeine)} = \frac{0.334}{0.00173} = 193.1 \text{ g mol}^{-1}$$

relative molecular mass of caffeine = 193.1

**Step 3**

$$97.1 \times n = 193.1$$

$$n = \frac{193.1}{97.1} = 1.989 \approx 2$$

The molecular formula of caffeine is  $(\text{C}_4\text{H}_5\text{N}_2\text{O})_2$  or  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ .

**\* Review exercise 12.5**

- 1 Citric acid, the sour substance in lemon juice, is composed of only carbon, hydrogen and oxygen. Its percentage composition is 37.5% carbon, 4.16% hydrogen and the remainder is oxygen. If the approximate relative molecular mass of citric acid is 192, what is its molecular formula?
- 2 The hormone epinephrine increases the body's metabolic rate. The percentage composition of this hormone is 56.8% carbon, 6.56% hydrogen, 28.4% oxygen and 8.28% nitrogen and its approximate relative molecular mass is 170. What is the molecular formula of epinephrine?
- 3 In an experiment, 0.310 g of phosphorus was burned in a plentiful supply of air to form 0.710 g of an oxide of phosphorus. This oxide has a relative molecular mass of 284. What are the empirical and molecular formulas of the oxide of phosphorus formed in the reaction?
- 4 Ethylene glycol is a colourless liquid often used as an antifreeze in car radiators. It consists of 38.7% carbon, 9.7% hydrogen and 51.6% oxygen. A 0.179 mol sample of ethylene glycol was found to have a volume of 10 mL, at 25°C. If the density of ethylene glycol is  $1.11 \text{ g mL}^{-1}$  at 25°C, what is its molecular formula?



## MAJOR IDEAS

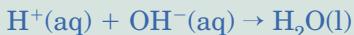
- Ionic equations are used for solution reactions to indicate more accurately the reaction taking place. Spectator ions are not included.
- The limiting reagent in a chemical reaction is the substance that is completely consumed in the reaction. A reactant that is not consumed completely is said to be present in excess.
- The flowchart given in Figure 12.8 can be used to map many of the steps in stoichiometric problems involving masses, volumes and concentrations of solutions and volumes of gases at STP.
- The empirical formula of a compound specifies the simplest whole-number ratio of the atoms of each element in the compound.
- The molecular formula of a compound specifies the actual number of atoms of each element in a molecule of the compound.

## QUESTIONS

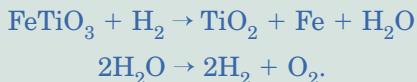
- 1 The following statements are referring to ionic equations for precipitation reactions. Identify the mistake in each equation.
  - a The equation for the reaction that occurs when a solution of barium chloride is mixed with a solution of ammonium sulfate is  
 $\text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$
  - b The equation for the reaction that occurs when a solution of nickel(II) nitrate is mixed with a solution of sodium hydroxide is  
 $\text{Ni}^{2+}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{Ni}(\text{OH})_2(\text{s})$
  - c The equation for the reaction that occurs when a solution of copper iodide is mixed with a solution of sodium sulfate is  
 $\text{Cu}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{CuSO}_4(\text{s})$
- 2 Write balanced ionic equations for the following reactions:
  - a When chlorine gas is bubbled into a solution of potassium iodide, the products formed are iodine and a solution of potassium chloride.
  - b Silver metal and a solution of zinc nitrate are formed if some small pieces of zinc are added to a solution of silver nitrate.
  - c Phosphoric acid is added to some solid potassium hydroxide to form water and a solution of potassium phosphate.

- d When nitric acid is mixed with some solid magnesium sulfite, the products formed are sulfur dioxide gas, water and a solution of magnesium nitrate.
  - e Solutions of aluminium nitrate and sodium sulfide are mixed.
  - f A solution of hydrogen peroxide reacts with a solution of sodium iodide, in the presence of nitric acid, to form iodine in solution, water, and a solution containing sodium nitrate.
- 3 When manganese dioxide reacts with concentrated hydrochloric acid, the products are manganese(II) chloride, chlorine gas and water. If 2.17 g of manganese dioxide is treated with hydrochloric acid containing 2.74 g of hydrogen chloride, determine the following:
    - a the limiting reagent
    - b the mass of chlorine produced
    - c the mass of the excess reagent left after the reaction.
  - 4 A solution containing 15.0 g of iron(III) chloride is mixed with another solution containing 12.0 g of sodium hydroxide, to produce a precipitate of iron(III) hydroxide. What is the mass of precipitate formed?  
 $\text{Fe}^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq}) \rightarrow \text{Fe}(\text{OH})_3(\text{s})$
  - 5 How many millilitres of 6.00 mol L<sup>-1</sup> HCl is required to precipitate the silver from 1.00 g of an alloy containing 72.0% by mass, of silver?
  - 6 2.50 g of a very impure sample of potassium carbonate required 25.0 mL of hydrochloric acid of concentration 10.0 g L<sup>-1</sup> for complete reaction. What is the percentage purity, by mass, of the potassium carbonate sample?  
 $\text{K}_2\text{CO}_3(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + 2\text{K}^+(\text{aq})$
  - 7 One possible definition of the salinity of a solution is the mass in grams of total salts dissolved in 1 kg of solution. The word ‘salts’ refers to the solids (usually ionic compounds) that remain after the water has been evaporated from the solution. A ‘salty’ solution being used by an agricultural scientist is known to contain twice as many mole of NaCl as MgSO<sub>4</sub>. When the scientist evaporated 500 g of this solution, 16.5 g of a salt residue was obtained. Calculate the percentages, by mass, of NaCl and MgSO<sub>4</sub> in the solution.

- 8 A human patient suffering from a duodenal ulcer has an HCl concentration of  $0.158 \text{ mol L}^{-1}$  in his gastric juice. If his stomach receives 3.00 L of gastric juice per day, what mass of patent medicine containing 2.60%, by mass,  $\text{Al(OH)}_3$  must he consume per day to react with all the acid?



- 9 The moon lacks water and oxygen. The soil, however, contains a mineral known as ilmenite,  $\text{FeTiO}_3$ . It has been proposed that explorers on the moon could produce water from lunar soil by reducing it in a solar furnace at  $1300^\circ\text{C}$ , initially using hydrogen transported from Earth. Some of the water could then be electrolysed to yield oxygen.



A 100 kg sample of lunar soil, containing 4.00% ilmenite, is to be processed.

- a What would be the expected mass of water?  
b If half of the water from part a is converted to oxygen, what volume of oxygen would result at  $0^\circ\text{C}$  and 101.3 kPa?
- 10 2.32 g of lead nitrate was dissolved in water to make 100 mL of solution, which was then added to 100 mL of 0.120 mol  $\text{L}^{-1}$  sodium sulfate solution. A white precipitate of lead sulfate formed.
- a Write an ionic equation for the reaction that occurred.  
b Calculate the mass of precipitate formed.  
c Calculate the concentration, in mol  $\text{L}^{-1}$ , of:  
i the nitrate ion in the final solution  
ii the sulfate ion in the final solution.

- 11 Determine the empirical formulas of the following compounds:
- a Teflon, which consists of 24% carbon and 76% fluorine  
b a uranium oxide, given that 59.0 g of the oxide produces 50.0 g of uranium.

- 12 Aspartame, an artificial sweetener that is 160 times sweeter than sucrose when dissolved in water, is 9.52% N by mass. If a molecule of aspartame contains two nitrogen atoms, what is the relative molecular mass of aspartame?

- 13 Glycerol (glycerine) consists of 39.1% carbon, 52.2% oxygen and the remainder is hydrogen. Calculate the empirical formula of glycerol. Given its relative molecular mass is 92.0, what is its molecular formula?

- 14 Despite the vast numbers of different species of insects that inhabit the Earth, insects of a particular species are able to identify each other (especially at mating time) by using special chemicals called pheromones to transmit chemical messages. The pheromone that serves as a sex attractant for (American) gypsy moths is called disparlure and contains the elements carbon, hydrogen and oxygen. Analysis of disparlure shows that a 0.1411 g sample contains  $8.00 \times 10^{-3}$  g of oxygen atoms and 0.114 g of carbon atoms. Disparlure has a molar mass of 282 g  $\text{mol}^{-1}$ . Determine the molecular formula of disparlure.

- 15 A poisonous compound isolated from rhubarb consists of 19.0% carbon, 4.8% hydrogen and 76.2% oxygen. Calculate its empirical formula. Given that the compound's relative molecular mass is 126.0 and it occurs as a dihydrate, what is its molecular formula?

16 *Empirical formula of copper oxide*

The empirical formula of ionic oxides can often be experimentally determined by reacting them with a chemical that will donate electrons and so change the positive metal ion into neutral metal atoms. This process is called 'reduction' and the chemical providing the electrons is called the 'reducing agent'.

In the following experiment to determine the empirical formula of copper oxide, the reducing agent is the methane,  $\text{CH}_4$ , in natural gas.

Read through the experiment instructions and then answer the questions.

**Experimental procedure for determining the empirical formula of copper oxide**

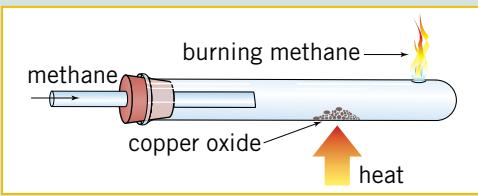
*Apparatus and materials*

copper oxide (a black powder)	Bunsen burner and mat stand and clamp
spatula	rubber tubing
hard glass test tube with small hole	electronic balance
natural gas supply	stopper fitted with glass tube
	safety goggles

*Procedure*

- 1 Weigh the test tube then add two spatula measures of copper oxide, and reweigh.
- 2 Using the clamp and stand, place the test tube and copper oxide in a horizontal position as shown in Figure 12.9.
- 3 Insert the stopper plus glass tube and connect the end of the tube to the natural gas supply.

- 4 Turn on the gas supply and adjust it to a gentle flow coming out of the small hole in the test tube. Light the gas.
- 5 Using a blue Bunsen burner flame, heat the copper oxide sample until it has changed completely to copper.
- 6 Turn off the Bunsen burner and allow gas to continue to flow over the copper while it is cooling.
- 7 When the test tube is cool, turn off the gas, carefully remove the stopper and reweigh the test tube and contents.



**Figure 12.9**

- a List the dangers involved in this experiment.
- b Why is the excess natural gas (methane) burnt as it emerges from the small hole in the test tube?
- c How would you know when, in step 5, the copper oxide has changed to copper?
- d Why, during the cooling process in step 6, is the natural gas still allowed to flow through the test tube?
- e The results obtained by three students for this experiment are shown in the following table.

	Student A	Student B	Student C
Mass of test tube	30.214 g	32.839 g	31.920 g
Mass of test tube + copper oxide	30.829 g	34.372 g	32.628 g
Mass of test tube + copper	30.616 g	33.341 g	32.493 g

Calculate the empirical formula of copper oxide from each of these sets of results.

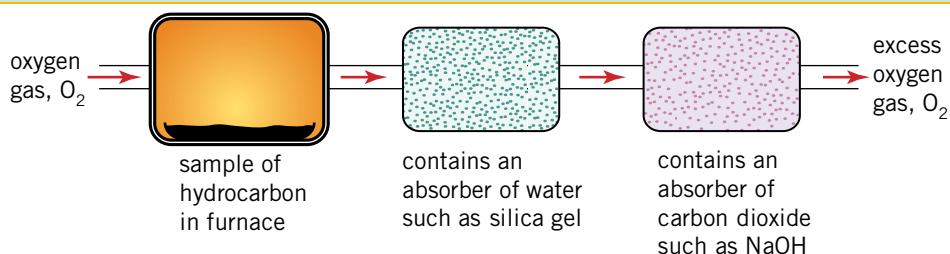
- f Which of these two empirical formulas would cause you to wonder about their accuracy? Explain your reasoning.
- g For these two seemingly incorrect empirical formulas, suggest what the students may have done during the experiment to cause these inaccuracies.
- h What could be done to confirm that the two formulas chosen in part f are incorrect?

### 17 Analysis by combustion

To determine the empirical formula of a hydrocarbon, chemists use a procedure involving combustion of the hydrocarbon.

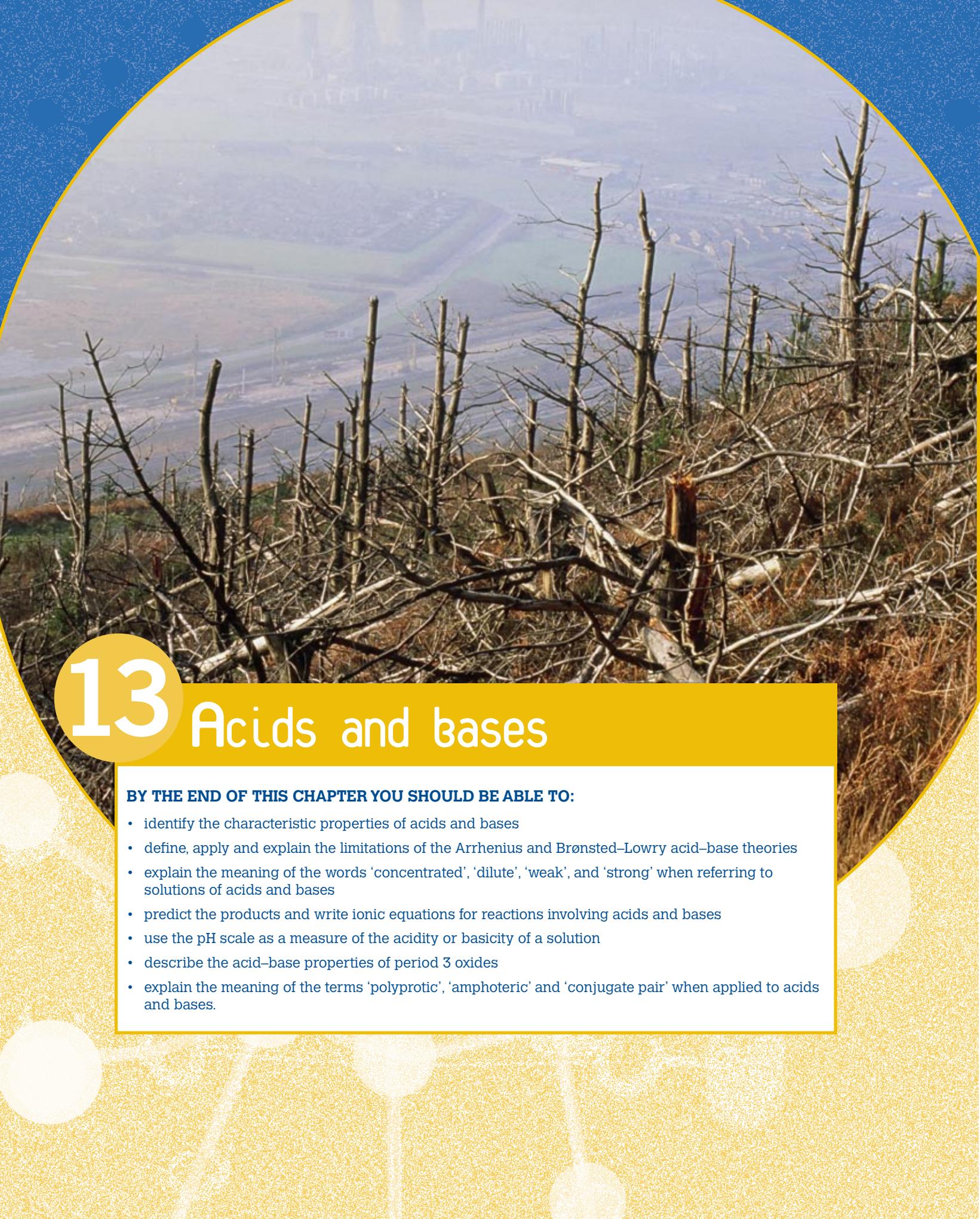
In this procedure, the hydrocarbon sample is burned in the presence of excess oxygen, which converts all the carbon in the hydrocarbon to carbon dioxide and all the hydrogen to water. The gaseous water and carbon dioxide gas produced are absorbed in two different stages and their masses determined by measuring the increase in mass of the absorbers (see Figure 12.10).

- a In an experiment, when a hydrocarbon sample was burned, 0.449 g of carbon dioxide and 0.274 g of water were formed.
  - i Calculate the mole of carbon dioxide formed in the combustion reaction.
  - ii How many mole of carbon atoms are present in this amount of carbon dioxide?
  - iii How many mole of carbon atoms must have been present in the hydrocarbon?
  - iv Calculate the mole of water,  $\text{H}_2\text{O}$ , formed in the combustion reaction.
  - v What amount in mole of hydrogen atoms are present in this amount of water?
  - vi What amount in mole of hydrogen atoms must have been present in the hydrocarbon?
  - vii Use the answers to iii and vi to calculate the empirical formula of the hydrocarbon.



**Figure 12.10** A simplified diagram of the device used in the analysis of hydrocarbons by combustion.

- b** i In a second experiment, a different hydrocarbon was burned and 0.386 g of carbon dioxide and 0.175 g of water were formed. Calculate the empirical formula of this hydrocarbon.
- ii If the relative molecular weight of this hydrocarbon is approximately 141, what is its molecular formula?
- c A 0.581 g sample of a hydrocarbon burns to give 0.899 g of water and some carbon dioxide. Calculate the empirical formula of this hydrocarbon.



# 13 Acids and bases

**BY THE END OF THIS CHAPTER YOU SHOULD BE ABLE TO:**

- identify the characteristic properties of acids and bases
- define, apply and explain the limitations of the Arrhenius and Brønsted–Lowry acid–base theories
- explain the meaning of the words ‘concentrated’, ‘dilute’, ‘weak’, and ‘strong’ when referring to solutions of acids and bases
- predict the products and write ionic equations for reactions involving acids and bases
- use the pH scale as a measure of the acidity or basicity of a solution
- describe the acid–base properties of period 3 oxides
- explain the meaning of the terms ‘polyprotic’, ‘amphoteric’ and ‘conjugate pair’ when applied to acids and bases.

Acids and bases have significant roles in our daily life, the environment, human biology, agriculture and industry. These roles range from essential and useful through to destructive. Digestion of food in the stomach, maintaining the correct pH level in living systems, formation of limestone caves, lemons tasting sour, starting the car with the lead–acid accumulator, cleaning ovens and floors, erosion of marble buildings by acid rain and flora devastation by emissions from metal extracting plants all happen because of acids and bases.



**Figure 13.1** Some acids and bases found in the home.

## 13.1 Properties of acids and bases

Since the earliest days of chemistry, scientists have labelled particular compounds acids or bases according to their properties. Examples of commonly known acids and bases are listed in Table 13.1.

**TABLE 13.1 COMMON ACIDS AND BASES**

	Examples	Use or occurrence
Acids	hydrochloric acid, HCl	produced in the stomach to assist digestion
	sulfuric acid, $\text{H}_2\text{SO}_4$	in car batteries
	sulfurous acid, $\text{H}_2\text{SO}_3$	damaging component in acid rain
	acetic acid, $\text{CH}_3\text{COOH}$	in vinegar, salad dressing, pickled onions, gherkins
	carbonic acid, $\text{H}_2\text{CO}_3$	in fizzy drinks
	lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$	in yogurt, sour milk, sour cream
	citric acid, $\text{C}_6\text{H}_8\text{O}_7$	in citrus fruit
	ammonium nitrate, $\text{NH}_4\text{NO}_3$	in fertilisers
Bases	sodium hydroxide, NaOH	in oven and drain cleaners
	ammonia, $\text{NH}_3$	in cleaning products, in manufacturing fertilisers
	calcium hydroxide, $\text{Ca}(\text{OH})_2$	in cement and plaster
	sodium hydrogen carbonate, $\text{NaHCO}_3$	a rising agent in baking
	calcium oxide (lime), CaO	to make soil less acidic
	sodium carbonate, $\text{Na}_2\text{CO}_3$	to soften hard water

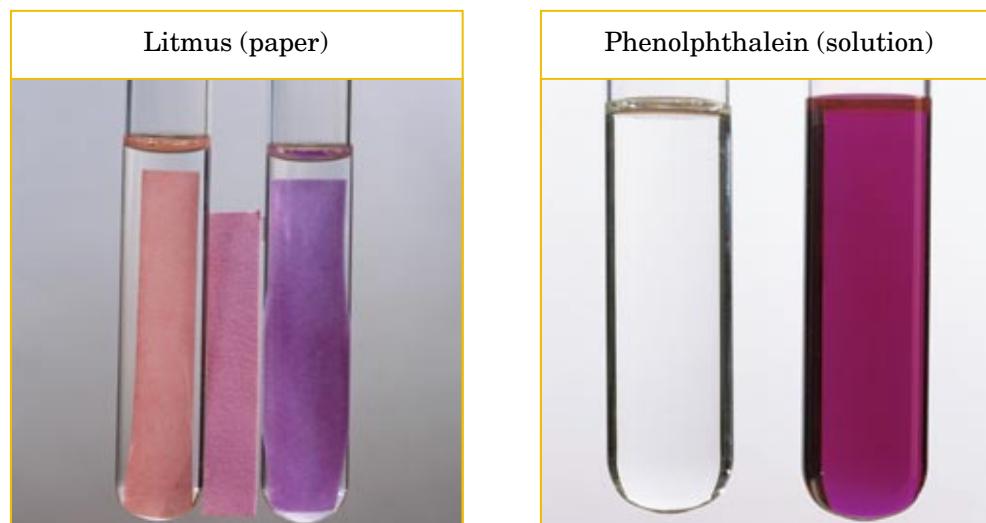
The characteristic properties of acids and bases are listed in Table 13.2.

**TABLE 13.2 CHARACTERISTIC PROPERTIES OF ACIDS AND BASES**

Acids
<ul style="list-style-type: none"><li>• taste sour</li><li>• cause indicators to change colour e.g. blue litmus changes to red</li><li>• are corrosive</li><li>• many solutions of acids conduct electricity</li><li>• react with carbonates e.g. marble, and hydrogencarbonates to form carbon dioxide and water</li><li>• react with some metals to form hydrogen</li><li>• react with bases to form water</li></ul>
Bases
<ul style="list-style-type: none"><li>• taste bitter</li><li>• feel slippery</li><li>• cause indicators to change colour e.g. red litmus changes to blue</li><li>• can be corrosive</li><li>• do not react with most metals</li><li>• many solutions of bases conduct electricity</li><li>• react with acids to form water</li></ul>

### Indicators

Indicators are often used to determine whether a solution is acidic or basic. An indicator is a chemical that changes to a different colour when added to a solution of an acid compared to when added to a solution of a base. Several common indicators used in the laboratory, together with their colours in hydrochloric acid (an acidic solution) and sodium hydroxide solution (a basic solution) are shown in Figure 13.2. Indicators can be used as a solution or impregnated in paper.



**Figure 13.2 Colours of the indicators litmus and phenolphthalein in hydrochloric acid (left test tube) and sodium hydroxide solution (right test tube).**

## \* Review exercise 13.1

- 1 One of the properties of acids listed in Table 13.2 is that they are corrosive.
  - a What is meant by the word ‘corrosive’?
  - b Some acids are much less corrosive than others. Name two acids that can be eaten, and give examples of the food or drink in which these acids are found.
  - c **RESEARCH** One acid that is regarded as highly corrosive is produced by the stomach in the human body. What is this acid, and how does the stomach cope with having this acid in it?
- 2 a Explain why it is that many people prefer not to eat lemons.  
b Why do the crushed petals of some flowers change colour when mixed with acids or bases?  
c What property of the sulfuric acid in a car battery explains why the battery can be recharged and discharged?  
d Why might sodium hydrogencarbonate powder be recommended for placing on an acid spill?



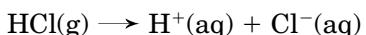
Figure 13.3 Corrosion of the terminal of a car battery, caused by sulfuric acid in the battery.

## 13.2 The Arrhenius theory of acids and bases

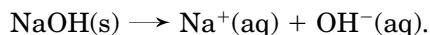
One of the earliest definitions of acids and bases, based on their chemical nature at a molecular level, was proposed by Svante Arrhenius in 1883. He suggested that

- an **acid** has H in its formula and dissolves in water to form hydrogen ions,  $\text{H}^+(\text{aq})$ , and
- a **base** has OH in its formula and when added to water forms hydroxide ions,  $\text{OH}^-(\text{aq})$ .

For example, according to the **Arrhenius theory**, in hydrochloric acid (a solution of  $\text{HCl(g)}$  in water) the  $\text{HCl}$  molecules are ionised according to the following reaction:



and when the base  $\text{NaOH}$  is dissolved in water, the following dissociation process takes place:



Examples of the ions formed by other Arrhenius acids and bases when they are added to water are shown in Table 13.3.



Figure 13.4 Swedish chemist Svante Arrhenius (1859–1927) in his laboratory. He won a Nobel Prize in 1903 for his ‘electrolytic theory on dissociation’. Also, he was possibly the first scientist to suggest that future problems may arise because of the ‘greenhouse effect’.

**TABLE 13.3 IONS FORMED WHEN SOME ACIDS AND BASES ARE ADDED TO WATER**

Acids	Ions formed	Bases	Ions formed
nitric acid, $\text{HNO}_3$	hydrogen ions, $\text{H}^+$ nitrate ions, $\text{NO}_3^-$	potassium hydroxide	potassium ions, $\text{K}^+$ hydroxide ions, $\text{OH}^-$
sulfuric acid, $\text{H}_2\text{SO}_4$	hydrogen ions, $\text{H}^+$ sulfate ions, $\text{SO}_4^{2-}$ hydrogensulfate ions, $\text{HSO}_4^-$	calcium hydroxide	calcium ions, $\text{Ca}^{2+}$ hydroxide ions, $\text{OH}^-$
acetic acid, $\text{CH}_3\text{COOH}$	hydrogen ions, $\text{H}^+$ acetate ions, $\text{CH}_3\text{COO}^-$		

The Arrhenius theory could be used to explain many of the properties of the acids and bases known in the late nineteenth century. For example:

- because all the acids have  $\text{H}^+$  ions in their solution, they all react with carbonates, hydrogencarbonates, and metals such as magnesium.
- solutions of acids can conduct electricity because of the  $\text{H}^+$  ions and the negative ions present in the solution.
- when mixed together, an acid and a base undergo a neutralisation reaction. That is, both the acid and base properties of the two substances are ‘cancelled’ or neutralised. This occurs because the  $\text{H}^+$  ions from the acid react with the  $\text{OH}^-$  ions from the base to form water, which, according to the Arrhenius theory, is neither an acid nor a base.

Despite its importance at the time it was first proposed, there are limitations to the Arrhenius theory. These include:

- some substances that behave as bases, that is, produce  $\text{OH}^-$  ions in solution, do not contain OH in their formula, for example, ammonia,  $\text{NH}_3$ , and the carbonate ion,  $\text{CO}_3^{2-}$ .
- the theory only applies to solutions of acids and bases in water and not to solutions in other solvents such as acetic acid or liquid ammonia.
- reactions such as that between  $\text{HCl(g)}$  and  $\text{NH}_3(\text{g})$ , to form  $\text{NH}_4\text{Cl(s)}$ , cannot be explained.
- not all salts (ionic compounds produced when an acid reacts with a base) are neutral. Many salts behave as acids or bases.
- the hydrogen ion,  $\text{H}^+$ , cannot exist for very long in water. It reacts with water to form  $\text{H}_3\text{O}^+(\text{aq})$ , the hydronium ion. That is, in an aqueous solution, an acid should be regarded as a substance that produces  $\text{H}_3\text{O}^+(\text{aq})$ .

The Arrhenius definition is still used today, although it is now usual to define acids and bases in more general terms to include a broader range of acids and bases that are known to exist and to include the use of other solvents apart from water.



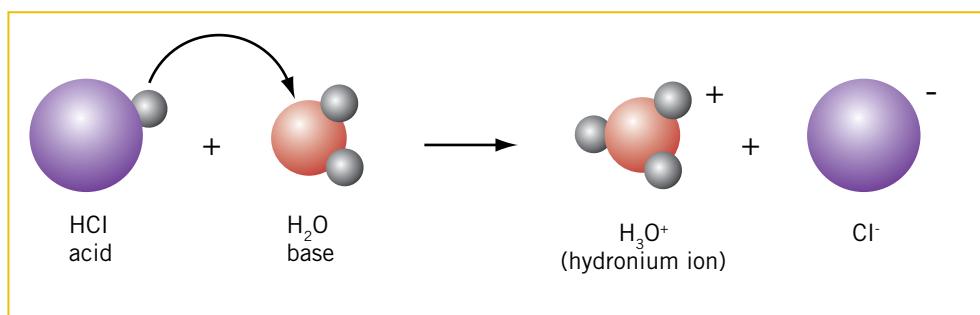
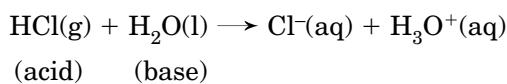
## \* Review exercise 13.2

- 1 The meanings of the words ‘ionise’ and ‘dissociate’ were discussed earlier in Chapter 8. What are the meanings of these words?
  - 2 Use the Arrhenius theory to write equations showing the ions you would expect to form when the following acids and bases are added to water: HBr, Ca(OH)<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>, HNO<sub>3</sub>.
  - 3 According to the Arrhenius theory, why might you expect all acids to turn litmus paper ‘red’ and all bases to turn litmus paper ‘blue’.
  - 4
    - a Draw electron dot diagrams to show what happens, according to the Arrhenius theory, when the following substances are added to water: HCl, CH<sub>3</sub>COOH, Ca(OH)<sub>2</sub>.
    - b Classify each of the examples shown in part a as an ionisation or dissociation process.
  - 5 Liquid HCl does not conduct electricity, yet a solution of HCl does. Explain this observation. Include electron dot diagrams of the relevant molecules or ions in HCl(l) and HCl(aq) in your answer.
  - 6 The heat of reaction for the reaction of potassium hydroxide with hydrochloric acid is the same as the heat of reaction for the reaction of sodium hydroxide with nitric acid. Use the Arrhenius theory of acids and bases to explain this observation.

### 13.3 The Brønsted–Lowry theory of acids and bases

In the acid–base theory developed independently by Johannes Brønsted and Thomas Lowry in 1923, an acid–base reaction is one that involves the transfer of a hydrogen ion (a proton) from one reactant to another. The reactant that loses the hydrogen ion,  $\text{H}^+$ , is called the **acid** and the reactant that gains the hydrogen ion is the **base**.

According to the **Brønsted-Lowry theory**, when hydrogen chloride molecules are dissolved in water, each hydrogen chloride molecule donates a hydrogen ion to a water molecule, as shown in Figure 13.5. The HCl acts as a Brønsted-Lowry acid and the  $\text{H}_2\text{O}$  acts as a Brønsted-Lowry base, according to the equation



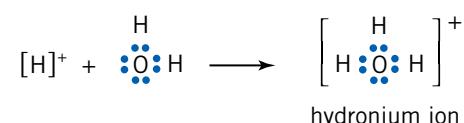
**Figure 13.5** The transfer of  $H^+$  that occurs when HCl acts as an acid and  $H_2O$  acts as a base.

When a  $\text{H}^+$  is pulled away from the neutral  $\text{HCl}$  molecule, the chloride ion formed has a  $-1$  charge and when the neutral  $\text{H}_2\text{O}$  molecule bonds with this  $\text{H}^+$  ion, it forms a hydronium ion with a  $+1$  charge.

The hydrogen ion,  $H^+$ , is actually just a proton. A neutral hydrogen atom is composed of a proton and an electron and if the electron is removed, to form  $H^+$ , only the proton remains. The definition of an acid and a base, according to the Brønsted–Lowry theory, can therefore be rephrased as

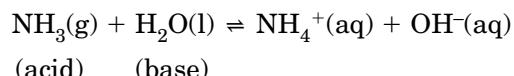
- **acids** are proton donors
  - **bases** are proton acceptors.

Hydrogen ions do not exist as  $H^+$  in an aqueous solution, instead they react with the water molecules and so are present as hydronium ions,  $H_3O^+$ , as shown in Figure 13.6. However, it is acceptable to write the formula of a hydronium ion in solution as  $H_3O^+(aq)$  or  $H^+(aq)$ . The hydronium ion is present in every solution of an acid, and it is this ion that gives these acidic solutions their common characteristic properties.

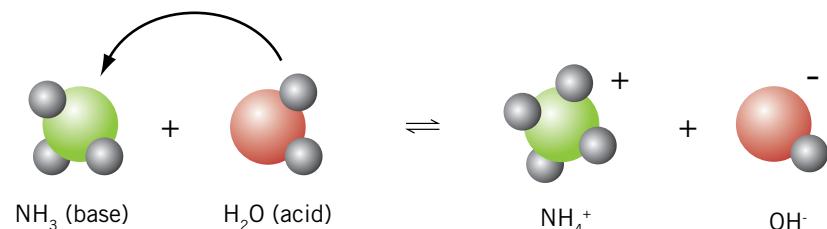


**Figure 13.6** An electron dot representation of the formation of hydronium ions from the reaction of hydrogen ions with water molecules.

Another example of a Brønsted–Lowry acid–base reaction is the reaction between ammonia and water. When ammonia gas is bubbled into water, the following reaction occurs:

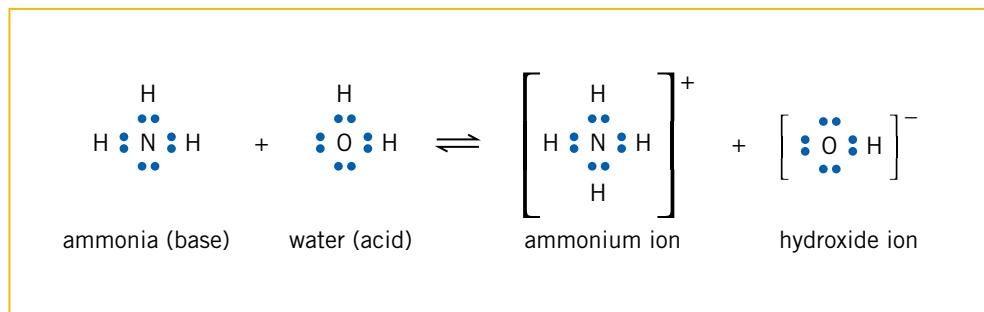


In this reaction, the  $\text{H}_2\text{O}$  loses a hydrogen ion (proton) and is acting as the acid, and the  $\text{NH}_3$  gains the hydrogen ion (proton) and so is acting as the base, as shown in Figure 13.7.



**Figure 13.7** A Brønsted–Lowry acid–base reaction showing the transfer of a  $\text{H}^+$  from a molecule of  $\text{H}_2\text{O}$  to a molecule of  $\text{NH}_3$ . The  $\text{H}_2\text{O}$  is acting as the acid and the  $\text{NH}_3$  is acting as the base.

This hydrogen ion transfer reaction can also be represented using electron dot diagrams:



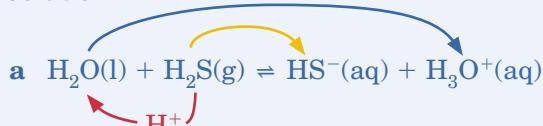
Note: The double arrows have been used in the reaction of  $\text{NH}_3$  with  $\text{H}_2\text{O}$  to indicate that the reaction does not go completion. Because of this, in an aqueous solution of  $\text{NH}_3$  there will always be some  $\text{NH}_3$  molecules as well as  $\text{NH}_4^+$  ions (and  $\text{OH}^-$  and  $\text{H}_2\text{O}$ ). This was explained in an earlier chapter in terms of the  $\text{NH}_3$  only partially ionising in water because it is a weak electrolyte.

#### → Example 13.1

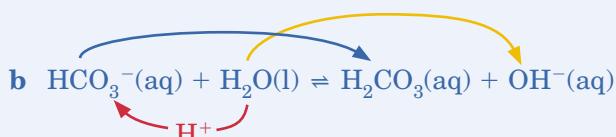
Identify which reactant is acting as the Brønsted–Lowry acid and which is acting as the Brønsted–Lowry base in the following reactions:

- $\text{H}_2\text{O(l)} + \text{H}_2\text{S(g)} \rightleftharpoons \text{HS}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- $\text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) + \text{OH}^-(\text{aq})$
- $\text{CH}_3\text{COOH(aq)} + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O(l)}$

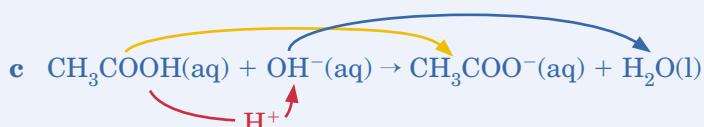
#### → Solution



- $\text{H}_2\text{O}$  has gained a  $\text{H}^+$  to form  $\text{H}_3\text{O}^+$   **$\text{H}_2\text{O}$  is the base.**
- $\text{H}_2\text{S}$  has lost a  $\text{H}^+$  to form  $\text{HS}^-$   **$\text{H}_2\text{S}$  is the acid.**
- $\text{H}^+$  ions have been transferred from  $\text{H}_2\text{S}$  (the acid) to  $\text{H}_2\text{O}$  (the base).



- $\text{HCO}_3^-$  has gained a  $\text{H}^+$  to form  $\text{H}_2\text{CO}_3$   **$\text{HCO}_3^-$  is the base.**
- $\text{H}_2\text{O}$  has lost a  $\text{H}^+$  to form  $\text{OH}^-$   **$\text{H}_2\text{O}$  is the acid.**
- $\text{H}^+$  ions have been transferred from  $\text{H}_2\text{O}$  (the acid) to  $\text{HCO}_3^-$  (the base).

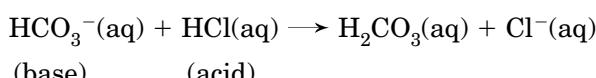
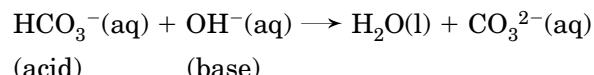


- $\text{OH}^-$  has gained a  $\text{H}^+$  to form  $\text{H}_2\text{O}$   **$\text{OH}^-$  is the base.**
- $\text{CH}_3\text{COOH}$  has lost a  $\text{H}^+$  to form  $\text{CH}_3\text{COO}^-$   **$\text{CH}_3\text{COOH}$  is the acid.**
- $\text{H}^+$  ions have been transferred from  $\text{CH}_3\text{COOH}$  (the acid) to  $\text{OH}^-$  (the base).

As with the Arrhenius theory, the Brønsted–Lowry theory also has its limitations. Since the theory defines an acid as a hydrogen ion donor, it excludes substances that have no hydrogen ions to donate from being classified as acids. In the 1930s, a more inclusive acid–base theory—the Lewis theory—was proposed. This theory describes a base as a substance with a lone pair of electrons that can form a bond with an acid, and an acid as the electron pair acceptor.

## Amphoteric substances

The reactions of hydrogen chloride, HCl, and of ammonia, NH<sub>3</sub>, with water, referred to earlier in this section, reveal that water is capable of accepting or donating a hydrogen ion, depending on whether it is reacting with an acid or a base. Substances that can act either as an acid or a base are called **amphoteric substances**. Another example of an amphoteric substance is the hydrogencarbonate ion. When the HCO<sub>3</sub><sup>-</sup> ion reacts with OH<sup>-</sup> ions, it acts as an acid, and when it reacts with HCl, it acts as a base, as shown in the following equations:



Since water is amphoteric, one water molecule can react with another water molecule in an acid–base reaction, as shown in the following equation:



One water molecule donates a hydrogen ion and the other accepts it. This reaction is called the **self-ionisation of water**.

## Conjugate acids and bases

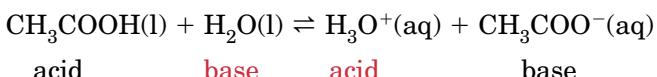
When a Brønsted–Lowry acid reacts by losing a hydrogen ion, the species it forms has the potential to act as a base. For example, when HCl loses a hydrogen ion to a base, it forms  $\text{Cl}^-$ . This  $\text{Cl}^-$  can, under certain conditions, act as a base by gaining a hydrogen ion from an acid to form HCl. An acid and the base it forms when it loses a hydrogen ion are called a **conjugate acid–base pair**. The HCl and  $\text{Cl}^-$  are a conjugate acid–base pair.

The molecules or ions of the acid and the base comprising a conjugate pair differ by one hydrogen ion. The acid, with one more hydrogen ion than the base, is said to be the conjugate acid of the base. For example, HCl is the conjugate acid of the base  $\text{Cl}^-$ . Likewise, the base, with one less hydrogen ion than the acid, is called the conjugate base of the acid.  $\text{Cl}^-$  is the conjugate base of HCl. Further examples of acids and their conjugate bases, together with bases and their conjugate acids, are given in Table 13.4. In this table, HA has been used as the general formula of an acid, and  $\text{A}^-$  its conjugate base.

TABLE 13.4 EXAMPLES OF ACID-BASE CONJUGATE PAIRS

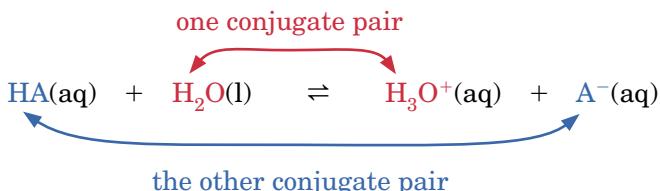
Acid (HA)	Conjugate base (A <sup>-</sup> )	Base (A <sup>-</sup> )	Conjugate acid (HA)
HCl	Cl <sup>-</sup>	F <sup>-</sup>	HF
HBr	Br <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	HNO <sub>3</sub>
H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	HPO <sub>4</sub> <sup>2-</sup>
CH <sub>3</sub> COOH	CH <sub>3</sub> COO <sup>-</sup>	H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>
H <sub>2</sub> O	OH <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	H <sub>2</sub> CO <sub>3</sub>
NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub>	S <sup>2-</sup>	HS <sup>-</sup>

Because the Brønsted–Lowry theory requires that acids react with bases, any acid–base reaction involves two conjugate pairs. This can be illustrated using the example of acetic acid with water:



In this reaction, one conjugate pair is  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$ , and the other is  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$ . The acetate ion,  $\text{CH}_3\text{COO}^-$ , is the conjugate base of acetic acid, while the hydronium ion,  $\text{H}_3\text{O}^+$ , is the conjugate acid of water.

These ideas can be generalised by considering the reaction of the general acid HA with water. The two conjugate acid–base pairs are  $\text{HA}/\text{A}^-$  and  $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ :



### → Example 13.2

Identify the conjugate pairs in the following reactions. Label the acid and the base in each pair.

- a  $\text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) + \text{OH}^-(\text{aq})$
- b  $\text{F}^-(\text{aq}) + \text{HSO}_4^{2-}(\text{aq}) \rightarrow \text{SO}_4^{2-}(\text{aq}) + \text{HF}(\text{aq})$

### → Solution

- a  $\text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) + \text{OH}^-(\text{aq})$
- One conjugate pair is  $\text{HCO}_3^-$  (base) and  $\text{H}_2\text{CO}_3$  (acid).  
 The second conjugate pair is  $\text{H}_2\text{O}$  (acid) and  $\text{OH}^-$  (base).  
 (For each pair, the molecule/ion with the larger number of H atoms in its formula is the acid.)
- b  $\text{F}^-(\text{aq}) + \text{HSO}_4^{2-}(\text{aq}) \rightarrow \text{SO}_4^{2-}(\text{aq}) + \text{HF}(\text{aq})$
- One conjugate pair is  $\text{F}^-$  (base) and HF (acid).  
 The second conjugate pair is  $\text{HSO}_4^{2-}$  (acid) and  $\text{SO}_4^{2-}$  (base).

### → Example 13.3

- a Give the formula of the conjugate acid of:
  - i  $\text{CN}^-$
  - ii  $\text{HPO}_4^{2-}$
- b Give the formula of the conjugate base of the following species:
  - i  $\text{H}_2\text{SO}_3$
  - ii  $\text{OH}^-$

### → Solution

- a The conjugate acid will have one more  $\text{H}^+$  ion than the base:
  - i  $(\text{CN}^- + \text{H}^+) = \text{HCN}$
  - ii  $(\text{HPO}_4^{2-} + \text{H}^+) = \text{H}_2\text{PO}_4^-$
- b The conjugate base will have one less  $\text{H}^+$  than the acid:
  - i  $(\text{H}_2\text{SO}_3 - \text{H}^+) = \text{HSO}_3^-$
  - ii  $(\text{OH}^- - \text{H}^+) = \text{O}^{2-}$

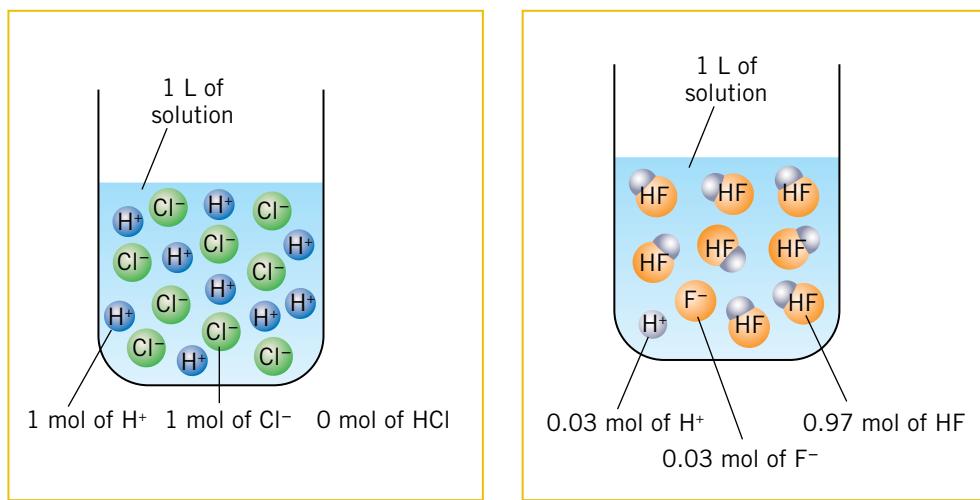
### \* Review exercise 13.3

- 1 Which of the following reactions are regarded as Brønsted–Lowry acid–base reactions? For these reactions identify which reactant is acting as the Brønsted–Lowry acid and which is acting as the Brønsted–Lowry base.
  - a  $\text{SO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HSO}_3^-(\text{aq}) + \text{OH}^-(\text{aq})$
  - b  $\text{HS}^-(\text{aq}) + \text{NH}_3(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{S}^{2-}(\text{aq})$
  - c  $\text{H}_2\text{O}_2(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
  - d  $\text{H}_2\text{O}(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$
- 2 Draw electron dot diagrams showing what happens when:
  - a gaseous HCl is added to water, according to the Brønsted–Lowry theory
  - b the carbonate ion acts as a Brønsted–Lowry base in its reaction with water.
- 3 Write equations for the dihydrogenphosphate ion reacting with water as a:
  - a Brønsted–Lowry acid
  - b Brønsted–Lowry base.
- 4 The hydrogensulfide ion,  $\text{HS}^-$ , is amphoteric.
  - a What is meant by the word ‘amphoteric’?
  - b When  $\text{HS}^-$  is added to hydrochloric acid, it acts as a Brønsted–Lowry base. Write the equation for the reaction between  $\text{HS}^-(\text{aq})$  and the hydronium ions in the hydrochloric acid.
  - c  $\text{HS}^-$  acts as a Brønsted–Lowry acid when it is added to a solution of sodium hydroxide. Write an equation for the reaction between  $\text{HS}^-(\text{aq})$  and the hydroxide ions in the sodium hydroxide solution.
- 5 Give the formulas for:
  - a the conjugate bases of HI,  $\text{HNO}_2$ ,  $\text{HCO}_3^-$ ,  $\text{PH}_4^+$
  - b the conjugate acids of  $\text{SO}_3^{2-}$ ,  $\text{O}^{2-}$ , HF,  $\text{NH}_3$ .
- 6 Identify the conjugate acid–base pairs in the following reactions:
  - a  $\text{HCN}(\text{g}) + \text{OH}^-(\text{aq}) \rightarrow \text{CN}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
  - b  $\text{H}_2\text{SO}_4(\text{l}) + \text{HNO}_3(\text{l}) \rightarrow \text{H}_3\text{SO}_4^+(\text{l}) + \text{NO}_3^-(\text{l})$ .

## 13.4 Strong and weak acids and bases

Some acids are used to sprinkle on food, add flavour and fizz to soft drinks and are in edible products like yoghurt. Other acids are treated with great care, and if they are spilt on skin, they need to be quickly washed off before they cause ‘burns’. Obviously, there are some important differences in the ‘amount of acidity’ in different acids. Acetic acid in vinegar, citric acid and carbonic acid in drinks, and lactic acid in yoghurt are classified as **weak acids**. The acids such as hydrochloric acid, nitric acid and sulfuric acid that can cause damage when spilt are identified as **strong acids**.

According to the Arrhenius theory, when strong acids are dissolved in water, all the acid molecules break up into hydrogen ions and negative ions. For instance, if 1 mole of HCl is dissolved in water, 1 mole of  $\text{H}^+$  ions and 1 mole of  $\text{Cl}^-$  ions are formed. No HCl molecules remain in the solution, as shown in Figure 13.8a. If a weak acid is added to water, only some of the molecules are ionised. For example, if 1 mole of hydrogen fluoride molecules, HF, is dissolved in 1 L of water, only approximately 0.03 mole of the molecules are ionised, forming around 0.03 mole of  $\text{H}^+$  ions and 0.03 mole of  $\text{F}^-$  ions.



a 1 L of  $1 \text{ mol L}^{-1}$  HCl solution,  
a strong acid

b 1 L of  $1 \text{ mol L}^{-1}$  HF solution,  
a weak acid

Figure 13.8 Different numbers of ions formed when 1 mole of a strong acid (HCl) and 1 mole of a weak acid (HF) are dissolved in 1 L of solution.

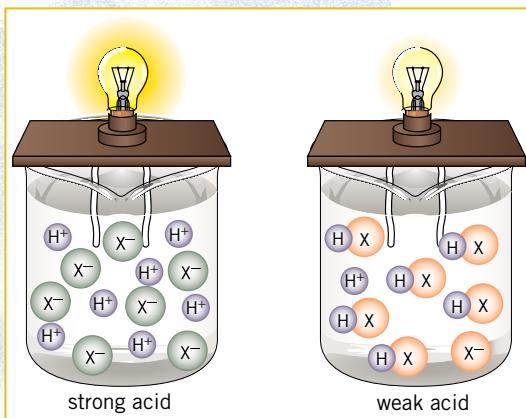
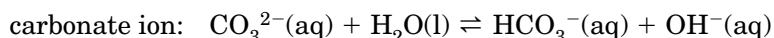
(Note: The hydrogen ions in solution are actually present as hydronium ions,  $\text{H}_3\text{O}^+$ .)

Similarly, with bases, a **strong base** completely breaks up into ions when added to water, but a **weak base** only partially ionises (or only some of the weak base molecules react with the water). For instance, when 1 mole of sodium hydroxide, a strong base, is added to water, it dissolves and completely breaks up into ions to form 1 mole of  $\text{OH}^-$  ions and 1 mole of  $\text{Na}^+$  ions. However, when 1 mole of ammonia molecules,  $\text{NH}_3$ , is dissolved in 1 L of water, only about 0.004 mole of the ammonia molecules ionise to form approximately 0.004 mole of  $\text{OH}^-$  ions and 0.004 mole of  $\text{NH}_4^+$  ions. Some examples of strong and weak acids and bases are given in Table 13.5.

**TABLE 13.5 SOME COMMON STRONG AND WEAK ACIDS AND BASES**

Strong acids	Weak acids	Strong bases	Weak bases
nitric acid, $\text{HNO}_3$ sulfuric acid, $\text{H}_2\text{SO}_4$ hydrochloric acid, $\text{HCl}$ hydrobromic acid, $\text{HBr}$ hydroiodic acid, $\text{HI}$ perchloric acid, $\text{HClO}_4$	acetic acid, $\text{CH}_3\text{COOH}$ hydrofluoric acid, $\text{HF}$ phosphoric acid, $\text{H}_3\text{PO}_4$ sulfurous acid, $\text{H}_2\text{SO}_3$ nitrous acid, $\text{HNO}_2$ hypochlorous acid, $\text{HClO}$ carbonic acid, $\text{H}_2\text{CO}_3$ hydrogen cyanide, $\text{HCN}$ hydrogen sulfide, $\text{H}_2\text{S}$ lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ citric acid, $\text{C}_6\text{H}_8\text{O}_7$ ammonium ion, $\text{NH}_4^+$ hydrogensulfate ion, $\text{HSO}_4^-$	metal hydroxides, e.g. sodium hydroxide, $\text{NaOH}$ potassium hydroxide, $\text{KOH}$ calcium hydroxide, $\text{Ca}(\text{OH})_2$	ammonia, $\text{NH}_3$ hydrogencarbonate ion, $\text{HCO}_3^-$ carbonate ion, $\text{CO}_3^{2-}$ sulfide ion, $\text{S}^{2-}$ phosphate ion, $\text{PO}_4^{3-}$ acetate ion, $\text{CH}_3\text{COO}^-$ fluoride ion, $\text{F}^-$

The hydroxide ions formed when a weak base is added to water are a result of the weak base reacting with water. Some examples of the reactions with water of some weak bases are given below. In each case, because the bases are weak, only a small amount of the dissolved base reacts with the water.



**Figure 13.9** A solution of a strong acid is a better conductor than a solution of a weak acid (assuming both solutions are of similar concentrations). (The wires and power source of the electrical circuits have not been shown in the diagrams.)

### Strong and weak, dilute and concentrated

In chemistry these four words have precise meanings, but in general conversation the meanings can be quite different. For example, when a person asks for a cup of weak tea, they are actually asking for a drink with very little tea dissolved in it. In other words, they want a cup of dilute tea. As described above, strong and weak acids and bases refer to the amount of the acid or base that ionises or dissociates when dissolved in water. However, dilute and concentrated refer to the amount of substance dissolved in a certain volume of solution. A  $0.01 \text{ mol L}^{-1}$   $\text{HCl}$  solution is an example of a dilute solution of a strong acid, and a  $10.0 \text{ mol L}^{-1}$   $\text{NH}_3$  solution is an example of a concentrated solution of a weak base.

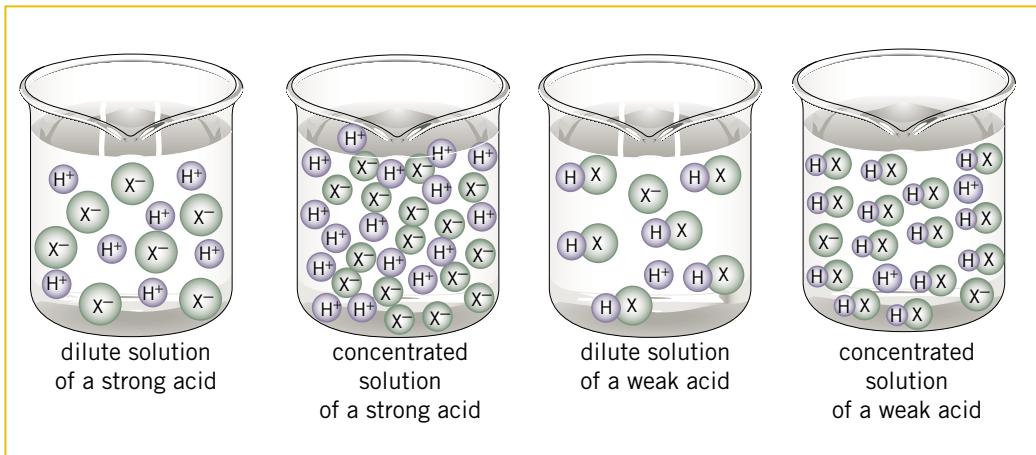


Figure 13.10 Strong or weak? Concentrated or dilute?

### \* Review exercise 13.4

- The photograph in Figure 13.11 shows the reaction between zinc and hydrochloric acid on the left and zinc and acetic acid on the right. The concentrations of the two acids are  $0.1 \text{ mol L}^{-1}$ . Using the words ‘concentrated’, ‘dilute’, ‘weak’, and ‘strong’, explain what is observed in these two test tubes.
- a**
  - Both ammonia and acetic acid are described as ‘weak’. Explain what is meant by this statement.
  - Predict and explain the conductivity of an aqueous solution of each of these compounds.
- b** A solution containing 0.1 mole of ammonia dissolved in water is added to a solution containing 0.1 mole of acetic acid dissolved in water. The new solution is an excellent conductor of electricity. Propose an explanation for this observation.

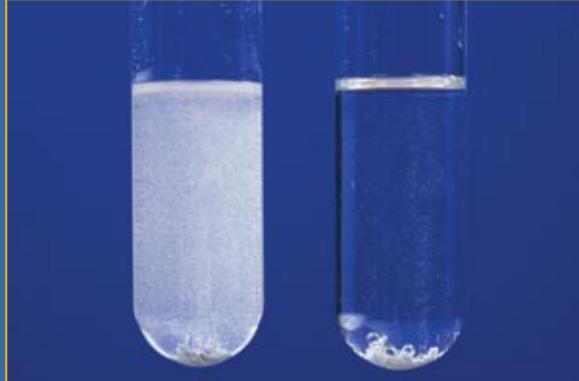
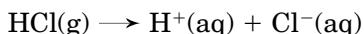


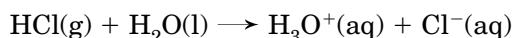
Figure 13.11 Different rates of reaction.

## 13.5 Polyprotic acids

Acids such as hydrochloric acid,  $\text{HCl}$ , nitric acid,  $\text{HNO}_3$ , and acetic acid,  $\text{CH}_3\text{COOH}$ , are commonly known as monoprotic acids because each molecule of the acid produces only one hydrogen ion during the ionisation process in aqueous solution. For example, the following equations show the  $\text{HCl}$  molecule producing one  $\text{H}^+$  ion during ionisation in water:

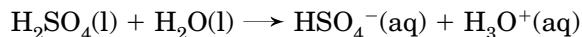


or, alternatively

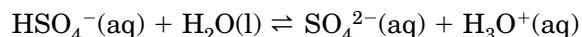


Some acids such as sulfuric acid,  $\text{H}_2\text{SO}_4$ , and phosphoric acid,  $\text{H}_3\text{PO}_4$ , produce more than one hydrogen ion when they dissolve in water. These acids are known as **polyprotic acids**.

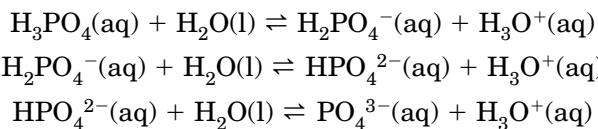
Sulfuric acid is an example of a diprotic acid. It is a strong acid, and so in water it completely loses its ‘first’ hydrogen ion:



The hydrogensulfate ion formed in this reaction then acts as a weak acid resulting in the loss of the ‘second’ hydrogen ion:



Phosphoric acid is a triprotic acid because it has three hydrogen ions it can lose or donate in a reaction with a base. For example, in water, the following progressive ionisations occur:



Phosphoric acid is a weak acid,  $\text{H}_2\text{PO}_4^-$  is a weaker acid and, in turn,  $\text{HPO}_4^{2-}$  is an even weaker acid. That is, the first ionisation reaction occurs to a greater extent than does the second reaction, which occurs to a greater extent than the third reaction.

### \* Review exercise 13.5

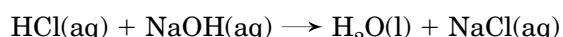
- 1 Write the complete set of equations for the reaction of each of the following polyprotic acids with water:
  - a carbonic acid,  $\text{H}_2\text{CO}_3$
  - b sulfurous acid,  $\text{H}_2\text{SO}_3$
  - c hydrogen sulfide,  $\text{H}_2\text{S}$ .
- 2 Acetic acid,  $\text{CH}_3\text{COOH}$ , has four hydrogen atoms in the formula but is described as a monoprotic acid.
  - a Draw an electron dot diagram of  $\text{CH}_3\text{COOH}$ .
  - b Propose an explanation for why acetic acid is only a monoprotic acid.
- 3 List, in order of increasing concentration, the ions present in a dilute solution of sulfuric acid.

## 13.6 Reactions of acids and bases

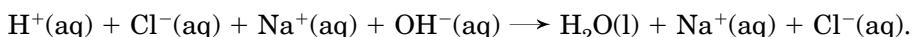
Acids react readily with a number of different substances to form predictable products. Some of these characteristic reactions are described below.

### Acids reacting with metal hydroxides

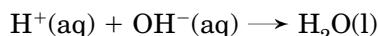
If hydrochloric acid,  $\text{HCl}$ , is mixed with a solution of sodium hydroxide, a reaction occurs to form water and a solution of sodium chloride. The molecular equation for this reaction is



This reaction is, however, more accurately represented by an ionic equation. As explained in Chapter 12, ionic equations show only the species that have undergone a change during the reaction. In writing the ionic equation, hydrochloric acid, the solution of sodium hydroxide and the solution of sodium chloride should be written as ‘separated ions’, not as neutral formulas:



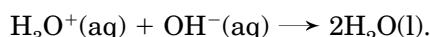
This form of the equation shows that the sodium ions and the chloride ions were dissolved in the solution before the reaction, and still remain dissolved in solution after the reaction. They have not undergone a chemical change during the reaction, and so should not be included in the ionic equation. They are the spectator ions. The ionic equation for this reaction is therefore



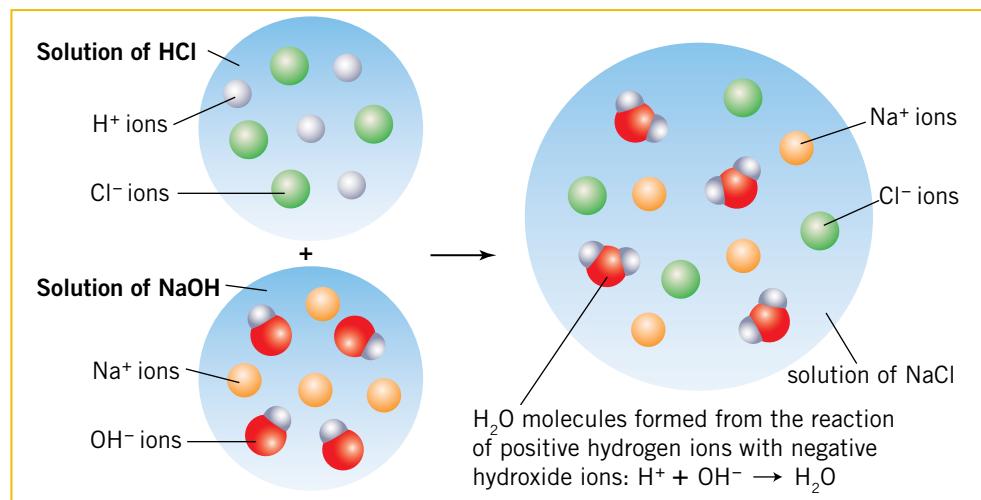
(Note: in all aqueous solutions, the hydrogen ion actually exists as the hydronium ion,  $\text{H}_3\text{O}^+$ , but for simplicity it is shown as  $\text{H}^+$  in the ionic equations for these acid reactions.)

The ionic equation shows that in this reaction of an acid with a metal hydroxide, the positive hydrogen ions from the acid join with the negative hydroxide ions to form water, as shown in Figure 13.12.

(This reaction can be interpreted using Brønsted–Lowry theory as it is actually a hydrogen ion transfer reaction. Because the  $\text{H}^+$  ions exist as  $\text{H}_3\text{O}^+$  ions in solution, the equation for the reaction could be shown as



The  $\text{H}_3\text{O}^+$  has lost a  $\text{H}^+$  ion and so has acted as the acid, and the  $\text{OH}^-$  ion has gained the  $\text{H}^+$  ion and so has acted as the base.)



**Figure 13.12 Reaction between  $\text{H}^+$  and  $\text{OH}^-$  ions that occurs when solutions of HCl and NaOH are mixed.**

The sodium chloride present in the final solution of this reaction is an example of a salt. **Salts** are composed of positive and negative ions and they are normally present in the solution formed in an acid–base reaction.

Because all acids contain hydrogen ions, any acid will undergo a similar reaction, to the one described above, with a metal hydroxide. As a result, a general word equation can be written to summarise the reaction of an acid with a metal hydroxide:



For example,

- nitric acid reacts with potassium hydroxide, to produce water and a solution of potassium nitrate
- sulfuric acid reacts with magnesium hydroxide, to produce water and a solution of magnesium sulfate.

The salts formed in the acid reactions described in this section are derived from the negative ion associated with the acid and positive ion from the metal hydroxide in the reaction. The negative ions produced by some common acids, in the formation of salts, are listed in Table 13.6.

**TABLE 13.6 NEGATIVE IONS CONTRIBUTED BY ACIDS IN THE FORMATION OF SALTS**

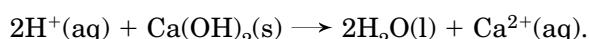
Acid	Negative ion
hydrochloric acid, HCl	chloride ion, Cl <sup>-</sup>
hydrobromic acid, HBr	bromide ion, Br <sup>-</sup>
nitric acid, HNO <sub>3</sub>	nitrate ion, NO <sub>3</sub> <sup>-</sup>
sulfuric acid, H <sub>2</sub> SO <sub>4</sub>	sulfate ion, SO <sub>4</sub> <sup>2-</sup>
acetic acid, CH <sub>3</sub> COOH	acetate ion, CH <sub>3</sub> COO <sup>-</sup>
phosphoric acid, H <sub>3</sub> PO <sub>4</sub>	phosphate ion, PO <sub>4</sub> <sup>3-</sup>

Examples of the salts formed in the reactions of some acids with metal hydroxides are given in Table 13.7.

**TABLE 13.7 EXAMPLES OF SALTS FORMED IN ACID + METAL HYDROXIDE REACTIONS**

Reactants (acid + metal hydroxide)	Name of salt formed	Formulas of ions present in the salt solution
hydrochloric acid + potassium hydroxide	potassium chloride	K <sup>+</sup> (aq) + Cl <sup>-</sup> (aq)
hydrochloric acid + magnesium hydroxide	magnesium chloride	Mg <sup>2+</sup> (aq) + Cl <sup>-</sup> (aq)
nitric acid + sodium hydroxide	sodium nitrate	Na <sup>+</sup> (aq) + NO <sub>3</sub> <sup>-</sup> (aq)
sulfuric acid + zinc hydroxide	zinc sulfate	Zn <sup>2+</sup> (aq) + SO <sub>4</sub> <sup>2-</sup> (aq)
phosphoric acid + potassium hydroxide	potassium phosphate	K <sup>+</sup> (aq) + PO <sub>4</sub> <sup>3-</sup> (aq)
acetic acid + calcium hydroxide	calcium acetate	Ca <sup>2+</sup> (aq) + CH <sub>3</sub> COO <sup>-</sup> (aq)

At times, the metal hydroxide is not added as a solution, but as a solid. The reaction between the acid and this solid hydroxide is the same as that described above, that is, the H<sup>+</sup> ions and the OH<sup>-</sup> ions combine to form H<sub>2</sub>O. However, the ionic equation appears a little different because it shows the metal hydroxide present in its solid form (written as the neutral formula), not as a solution. For example, when dilute hydrochloric acid is added to solid calcium hydroxide, the ionic equation for the reaction is



The chloride ions act as spectator ions.

Also, if a weak acid is used in the reaction, the ionic equation is slightly different because the weak acid is represented as its neutral formula rather than separated ions. For example, if a solution of acetic acid is mixed with a solution of sodium hydroxide, the ionic equation becomes



The sodium ions are the spectator ions.

#### → Example 13.4

Write ionic equations for the following reactions:

- dilute nitric acid is added to a solution of calcium hydroxide
- a solution of sulfuric acid is mixed with a little solid aluminium hydroxide
- vinegar (solution of acetic acid) is added to solid lithium hydroxide

(Note: when writing ionic equations using the ‘rules’ described in Section 12.1, the equations are not balanced until the final step.)

#### → Solution

- a Step 1:** Write reactants in their correct form for an ionic equation.

- nitric acid—a strong acid, so is written as ‘separated ions’,  $\text{H}^+ + \text{NO}_3^-$
- solution of calcium hydroxide—because this is a solution of an ionic compound, it is written as ‘separated ions’,  $\text{Ca}^{2+} + \text{OH}^-$

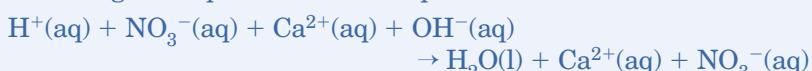
That is, the reactants are shown as



- Step 2:** Determine the products in the reaction.

- acid + hydroxide → water + salt solution
- water—written as  $\text{H}_2\text{O}$
- the salt formed is calcium nitrate and, as a solution, is written as ‘separated ions’,  $\text{Ca}^{2+} + \text{NO}_3^-$

Including these products in the equation:



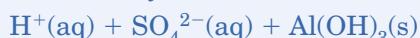
- Step 3:** Cancel out the spectator ions, and balance the equation.

The spectator ions (the ions that remain unchanged) are  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$ .

The balanced ionic equation is  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$

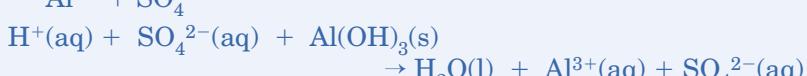
- b Step 1:** Reactants:

- sulfuric acid—a strong acid, written as  $\text{H}^+ + \text{SO}_4^{2-}$
- solid aluminium hydroxide—written as  $\text{Al(OH)}_3$

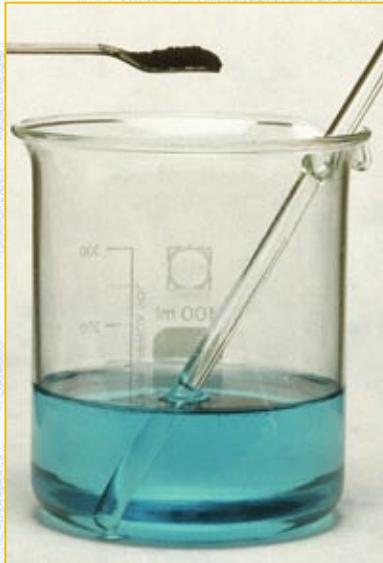


- Step 2:** Products:

- acid + hydroxide → water + salt solution
- the salt formed is aluminium sulfate (solution)—written as  $\text{Al}^{3+} + \text{SO}_4^{2-}$



*continued*



**Figure 13.13** Copper oxide added to warm sulfuric acid, forming a blue solution of copper sulfate.

**Figure 13.14** Reaction of hydrogen ions from sulfuric acid with oxide ions from copper oxide. A representation of the reaction mixture during the reaction.

**Step 3:** The spectator ion is  $\text{SO}_4^{2-}$ .

The balanced ionic equation is therefore



**c Step 1:** Reactants:

- acetic acid—a weak acid, written as  $\text{CH}_3\text{COOH}$
- solid lithium hydroxide—written as  $\text{LiOH}$



**Step 2:** Products:

- acid + hydroxide  $\rightarrow$  water + salt solution
- the salt formed will be lithium acetate (solution)—written as  $\text{Li}^+ + \text{CH}_3\text{COO}^-$



**Step 3:** There are no spectator ions.

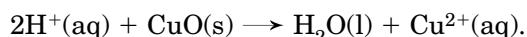
The balanced ionic equation is



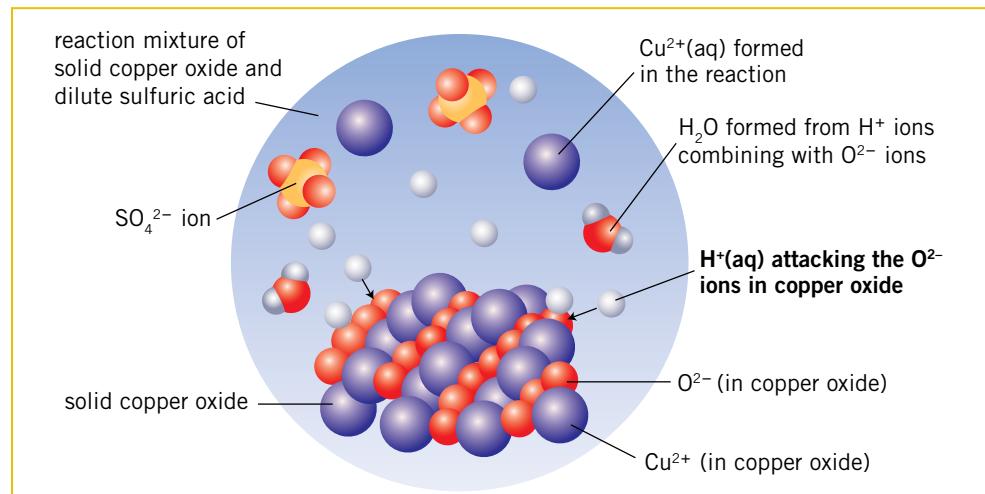
The reaction between an acid and a metal hydroxide is often called a neutralisation reaction because when the hydrogen ions and the hydroxide ions react, they are ‘removed’ from the solution to form water, a neutral substance. However, the solution formed in such a reaction is not always neutral; it depends on the nature of the salt formed. This observation will be further discussed in Unit 3.

### Acids reacting with metal oxides

Acids react with metal oxides to form water and a salt solution. For example, when a solution of sulfuric acid is added to some copper oxide and the mixture is heated, the hydrogen ions from the acid join with the oxide ions to form water, as shown in Figure 13.13. A blue-coloured solution of copper sulfate is present at the completion of the reaction. The ionic equation for this reaction is:



The sulfate ions act as spectator ions.



The general word equation for the reaction of an acid with a metal oxide is:



→ **Example 13.5**

Write an ionic equation and give observations for the reaction that occurs when dilute acetic acid is added to solid nickel oxide.

→ **Solution**

Reactants: acetic acid (weak acid):  $\text{CH}_3\text{COOH}$

solid nickel oxide:  $\text{NiO}$



Products: water:  $\text{H}_2\text{O}$

solution of nickel acetate:  $\text{Ni}^{2+} + \text{CH}_3\text{COO}^-$



Spectator ions: none

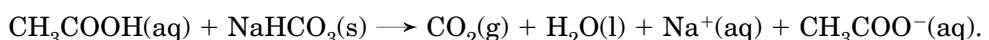
Balanced ionic equation:



**Observations:** Green solid dissolves to form a green solution and the vinegar smell may disappear (if an excess of the oxide is used).

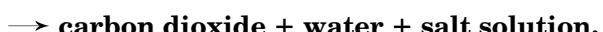
### Acids reacting with metal hydrogencarbonates and metal carbonates

When vinegar is mixed with some sodium hydrogencarbonate (sodium bicarbonate), the mixture fizzes rapidly (see Figure 9.3b). The fizzing is due to the formation of a colourless gas during the reaction of the acetic acid in the vinegar with the hydrogencarbonate ions. This gas is carbon dioxide. Two other products also formed in this reaction are water and a solution of sodium acetate. The reaction can be represented by the ionic equation



Very similar reactions occur when most acids are mixed with a compound containing the hydrogencarbonate ion. That is, carbon dioxide, water and a solution containing a salt are formed:

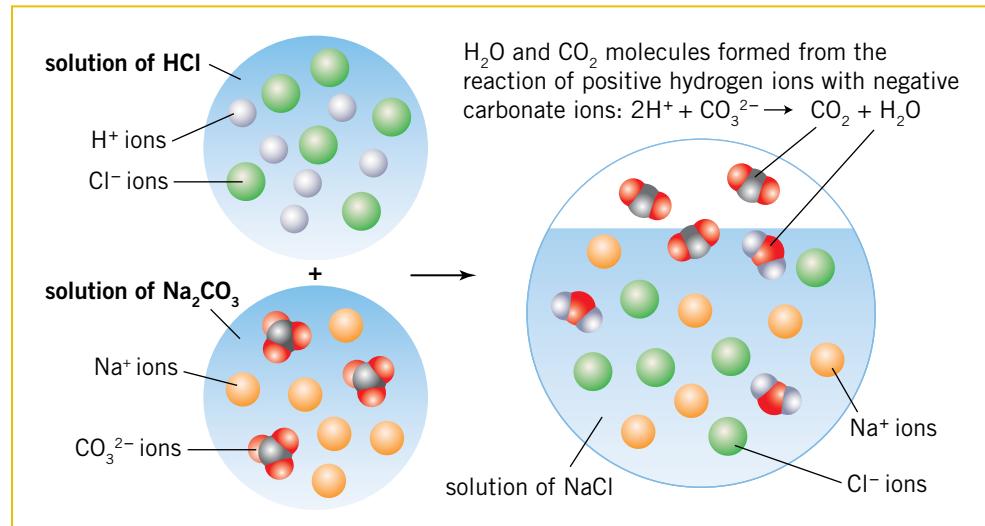
**acid + metal hydrogencarbonate**



Carbon dioxide, water and a salt solution are also formed when a compound containing a carbonate ion reacts with an acid. For example, when dilute hydrochloric acid is poured into a solution of sodium carbonate, the mixture fizzes rapidly due to the formation of a colourless gas. The colourless gas is carbon dioxide that is formed, together with water, when the carbonate ions interact with the hydrogen ions, as shown in Figure 13.15.



**Figure 13.16** Magnesium carbonate reacting with acid.



**Figure 13.15** Representation, at the atomic level, of the reaction of solutions of sodium carbonate and hydrochloric acid.

The ionic equation for this reaction is as follows, with sodium ions and chloride ions acting as spectator ions:

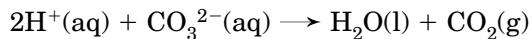


Figure 13.16 shows the reaction of hydrochloric acid with a solid carbonate, magnesium carbonate. The bubbles are due to the carbon dioxide formed in the reaction. The ionic equation for this reaction is



The reaction of a metal carbonate with an acid can be summarised with the following general word equation:

**acid + metal carbonate → carbon dioxide + water + salt solution.**

#### → Example 13.6

Give the ionic equations and observations for the following two reactions:

- a a 0.1 mol L<sup>-1</sup> sulfuric acid solution is added to solid copper carbonate.
- b a solution of potassium hydrogencarbonate is mixed with dilute nitric acid.

#### → Solution

- a Reactants: sulfuric acid (strong acid):  $\text{H}^+ + \text{SO}_4^{2-}$   
solid copper carbonate:  $\text{CuCO}_3$

Products: carbon dioxide and water:  $\text{CO}_2 + \text{H}_2\text{O}$   
solution of copper sulfate:  $\text{Cu}^{2+} + \text{SO}_4^{2-}$



Spectator ion: sulfate ions,  $\text{SO}_4^{2-}$

Balanced ionic equation:



**Observations:** Green solid dissolves to form a colourless, odourless gas and a blue solution.

**b** Reactants: solution of potassium hydrogencarbonate:  $\text{K}^+$  and  $\text{HCO}_3^-$   
solution of nitric acid:  $\text{H}^+$  and  $\text{NO}_3^-$   
Products: carbon dioxide and water:  $\text{CO}_2 + \text{H}_2\text{O}$   
solution of potassium nitrate:  $\text{K}^+ + \text{NO}_3^-$

$$\text{K}^+(\text{aq}) + \text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{K}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$$

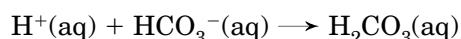
Spectator ions: potassium ions,  $\text{K}^+$  and nitrate ions,  $\text{NO}_3^-$

Balanced ionic equation:

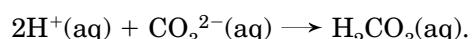


**Observations:** Two colourless solutions produce a colourless, odourless gas, and a colourless solution remains.

Even though it is not obvious by examining the products formed, the reactions of acids with hydrogencarbonates and carbonates are actually very similar to precipitation reactions and the reactions of acids with oxides and hydroxides. The similarity is that positive ions and negative ions attract one another and ‘join up’ during the reaction. In the carbonate and hydrogencarbonate reactions, however, an unstable product, carbonic acid, is formed when the positive hydrogen ions combine with the negative carbonate and hydrogencarbonate ions:



and



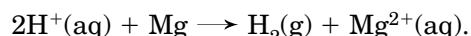
The carbonic acid then decomposes to form carbon dioxide and water:



When writing equations for the reactions of acids with carbonates and hydrogencarbonates, these intermediate steps are normally not given; just the final production of carbon dioxide and water is shown.

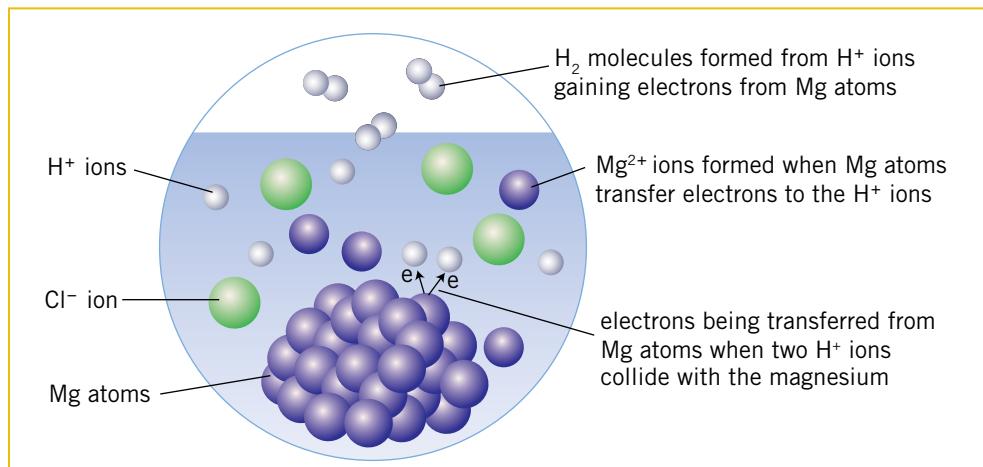
### Acids reacting with metals

Some metals react with acids to form hydrogen gas and a salt. For example, when hydrochloric acid is added to magnesium, bubbles of hydrogen gas and a colourless solution of magnesium chloride are formed. The ionic equation for this reaction is:



The chloride ions are spectator ions in this reaction.

This reaction is an example of an electron transfer reaction, often called an oxidation-reduction reaction. Electrons have been transferred from the magnesium to the hydrogen ions in the hydrochloric acid solution, as shown in Figure 13.17. The magnesium is said to have been oxidised and the hydrogen ions to have been reduced. Oxidation–reduction reactions will be discussed further in Chapters 14 and 15.



**Figure 13.17** The transfer of electrons that occurs when the hydrogen ions in hydrochloric acid react with magnesium.

The reaction of most acids with the more reactive metals can be summarised as  
**acid + metal → hydrogen + salt solution**

→ **Example 13.7**

Write an ionic equation and give observations for the reaction of aluminium with warm dilute hydrochloric acid.

→ **Solution**

Reactants: aluminium (a metallic element): Al  
hydrochloric acid:  $H^+ + Cl^-$

Products: hydrogen:  $H_2$   
solution of aluminium chloride:  $Al^{3+} + Cl^-$



Spectator ion: chloride ions,  $Cl^-$

Balanced ionic equation



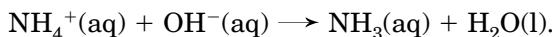
**Observations:** Silver-grey solid dissolves when added to a colourless solution and produces a colourless, odourless gas and a colourless solution.

Not all metals react with acids to form hydrogen gas. Some metals such as sodium and calcium are much more reactive than others such as gold. The differences in reactivities of metals with acid will be discussed further in Chapter 14. Also, depending on the acid used and its concentration, different products apart from hydrogen can be formed when an acid is added to a metal. For example, concentrated nitric acid usually forms nitrogen dioxide,  $NO_2$ , and water when it reacts with a metal. These metal/acid reactions that form other products instead of hydrogen will be looked at in more detail in Unit 3.

### Bases reacting with acids

Metal hydroxide bases react with acids to form water and a salt solution. This type of reaction was discussed earlier in this section. Oxide ions, carbonate ions and hydrogencarbonate ions are also bases and their reactions with acids have also previously been explained.

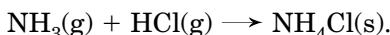
Bases also react with compounds containing the ammonium ion, such as ammonium chloride,  $\text{NH}_4\text{Cl}$ , or ammonium nitrate,  $\text{NH}_4\text{NO}_3$ . In these reactions, the ammonium ion,  $\text{NH}_4^+$ , acts as an acid and donates a hydrogen ion to the base, to form ammonia,  $\text{NH}_3$ . For example, when a solution of ammonium chloride is mixed with a solution of sodium hydroxide, ammonia and water are formed:



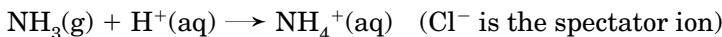
The  $\text{Na}^+$  and  $\text{Cl}^-$  ions act as spectator ions.

Ammonia, a weak base, reacts with acids, but unlike most of the other acid–base reactions, water is not one of the products in these ammonia reactions. Some reactions of ammonia with acids are:

- the reaction of gaseous ammonia with gaseous hydrogen chloride. In this reaction in the gas state,  $\text{H}^+$  ions are transferred from the  $\text{HCl}$  molecules to the  $\text{NH}_3$  molecules to form ammonium ions,  $\text{NH}_4^+$  and chloride ions,  $\text{Cl}^-$ . However, because no water is present, the ammonium ions and the chloride ions form as the ionic solid, ammonium chloride. This ionic solid appears as a white smoke, as can be seen in Figure 13.18.



- gaseous ammonia or a solution of ammonia reacting with an acid solution to form a solution containing an ammonium salt. For example, when ammonia gas is bubbled through hydrochloric acid, a solution of ammonium chloride is formed:



- the reaction of an ammonia solution with acetic acid:



**Figure 13.18** Ammonia gas, coming from the petri dish, reacts with hydrogen chloride gas in the conical flask to form ammonium chloride, which appears as a white smoke.

### \* Review exercise 13.6

- Write ionic equations and give observations for the following reactions (if there is no reaction then note this as NO REACTION)
  - A solution of lithium hydroxide is mixed with a solution of nitric acid.
  - Solid barium hydroxide is added to a solution of hydrochloric acid.
  - Sulfuric acid is added to solid magnesium oxide.
  - Solid cobalt carbonate is added to a solution of nitric acid.
  - Zinc is added to a solution of sulfuric acid.
  - Ammonia solution is mixed with a solution of sodium hydrogencarbonate.
  - A solution of ammonium sulfate and a solution of barium hydroxide are mixed together.
  - A solution of sodium hydrogencarbonate is added to a solution of nitric acid.
  - Acetic acid is added to copper oxide and warmed.
- a Describe how you would prepare a sample of solid sodium chloride if given solid sodium carbonate and hydrochloric acid.  
b How would you prepare a sample of solid barium sulfate starting with solid barium oxide and one other substance?
- Draw the electron dot diagram for the reaction of calcium with hydrochloric acid, showing how the electrons are rearranged in the reaction.

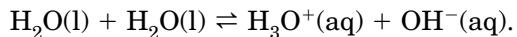
*continued*

### Review exercise 13.6 — *continued*

- 4 Write an ionic equation for a possible reaction that would fit with the following observations.
  - a A white solid produces a colourless gas when added to a colourless solution.
  - b A silver grey solid added to a colourless solution produces a colourless, odourless gas and a pink solution.
  - c A black solid disappears in a colourless solution and is replaced by a blue solution.
  - d Two colourless solutions are mixed and a colourless, odourless gas is produced.
  - e A deep green solid disappears in a colourless solution and is replaced by a deep green solution.
  - f Two colourless solutions are mixed and gently warmed. A colourless, pungent gas that turns red litmus blue is produced.
- 5 500 mL of concentrated ( $18.0 \text{ mol L}^{-1}$ )  $\text{H}_2\text{SO}_4$  has been spilled. What mass of sodium hydrogencarbonate would be required to completely neutralise this spilt acid?

## 13.7 pH

As described in Section 13.3, water undergoes self-ionisation according to the following equation:



This reaction only occurs to a very slight extent. In pure water at  $25^\circ\text{C}$ , the concentration of  $\text{H}_3\text{O}^+$  is just  $1 \times 10^{-7} \text{ mol L}^{-1}$ . Since  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are formed in equal amounts in the self-ionisation reaction, the concentration of  $\text{OH}^-$  in pure water must also be  $1 \times 10^{-7} \text{ mol L}^{-1}$ . Solutions in which the concentration of  $\text{H}_3\text{O}^+$  and the concentration of  $\text{OH}^-$  are equal are said to be **neutral**.

When an acid is added to pure water, the acid ionises to form  $\text{H}_3\text{O}^+$  ions. This means that in the acid solution or **acidic solution**, the concentration of  $\text{H}_3\text{O}^+$  must be greater than that in pure water. If a base, such as sodium hydroxide, is added to water,  $\text{OH}^-$  ions in solution are formed and so in the **basic solution** the concentration of  $\text{OH}^-$  must be greater than that in pure water. It therefore can be said that, at  $25^\circ\text{C}$ :

- in neutral solutions, such as pure water:  
concentration of  $\text{H}_3\text{O}^+$  = concentration of  $\text{OH}^-$  =  $1 \times 10^{-7} \text{ mol L}^{-1}$
- in acidic solutions:  
concentration of  $\text{H}_3\text{O}^+$  is greater than  $1 \times 10^{-7} \text{ mol L}^{-1}$
- in basic solutions: concentration of  $\text{OH}^-$  is greater than  $1 \times 10^{-7} \text{ mol L}^{-1}$ .

Some solutions of acids are more acidic or have greater acidity than others. For example, in  $1 \text{ mol L}^{-1}$  HCl solution, the concentration of  $\text{H}_3\text{O}^+$  is  $1.0 \text{ mol L}^{-1}$ . This is true because HCl is a strong acid and when it dissolves in water, all of the HCl molecules ionise to form  $\text{H}_3\text{O}^+$ . However, in a  $1 \text{ mol L}^{-1}$   $\text{CH}_3\text{COOH}$  solution, the concentration of  $\text{H}_3\text{O}^+$  is only about  $0.004 \text{ mol L}^{-1}$ . This is because  $\text{CH}_3\text{COOH}$  is a weak acid and only some of the dissolved acid molecules ionise to form  $\text{H}_3\text{O}^+$ . The  $1 \text{ mol L}^{-1}$  HCl solution is said to be more acidic or possess greater acidity than the  $1 \text{ mol L}^{-1}$   $\text{CH}_3\text{COOH}$  solution.

The same situation also occurs for bases. For example, because NaOH is a stronger base than ammonia,  $\text{NH}_3$ , a  $1.0 \text{ mol L}^{-1}$  NaOH solution will contain a greater

concentration of  $\text{OH}^-$  ions and so be more basic or possess greater basicity than a  $1.0 \text{ mol L}^{-1}$   $\text{NH}_3$  solution. The concentration of  $\text{OH}^-$  ions in a  $1 \text{ mol L}^{-1}$   $\text{NH}_3$  solution is about  $0.004 \text{ mol L}^{-1}$ .

The concentration of hydrogen ions,  $\text{H}^+$  (or  $\text{H}_3\text{O}^+$ ), provides a measure of the acidity of a solution. However, the small values that are generally involved make it inconvenient to use such values, particularly when it comes to providing consumers with information about how acidic or basic a product may be. In 1909, Soren Sörensen introduced the concept of pH, which he called the 'hydrogen ion exponent', to make the expression of acidity possible through a set of more convenient numbers.

The pH of an aqueous solution is defined as:

$$\text{pH} = -\log(\text{concentration of } \text{H}^+)$$

The relationship between pH and the concentration of  $\text{H}^+$  can also be represented in the following way:

if the concentration of  $\text{H}^+ = 10^{-x}$  then the pH =  $x$

For example, at  $25^\circ\text{C}$ , the concentration of  $\text{H}^+$  in:

- pure water is  $10^{-7} \text{ mol L}^{-1}$ , so the pH is 7
- $0.1 \text{ mol L}^{-1}$   $\text{HCl}$  is  $10^{-1} \text{ mol L}^{-1}$ , so the pH is 1
- $1 \text{ mol L}^{-1}$   $\text{CH}_3\text{COOH}$  is approximately  $10^{-3} \text{ mol L}^{-1}$ , so the pH is approximately 3.

It therefore follows that at  $25^\circ\text{C}$  acidic solutions are solutions whose pH values are less than 7 and that neutral solutions have a pH of 7. Solutions whose pH values are greater than 7 are basic. The relationships between the concentration of  $\text{OH}^-$ , concentration of  $\text{H}^+$  and pH in basic solutions will be explained in Unit 3. At this stage in this chemistry course, it is sufficient to recognise that at  $25^\circ\text{C}$  basic solutions have pH values greater than 7 and the more basic the solution, the greater its pH.

pH values for aqueous solutions can range from a little below –1 all the way through to values slightly above 15. Figure 13.19 shows the range of pH values for acidic, basic and neutral solutions and the pH values of some commonly used substances.

In summary, some generalisations that can be made about pH include:

- the pH of a neutral solution at  $25^\circ\text{C}$  is 7 exactly
- pH falls as the concentration of  $\text{H}^+$  increases
- acidic solutions have pH values below 7, while basic solutions have pH values above 7, at  $25^\circ\text{C}$
- the greater the acidity the lower the pH of the solution
- every change in pH by one unit represents a tenfold change in the concentration of  $\text{H}^+$ .

There are various ways of measuring the pH of a substance, depending on the degree of precision required:

- universal indicator solution (a mixture of several acid–base indicators), changes different colours depending on the pH of the substance. Universal indicator solution is the indicator that is provided with many soil-testing kits. Figure 13.19 shows the colours that universal indicator solution presents at various pH values.

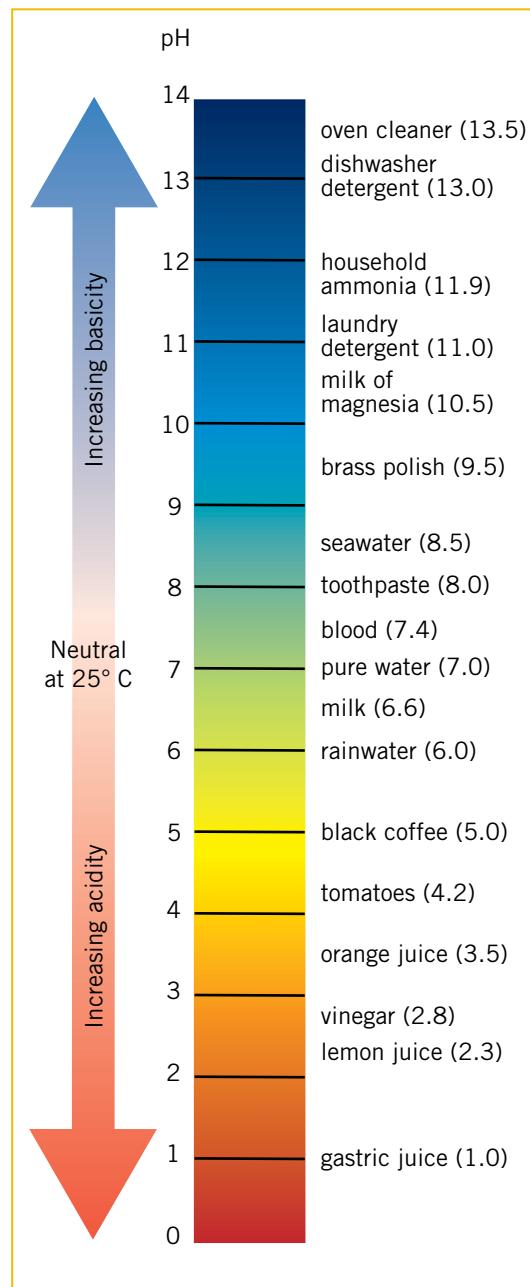


Figure 13.19 The pH values of some familiar substances. The colours ranging from red through green to blue are universal indicator colours.



Figure 13.20 A pH meter being used to measure the pH of rainwater.

- pH paper comes in several varieties depending on the precision desired for the pH determination. Paper soaked in universal indicator solution is commonly used where a general idea of pH is required. The paper produces a different colour for different pH values. However, pH papers are available with a narrower range of pH values. For example, pH paper used to measure the pH of urine may only have a range of 5.0–7.0.
- pH meters are electronic devices that are more sensitive to subtle differences in pH values and are more precise in their measurements.

Acid–base indicators are complex organic molecules that have a different colour form in an acidic solution to that in a basic solution. Many of the indicators that are commonly used are themselves weak acids. They change colour as a result of donating their acidic hydrogen ion to a base. The pH at which the colour change occurs is different for different indicators. As a result, the mixture known as the ‘universal indicator’ shows several colour changes as each successive indicator changes from one form to the other.

The pH values of solutions making up living systems are around 7. If the pH of solutions in a cell or around a cell are changed by only a small amount the chemicals making up the cell will decompose and the cell will be damaged or killed. Soaps, shampoos, water, food, drinks or any chemical that comes in contact with the body, both within and on the outside must have a pH close to 7. If the pH is too high or too low, damage will occur. There is, however, one part of the body that can withstand a pH of close to 1. This is the stomach. To assist in the digestion of food, the stomach produces hydrochloric acid with a concentration of about  $0.1 \text{ mol L}^{-1}$ , but it has a very special lining that does not decompose under these quite acidic conditions. If, however, the acidic stomach contents come in contact with other parts of the body, such as the oesophagus and teeth, for example, if a person is continually vomiting, then these body parts can be damaged.

Some of the ways in which pH values are used include:

- monitoring the environment to check that industry is not producing harmful quantities of acidic gases
- checking that blood and other body fluids are at optimum pH values, or for testing for signs of infection
- checking soil and waterways for evidence of acid (or base) contamination
- checking soil pH for growth of particular plants that may prefer acidic or basic conditions
- industrial processes that may need a measure of pH control to optimise production
- monitoring chemical reactions in the laboratory.

### \* Review exercise 13.7

- 1 Order the following solutions from lowest pH to highest pH (assume they are all of equal concentration).  
NaOH, NH<sub>3</sub>, HNO<sub>3</sub>, Ca(OH)<sub>2</sub>, H<sub>2</sub>O, CH<sub>3</sub>COOH
- 2 Which one of the following pairs of solutions could be mixed to produce a final solution with a pH of 7?
  - a Solution A with pH 3 and solution B with pH 4
  - b Solution C with pH 5 and solution D with pH 7

- c Solution E with pH 8 and solution F with pH 2
- d Solution G with pH 8 and solution H with pH 10
- 3 By what factor (increase or decrease) does the concentration of  $\text{H}^+(\text{aq})$  change in the following:
- a solution of pH 3 is diluted until the pH is 5
  - hydrochloric acid is added to a solution of pH 10 to produce a neutral solution
  - 10.0 mL of a solution of pH 1 is added to 9990 mL of water.
- 4 What is the concentration of  $\text{H}^+$  and what is the pH in each of the solutions formed in the following ways?
- 0.100 mol of hydrogen chloride is made up to 1.00 L with water
  - a  $1.00 \text{ mol L}^{-1}$  solution of nitric acid is diluted by a factor of 10 000
  - 100 L of a  $0.01 \text{ mol L}^{-1}$  solution of hydrochloric acid is concentrated by careful evaporation of the water only to a final volume of 10.0 L.

## 13.8 Acid–base properties of oxides

Oxides are formed by both metal and non-metal elements. Magnesium oxide, copper oxide and aluminium oxide are examples of metal oxides and carbon dioxide, silicon dioxide and water are example of non-metal oxides.

Metal oxides are ionic compounds; they are composed of positive metal ions and negative oxide ions. However, non-metal oxides are either covalent molecular or covalent network compounds in which the oxygen atoms are covalently bonded to the other non-metal atoms.

Oxides can be classified into four groups according to their acid–base properties:

- basic oxides—display basic properties but not acidic properties
- acidic oxides—display acidic properties but not basic properties
- amphoteric oxides—display both basic and acidic properties, depending on the reaction conditions
- neutral oxides—display neither acidic nor basic properties.

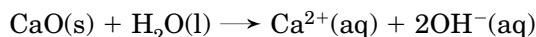
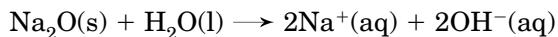
In identifying, by experiment, the acidic and basic properties of the oxides, it is necessary to broaden the meaning of ‘acidic’ and ‘basic’ given in Section 13.7. If an oxide is soluble in water, then the pH of its solution can be tested to determine whether it is an acidic or basic oxide. However, if the oxide is insoluble in water, then the test involves reacting the oxide with an acid and a base. These tests are summarised in Table 13.8.

**TABLE 13.8 DIFFERENT TYPES OF OXIDES**

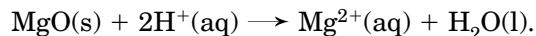
Type of oxide	Examples	pH of solution	Reaction with acid	Reaction with base ( $\text{OH}^-$ )
Basic	$\text{Na}_2\text{O}$ , $\text{MgO}$ , $\text{CaO}$ , $\text{CuO}$	greater than 7 (for soluble oxides)	react to form salt + water	do not react
Acidic	$\text{CO}_2$ , $\text{SiO}_2$ , $\text{SO}_2$ , $\text{SO}_3$	less than 7 (for soluble oxides)	do not react	react to form polyatomic ions (see next page)
Amphoteric	$\text{Al}_2\text{O}_3$ , $\text{ZnO}$	—	react to form salt + water	react to form complex ions (see next pages)
Neutral	$\text{CO}$ , $\text{N}_2\text{O}$	7	do not react	do not react

## Basic oxides

All basic oxides are metal oxides. However, not all metal oxides are basic oxides because some are amphoteric, such as,  $\text{ZnO}$  and  $\text{Al}_2\text{O}_3$ . If a metal oxide is soluble in water, it reacts with the water to form hydroxide ions. This explains why the pH of the solution is greater than 7. For example, the reactions of  $\text{Na}_2\text{O}$  and  $\text{CaO}$  with water are shown below:



Basic oxides will also react with acids to form water and salt solutions. For example, the ionic equation for the reaction of magnesium oxide with hydrochloric acid is



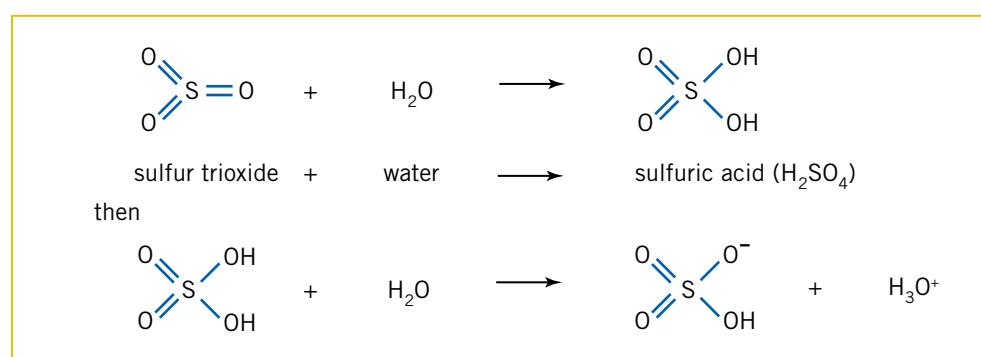
## Acidic oxides

Most acidic oxides are non-metal oxides, even though a small number of transition metals form acidic oxides. For instance, chromium(VI) oxide,  $\text{CrO}_3$ , is an acidic oxide. If an acidic oxide is soluble in water, it reacts with the water to form a hydroxy compound, which is an acid. This acid produces hydrogen ions in solution, resulting in the solution of the oxide having a pH less than 7. The acids formed when some non-metal oxides dissolve in water are given in Table 13.9.

**TABLE 13.9 ACIDS FORMED WHEN SOME NON-METAL OXIDES ARE DISSOLVED IN WATER**

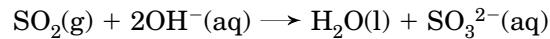
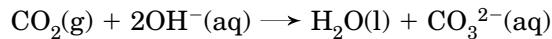
Non-metal oxide	Acid formed when oxide is added to water
$\text{CO}_2$	carbonic acid: $\text{CO(OH)}_2$ or $\text{H}_2\text{CO}_3$
$\text{NO}_2$	nitric acid + nitrous acid: $\text{NO}_2(\text{OH}) + \text{NO}(\text{OH})$ or $\text{HNO}_3 + \text{HNO}_2$
$\text{SO}_2$	sulfurous acid: $\text{SO}(\text{OH})_2$ or $\text{H}_2\text{SO}_3$
$\text{SO}_3$	sulfuric acid: $\text{SO}_2(\text{OH})_2$ or $\text{H}_2\text{SO}_4$
$\text{P}_4\text{O}_6$	phosphorous acid: $\text{P}(\text{OH})_3$ or $\text{H}_3\text{PO}_3$
$\text{P}_4\text{O}_{10}$	phosphoric acid: $\text{PO}(\text{OH})_3$ or $\text{H}_3\text{PO}_4$
$\text{Cl}_2\text{O}_7$	perchloric acid: $\text{ClO}_3(\text{OH})$ or $\text{HClO}_4$

These acids formed by the non-metal oxides are called hydroxy acids because they contain OH groups within the molecular structure. However, in water these OH groups do not form  $\text{OH}^-$ . Instead, they form  $\text{H}^+$  ions as shown for sulfuric acid in Figure 13.21. This makes the solution acidic.



**Figure 13.21 Structural equation showing the ionisation of sulfuric acid in water.**

When mixed with a solution containing  $\text{OH}^-$ , such as a solution of sodium hydroxide, the acidic oxides produce water and a polyatomic ion. This ion is the polyatomic ion of the acid the oxide forms when it is added to water, that is, the negative ion of the acid listed in Table 13.9. For example, when carbon dioxide and sulfur dioxide are bubbled through solutions of sodium hydroxide, the following reactions occur:

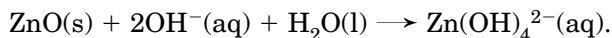


### Amphoteric oxides

Amphoteric oxides react with both acids and bases. Water and a salt solution are formed when amphoteric oxides react with an acid. For example, aluminium oxide reacts with hydrochloric acid according to the following equation:



In the reaction of an amphoteric oxide with a solution containing  $\text{OH}^-$  ions, an ion composed of two different ions, the metal ion and  $\text{OH}^-$  ion, is formed. This type of ion is called a complex ion. Water also acts as a reactant in this reaction. The equations for the reactions of two amphoteric oxides,  $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$ , with a solution of sodium hydroxide are shown below:



### Neutral oxides

The neutral oxides are all non-metallic oxides and they display no acid/base properties. They form neutral solutions when dissolved in water and they do not react with acids or bases.

### Periodic trends in acid/base properties of oxides

Moving across the periodic table, there is a gradual transition in the acid-base properties of the oxides, from basic to amphoteric to acidic, as shown in Figure 13.22. Going down a group the oxides become less acidic (more basic).

**Figure 13.22** The acid–base properties of some oxides in the periodic table.

This gradual trend can also be observed if the properties of the oxides from one particular period are examined. The bonding and acid–base properties of the period 3 oxides (of highest oxidation number) are summarised in Table 13.10.

**TABLE 13.10 ACID–BASE PROPERTIES OF OXIDES OF PERIOD 3 ELEMENTS**

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Formula of oxide	$\text{Na}_2\text{O}$	$\text{MgO}$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{P}_4\text{O}_{10}$	$\text{SO}_3$	$\text{Cl}_2\text{O}_7$	does not form an oxide
Bonding and structure	ionic	ionic	ionic	covalent, network	covalent, molecular	covalent, molecular	covalent, molecular	
Reaction with water	forms $\text{NaOH}$	insoluble	insoluble	insoluble	forms $\text{H}_3\text{PO}_4$	forms $\text{H}_2\text{SO}_4$	forms $\text{HClO}_4$	
Reaction with acid	forms $\text{H}_2\text{O} + \text{Na}^+$	forms $\text{H}_2\text{O} + \text{Mg}^{2+}$	forms $\text{H}_2\text{O} + \text{Al}^{3+}$	no reaction	no reaction	no reaction	no reaction	
Reaction with $\text{OH}^-(\text{aq})$	no reaction	no reaction	forms $\text{Al}(\text{OH})_4^-$	forms $\text{SiO}_3^{2-}$	forms $\text{PO}_4^{3-}$	forms $\text{SO}_4^{2-}$	forms $\text{ClO}_4^-$	
Acid/base properties	strongly basic	strongly basic	amphoteric	weakly acidic	moderately acidic	strongly acidic	strongly acidic	

### \* Review exercise 13.8

- Write ionic equations for the reactions of the following oxides with water.
  - $\text{K}_2\text{O}(\text{s})$
  - $\text{CO}_2(\text{g})$
  - $\text{NO}_2(\text{g})$
  - $\text{BaO}(\text{s})$
- Write balanced ionic equations to show the amphoteric nature of aluminium oxide.
- Explain, using equations, why the pH of rainwater is around 5.5 rather than 7.
- Explain in terms of the bonding of the oxide why sodium oxide is basic but sulfur dioxide is acidic.
- The properties of the oxides of elements X, Y and Z are tabulated below. Use these properties to predict whether the oxide is likely to be acidic or basic.

	Oxide of X	Oxide of Y	Oxide of Z
Appearance	White solid	White solid	Colourless gas
Conductivity of molten oxide	Non-conductor	Conductor	Non-conductor
Conductivity of aqueous solution	High	High	High



## MAJOR IDEAS

- The characteristic properties of aqueous solutions of acids and bases are shown in Table 13.11.

TABLE 13.11

Properties of acids	Properties of bases
<ul style="list-style-type: none"> <li>turn litmus red.</li> <li>conduct an electric current.</li> <li>taste sour.</li> <li>react with reactive metals to produce hydrogen gas and a salt.</li> <li>react with carbonates and hydrogencarbonates to form carbon dioxide, water and a salt.</li> <li>react with metal hydroxides and oxides to produce a salt and water.</li> </ul>	<ul style="list-style-type: none"> <li>turn litmus blue.</li> <li>conduct an electric current.</li> <li>taste bitter.</li> <li>react with acids to form a salt and water.</li> <li>react with <math>\text{NH}_4^+</math> to form <math>\text{NH}_3</math> and water.</li> </ul>

- Arrhenius theory of acids and bases:
  - An acid is a substance that produces  $\text{H}^+(\text{aq})$  in solution.
  - A base is a substance that produces  $\text{OH}^-(\text{aq})$  in solution.
  - A neutralisation reaction is the reaction between an acid and a base.
- Brønsted–Lowry theory of acids and bases:
  - An acid is a proton ( $\text{H}^+$ ) donor.
  - A base is a proton ( $\text{H}^+$ ) acceptor.
  - Amphoteric substances can react as acids or bases.
  - Every acid has a conjugate base which is related in the following way:  
 $\text{HX} \rightleftharpoons \text{H}^+ + \text{X}^-$  where HX is the acid and  $\text{X}^-$  is its conjugate base
- Water is a weak electrolyte that ionises to form  $\text{H}^+(\text{aq})$  and  $\text{OH}^-(\text{aq})$  to a small extent.
- At 25°C
  - Neutral solutions have a pH of 7
  - Acidic solutions have a pH less than 7
  - Basic solutions have a pH greater than 7
- Strong acids (for example,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ) and strong bases (for example,  $\text{NaOH}$ ) are essentially completely ionised or dissociated into ions in aqueous solution.
- For weak acids (for example,  $\text{CH}_3\text{COOH}$ ,  $\text{H}_3\text{PO}_4$ ) and weak bases (for example,  $\text{NH}_3$ ) only a small proportion of the molecules are ionised in aqueous solution.
- Polyprotic acids (for example,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ) contain more than one acidic or ionisable hydrogen per molecule of the acid.

- For polyprotic acids, successive ionisations occur to successively smaller extents.
- Oxides increase in acidity across periods in the periodic table.
- Oxides decrease in acidity down groups in the periodic table.

## QUESTIONS

- In each of the following reactions, which reactant is acting as an acid and which reactant is acting as a base (according to the Brønsted–Lowry definition)?
  - $\text{HCN} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{CN}^-$
  - $\text{PH}_3 + \text{HI} \rightarrow \text{PH}_4^+ + \text{I}^-$
  - $\text{H}_2\text{O} + \text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}_3\text{O}^+$
  - $\text{OH}^- + \text{H}_3\text{O}^+ \rightarrow 2\text{H}_2\text{O}$
  - $\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_2\text{PO}_4^-$
  - $\text{HClO}_4 + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COOH}_2^+ + \text{ClO}_4^-$
- a Write equations to show each of the following acting as an Arrhenius acid or base:
  - $\text{HNO}_3$
  - $\text{Mg}(\text{OH})_2$
  - $\text{H}_3\text{PO}_4$
- b Write an equation to show each of the following acting as a Brønsted–Lowry acid:
  - $\text{HPO}_4^{2-}$
  - $\text{NH}_4^+$
  - $\text{H}_2\text{O}$
- c Write an equation to show each of the following acting as a Brønsted–Lowry base:
  - $\text{Cl}^-$
  - $\text{H}_2\text{O}$
  - $\text{NH}_3$
- a Give the conjugate acids of the following species:
  - $\text{OH}^-$
  - $\text{HPO}_4^{2-}$
  - $\text{PH}_3$
- b Give the conjugate bases of the following species:
  - $\text{CH}_3\text{COOH}$
  - $\text{HSO}_4^-$
  - $\text{H}_2\text{O}$
- 4 Write balanced ionic equations for the following reactions:
  - Rust,  $\text{Fe}_2\text{O}_3$ , on a wrought-iron gate is treated with spirits of salts,  $\text{HCl}$ , to remove the rust.
  - Acid rain containing sulfurous acid,  $\text{H}_2\text{SO}_3$ , reacts with marble,  $\text{CaCO}_3$ , statues in a city park.
  - Baking powder, which includes the acid potassium hydrogentartrate,  $\text{KHC}_4\text{H}_4\text{O}_6$ , and sodium hydrogencarbonate,  $\text{NaHCO}_3$ , is moistened to allow reaction between the components.

- 5** Write an ionic equation and give the observations for each of the following reactions:
- Dilute hydrochloric acid is added to solid nickel carbonate
  - Calcium is added to very dilute nitric acid.
  - A solution of potassium hydroxide is mixed with a solution of sulfuric acid.
  - Copper oxide is added to dilute nitric acid.
  - Hydrobromic acid solution and a solution of sodium carbonate are mixed together.
  - A solution of acetic acid is added to a solution of potassium hydrogencarbonate.
  - Solid ammonium nitrate is gently warmed with a solution of lithium hydroxide.
  - A solution of ammonia is added to dilute sulfuric acid.
- 6** 2.00 L of a solution of hydrochloric acid is found to produce 4.76 L of hydrogen at 0°C and 101.3 kPa when reacted with excess magnesium.
- Write an ionic equation for the reaction.
  - What is the concentration, in mol L<sup>-1</sup>, of the hydrochloric acid?
- 7** In the following table match the solution on the left with the correct pH on the right:
- |   |            |
|---|------------|
| a 0.1 mol L <sup>-1</sup> NH <sub>3</sub>       | i pH = 13  |
| b 0.1 mol L <sup>-1</sup> HNO <sub>3</sub>      | ii pH = 7  |
| c 0.1 mol L <sup>-1</sup> LiOH                  | iii pH = 4 |
| d 0.1 mole L <sup>-1</sup> CH <sub>3</sub> COOH | iv pH = 10 |
| e water   | v pH = 1   |
- 8** Elements X, Y and Z are from the same period of the periodic table. The oxide of X reacts with water to produce a solution that turns blue litmus red. The oxide of Y dissolves in water to produce a solution with a pH of 12. The oxide of Z reacts with both acids and bases. Place these three elements in the correct order, from left to right, in the period.
- 9** The electrolyte in car batteries is sulfuric acid, H<sub>2</sub>SO<sub>4</sub>.
- Solutions of electrolytes conduct electricity. Why would you expect sulfuric acid, H<sub>2</sub>SO<sub>4</sub>(aq), to conduct electricity?
  - Sulfuric acid is an example of a diprotic acid. Explain what the term ‘diprotic acid’ means. Support your answer with the appropriate equations.
- c** A curious student decided to determine the concentration of sulfuric acid in a well-charged battery by taking exactly 2.00 g of the battery acid and titrating (reacting) it with 1.16 mol L<sup>-1</sup> sodium hydroxide solution. 17.1 mL of the sodium hydroxide solution was required for a complete neutralisation reaction. Calculate the percentage composition, by mass, of the sulfuric acid solution in the well-charged battery.
- 10** The heats of solution for a number of substances are listed below. Heat of solution is a measure of the energy change for the general reaction
- $$AB + H_2O(l) \rightarrow A^+(aq) + B^-(aq)$$
- |                      |                                    |
|----------------------|------------------------------------|
| HCl                  | $\Delta H_{soln} = -75\text{ kJ}$  |
| NH <sub>3</sub>      | $\Delta H_{soln} = -30\text{ kJ}$  |
| CH <sub>3</sub> COOH | $\Delta H_{soln} = -1.5\text{ kJ}$ |
| KOH                  | $\Delta H_{soln} = -56\text{ kJ}$  |
- Propose a tentative explanation for these observations in terms of the strengths of these substances as acids and bases.
- 11** The following block diagram summarises the results of a number of simple chemical reactions:
- 
- ```

graph TD
    A[White crystalline solid A] -- "concentrated H2SO4" --> B[Colourless gas B]
    B -- "NH3 gas" --> C[Dense white fumes in air — white solid C]
    D[Acid solution D] -- "lead nitrate solution" --> E[White precipitate E]
    D -- "NaOH" --> A
  
```

- Identify the substances A–E, giving the correct chemical name and formula.
- B is made from A by warming solid A with concentrated sulfuric acid. Write a balanced equation for this reaction.
- How does the structure of B differ from that of D?
- Write the ionic equation for the conversion of D to E.
- What other solution could be used to produce the same observations (that is, a white precipitate), with D, as the lead nitrate solution?

- 12** Indium, In, is in the same group in the periodic table as aluminium and forms an amphoteric oxide. Write equations that would show the amphoteric nature of this oxide.
- 13** Explain the following statements. Use equations where appropriate.
- Ammonia gas is very soluble in water. It forms a concentrated solution even though it is described as a weak base.
  - Beryllium oxide, BeO, is an amphoteric oxide.
  - The hydrogencarbonate ion is the conjugate base of carbonic acid but the conjugate acid of the carbonate ion.
  - Liquid hydrogen chloride is a non-conductor of electricity but its solution in water is an excellent conductor.
  - A dilute solution of nitric acid is a better electrical conductor than a concentrated solution of acetic acid.
- 14** **a** What volume of  $0.100 \text{ mol L}^{-1}$  hydrochloric acid is required to react completely with 25.0 mL of  $0.200 \text{ mol L}^{-1}$  barium hydroxide?
- b** Identify which of the following solutions has the greatest number of ions in 10.0 mL and explain your answer.
- $2.0 \text{ mol L}^{-1}$  acetic acid
  - $1.0 \text{ mol L}^{-1}$  phosphoric acid
  - $1.0 \text{ mol L}^{-1}$  calcium hydroxide
  - $2.0 \text{ mol L}^{-1}$  ammonia
- c**  $0.1 \text{ mol L}^{-1}$  nitric acid has a pH of 1, yet  $0.1 \text{ mol L}^{-1}$  phosphoric acid has a pH of 3. Explain these differences.
- 15** The label for a particular brand of toilet cleaner states that it contains a solution of dilute hydrochloric acid and is effective in removing lime scale (calcium carbonate) and rust (iron(III) oxide). Write balanced ionic equations for the reaction of the toilet cleaner with both lime scale and rust.
- 16** 1 L of  $2 \text{ mol L}^{-1}$  NaOH is added to 1 L of  $1 \text{ mol L}^{-1}$   $\text{H}_2\text{SO}_4$ . For each of the solutions i, ii and iii described in the next column identify:
- all of the species present (remember that  $\text{H}_2\text{SO}_4$  is a strong acid, but  $\text{HSO}_4^-$  is a weak acid)
  - the most abundant species other than water.
- i** in the separate solutions before they are mixed
- ii** when half the NaOH solution has been added to the  $\text{H}_2\text{SO}_4$  solution
- iii** when all the NaOH solution has been added to the  $\text{H}_2\text{SO}_4$  solution.
- 17** Tooth enamel is made from the ionic compound hydroxyapatite, whose formula is  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ .
- What ions are present in this compound?
  - After a meal, the pH of saliva may be around 5.
    - Is the saliva acidic or basic? Explain your answer.
    - Which of the ions in hydroxyapatite is most likely to react under these conditions? Write the ionic equation for the reaction.
- 18** An antacid tablet contains 750 mg  $\text{CaCO}_3$  and 200 mg  $\text{Al(OH)}_3$ .
- Write equations to represent the reactions between  $\text{CaCO}_3$  and  $\text{Al(OH)}_3$  and gastric juice acid, HCl.
  - Assuming gastric juice is  $0.15 \text{ mol L}^{-1}$  HCl, calculate the volume of gastric juice that would be neutralised by the antacid tablet.
- 19** Consider the following quote from a gardening website:  
'It is necessary to appreciate the fact that acids are produced as byproducts of even the most favorable decay and that too much acid will spoil compost. This problem can be overcome if some lime is included in the heap. This can be done if some powdered chalk or limestone is sprinkled on alternate layers of waste vegetation. A fertiliser or a dressing containing lime such as Nitrochalk can be used instead. It is important to note that lime and chalk must not be allowed to come into contact with sulphate (sic) of ammonia which might be used as an accelerator. If this is done, ammonia will be liberated and nitrogen lost as ammonia gas.'
- <http://www.backyardgardener.com/compost/index.html>
- Why does the author claim that too much acid will spoil the compost?
  - The remedy proposed is to add powdered chalk or limestone. Write an ionic equation to show how limestone would react with acid in the compost heap.
  - Assuming that the lime referred to in the article is either calcium oxide or calcium hydroxide, explain, using equations, the concern in the last two sentences about the loss of nitrogen from the heap.

The diagram below shows the availability of various plant nutrients and micronutrients at different soil pH values.

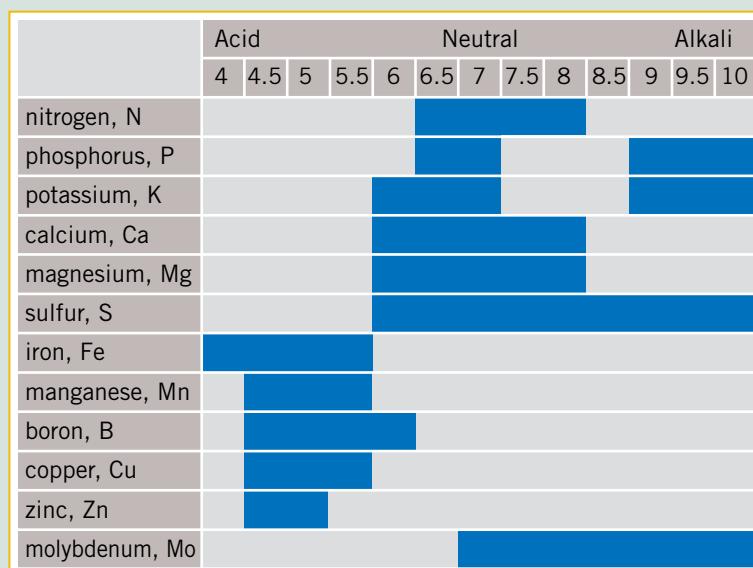


Figure 13.23 Elements available to plants at different pH values.

- d Why is it that iron, copper and zinc are more readily available to plants at low pH values, but potassium, calcium and magnesium are more likely to be available to plants at higher pH values?
- e A particular plant needs to have access to nitrogen, phosphorus, potassium, and molybdenum for best growth. What is the optimum pH range for the soil to provide the best growth for this plant?

- 20 A report on a particular archaeological site makes the following comment.

'An archaeological excavation by the Museum of London Archaeology Service at Priory Crescent, Prittlewell, Essex in autumn 2003 unearthed a 7th century grave that is perhaps the most spectacular discovery of its kind made during the past 50 years—the grave is probably that of an Anglo-Saxon King of Essex. The range and combination of objects and how they were placed in the grave to create a setting for the dead king is unique. Weapons, equipment for feasting and personal possessions were found. The coffin contained items that had been placed on the body as part of the burial ritual. These included two small gold foil crosses, two gold coins and a gold belt buckle. The survival of the chamber and its contents is due to the mound above the grave collapsing into the open chamber as the roof timbers decayed. However, the high acidity of the sand filling the burial chamber has meant that no trace of a body survived. The objects in the grave such as the sword suggest it was almost certainly that of a man. The contents of the burial chamber, down to the 'king's' shoe buckles, were still in place.'

[http://www.britarch.ac.uk/archaeoblog/blogger\\_rss.xml](http://www.britarch.ac.uk/archaeoblog/blogger_rss.xml)

- a In many archaeological sites human remains are found as bones. In this case, no human remains were found. If human bone comprises a large amount of calcium carbonate and calcium phosphate, write equations to explain the absence of any bone in this particular site.
- b Despite the absence of bone, gold coins and other artefacts made of gold were found. Why did the gold not react with the highly acidic sand?

# 14

# Oxidation and reduction reactions

## BY THE END OF THE CHAPTER YOU SHOULD BE ABLE TO:

- explain oxidation and reduction as an electron transfer process
- use oxidation numbers to identify the oxidant and reductant in an oxidation–reduction reaction
- write and balance simple redox equations
- give examples of metal and halogen displacement reactions.

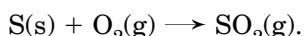
## 14.1 Definition of oxidation and reduction

### Historical definition



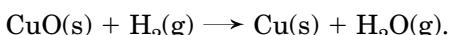
Figure 14.1 Sulfur burns with a blue flame.

Combustion reactions were one of the first types of reaction studied by early chemists. This type of reaction involves the burning substance reacting with oxygen from the air. For example, when sulfur is burnt, it reacts with oxygen to form sulfur dioxide:



Historically, the process in which a substance gains oxygen was called oxidation. It can therefore be said that sulfur is oxidised during the reaction in the above example.

Removal of oxygen was defined as reduction by these early chemists. For example, copper oxide is said to be reduced when it is heated in the presence of hydrogen:



These earliest definitions of oxidation and reduction were also extended to include the loss or gain of hydrogen. In a reaction such as the combustion of methane



the methane was said to be oxidised because it lost hydrogen, while the oxygen has been reduced since it has gained hydrogen. From studying reactions such as these last two, it also became obvious that the processes of oxidation and reduction are interdependent. During the combustion of methane for example, as one substance ( $\text{CH}_4$ ) loses hydrogen and is oxidised, another substance ( $\text{O}_2$ ) gains the hydrogen and is reduced.

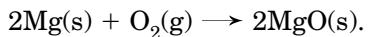
If oxidation and reduction reactions were reserved just for processes in which oxygen and hydrogen are gained or lost, this classification would have limited use in chemistry. With the development of the atomic theory, it was recognised that oxidation and reduction as a process has a much broader scope and could be explained in terms of the transfer of electrons.



Figure 14.2 Magnesium burning. The white smoke formed is magnesium oxide.

### Oxidation and reduction as an electron transfer process

When magnesium is heated in a Bunsen burner flame, it burns vigorously. This reaction of magnesium with oxygen can be summarised in the equation:



According to the historical definition, the magnesium has been oxidised. In this oxidation process, the originally neutral magnesium atoms have become magnesium ions,  $\text{Mg}^{2+}$ , in magnesium oxide. Each magnesium atom has lost two electrons to form magnesium ions, as shown in the following equation:



If a substance loses electrons, as the magnesium has, it is said to have been oxidised or to have undergone **oxidation**.

During the combustion of magnesium, the originally neutral, covalently bonded oxygen molecules have been converted to oxide ions,  $\text{O}^{2-}$ . In this part of the reaction, each oxygen molecule has gained four electrons to form two oxide ions,  $\text{O}^{2-}$ :



A substance that gains electrons in a reaction, like the  $O_2$  molecules, is said to have been reduced or to have undergone **reduction**.

In summary, during the reaction of magnesium with oxygen, electrons have been transferred from the magnesium atoms to the oxygen molecules, as shown in the electron dot representation of the reaction in Figure 14.3. As a result, the magnesium has been oxidised and the oxygen has been reduced.

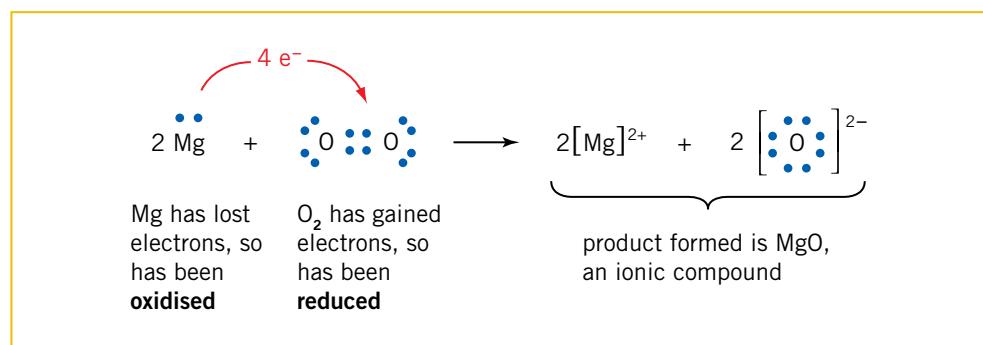


Figure 14.3 Electron dot representation of magnesium reacting with oxygen.

A reaction in which one substance has been oxidised and another has been reduced is called an **oxidation-reduction** or **redox reaction**. The two equations showing the loss of electrons (by Mg atoms) and the gain of electrons (by the  $O_2$  molecules) are called **half-equations**.

The definitions of oxidation and reduction, in terms of a transfer of electrons, are

- oxidation—loss of electrons
- reduction—gain of electrons.

Sometimes it is easier to learn definitions by changing them into acronyms. Two that are commonly used to describe redox reactions are:

**OIL RIG—Oxidation Is Loss, Reduction Is Gain**

**LEO says GER—Loss of Electrons Oxidation, Gain of Electrons Reduction.**

In addition to defining the oxidation-reduction process in terms of electron transfer, the reactants can also be described by referring to the change they have made happen during the reaction:

- The reactant that causes the oxidation of another substance is called the **oxidant** or the **oxidising agent**. In the process of removing electrons from the other reactant, the oxidant gains these electrons and so is reduced.
- A **reductant** or **reducing agent** is a substance that causes another substance to undergo reduction. This means a reductant gives electrons to another substance, and in this process the reductant is oxidised.

For example, in the combustion reaction of magnesium, the magnesium is oxidised and so has acted as the reductant. The oxygen has been reduced and so has acted as the oxidant.

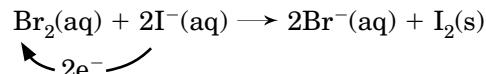
To summarise:

- reductants undergo oxidation and lose electrons in a redox reaction
- oxidants undergo reduction and gain electrons in a redox reaction.

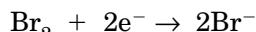


Figure 14.4 A redox reaction between aluminium and bromine.

Several further examples of the oxidants and reductants involved in oxidation-reduction reactions are given below:

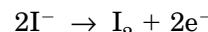


**Br<sub>2</sub>** has gained electrons to become Br<sup>-</sup>

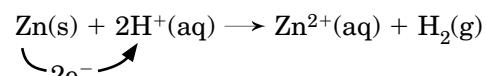


Br<sub>2</sub> has been reduced and has acted as the oxidant

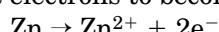
I<sup>-</sup> has lost electrons to become I<sub>2</sub>



I<sup>-</sup> has been oxidised and has acted as the reductant

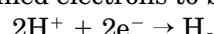


**Zn** has lost electrons to become Zn<sup>2+</sup>

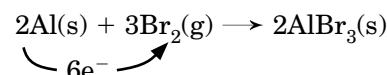


Zn has been oxidised and has acted as the reductant

**H<sup>+</sup>** has gained electrons to become H<sub>2</sub>

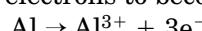


H<sup>+</sup> has been reduced and has acted as the oxidant



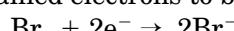
(AlBr<sub>3</sub> is composed of Al<sup>3+</sup> and Br<sup>-</sup> ions.)

**Al** has lost electrons to become Al<sup>3+</sup>



Al has been oxidised and has acted as the reductant

**Br<sub>2</sub>** has gained electrons to become Br<sup>-</sup>



Br<sub>2</sub> has been reduced and has acted as the oxidant

#### → Example 14.1

Identify which reactant has been oxidised and which has been reduced in the following reactions:



#### → Solution

a Fe<sup>3+</sup> has gained electrons to form Fe<sup>2+</sup>:  $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$

Cu has lost electrons to form Cu<sup>2+</sup>:  $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$ .

**Fe<sup>3+</sup> has been reduced, Cu has been oxidised.**

b Br<sub>2</sub> has gained electrons to form Br<sup>-</sup>:  $\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$ .

S<sup>2-</sup> has lost electrons to form S:  $\text{S}^{2-} \rightarrow \text{S} + 2\text{e}^-$ .

**Br<sub>2</sub> has been reduced, S<sup>2-</sup> has been oxidised.**

c PbCl<sub>2</sub> is an ionic compound composed of Pb<sup>2+</sup> and Cl<sup>-</sup> ions.

The Pb<sup>2+</sup> and Cl<sup>-</sup> ions have remained as the same ions during the reaction, that is, they have not gained or lost electrons. This is **not an oxidation-reduction reaction**.

### → Example 14.2

Identify the reductant and oxidant in the following reactions:

- a  $\text{Cu(s)} + \text{Br}_2(\text{g}) \rightarrow \text{CuBr}_2(\text{s})$
- b  $2\text{Ag}^+(\text{aq}) + \text{Mg(s)} \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{Ag(s)}$ .

### → Solution

- a  $\text{CuBr}_2$  is composed of  $\text{Cu}^{2+}$  and  $\text{Br}^-$  ions  
Cu has lost electrons to form  $\text{Cu}^{2+}$  and so has been oxidised.  
 $\text{Br}_2$  has gained electrons to form  $\text{Br}^-$ , and so has been reduced.  
**Cu is the reductant,  $\text{Br}_2$  is the oxidant.**
- b  $\text{Ag}^+$  has gained electrons to form Ag, and so has been reduced.  
Mg has lost electrons to form  $\text{Mg}^{2+}$  and so has been oxidised.  
 **$\text{Ag}^+$  is the oxidant, Mg is the reductant.**

### \* Review exercise 14.1

- 1 When chlorine gas,  $\text{Cl}_2$ , is bubbled through a solution of potassium iodide, the resulting products are iodine,  $\text{I}_2$ , and a solution of potassium chloride.
  - a Write an ionic equation for this reaction.
  - b Explain in terms of electron transfer why this reaction can be classified as an oxidation-reduction reaction.
  - c Draw electron dot diagrams to show the transfer of valence electrons during this reaction.
- 2 Identify the species being oxidised and being reduced in the following reactions:
  - a  $2\text{Al(s)} + 3\text{Ni}^{2+}(\text{aq}) \rightarrow 2\text{Al}^{3+}(\text{aq}) + 3\text{Ni(s)}$
  - b  $2\text{I}^-(\text{aq}) + \text{F}_2(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2\text{F}^-(\text{aq})$
  - c  $2\text{Fe}^{3+}(\text{aq}) + \text{Sn}^{2+}(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{Sn}^{4+}(\text{aq})$
  - d  $\text{Zn(s)} + \text{Cl}_2(\text{g}) \rightarrow \text{ZnCl}_2(\text{s})$
  - e  $2\text{Cu}^+(\text{aq}) \rightarrow \text{Cu(s)} + \text{Cu}^{2+}(\text{aq})$
- 3 Identify the oxidant and reductant in the following reactions:
  - a  $\text{Co(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Cu(s)} + \text{Co}^{2+}(\text{aq})$
  - b  $\text{Cl}_2(\text{g}) + \text{Ca(s)} \rightarrow \text{CaCl}_2(\text{s})$
  - c  $\text{Hg}^{2+}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Hg(l)} + 2\text{Fe}^{3+}(\text{aq})$

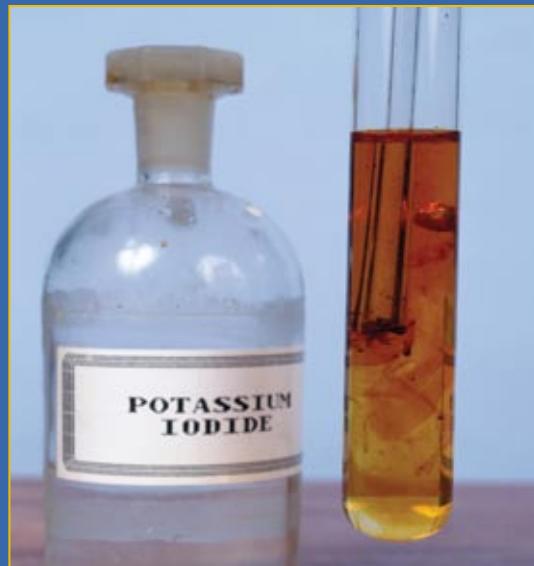


Figure 14.5 The reaction of chlorine with iodide ions. The dark colouring in the solution is due to the formation of iodine.

## 14.2 Oxidation number

For some reactions, particularly those involving covalent molecular or covalent network substances, it is difficult to determine which reactant has lost electrons and which has gained electrons. For example, for the combustion of methane



that has already been identified as a redox reaction, there are no ions involved in this reaction. Indeed, there is no obvious sign of any electron transfer happening.

To allow this and other similar reactions to be classified as redox reactions, chemists have devised an arbitrary set of rules to assign what are known as oxidation numbers to the atoms. The concept of **oxidation number** is based on the assignment of the equivalent of an ionic charge to every atom in the chemical formula of a substance. Obviously, this contradicts the concept of covalent bonding presented in this textbook, where it has been assumed that little or no ionic bonding is involved. However, the assignment of oxidation numbers to atoms is a valuable tool for identifying the full range of redox reactions.

### Rules for assigning oxidation numbers

- Oxidation numbers for the atoms in an element are zero. For example, for the atoms in Mg, Al, Zn, O<sub>2</sub>, P<sub>4</sub> and S<sub>8</sub> the oxidation number (ON) is zero.
- The oxidation number for a monatomic ion is the charge on the ion. For example, Na<sup>+</sup> (ON = +1); Cr<sup>3+</sup> (ON = +3); P<sup>3-</sup> (ON = -3), Br<sup>-</sup> (ON = -1).
- The oxidation number of oxygen in its compounds is -2. For example, the ON of oxygen in CO<sub>2</sub> is -2, and in Na<sub>2</sub>SO<sub>4</sub> it is also -2. The exceptions to this are in peroxides, for example the O<sub>2</sub><sup>2-</sup> ion, where the oxidation number of oxygen is -1, and in F<sub>2</sub>O, where the oxygen is assigned an oxidation number of +2.
- The oxidation number of hydrogen in its compounds is +1. The exception to this is for metal hydrides, containing the hydride ion, H<sup>-</sup>, which has the oxidation number of -1.
- The sum of the oxidation numbers of the atoms in a neutral molecule must add up to zero. For example, when the oxidation numbers are assigned to the carbon atom and two oxygen atoms in carbon dioxide, CO<sub>2</sub>, the result of adding together all three numbers (including the sign) must be zero.
- The sum of the oxidation numbers of the atoms in a polyatomic ion must add up to the charge on the ion. For example, when the oxidation numbers are assigned to the nitrogen and three oxygen atoms in the nitrate ion, NO<sub>3</sub><sup>-</sup>, they must add up to -1.

A particular atom often exhibits different oxidation numbers (or exists in different oxidation states) in different compounds. For example, as well as having an oxidation number of zero in the free element, chlorine exhibits five other oxidation numbers, as shown in the acids listed in Table 14.1.

**TABLE 14.1 DIFFERENT OXIDATION NUMBERS OF CHLORINE IN VARIOUS ACIDS**

| Acid         | Formula           | Oxidation number of chlorine |
|--------------|-------------------|------------------------------|
| hydrochloric | HCl               | -1                           |
| hypochlorous | HClO              | +1                           |
| chlorous     | HClO <sub>2</sub> | +3                           |
| chloric      | HClO <sub>3</sub> | +5                           |
| perchloric   | HClO <sub>4</sub> | +7                           |

Hydrogen and oxygen, however, have an oxidation number of +1 and -2, respectively, in nearly all of their compounds. (The exceptions were listed in the oxidation number rules).

→ **Example 14.3**

Assign oxidation numbers to the atoms in the following species:

- a  $\text{O}_3$
- b  $\text{S}^{2-}$
- c  $\text{P}_2\text{O}_3$
- d  $\text{SiO}_3^{2-}$
- e  $\text{MgH}_2$
- f  $\text{K}_3\text{PO}_4$

→ **Solution**

a Despite the presence of three atoms,  $\text{O}_3$  is an element and all atoms have ON = **0**

b The oxidation number of S is the ionic charge; ON = **-2**

c The sum of the oxidation numbers of the two P atoms and the three O atoms must be zero.

Each **O** atom in the compound has an oxidation number of **-2** (this is not a peroxide).

Each **P** atom must have an oxidation number of **+3**, for the sum of all oxidation numbers to be zero, that is  $[2 \times (+3)] + [3 \times (-2)] = 0$ .

d The sum of the oxidation numbers of the one Si atom and the three O atoms must be -2.

Each **O** atom in the species has an oxidation number of **-2** (this is not a peroxide).

The **Si** atom must have an oxidation number of **+4** for the sum of the oxidation numbers to be equal to -2, that is  $(+4) + [3 \times (-2)] = -2$ .

e This is an ionic compound composed of  $\text{Mg}^{2+}$  ions and  $\text{H}^-$  (hydride) ions.

The oxidation number of **Mg** is **+2**.

The oxidation number of **H** is **-1**.

f This is an ionic compound composed of  $\text{K}^+$  ions and  $\text{PO}_4^{3-}$  ions.

The oxidation number of **K** is **+1**.

The oxidation number of each **O** atom in the phosphate ion is **-2**.

The oxidation number of the **P** atom in the phosphate ion must be **+5** for the sum of the oxidation numbers of atoms in this ion to equal -3, that is  $(+5) + [4 \times (-2)] = -3$

## Identification of redox reactions using oxidation numbers

With a means to assign oxidation numbers to every atom in a formula, it is possible to redefine oxidation and reduction in terms of changes in oxidation numbers:

- **Oxidation** occurs when the oxidation number of an atom increases.
- **Reduction** occurs when the oxidation number of an atom decreases.

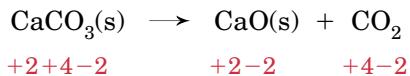
Determining if a particular chemical reaction is a redox reaction therefore involves assigning oxidation numbers to all the atoms in the chemical equation (both reactants and products) and determining whether there has been any change in these oxidation numbers. If a given atom has a higher oxidation number in the product than it has in the reactant, the reactant molecule or ion containing the atom is said to be oxidised. Similarly, if a given atom has a lower oxidation number in the product than it has in the reactant, the reactant molecule or ion containing the atom is said to be reduced.

For example, it is possible to show that the combustion of methane is a redox reaction using oxidation numbers. The oxidation numbers of the individual atoms relevant to the reaction are shown below the atoms in the equation:



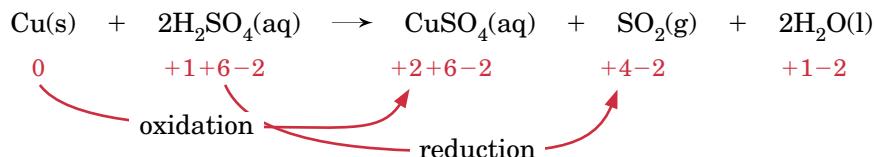
The oxidation number of carbon has increased from -4 in  $\text{CH}_4$  to +4 in  $\text{CO}_2$  and so oxidation has occurred. The oxidation number of oxygen has decreased from 0 in  $\text{O}_2$  to -2 in  $\text{H}_2\text{O}$  and so has been reduced. From this it can be concluded that methane has been oxidised and oxygen has been reduced in this reaction or that methane is the reductant and oxygen is the oxidant.

If there has been no change in the oxidation numbers of the atoms, then the reaction is not an oxidation-reduction reaction. In the reaction:



the oxidation numbers of Ca, C and O have not changed, so this is not an oxidation-reduction reaction.

A further example of an oxidation-reduction reaction and identification of the reactants being reduced and oxidised is:



For copper, Cu, its oxidation number has increased from 0 to +2, that is, it has been oxidised, and has acted as the reductant.

For sulfuric acid,  $\text{H}_2\text{SO}_4$ , the oxidation number of S has decreased from +6, to +4 in  $\text{SO}_2$ , so sulfuric acid has been reduced, and has acted as the oxidant.

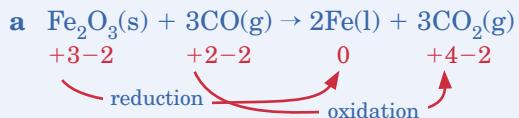
(Note that the balancing coefficients in the equation are not relevant to the determination of the oxidation numbers of the atoms of the substances involved in a reaction.)

#### → Example 14.4

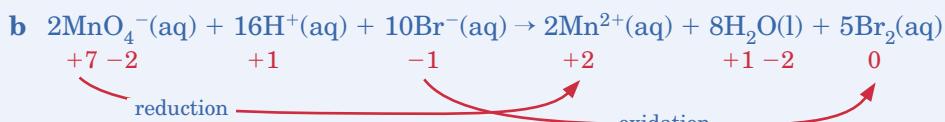
Identify which reactant has been oxidised and which has been reduced in the following reactions. Also, identify the oxidising agent and the reducing agent:

- $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \rightarrow 2\text{Fe}(\text{l}) + 3\text{CO}_2(\text{g})$
- $2\text{MnO}_4^-(\text{aq}) + 16\text{H}^+(\text{aq}) + 10\text{Br}^-(\text{aq}) \rightarrow 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O}(\text{l}) + 5\text{Br}_2(\text{aq})$
- $2\text{HF}(\text{aq}) + \text{CaCO}_3(\text{s}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{Ca}^{2+}(\text{aq}) + 2\text{F}^-(\text{aq})$

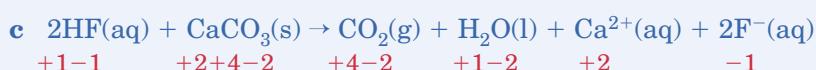
#### → Solution



**Fe<sub>2</sub>O<sub>3</sub>** has been **reduced** and so has acted as the **oxidising agent**.  
**CO** has been **oxidised** and so has acted as the **reducing agent**.



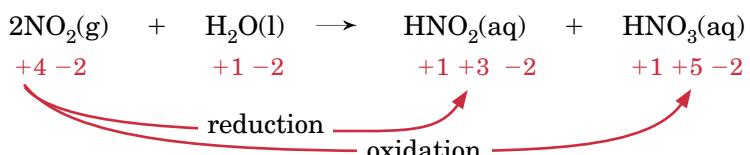
**MnO<sub>4</sub><sup>-</sup>** has been **reduced** and so has acted as the **oxidising agent**.  
**Br<sup>-</sup>** has been **oxidised** and so has acted as the **reducing agent**.



Because there has been no change in oxidation numbers, neither of the reactants has undergone oxidation or reduction.

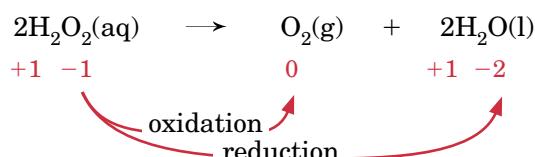
## Disproportionation

In the formation of acid rain, one of the oxides of nitrogen, NO<sub>2</sub>, combines with water to produce a mixture of nitrous and nitric acid.



In this unusual reaction, the oxidation number of nitrogen in nitrogen dioxide has gone up from +4 to +5 in HNO<sub>3</sub> (oxidation), and has also gone down from +4 to +3 in HNO<sub>2</sub> (reduction). That is, the nitrogen dioxide has been both oxidised and reduced. Or an alternative way of looking at it, the nitrogen dioxide has acted as both the oxidant and the reductant. Reactions such as this, in which a single substance undergoes both oxidation and reduction, are called **disproportionation reactions**.

A second example of a disproportionation reaction is the decomposition of hydrogen peroxide to produce oxygen and water:



In this reaction the oxidation number of the oxygen atoms in H<sub>2</sub>O<sub>2</sub> has changed from -1 to 0 and -2. That is, the H<sub>2</sub>O<sub>2</sub> has undergone both oxidation and reduction.

## \* Review exercise 14.2

- 1 Plants are unable to obtain the nitrogen essential to the production of protein and other biologically active molecules directly from atmospheric nitrogen. Instead, they rely on natural processes such as lightning to convert the nitrogen into a dilute solution of nitric acid and nitrous acid,  $\text{HNO}_2$ , in the soil after rain. Also, some bacteria in the soil can convert nitrogen in the atmosphere directly or indirectly to nitrates, nitrites and ammonium ions.

Write the formulas and give the oxidation numbers for all of the nitrogen-containing species mentioned in the paragraph above.

- 2 Assign oxidation numbers to the atoms in the following substances:

- |                           |                                              |                                    |
|---------------------------|----------------------------------------------|------------------------------------|
| a Cs                      | d $\text{NaIO}_3$                            | g $\text{BaH}_2$                   |
| b $\text{As}_2\text{O}_5$ | e $\text{HOBr}$                              | h $\text{H}_2\text{S}_2\text{O}_7$ |
| c $\text{CaI}_2$          | f $\text{H}_2\text{O}_2$ (hydrogen peroxide) | i $\text{KMnO}_4$                  |

- 3 Assign oxidation numbers to the atoms in each of the following equations and indicate which of these are redox reactions. Also, identify the oxidant and the reductant.

- a  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$   
b  $\text{CuCO}_3(\text{s}) \rightarrow \text{CuO}(\text{s}) + \text{CO}_2(\text{g})$   
c  $2\text{KClO}_3(\text{s}) \rightarrow 2\text{KCl}(\text{s}) + 3\text{O}_2(\text{g})$   
d  $\text{Ba(OH)}_2(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$

- 4 Show that the following reaction between chlorine and water is a disproportionation reaction.



- 5 Chrome-plating of ornaments and car bumpers and grilles results in the production of two toxic waste products, cyanide ions and chromate ions. In the past these products were dumped into the waterways, but today chemical treatments generally remove a large amount of them before the water is released to the environment.

The cyanide ions are treated with chlorine and the following reaction occurs



The products formed are less toxic than cyanide. Sulfur dioxide is used to treat the chromate ions as shown in the following equation



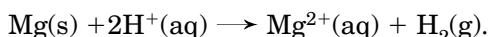
The chromium(III) ions are sufficiently insoluble in basic conditions and so can be easily removed from the water.

Both of the reactions described above are redox reactions. For each reaction, identify which reactant has been oxidised and which has been reduced. Also, identify the oxidant and the reductant for each reaction.

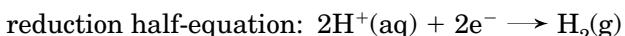
## 14.3 Writing equations for oxidation and reduction reactions

### Half-equations

As shown in Section 14.1 for the reaction of magnesium with oxygen, it is sometimes useful to split a redox equation into its two parts to show which reactant has lost electrons and which has gained electrons. These equations that represent the oxidation and the reduction processes separately are called **half-equations**. For example, when magnesium reacts with an acid to form magnesium ions and hydrogen gas, the overall equation is



This equation can be split into its two half-equations as follows:



For redox reactions involving monatomic ions, the method used to derive a half-equation is relatively simple. The steps in this method are described, together with an example, below:

| Method                                                                | EXAMPLE: derive the half-equation for the reduction of solid iodine to iodide ions in solution |
|-----------------------------------------------------------------------|------------------------------------------------------------------------------------------------|
| a Write down the oxidant (or the reductant) and the product it forms. | $\text{I}_2 \rightarrow \text{I}^-$                                                            |
| b Balance the atoms undergoing reduction (or oxidation).              | $\text{I}_2 \rightarrow 2\text{I}^-$                                                           |
| c Balance charges by adding electrons where necessary.                | $\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$                                             |
| d Introduce state symbols to complete the half-equation.              | $\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$                        |

#### → Example 14.5

Give the oxidation half-equation and the reduction half-equation for the reaction of an aqueous solution containing iron(III) ions and nickel:



#### → Solution



ON      +3      0      +2      +2

*continued*

| Method                                                                       | <b>Fe<sup>3+</sup></b><br>$\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$                       | <b>Ni</b><br>$\text{Ni} \rightarrow \text{Ni}^{2+}$                            |
|------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------|
| <b>1</b> Write down the oxidant (or the reductant) and the product it forms. | $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$                                                 | $\text{Ni} \rightarrow \text{Ni}^{2+}$                                         |
| <b>2</b> Balance the atoms undergoing reduction (or oxidation).              | $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$                                                 | $\text{Ni} \rightarrow \text{Ni}^{2+}$                                         |
| <b>3</b> Balance charges by adding electrons where necessary.                | $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$                                    | $\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$                           |
| <b>4</b> Introduce state symbols to complete the half-equation.              | <b>Fe<sup>3+(aq)</sup> + e<sup>-</sup> → Fe<sup>2+(aq)</sup></b><br>reduction half-equation | <b>Ni(s) → Ni<sup>2+(aq)</sup> + 2e<sup>-</sup></b><br>oxidation half-equation |

### Balancing redox equations

The balanced overall equation for a redox reaction can be obtained by combining the two relevant half-equations. In a redox reaction the number of electrons donated by one reactant must equal the number of electrons accepted by another reactant. To ensure that this situation is reflected in the balanced overall redox equation, that is, that no electrons appear in this overall equation, one or both of the half-equations may need to be multiplied by factors before they are combined. With equal numbers of electrons shown on opposite sides in the two half-equations, when these half-equations are added together, the electrons will cancel out.

For example, the two half-equations for the reaction of sodium with magnesium ions are



Before these two half-equations can be added together to give the balanced overall equation, the first half-equation must be multiplied by the factor of two to give



This half-equation can then be added to the magnesium ion half-equation:



Because there are an equal number of electrons on both sides of this equation, they will be cancelled to give the overall balanced ionic equation of



Providing the half-equations have been manipulated in the correct way to ensure that the number of electrons are equal in each, the final overall ionic equation obtained this way should be balanced.

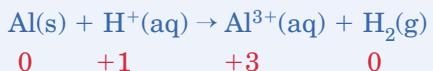
### → Example 14.6

Balance the following equation, for the reaction of aluminium with hydrochloric acid, by first breaking it up into two half-equations:



### → Solution

**Step 1:** Use oxidation numbers to determine what is oxidised and what is reduced.



**Step 2:** Write the two balanced half-equations.



**Step 3:** Multiply each equation by an appropriate factor to ensure that they both have the same number of electrons.

– multiply Al half-equation by 2, to give 6 electrons:



– multiply H<sup>+</sup> half-equation by 3, to give 6 electrons:



**Step 4:** Add the two half-equations and cancel the electrons.



**Step 5:** Add state symbols to the species.



(This process will give the balanced ionic equation for the reaction—the chloride ion is a spectator ion).

### \* Review exercise 14.3

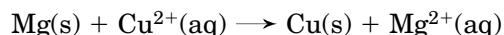
- 1 Write half-equations for each of the following:
  - a elemental sulfur can be reduced to sulfide ions.
  - b gold can be oxidised to gold(III) ions.
  - c copper(II) ions can be reduced to copper(I) ions.
  - d iodide ions can be oxidised to iodine.
- 2 Balance the following redox reactions by first writing the oxidation and reduction half-equations and then joining them to derive the balanced equation.
  - a  $\text{Cr(s)} + \text{Cl}_2(\text{aq}) \rightarrow \text{Cr}^{3+}(\text{aq}) + \text{Cl}^-(\text{aq})$
  - b Silver nitrate solution reacts with iron to produce metallic silver and a solution of iron(III) nitrate.
  - c  $\text{Sc(s)} + \text{H}^+(\text{aq}) \rightarrow \text{Sc}^{3+}(\text{aq}) + \text{H}_2(\text{g})$
  - d A solution of iron(III) nitrate reacts with aluminium to produce a solution containing iron(II) nitrate and aluminium nitrate.



Figure 14.6 The redox reaction between chlorine and bromide ions.

## 14.4 Redox displacement reactions

During a redox displacement reaction, an element either oxidises or reduces ions in a solution causing these ions to become neutral atoms (of an element). In this process it is said that one substance ‘displaces’ ions of a different substance from solution. For example, in the reaction of magnesium with copper ions to form solid copper and magnesium ions:



the magnesium displaces the copper ions from solution.

### Halogen displacement reactions

When chlorine,  $\text{Cl}_2$ , is bubbled through a colourless solution of potassium bromide, the solution turns a yellow-orange colour as bromine,  $\text{Br}_2$ , is formed (Figure 14.6). Chloride ions in solution also form in this reaction.

The two half-equations and the overall ionic equation for this reaction are:



In this reaction the chlorine has removed electrons from the bromide ions, and in doing so has acted as an oxidant. All the halogens,  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$ , are oxidants, that is, they react by removing electrons from other substances. But not all halogens are able to oxidise all halide ions. For example, when chlorine,  $\text{Cl}_2$ , is mixed with fluoride ions,  $\text{F}^-$ , no reaction occurs. The results obtained when the halogens are mixed with solutions containing the different halide ions are shown in Table 14.2.

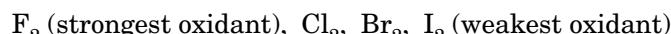
TABLE 14.2 OBSERVATIONS OF REACTIONS OF HALOGENS WITH HALIDE IONS

| halogens<br>halide ion   | $\text{F}_2$                | $\text{Cl}_2$               | $\text{Br}_2$               | $\text{I}_2$ |
|--------------------------|-----------------------------|-----------------------------|-----------------------------|--------------|
| $\text{F}^-(\text{aq})$  | no reaction                 | no reaction                 | no reaction                 | no reaction  |
| $\text{Cl}^-(\text{aq})$ | reaction occurs             | no reaction                 | no reaction                 | no reaction  |
| $\text{Br}^-(\text{aq})$ | mixture turns brown         | mixture turns brown         | no reaction                 | no reaction  |
| $\text{I}^-(\text{aq})$  | mixture turns a dark colour | mixture turns a dark colour | mixture turns a dark colour | no reaction  |

From these results, it can be seen that:

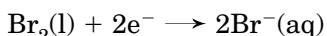
- fluorine is a sufficiently strong oxidant to remove electrons from (oxidise)  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  ions
- chlorine can oxidise  $\text{Br}^-$  and  $\text{I}^-$
- bromine can oxidise  $\text{I}^-$
- iodine is not a strong enough oxidant to remove electrons from (oxidise) any of the halide ions.

It can therefore be concluded that the order of oxidising strength of the halogens is



This order reflects the arrangement of the halogens (group 17 elements) in the periodic table, with their oxidising strength decreasing down the group.

The equations for the reactions of the halogens with the halide ions can be determined by using the following half-equations (in the forward direction for the halogens, and the reverse direction for the halides).



These half-equations have been listed in order from strongest oxidant ( $\text{F}_2$ ) to weakest oxidant ( $\text{I}_2$ ). When listed this way, predictions can be made concerning which halide ion each halogen will react with. The ‘rule’ is that a halogen will oxidise a halide ion lower on the list. For example, bromine,  $\text{Br}_2$ , will oxidise iodide ions,  $\text{I}^-$ , but not chloride ions,  $\text{Cl}^-$ .

#### → Example 14.7

For the following mixtures, predict whether or not a reaction will occur.

Write an ionic equation for the reactions that occur.

- a Fluorine gas is bubbled into a solution of sodium bromide.
- b Chlorine gas is bubbled into a solution of sodium fluoride.
- c A few crystals of iodine are added to a solution of potassium bromide.

#### → Solution

- a Fluorine,  $\text{F}_2$ , will oxidise the bromide ions,  $\text{Br}^-$ , in the sodium bromide solution. The sodium ions do not react.



The ionic equation for the reaction is therefore



- b A reaction will not occur.
- c A reaction will not occur.

### Metal displacement reactions

In a similar way to halogens, metals also undergo redox displacement reactions, and they can be listed in order of reactivity (or activity as it is sometimes called). There is, however, a major difference between halogen and metal reactions in that metals act as reductants and not oxidants. Metals donate electrons to other substances, but halogens take electrons from other substances. Table 14.3 gives an activity or reactivity series of some commonly used metals, shown as their half-equations. The metals are organised in order from most reactive to least reactive, or from strongest reductant to weakest reductant.

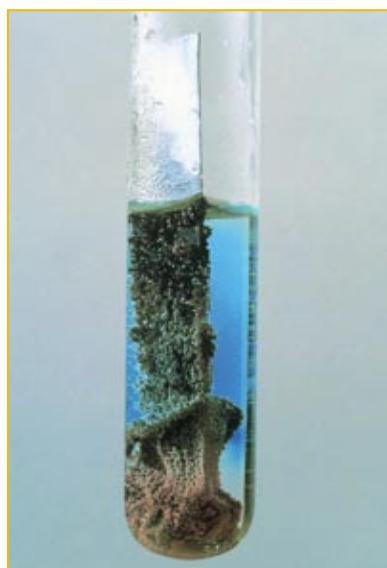


Figure 14.7 A redox displacement reaction of zinc reacting with copper ions in solution.



Figure 14.8 Sodium reacting with water.



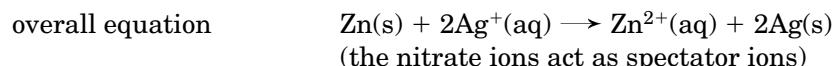
Figure 14.9 Zinc reacting with dilute hydrochloric acid.

TABLE 14.3 AN ACTIVITY SERIES OF METALS, SHOWN AS THEIR HALF-EQUATIONS, ORDERED FROM THE STRONGEST REDUCTANT TO WEAKEST REDUCTANT

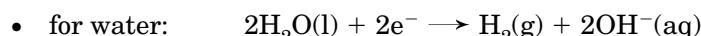
| Strength as a reductant<br>↑ | $K(s) \rightarrow K^+(aq) + e^-$<br>$Na(s) \rightarrow Na^+(aq) + e^-$<br>$Ca(s) \rightarrow Ca^{2+}(aq) + 2e^-$<br>$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$<br>$Al(s) \rightarrow Al^{3+}(aq) + 3e^-$<br>$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$<br>$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$<br>$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$<br>$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$<br>$Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$<br>$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$<br>$Ag(s) \rightarrow Ag^+(aq) + e^-$<br>$Au(s) \rightarrow Au^+(aq) + e^-$ | metals DO react with acid ( $H^+$ ) | metals DO NOT react with acid | metals DO NOT react with water |
|------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|-------------------------------|--------------------------------|
|------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|-------------------------------|--------------------------------|

This table shows that, for example, potassium donates electrons more readily than calcium, which in turn donates electrons more readily than copper. It also enables the prediction of which metals will react with which metal ions. A metal will react with, or reduce, a metal ion whose ‘parent’ metal is lower in the activity series. For example, calcium will react with magnesium ions, but not with sodium ions.

The overall equation for the reaction of a metal with a metal ion can be determined by adding the two relevant half-equations together. When zinc reacts with a solution of silver nitrate, the half-equations and the overall ionic equation are:

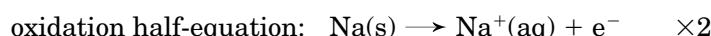


The activity series also enables the prediction of which metals will react with acid to form hydrogen gas, and which will react with water to form hydrogen and hydroxide ions. The two relevant half-equations for the acid and water in these reactions with metals are:



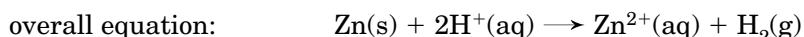
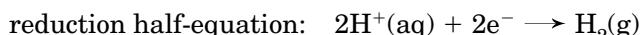
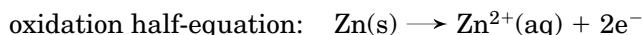
Metals ‘above’ zinc in the activity series react with water. For example, gold will not react with water but sodium will.

The half-equations and overall ionic equation for the reaction of sodium with water are given below:



The reaction of magnesium with water is very slow, but its rate can be increased by using hot water. Aluminium does not react with water unless its strong protective oxide coating is first removed. However, magnesium, aluminium and zinc will react with steam (gaseous water) to form hydrogen and the oxide.

Metals ‘above’ copper on the activity series will react with the hydrogen ions in acids to produce hydrogen. Zinc, for example, will react with dilute hydrochloric acid, but silver will not. The half-equations and overall equation for the zinc with dilute hydrochloric acid reaction are:



#### → Example 14.8

Predict if the following mixtures of substances will result in a reaction. Give ionic equations for these reactions.

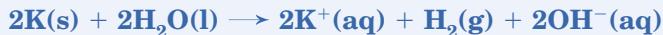
- a A small piece of potassium is dropped into a beaker of water.
- b Copper and dilute hydrochloric acid are mixed.
- c Water is poured onto some pieces of nickel.
- d Dilute sulfuric acid is poured onto some magnesium.

#### → Solution

- a Potassium will react with water, according to the following half-equations:



The overall equation for the reaction is:



- b **Copper will not react** with the hydrogen ions (or the chloride ions) in the hydrochloric acid.
- c **Nickel will not react** with water.
- d Magnesium will react with the hydrogen ions in sulfuric acid according to the following half-equations:



The overall equation for the reaction is:



## \* Review exercise 14.4

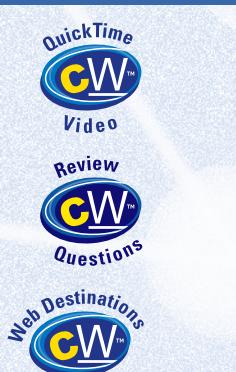
- 1 'Before' and 'after' photos of the reaction of copper with a solution of silver nitrate are depicted in Figure 14.10. Describe what is happening in this reaction and write the two half-equations, together with an overall ionic equation, to summarise the process.



Figure 14.10 Reaction of copper with silver nitrate solution.

- 2 For each of the following predict whether a reaction occurs. If it does, identify and write the separate oxidation and reduction half-equations and derive the overall ionic equation for the reaction. Also, give observations for each reaction.
- Chlorine is bubbled through a solution of sodium iodide.
  - Copper is added to dilute sulfuric acid.
  - A solution of potassium bromide is poured into a gas jar of chlorine.
  - Hydrochloric acid is added to calcium.
- 3 The ions  $\text{A}^{3+}$ ,  $\text{B}^{3+}$ ,  $\text{C}^{3+}$ , and  $\text{D}^{3+}$  can be reduced to their respective  $2+$  ions under certain conditions. The following observations have been made in a particular series of experiments:
- A solution of  $\text{B}^{3+}$  reacts with a solution containing  $\text{A}^{2+}$  to produce  $\text{B}^{2+}$  and  $\text{A}^{3+}$ .
  - There is no reaction when  $\text{C}^{3+}$  is mixed with a solution containing  $\text{A}^{2+}$ .
  - When a solution containing  $\text{B}^{2+}$  is mixed with a solution containing  $\text{D}^{3+}$  a reaction takes place to produce  $\text{D}^{2+}$  and  $\text{B}^{3+}$ .

Use this information to place the oxidising agents in these reactions in order of increasing oxidant strength.



## MAJOR IDEAS

- Oxidation and reduction can be defined as shown in Table 14.4.

TABLE 14.4

| Oxidation                         | Reduction                           |
|-----------------------------------|-------------------------------------|
| The loss or donation of electrons | The gain or acceptance of electrons |
| An increase in oxidation number   | A decrease in oxidation number      |

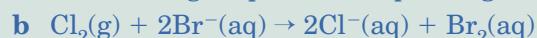
- An oxidising agent or oxidant causes the oxidation of another species and is itself reduced.
- A reducing agent or reductant causes the reduction of another species and is itself oxidised.
- Oxidation number is a real or imaginary charge on an atom which indicates its state of oxidation.
- Disproportionation involves the simultaneous oxidation and reduction of a reactant in a redox reaction.
- An oxidation half-equation shows loss of electrons. A reduction half-equation shows gain of electrons.
- A redox equation is obtained by adding half-equations that have been multiplied by factors so that the number of electrons is the same in both half-equations.
- An activity series for metals ranks them in order from the most reactive (strongest reductant) to least reactive. Metals higher in the series can donate electrons to ions of metals lower in the series.
- An activity series for halogens ranks them in order from the most reactive (strongest oxidant) to least reactive. Halogens higher in the series can take electrons from ions of halogens (halides) lower in the series.

## QUESTIONS

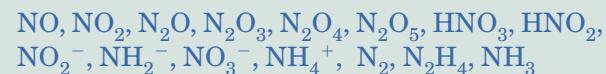
- Explain why the modern definition of oxidation and reduction in terms of electron exchange is superior to the historical definitions based on the exchange of oxygen or hydrogen.
- a** Use oxidation numbers to identify the oxidising agent in each of the following.
  - $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \rightarrow 2\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g})$
  - $2\text{Na}_2\text{O}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{Na}^+(\text{aq}) + 4\text{OH}^-(\text{aq}) + \text{O}_2(\text{g})$
  - $3\text{MnO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + 2\text{MnO}_4^-(\text{aq}) + \text{MnO}_2(\text{s})$
  - $\text{CaH}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{s}) + 2\text{H}_2(\text{g})$

- b** Which one of the reactions in part **a** is a disproportionation reaction?

- 3** Rewrite each of the following as two half-equations and label each as oxidation or reduction.



- 4** **a** Determine the oxidation state of nitrogen in each of the following species and then group them together in order of increasing oxidation number.



- b** Propose an explanation for why the maximum oxidation state of nitrogen is +5 and the minimum oxidation state is -3.

- 5** Why is it that metals usually behave as reducing agents in their reactions?

- 6** One of the main sources of acid rain is the sulfur oxides,  $\text{SO}_2$  and  $\text{SO}_3$ , emitted from coal-burning power plants and metal smelters. When these two oxides dissolve in water, they form sulfurous acid and sulfuric acid, respectively. Objects made of metal, such as iron, and limestone and marble (calcium carbonate) are corroded when the acidic rain falls on them.

- a** Write balanced equations for the following reactions:

**i** the formation of sulfurous acid from sulfur dioxide

**ii** the formation of sulfuric acid from sulfur trioxide

**iii** the corrosion of iron by sulfuric acid (assume iron(II) sulfate is formed in this reaction)

**iv** the corrosion of calcium carbonate by sulfurous acid.

- b** Use oxidation numbers to show which reactions described in part **a** are redox reactions.

- 7** The following table summarises some of the reactions of metals Cd, Co, Mn and Ni with solutions containing the 2+ ions of each of these metals. The blank spaces mean the combinations were not tested.

|                  | Cd | Co          | Mn                                                   | Ni          |
|------------------|----|-------------|------------------------------------------------------|-------------|
| Cd <sup>2+</sup> |    | No reaction | Grey solid formed, solution appeared to be unchanged |             |
| Co <sup>2+</sup> |    |             |                                                      | No reaction |
| Mn <sup>2+</sup> |    |             |                                                      |             |
| Ni <sup>2+</sup> |    |             |                                                      |             |

From the information given, predict whether or not reactions will occur for the untested combinations and record all the expected observations. Assume that if a metal reacts it forms its +2 ion.

- 8 Lead is used extensively in the manufacture of lead–acid accumulators (batteries) for vehicles. The main ore from which lead is extracted is galena, PbS. As with all metal extraction processes, the production of lead from galena involves oxidation–reduction reactions. In the first step, the galena ore is heated, or roasted, at a high temperature. Under these conditions the galena reacts with oxygen to form lead(II) oxide and sulfur dioxide. Then, in the second step, the lead(II) oxide is treated with carbon monoxide to form lead and carbon dioxide.
- a Write balanced equations for the two reactions involved in the extraction of lead from its ore.  
b Using oxidation numbers, show that these two reactions are indeed oxidation–reduction reactions.  
c For each of the two reactions, identify the substances that have been oxidised and reduced, and the oxidant and the reductant.  
d The by-products in these two reactions are well-known pollutants. Describe the damage each of these two by-products can cause to the environment if they are freely released into the atmosphere.
- 9 a What is the highest oxidation number that the following atoms can have in compounds or ions?  
i aluminium  
ii chlorine  
iii phosphorus  
b What do you notice about this highest value and the number of valence electrons in the atom?

- c Some household cleaners include labels describing the cleaner as ‘oxy-plus’ or ‘oxy-bleach’. The active ‘oxy’ ingredient in some of these cleaners is sodium perborate, NaBO<sub>3</sub>.
- i Use simple oxidation number rules to determine the oxidation number of boron in sodium perborate.  
ii How many valence electrons does boron have?  
iii If your answer to part b is correct, what can be concluded about the answer to c(i)?  
iv Assuming that the perborate ion can be represented as BO<sub>3</sub><sup>-</sup>, what alternative assignment of oxidation numbers can be given to some of the oxygen atoms in this ion?
- d Sodium persulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, is an ingredient in some hair bleaches.
- i Use simple oxidation number rules to calculate the oxidation number of sulfur in sodium persulfate.  
ii Sulfur is in group 16 of the periodic table, so why is your answer to (i) difficult to justify?  
iii If the sulfur in the persulfate ion has the same oxidation number as the sulfur in the sulfate ion, suggest a reason for the persulfate ion having a charge of -2.
- 10 In waterways, most organic matter in human sewage can be broken down by micro-organisms. This biodegradation can be either aerobic or anaerobic. With adequate dissolved oxygen, aerobic bacteria degrade the organic matter to carbon dioxide, water and a variety of inorganic ions such as nitrate, phosphate, sulfate and hydrogencarbonate ions. When too much organic matter in the water depletes the dissolved oxygen, anaerobic decay processes take place. The anaerobic bacteria produce foul-smelling substances such as hydrogen sulfide, ammonia, methanethiol (CH<sub>3</sub>SH) and aminomethane, CH<sub>3</sub>NH<sub>2</sub>.
- a Draw up a table listing the substances and their formulas formed under aerobic conditions and anaerobic conditions, described above.  
b Determine the oxidation numbers of the atoms in each of the formulas listed in your table.  
c Explain which of the two types of bacteria, aerobic or anaerobic, reduces the organic matter in sewage and which oxidises the organic matter. Use examples of compounds produced by these bacteria to support your answer.

**d**  **RESEARCH** Relatively clean water is usually produced by the aerobic processes. However, the production of too many nitrate and phosphate ions can lead to excessive eutrophication of the waterway, which can finally lead to the 'death' of a lake or river.

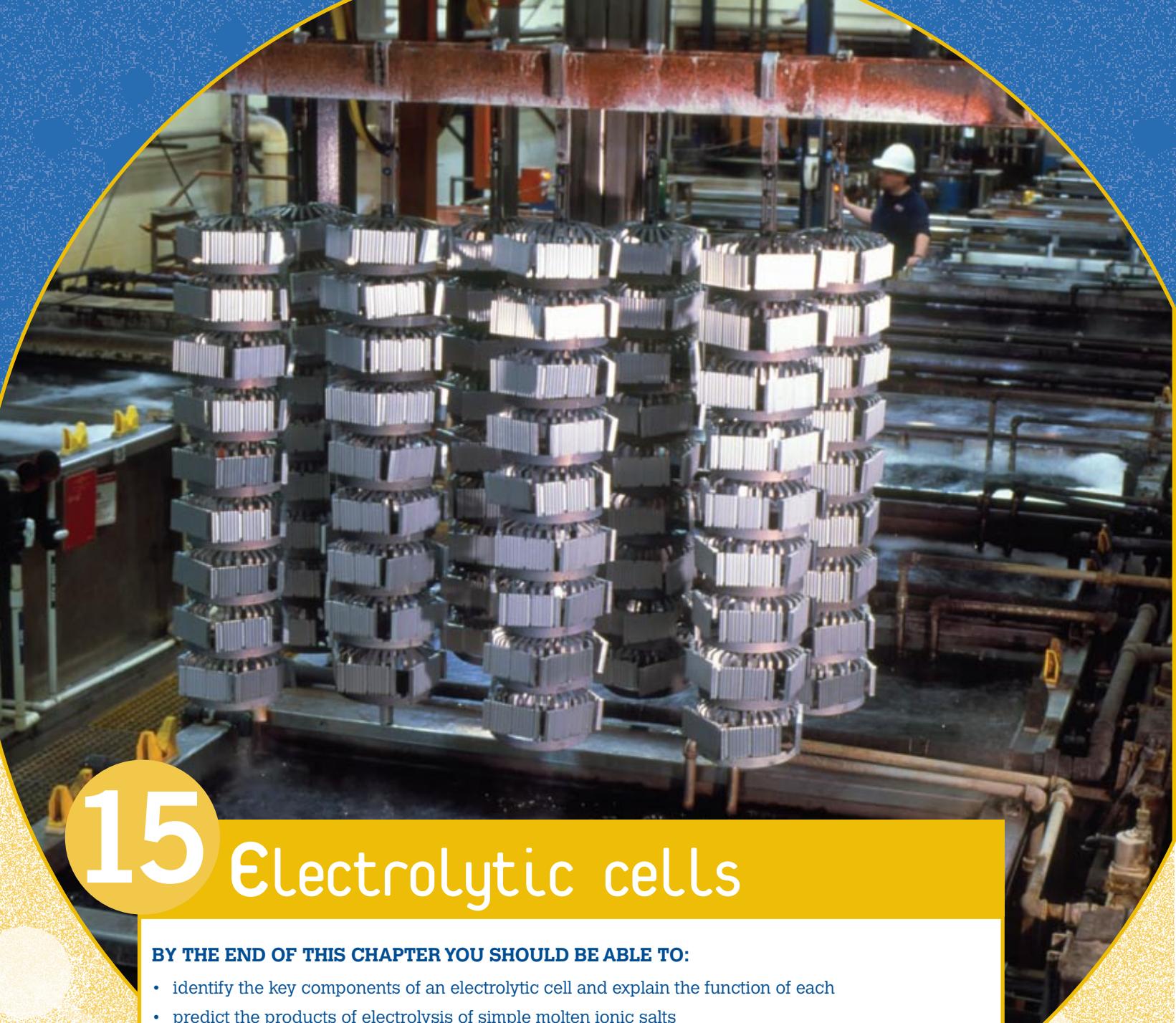
- i** What is eutrophication?
- ii** How can an excess of nitrate and phosphate ions in the water possibly lead to the 'death' of the waterway?

# 15

## Electrolytic cells

**BY THE END OF THIS CHAPTER YOU SHOULD BE ABLE TO:**

- identify the key components of an electrolytic cell and explain the function of each
- predict the products of electrolysis of simple molten ionic salts
- distinguish between electrowinning, electrorefining and electroplating and explain the redox chemistry associated with each.



## 15.1 Electric current and electrical energy

Without the electrical energy stored in a battery, your iPod and mobile phone would be useless. For the mp3 player or phone to work, the energy stored in the battery has to reach the electronic gadget. For this to happen an electric current must flow through the wires from the battery to the gadget.

In all of the battery-operated electronic appliances you use, this electric current is a flow of electrons, the same electrons that were introduced earlier as one of the fundamental particles that make up all atoms. Electrons have a negative charge and when they flow through an electric circuit can carry the energy necessary to operate the phone, iPod, digital camera, laptop computer, and so on. An electric current is therefore a flow of charged particles, in this case, electrons. The battery provides the electrons with the energy necessary to do the work that makes the electronic device operate. The battery and appliance make up part of what is called an **electric circuit**.

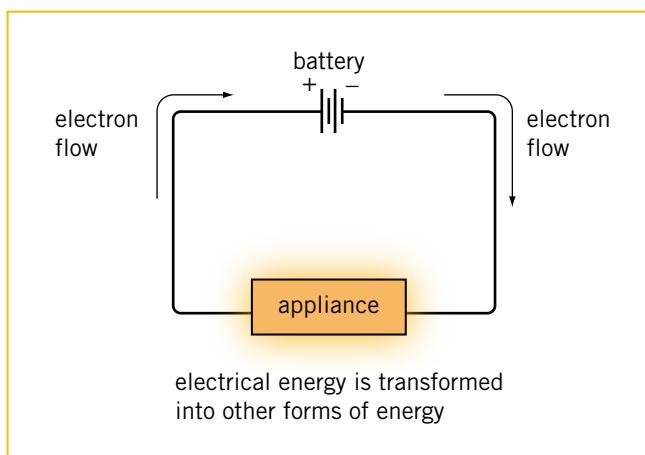


Figure 15.1 Transfer of energy and the flow of an electric current (electron current) in a simple circuit.

Figure 15.1 shows that in an electric circuit, the current, as a flow of electrons, comes out of one part of the battery (called a terminal), through the appliance, and back to the other terminal of the battery.



Figure 15.2 The positive and negative terminals of a 9 volt battery.

An electric current is defined as a flow of charge, with the charges being electrons or ions. Therefore, if electrons flow in a wire, or ions move in a particular direction in a solution or molten ionic salt, an electric current is flowing. The unit that has been chosen to represent electric charge is much bigger than the charge on a single electron. This unit is called the **coulomb (C)** and it is the amount of electric charge on about  $6.25 \times 10^{18}$  electrons.

For an electric current to flow the charged particles must be given energy. A battery, for example, can provide energy to the electrons that flow around a complete circuit. Evidence for the energy carried by an electric current can be gained by placing a lamp in the circuit. The electrical energy that the battery has given to the electrons is given off in the lamp as heat and light, when the electrons move through the lamp. This same electrical energy is transformed to sound energy in a mp3 player, or light energy in the flash of a digital camera.

The unit of energy is the **joule (J)**. For example, if this textbook falls from a desk to the floor it will release about 10 J of sound energy when it hits the floor. Rather than measure the electrical energy in terms of joules carried by an individual particle like an electron, electrical energy is measured as the number of joules of energy that a coulomb of charge carries. If one coulomb of charge ( $6.25 \times 10^{18}$  electrons) carries a total energy of one joule, the electrical energy carried is defined as one **volt** (or 1 joule per coulomb,  $J C^{-1}$ ).

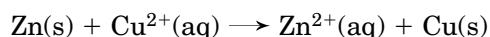
In summary, an electric current is a flow of charge. The charged particles can include electrons, positive ions (called cations) or negative ions (called anions). The moving charges in an electric current carry electrical energy and can be made to transform this energy into other forms of energy in an electric circuit. In a 1.5 volt battery, for example, each coulomb of charge carries a total energy of 1.5 joules.

### \* Review exercise 15.1

- 1 What is the difference between an electric current and electrical energy?
- 2 In which of the following is there an electric current flowing?
  - a The ions in a solution of sodium chloride moving randomly throughout the solution.
  - b The electrons travelling through a power cord connected to a television set that is switched on.
  - c The sodium ions in molten sodium chloride all moving towards a piece of carbon attached to the negative terminal of a battery.
  - d The electrons in a piece of copper wire that is being carried down a road by a truck.

## 15.2 Electrolysis—electrical energy to chemical energy

Oxidation–reduction or redox reactions involve electron transfer. The reductant in a redox reaction gives up electrons and is oxidised. The oxidant gains these electrons and is reduced. If a reactive metal such as zinc is placed in a solution of copper(II) sulfate, the zinc undergoes oxidation and the copper ions in solution are reduced. This reaction can be represented by the ionic equation

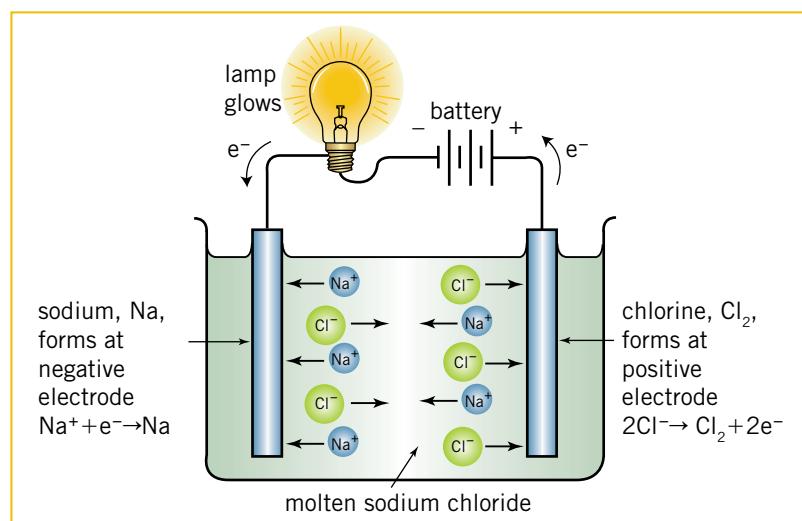


In Unit 3 the production of electrical energy from reactions such as this will be introduced. The process of electron transfer from the zinc to the copper(II) ion must involve an electric current. In this reaction chemical energy can be converted to electrical energy

**TABLE 15.1 REVIEW OF REDOX TERMINOLOGY**

| Redox property | Definition                                                                                                                                  |
|----------------|---------------------------------------------------------------------------------------------------------------------------------------------|
| Oxidation      | Loss of electrons in a chemical reaction; increase in oxidation number                                                                      |
| Reduction      | Gain of electrons in a chemical reaction; decrease in oxidation number                                                                      |
| Oxidant        | Causes one of the other reactants to be oxidised and undergoes reduction in the process; gains electrons; has its oxidation number reduced  |
| Reducant       | Causes one of the other reactants to be reduced and undergoes oxidation in the process; loses electrons; has its oxidation number increased |

What happens when an electric current is passed through a molten ionic compound or a solution of an ionic compound? Is it possible that electrical energy can be used to drive chemical reactions? Can electrical energy be used to make atoms or ions gain or lose electrons in a redox reaction?

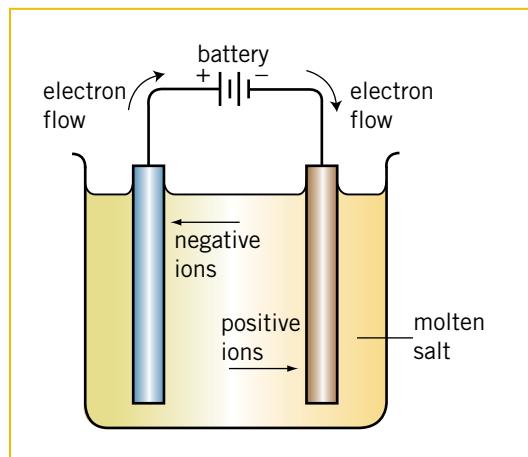


**Figure 15.3 Electrolysis of molten sodium chloride.**

Figure 15.3 highlights the various changes that take place when an electric current is passed through molten sodium chloride. In addition to the lamp, wire, battery and container of molten sodium chloride, this arrangement includes two pieces of carbon inserted into the molten salt. These graphite rods are called **electrodes**. The process occurring at these electrodes is called **electrolysis** and the arrangement of the battery, molten salt (the electrolyte) and electrodes is called an **electrolytic cell**.

The nature of the electrodes in an electrolytic cell is very important. Generally, they should not react with any of the contents of the cell, but they must be able to conduct an electric current as they provide the pathway for electrons to move to and from the cell contents.

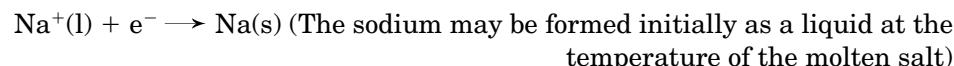
In an electrolytic cell, the conducting wire and electrodes provide a pathway for electrons, while the molten salt (or salt solution) provides a region in which positive and negative ions can move. Since an electric current is defined as a flow of charge, it is possible for these charges to be electrons in one part of a circuit and ions in another part. The only requirement is that the negatively charged particles all move in the same direction, as shown in Figure 15.4. The positive ions in the molten salt move in the opposite direction to the negative ions.



**Figure 15.4** Electrons travel through the wire and negative ions through the molten salt.

In summary, in an electrolytic cell, the electric current is a flow of electrons in the wire and electrodes, and a flow of positive and negative ions in the electrolyte (molten salt or salt solution).

At the negative electrode of an electrolytic cell there will be an excess of electrons that have been supplied by the battery or power source. In molten sodium chloride the positive sodium ions move towards the negative electrode and 'pick up' electrons to form sodium metal.



Since electrons are being gained in this reaction it is an example of reduction and the sodium ion is the oxidant. In general, reduction is the process that takes place at the negative electrode of an electrolytic cell. This electrode where reduction takes place is often called the **cathode**.

If positive ions are attracted to the negative electrode, then negative ions will be moving in the opposite direction towards the positive electrode. In molten sodium chloride, the chloride ions move towards the positive electrode where each gives up one electron.



The electrons from the chloride ions then complete the circuit, travelling to the positive terminal of the battery. The loss of electrons from the chloride ion is an oxidation reaction. Oxidation takes place at the positive electrode in an electrolytic cell and this electrode is often called the **anode**.

A substance that produces mobile ions when molten or when dissolved in water is referred to as an **electrolyte**. Consequently, electrolysis is defined as the passage of an electric current through an electrolyte resulting in a chemical change at the electrodes.

### → Example 15.1

An electrolytic cell is set up with molten zinc iodide in a beaker together with two graphite electrodes and a power supply. One graphite rod is attached to the negative terminal of the power source and the other rod to the positive terminal.

Zinc has a melting point of 419°C, zinc iodide melts at 446°C, and iodine boils at 184°C.

- What would be observed at each electrode when electricity flows through the cell?
- Write equations for the reactions that take place at each electrode.
- Draw a labelled diagram of the electrolytic cell identifying the positive and negative electrodes, anode, cathode, direction of electron flow, direction of ion flow and where oxidation and reduction take place.

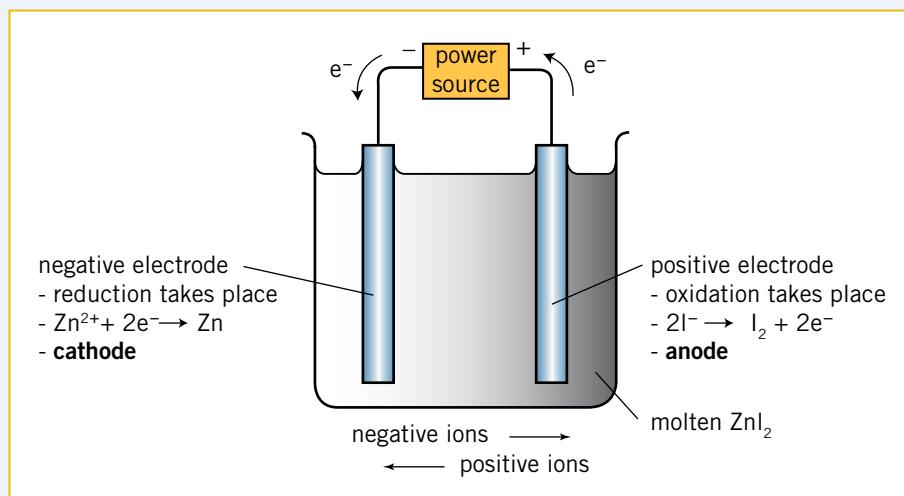
### → Solution

- At the negative electrode a shiny, silver-grey liquid would be seen to form (at the temperature of molten zinc iodide the zinc would be a liquid).

At the positive electrode a purple gas would be given off (at the temperature of the molten zinc iodide, iodine would be a gas).



c



In summary:

- An electrolytic cell consists of the following parts:
  - a battery or power source that provides electrons to one electrode and removes electrons from the other.
  - two electrodes that do not react with the chemicals in the cell, but are conductors of electricity. Carbon in the form of graphite is commonly used as electrode material. Metals can also be used. One electrode is connected to the negative terminal of the battery and the other to the positive terminal.
  - the cell contents, which may be a molten salt or a solution of a salt. While electrons carry the current through the external circuit of wires and electrodes, ions carry the current in the cell itself.

- In an electrolytic cell:
  - electrical energy from the battery has been converted to chemical energy in a redox reaction.
  - reduction takes place at the negative electrode, that is, at the cathode. Positive ions or cations move towards the cathode in the cell.
  - oxidation takes place at the positive electrode, that is, the anode. Negative ions or anions move towards the anode in the cell.

### \* Review exercise 15.2

- 1 **a** Potassium chloride is placed in an evaporating basin and melted. Two carbon rods are added, one attached to the positive terminal of a 9 volt battery and the other to the negative terminal. What would be observed at each electrode if the circuit was completed? Write equations for the electrode reactions and identify the oxidation and reduction processes.  
**b** The experiment is repeated but this time with a 1.5 volt battery. There is no noticeable change. Why is there no reaction in this cell?
- 2 **a** In an electrolytic cell, what is the name given to the electrode at which the electrons first come in contact with the electrolyte?  
**b** What is the general name given to the type of ion that is attracted to this electrode?  
**c** Assuming that the ion reacts at this electrode, what is the name of the process that it undergoes?
- 3 In a particular electrolytic cell, one of the electrodes is observed to give off a brown gas, later identified as bromine. At the other electrode, a silvery-grey metal is produced and this is determined to be tin. Draw a fully labelled diagram of this cell showing the battery (power source), electrodes, direction of electron movement, nature of the material in the cell itself, direction of movement of ions in the cell and the individual reactions taking place at each electrode.

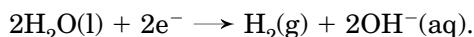
## 15.3 Electrolysis of solutions

Predicting the products formed and reactions at each electrode in the electrolysis of a simple, molten ionic compound is relatively easy. However, the electrolysis of aqueous solutions of salts introduces the possibility that water itself may be involved in the electrode reaction. Water can behave as an oxidant or a reductant during the electrolysis of aqueous solutions.

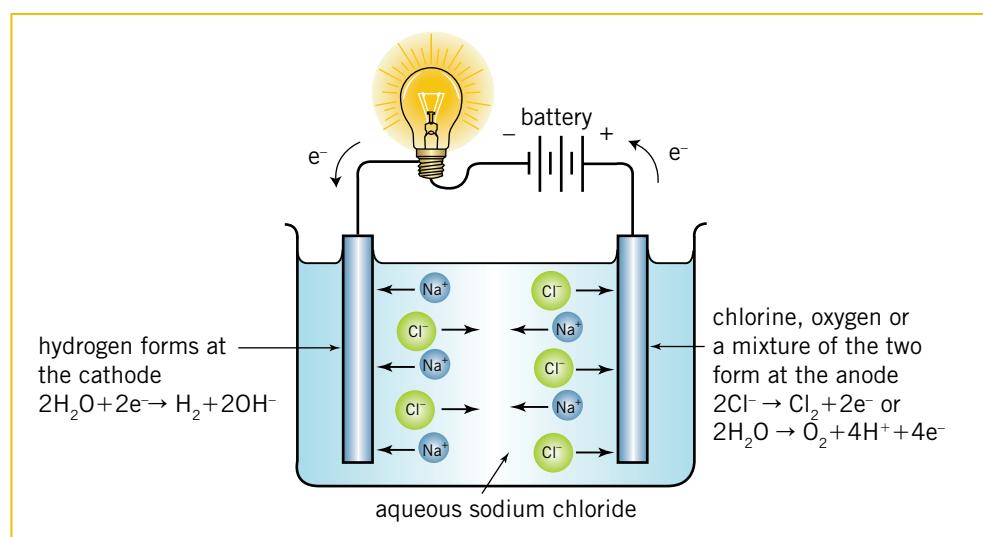
When a salt dissolves in water the solution conducts electricity due to the presence of the dissolved positive and negative ions. These ions are able to move towards the positive and negative electrodes in an electrolytic cell and so possibly undergo reduction or oxidation.

If an electric current is passed through a solution of sodium chloride in water, the products formed at the electrodes are not the same as those formed during the electrolysis of molten sodium chloride. At the cathode, hydrogen gas is obtained, while at the anode the product may be chlorine, oxygen, or a mixture of chlorine and oxygen, depending on the concentration of the sodium chloride solution (and also the voltage of the battery). During the electrolysis of the molten sodium chloride, sodium is formed at the cathode and chlorine at the anode.

During the electrolysis of a solution of sodium chloride, the production of hydrogen at the cathode results from the oxidation of water rather than of sodium ions. Oxidants and reductants have different strengths, depending on how readily they gain or lose electrons. The activity series of metals is an example of the different strengths of metal ions as oxidants (as well as the different reductant strengths of the metals themselves). In electrolytic cells where more than one oxidant or reductant is present, the strongest one will react at the electrode first. The formation of hydrogen, rather than sodium, at the cathode in the electrolysis of a solution of sodium chloride demonstrates that water is a stronger oxidant than the sodium ion. The reaction at the cathode can be represented as

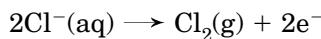


Further evidence for this reaction at the cathode is obtained by placing a small amount of an acid–base indicator, such as phenolphthalein in the solution. In the vicinity of the cathode the electrolyte turns pink due to the formation of hydroxide ions that raise the pH.

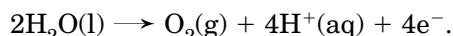


**Figure 15.5** Electrolysis of a solution of sodium chloride.

The observation that chlorine, oxygen or a mixture of these two can be produced at the anode indicates that both chloride ions and water can be oxidised. The two reactions are



or



While there is other evidence that the chloride ion is not as strong a reductant as water, the effect of concentration on the products of electrolysis makes prediction of what is likely to be observed at the anode difficult. In this course, making such predictions will not be expected.

### \* Review exercise 15.3

- 1 Solutions of potassium chloride and copper(II) chloride are electrolysed using carbon electrodes. The potassium chloride solution produces hydrogen gas at the cathode while the carbon cathode is coated with a red solid in the copper(II) chloride solution.
  - a Write the cathode equations for these two reactions.
  - b Use this experimental information to place water, potassium ions and copper(II) ions in order of increasing oxidant strength.
- 2 Electrolysis of a solution of sodium sulfate produces hydrogen at the cathode and oxygen at the anode.
  - a Write the equation for the two reactions and identify these as oxidation or reduction reactions.
  - b What changes would you expect to observe in the pH around each of the electrodes?
  - c Write the equation for the overall reaction involved in the electrolysis of a sodium sulfate solution.
- 3 Three  $0.1 \text{ mol L}^{-1}$  solutions of sodium chloride, sodium bromide and sodium iodide undergo electrolysis. Table 15.2 records the observations made.

**TABLE 15.2** PRODUCTS OF ELECTROLYSIS OF SODIUM HALIDES

| Solution        | Products at anode                                                                            | Product at cathode |
|-----------------|----------------------------------------------------------------------------------------------|--------------------|
| sodium chloride | mostly oxygen with a small amount of chlorine                                                | hydrogen           |
| sodium bromide  | mixture of oxygen gas, bromine gas and dissolved bromine forming an orange-coloured solution | hydrogen           |
| sodium iodide   | brown solution containing dissolved iodine, no other gas produced                            | hydrogen           |

Use this data to predict the order of reductant strength of the halide ions from weakest to strongest. Justify your answer in terms of the observations made.

## 15.4 Applications of electrolysis

### Production of sodium—the Downs Cell

Sodium is made commercially by the electrolysis of molten sodium chloride. Sodium chloride normally melts at temperatures around  $800^{\circ}\text{C}$  but this can be lowered to around  $600^{\circ}\text{C}$  by adding calcium chloride to the mixture. This saves energy in the commercial production and any small amount calcium formed can be readily separated from the sodium.

Figure 15.6 shows a commercial Downs Cell used for the production of sodium chloride.

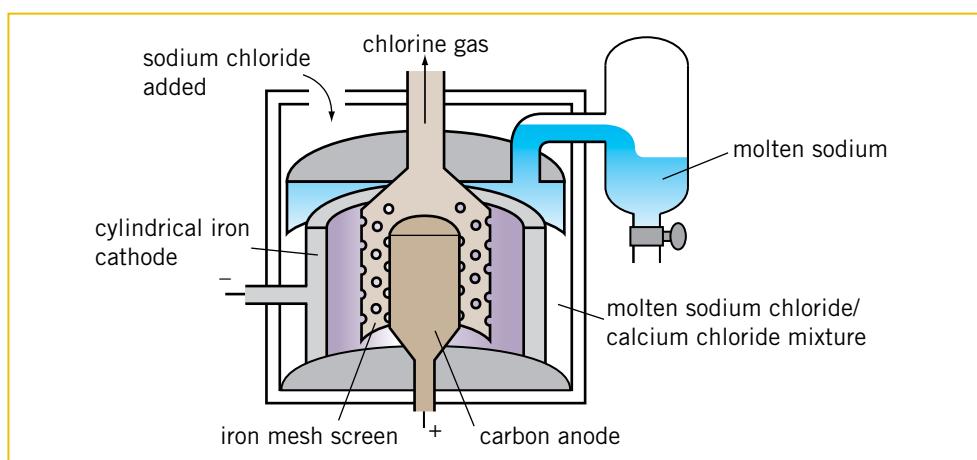
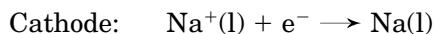
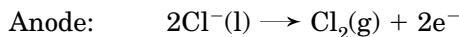


Figure 15.6 A Downs Cell.

The anode is made of graphite while the cathode is iron. At the anode, the only reaction is the oxidation of chloride ions to form chlorine. The key reaction at the cathode is the reduction of sodium ions to form sodium.



As sodium and chlorine are so reactive, care must be taken to keep the products separated. The chlorine gas is piped out at the top of the cell and there is a porous screen between the central anode and the cathode to ensure that the sodium and chlorine do not come into contact in the cell. The sodium is a liquid at the temperature of the molten mixture and would float on the molten sodium chloride. By encasing the cathode in a metal compartment the liquid sodium can be tapped off and collected in the absence of air that would immediately oxidise the reactive, molten metal.

Approximately 70 000 tonnes of sodium is made by electrolysis annually, although demand for the metal has decreased in recent years. Some of the sodium is used as a heat transfer agent in certain nuclear reactors where the use of water would reduce the efficiency of the reactor. Sodium melts at around  $100^{\circ}\text{C}$  and is an excellent conductor of heat. As a result, it can be used to transfer the heat energy produced in the core of the nuclear reactor to water that circulates in pipes positioned in the molten sodium. The water in the pipes is converted to steam which is then used to run turbines in the same way as in a fossil-fuel power station.



Figure 15.7 Anodised cups.

Other reactive metals like calcium and magnesium are also produced commercially by electrolysis of molten calcium chloride and magnesium chloride respectively. In addition, aluminium is commercially prepared in the electrolysis of a molten salt, aluminium oxide, obtained from the ore bauxite (see Section 17.1). **Electrowinning** is the general name given to these commercial electrolysis processes where metals are prepared from their molten salts using inert electrodes.

### Anodised aluminium

Aluminium is a very versatile metal, second only to iron in terms of world production. It is widely used in the construction industry and is often alloyed with other metals. In addition to its use in cars, aircraft, bicycle frames, boats and house construction, aluminium is used in packaging, cooking utensils and electrical transmission lines.

Despite aluminium being quite a reactive metal it is able to be used in situations where other, less reactive metals such as iron, might cause problems. Aluminium rapidly oxidises in air to form a thin, impervious oxide coating that protects the underlying metal from further reaction. However, in situations where even greater corrosion resistance is required, the aluminium may be anodised to give a thicker oxide coating.

Anodising aluminium involves making the aluminium the anode in an electrolytic cell containing sulfuric acid (Figure 15.8). At the anode, water is the strongest reductant and is oxidised to produce oxygen.

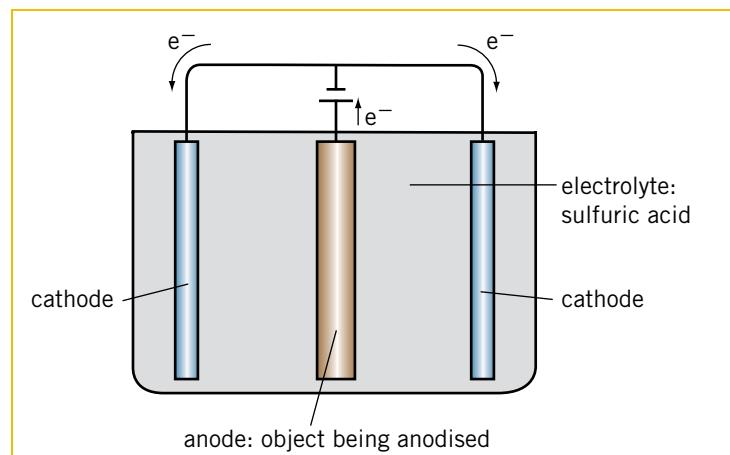
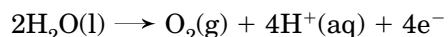


Figure 15.8 Anodising aluminium.

The oxygen reacts with the aluminium to produce a uniform oxide coating that acts as a protective surface. Various dyes can be introduced into the anodising process to produce the coloured aluminium surfaces that can be seen in items such as iPods, digital cameras, cookware and sporting goods.

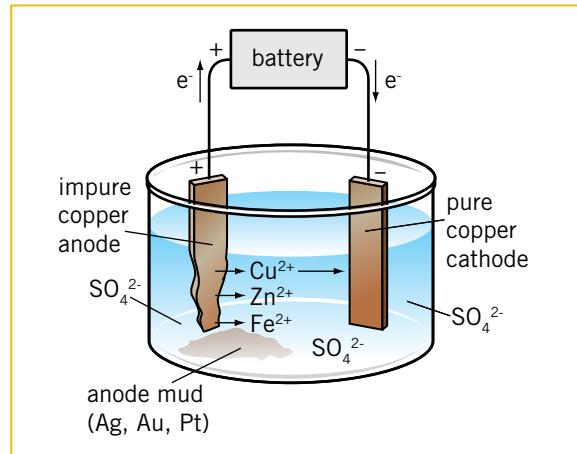
### Electrolytic refining of copper

Copper that is made from the smelting or refining of various copper-containing ores is not pure. This impure copper may contain approximately 98% copper, with other metals such as silver, platinum, zinc, iron and nickel also present. For purposes such as electrical wiring the copper needs to be well in excess of 99% pure, so the final step in the production of pure copper is an electrolytic process known as **electrorefining**. Electrorefining differs from electrowinning because the refining process involves the oxidation of the anode. That is the anode is not

inert as it is in the electrowinning process. While the use of electrodes made of graphite or unreactive metals such as platinum ensures that only those species present in the electrolyte undergo oxidation or reduction, where a more reactive metal is used as the positive electrode it is possible for the electrode to be oxidised in preference to any other reductant in the cell.



a

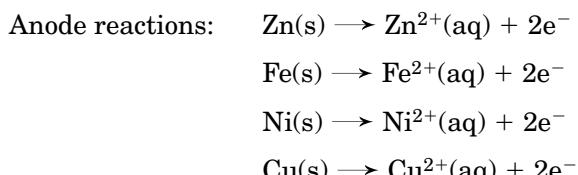


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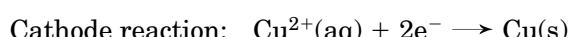
**Figure 15.9** Electrorefining of copper. a Copper cathodes being removed from the electrolytic cells b An illustration of the copper electrorefining cell.

The crude copper is made into anodes in an electrolytic cell. Thin pure copper electrodes form the cathode and both electrodes are placed in an acidic solution of copper(II) sulfate.

By careful adjustment of the voltage applied to the cell, the copper is oxidised, together with the more reactive metal impurities such as iron, zinc and nickel. The less reactive metals such as silver, gold and platinum do not undergo oxidation and as the anode oxidises and dissolves, these precious metals fall to the bottom of the cell as a sludge or mud.



At the cathode only the copper ions are reduced.



This is partly because of the much higher concentration of copper ions in the electrolyte, and partly because the copper ion is a stronger oxidant than the ions of the more reactive metals.

In this process, copper with purity in excess of 99.99% is plated onto the cathode.

### Electroplating of silver

The process of electroplating involves depositing a thin layer of one metal over another. The coating may serve as protection for the metal beneath or may provide a surface with a nicer appearance than the original.

A layer of silver can be deposited onto another metal object by making that object the cathode in an electrolytic cell. A piece of pure silver is used as the anode and the two metals are immersed in a solution containing silver ions. In commercial silver-plating the nature of the electrolyte needs to be carefully controlled using cyanide ion,  $\text{CN}^-$ , to keep the concentration of the silver ion low enough to allow the silver metal that forms on the surface to be a thin, controlled layer. The electrode reactions for this cell are:



### \* Review exercise 15.4

- 1 It is possible to obtain nickel from the crude metal that is obtained during the smelting and roasting of nickel ores. How would you set up an electrorefining cell to produce pure nickel from the crude metal?
- 2
  - a Sodium hydroxide and chlorine are obtained commercially by the electrolysis of sodium chloride solutions. Write the anode and cathode reactions for this process and explain how these two substances are formed from sodium chloride. What other important substance is obtained in this cell?
  - b In commercial cells a membrane separates the cathode from the sodium chloride solution. This membrane is made from a material that only allows ions of a particular charge (positive or negative) and water to pass through. If you were designing such a cell, which ions would you permit to pass into the region near the cathode? Explain your answer.
- 3 Describe an electrolytic cell that could be used to gold plate a piece of silver. Make sure you identify the materials you would use to make the cathode and the anode, and the nature of the electrolyte.



## MAJOR IDEAS

- An electric current is a flow of electric charge.
- Electric charge is measured in coulomb.
- Electrical energy is the energy that is carried by an electric charge.
- An electrolytic cell consists of a battery to supply the electric charges, two electrodes and an electrolyte.
- Electrodes are electrical conductors such as metals or graphite. In general, they do not react with anything in the electrolytic cell, although they may be changed in the electrolysis process.
- An electrolyte contains ions that are free to move. This may be a molten salt or an aqueous solution of a salt.
- A battery or power supply supplies electrons from its negative terminal that move through a wire to an electrode that is called the cathode.
- The positive terminal of the battery or power supply is connected to an electrode that is called the anode.
- Electric current in the wires of an electrolytic cell is due to the movement of electrons.
- In the electrolyte the current is due to the movement of ions.
- Anions migrate through the electrolyte to the anode and cations migrate to the cathode.
- Electrolysis is the passage of an electric current through an electrolyte with oxidation taking place at the anode and reduction at the cathode.
- A useful mnemonic for the electrode processes is AN OIL RIG CAT. Anode Oxidation is Loss of electrons and Reduction is Gain of electrons at the Cathode.
- During electrolysis electrical energy carried by the moving charges is transformed into chemical energy as new substances are formed at the electrodes.
- Molten metal halides produce the metal at the cathode and the halogen at the anode during electrolysis.
- Some commercially important metals are purified in an electrorefining process, where the crude metal is made the anode in an electrolytic cell and the pure metal plates onto the cathode.
- Anodising is the process in which a metal anode has an oxide coating built on it by performing the electrolysis in an aqueous medium where the water is oxidised at the anode to produce oxygen.
- Electroplating involves making the object that is to be plated the cathode and performing the electrolysis in a solution containing ions of the metal that is to be plated on the object.

## QUESTIONS

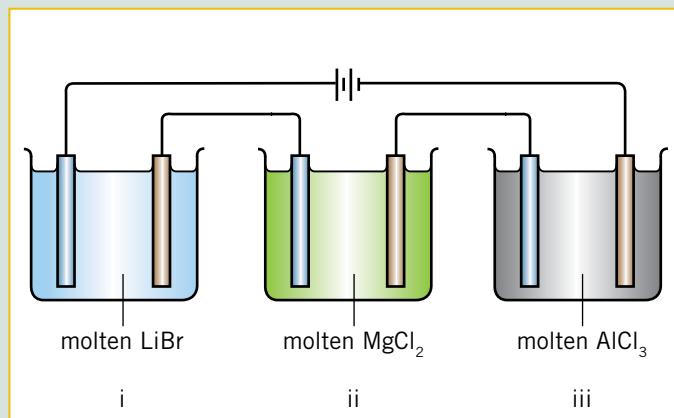
- 1 Predict the products formed in the electrolysis of the following substances, using carbon as the electrodes in each case. Write the anode and cathode reactions.
  - a molten lead(II) bromide
  - b molten potassium iodide
  - c a solution of copper(II) sulfate
  - d molten strontium chloride
  - e molten aluminium oxide
- 2 The same amount of electricity is passed through three electrolytic cells connected in series (one after another). The three cells contain graphite electrodes in
  - i molten zinc iodide
  - ii molten lithium chloride
  - iii molten magnesium bromide
  - a How does the amount (in mole) of product formed at the anode in each cell compare? Write equations to justify your answer.
  - b Compare the amount (in mole) of product formed at the cathode. Write equations to justify your answer.
- 3 Distinguish between the terms electrolysis and electrolyte.
- 4 Compare and contrast ion migration and electron movement in an electrolytic cell.
- 5 Draw fully labelled diagrams to show the similarities and differences between the electrolysis of a copper(II) sulfate solution using copper electrodes and the same solution using graphite electrodes.
- 6
  - a A mixture of sodium chloride and zinc iodide is melted and an electric current is passed through the mixture using graphite electrodes. Draw a labelled diagram of the cell showing the battery, flow of electrons, anode, cathode, ions present in the mixture, and direction in which the ions migrate.
  - b For metals, a conjugate redox pair is defined as the metal reductant and the cation that it produces (the conjugate oxidant) by loss of electrons. For the halogens, a conjugate redox pair is defined as the halogen itself (the oxidant) and the halide ion (reductant) produced when electrons are gained. Given that the strongest oxidant will have the weakest conjugate

reductant and the strongest reductant the weakest conjugate oxidant, predict what would be produced at the anode and the cathode in the cell described in a at the commencement of electrolysis. Explain your predictions.

- 7 When titanium is anodised the thickness of the coating controls the colour of the surface, which can range from pale blue through to red, silver, or gold depending on the voltage chosen and hence the thickness of the coating.

Draw and label an electrolytic cell in which titanium could be anodised and write the equations for the formation of the coating on the anode.

- 8 Three electrolytic cells are connected as shown in Figure 15.10. Assume the electrodes are graphite.



**Figure 15.10** Electrolysis of molten lithium bromide, magnesium chloride and aluminium chloride.

The same amount of electricity is passed through all three cells and 13.88 g of lithium is produced in cell 1.

- a Write the equations for the reactions at the anode and cathode in each cell.  
 b Determine the mass of magnesium, aluminium and chlorine that would be formed at the same time as the lithium.  
 9 Two processes involving electrolysis are described below.

Process A: Magnesium is obtained from seawater by precipitating the dissolved magnesium ions by adding solid calcium oxide to the seawater. The sparingly soluble magnesium hydroxide is collected, and acidified with hydrochloric acid to produce a solution of magnesium chloride. The solution is evaporated to produce crude solid magnesium

chloride. This solid is mixed with sodium chloride and calcium chloride and the molten mixture electrolysed at around 700–750°C.

Process B: The lead-containing electrodes from old car batteries can be converted back to pure lead by making the crude lead into anodes and performing electrolysis in a solution of a suitable lead salt.

- a Write the equations for the reactions that take place when calcium oxide is added to seawater to precipitate magnesium hydroxide.  
 b Write the equation for the anode reaction in the electrolysis cell containing lead from car batteries.  
 c Explain why one of these processes is an example of electrorefining and the other is an example of electrowinning.  
 d Why do the calcium ions and sodium ions present with the magnesium ions in Process A not undergo reduction at the cathode?

- 10 When silver coins are retrieved from ancient shipwrecks they are usually covered with an almost impervious corrosion layer of silver sulfide and an encasement of calcium carbonate. To restore the coins without destroying their detailed engravings, they are first soaked in an acidic bath to remove the calcium carbonate layer. Then electrolysis is used to remove the silver sulfide. The coin is used as one of the electrodes and usually graphite as the other, with the electrolyte being a dilute aqueous solution of sodium hydroxide. When electricity flows into the electrolysis cell, the silver ions in the silver sulfide layer are reduced to form silver metal:



Using this procedure, the coins are restored to almost the condition they were in before the ship was wrecked.

- a Give an ionic equation for the first stage of the restoration that results in the removal of the calcium carbonate deposit on the coin.  
 b Draw a labelled diagram of the electrolysis cell that could be used in the second stage of the restoration. Include in your diagram  
 i the electrodes, labelled as anode and cathode  
 ii the electrolyte  
 iii the reaction occurring on the surface of the coin  
 iv the direction of electron flow

- v the flow of positive and negative ions, including the identification of these ions
- c Why is an anode of silver not used in the electrolysis?
- d If an acidic electrolyte was used in the electrolysis cell, a dangerous gas would be produced as one of the products. What is this gas?

**11** Brass is an alloy of copper and zinc. A layer of brass can be produced on an object by simultaneously electroplating the two metals, copper and zinc, from a solution containing their +2 ions. In a particular electroplating cell, 65% of the electrons flowing into the cell were used to plate copper and 35% of the electrons to plate zinc. Calculate the mass percent of zinc in the brass layer formed on the object.



# 16

## Carbon compounds

### BY THE END OF THIS CHAPTER YOU SHOULD BE ABLE TO:

- distinguish between organic and inorganic chemistry
- explain the diversity of carbon-based compounds
- draw and name a range of simple hydrocarbon molecules
- discuss the refining of crude petroleum by fractional distillation
- explain the reason for the cracking of hydrocarbons in petroleum refining
- compare the properties and reactions of alkanes and alkenes
- distinguish between hydrocarbons as fuels and hydrocarbons as a source of raw materials for the petrochemical industry
- explain how benzene differs structurally from alkanes and alkenes.

## 16.1 Carbon—the most versatile element on Earth

Of all the atoms making up the Earth, only about 0.2% are carbon atoms, yet carbon compounds outnumber the compounds of all other elements put together. Many of these carbon compounds exist naturally in the atmosphere, in the oceans, in the Earth's crust and in living things, but a large number have also been manufactured by chemists over the years. The study of the compounds of carbon is described as organic chemistry, with the study of all the other compounds and elements being called inorganic chemistry. However, the boundary between organic and inorganic compounds is not always well defined. For example, carbonates and hydrogencarbonates as well as the oxides of carbon are normally regarded as inorganic compounds, while methanoic acid,  $\text{H}_2\text{CO}_2$ , is an organic compound.

It is in the chemistry of living things that organic chemistry sees perhaps its most important application. However, the petrochemicals derived from crude oil have also changed our lifestyle through the use of polymers, plastics, pharmaceuticals, dyes, insecticides, detergents and synthetic fabrics. Around 90% of crude petroleum is used in the production of various fuels and oils, leaving just 10% to service a petrochemical industry that provides such a vast array of important and useful substances. Indeed, around 20 million organic compounds are currently known. (It is estimated that there are around 100 000 known inorganic compounds.)

### What is so special about carbon?

With an electron configuration of 2, 4, carbon atoms have four outer shell or valence electrons. As a result carbon tends to form compounds in which each carbon atom gains a share of four extra electrons. This is often achieved by carbon forming four covalent (single) bonds with four other atoms. For example, when a carbon atom bonds with four hydrogen atoms, a molecule of  $\text{CH}_4$ , or methane is formed. The electron dot diagram for this molecule is shown in Figure 16.1a.

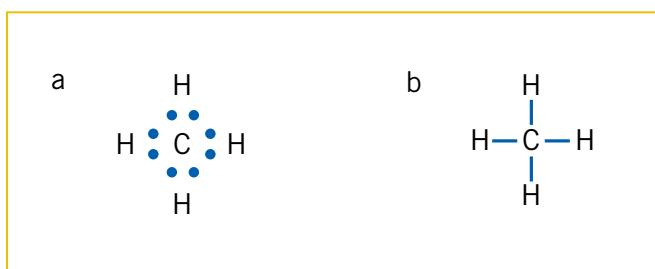


Figure 16.1 a Electron dot representation of methane,  $\text{CH}_4$ . b Structural formula of methane.

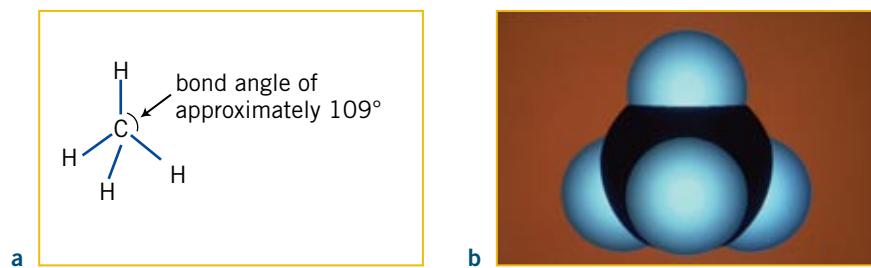
When two electrons are shared between two atoms, it is said that the two atoms are joined by a single covalent bond. That is, in a methane molecule the carbon atom forms four single covalent bonds and each hydrogen atom forms one single covalent bond.

Organic chemists sometimes draw structural formulas to represent molecules. In these diagrams, lines are used to show the bonds between atoms. The structural formula for methane is often drawn as shown in Figure 16.1b. Each line in a structural formula represents a pair of valence electrons.



Methane is the main component in the natural gas that is commonly used as a source of heat for cooking and for heating homes. Methane is obtained from underground deposits of natural gas that have locked carbon away for millions of years. The percentage of methane in these deposits is approximately 90%. The origin of this gas is still being debated, but the most popular theory suggests that most deposits come from the burial and breakdown of marine organisms in an environment in which the carbon compounds could not be oxidised to carbon dioxide, but rather were reduced to methane.

The diagram in Figure 16.1b does not accurately show the three-dimensional arrangement of the atoms around the central carbon atom. Because the four pairs of electrons, or electron clouds, around the carbon atom are negatively charged, they will repel one another, and be positioned as far apart as possible. As a result, the hydrogen atoms are arranged in what is known as a tetrahedral arrangement, with the angles between the bonds being approximately  $109^\circ$ . This arrangement of atoms is shown as a line structure in Figure 16.2a and as a space-filling model in Figure 16.2b.



**Figure 16.2** The arrangement and shape of a methane molecule shown as a line drawing (a) and a space-filling model (b).

For simplicity of representation most of the structures depicted in this chapter will be similar to that in Figure 16.1b. However, it is important to recognise that the bond angles are not the  $90^\circ$  angles implied in the diagrams.

Carbon is not restricted to forming single bonds. Combinations of single, double and triple bonds add to carbon's diversity of bonding options. A double bond forms when four electrons, or two electron pairs, are shared between two atoms. For a triple bond, six electrons, or three pairs of electrons, are shared. Examples of molecules in which carbon forms double and triple bonds are shown in Table 16.1.

**TABLE 16.1 MULTIPLE BONDS FORMED BY CARBON**

|                 |                 |
|-----------------|-----------------|
| <br>Double bond | <br>Triple bond |
|-----------------|-----------------|

Apart from carbon, other elements commonly found in organic compounds include hydrogen, oxygen, sulfur, nitrogen, fluorine, chlorine, bromine and iodine. The number of covalent bonds each of these elements usually forms in organic compounds is shown in Table 16.2

**TABLE 16.2 BONDING OF COMMON ATOMS IN ORGANIC COMPOUNDS**

| Element                             | Number of covalent bonds | Possible combinations of covalent bonds                          |
|-------------------------------------|--------------------------|------------------------------------------------------------------|
| carbon                              | 4                        | 4 single; 1 double and 2 single; 2 double; 1 triple and 1 single |
| nitrogen, phosphorus                | 3                        | 3 single; 1 double and 1 single; 1 triple                        |
| oxygen, sulfur                      | 2                        | 2 single; 1 double                                               |
| hydrogen                            | 1                        | 1 single                                                         |
| fluorine, chlorine, bromine, iodine | 1                        | 1 single                                                         |

Some more examples of compounds in which carbon is bonded to different elements, together with their uses, are given in Table 16.3

**TABLE 16.3 STRUCTURAL FORMULAS OF SOME SIMPLE ORGANIC MOLECULES**

|                    |                                                                                                                                                                                                                                        |                                                                                                                                 |                                                                                                                                                                                                                                              |
|--------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Name of compound   | chlorotrifluoromethane, freon 13                                                                                                                                                                                                       | trichloromethane, chloroform                                                                                                    | methanol                                                                                                                                                                                                                                     |
| Molecular formula  | $\text{CClF}_3$                                                                                                                                                                                                                        | $\text{CHCl}_3$                                                                                                                 | $\text{CH}_3\text{OH}$ (or $\text{CH}_4\text{O}$ )                                                                                                                                                                                           |
| Structural formula |                                                                                                                                                                                                                                        |                                                                                                                                 |                                                                                                                                                                                                                                              |
| Uses               | Used to clean metal surfaces. Until recently, freon 13 has been used as a coolant in commercial and industrial air-conditioners and as an ingredient in aerosol sprays. One of the CFCs thought to cause depletion of the ozone layer. | Was once used as an anaesthetic and in cough mixtures, but has now been banned from use because of its carcinogenic properties. | Used as a solvent and in the manufacture of other organic chemicals such as acetic acid. It is a potential clean-burning fuel for engines and fuel cells (devices that transform the energy from exothermic reactions to electrical energy). |

The ability of carbon to form multiple covalent bonds and to bond to other kinds of atoms, while important, does not completely explain the existence of the huge number of organic compounds. Perhaps the most important reason for this diversity is the ability of carbon to bond with other carbon atoms in chains that can extend hundreds of atoms in length without loss of stability, or in rings with as few as three and as many as thirty carbon atoms. Combine this with the ability to add other atoms and multiple bonding to the chain and the possibilities for a huge number of combinations become more obvious. Tables 16.4 and 16.5 show some carbon-based molecules involving chains and rings.

**TABLE 16.4 EXAMPLES OF COMPOUNDS WITH LINEAR CHAINS OF CARBON ATOMS**

|                    |                                  |                                                            |                                                                         |
|--------------------|----------------------------------|------------------------------------------------------------|-------------------------------------------------------------------------|
| Name of compound   | ethanol                          | octane                                                     | poly(tetrafluoroethene), Teflon™                                        |
| Formula            | $C_2H_5OH$ (or $C_2H_6O$ )       | $C_8H_{18}$                                                | $CF_3(CF_2)_nCF_3$ where n is a very large number, perhaps in the 1000s |
| Structural formula |                                  |                                                            |                                                                         |
| Uses               | The alcohol in alcoholic drinks. | One of hundreds of molecules present in petrol (gasoline). | Used as a non-stick coating on cooking utensils.                        |

**TABLE 16.5 EXAMPLES OF SIMPLE CYCLIC STRUCTURES BASED ON CARBON**

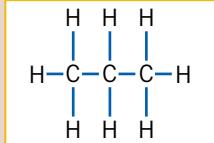
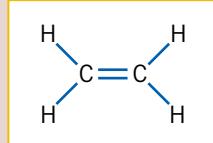
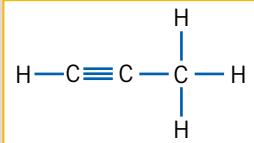
|                    |                              |                                                                           |
|--------------------|------------------------------|---------------------------------------------------------------------------|
| Name of compound   | cyclopentane                 | glucose                                                                   |
| Formula            | $C_5H_{10}$                  | $C_6H_{12}O_6$                                                            |
| Structural formula |                              |                                                                           |
| Uses               | Used as a solvent in paints. | Reacts with oxygen in the respiration process that is essential for life. |

What makes carbon unique, then, is this combination of properties – capacity to bond to many other atoms, capacity to bond to other carbon atoms in stable chains and rings, and capacity to form multiple bonds with itself and other atoms.

### Writing formulas of organic compounds and naming them

There are several different types of formulas used to represent an organic molecule. A **molecular formula** such as  $C_2H_6$ , for ethane, and  $C_2H_4O_2$ , for acetic acid, shows the number of each type of atom in a molecule of the compound. Molecular formulas contain important information, though a more useful formula is the **structural formula** that shows the bonding arrangement of the atoms in a molecule. Structural formulas can be written in a variety of ways, as shown in Table 16.6.

**TABLE 16.6 MOLECULAR AND STRUCTURAL FORMULAS OF SOME ORGANIC COMPOUNDS**

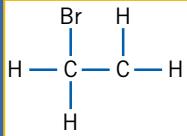
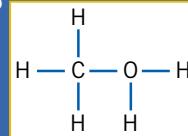
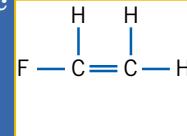
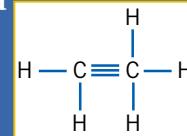
|                                                               |                                                                                                                         |                                                                                                                  |                                                                                                                       |
|---------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------|
| Name of compound                                              | propane                                                                                                                 | ethene                                                                                                           | propyne                                                                                                               |
| Molecular formula of compound                                 | $C_3H_8$                                                                                                                | $C_2H_4$                                                                                                         | $C_3H_4$                                                                                                              |
| Different ways in which the structural formula can be written | $CH_3-CH_2-CH_3$<br>$CH_3CH_2CH_3$<br> | $CH_2 = CH_2$<br>$CH_2CH_2$<br> | $CH \equiv C-CH_3$<br>$CHCCH_3$<br> |

Keeping track of such a vast number of compounds requires a systematic method of naming. Originally, chemists named newly-discovered carbon compounds in an arbitrary way. For example, the names acetic acid ( $CH_3COOH$ ), chloroform ( $CHCl_3$ ), ethylene ( $CH_2CH_2$ ), acetylene ( $CHCH$ ) and acetone ( $CH_3COCH_3$ ) were not systematically determined. As the number and diversity of known compounds grew, this informal method of nomenclature (naming) became chaotic. In 1892 the International Union of Pure and Applied Chemistry (IUPAC) drafted a set of rules for the systematic naming of organic compounds. These rules have been reviewed regularly to accommodate the millions of new compounds that have been identified since the late 1800s. However, the use of traditional names for some compounds is so entrenched that they are still commonly used. Table 16.7 lists some of the non-systematic names that are still in common use. Rules for the systematic naming of organic compounds will be introduced, as necessary, later in this chapter.

**TABLE 16.7 TRADITIONAL AND SYSTEMATIC NAMES OF SOME COMMON ORGANIC COMPOUNDS**

| Traditional name     | Systematic (IUPAC) name | Formula                |
|----------------------|-------------------------|------------------------|
| ethylene             | ethene                  | $CH_2CH_2$             |
| acetylene            | ethyne                  | $CHCH$                 |
| formaldehyde         | methanal                | $HCHO$                 |
| acetaldehyde         | ethanal                 | $CH_3CHO$              |
| acetone              | propanone               | $CH_3COCH_3$           |
| formic acid          | methanoic acid          | $HCOOH$                |
| acetic acid          | ethanoic acid           | $CH_3COOH$             |
| oxalic acid          | ethanedioic acid        | $HOOCCOOH$             |
| ethyl acetate        | ethyl ethanoate         | $CH_3COOCH_2CH_3$      |
| vinyl chloride       | chloroethene            | $CH_2CHCl$             |
| chloroform           | trichloromethane        | $CHCl_3$               |
| carbon tetrachloride | tetrachloromethane      | $CCl_4$                |
| glycerol             | propane-1,2,3-triol     | $CH_2(OH)CH(OH)CH_2OH$ |

## \* Review exercise 16.1

- 1 What are four properties of carbon that help to explain the number and diversity of carbon-containing compounds?
  - 2 How does organic chemistry differ from inorganic chemistry?
  - 3
    - a What is the average oxidation number of carbon in glucose?
    - b What is the oxidation number of carbon in methane?
    - c Assuming natural gas is made from the decomposition of molecules such as glucose, what sort of reaction does glucose need to undergo to be converted to methane?
  - 4 Why are the bonds in methane arranged in a tetrahedral fashion?
  - 5 Which of the following structural formulas are not correct?  
Explain what is wrong with each incorrect formula.
- a** 
- b** 
- c** 
- d** 
- 6 Draw structural formulas for the following organic compounds:
    - a methylene chloride, or dichloromethane,  $\text{CH}_2\text{Cl}_2$ , which is used in paint strippers and in aerosol spray paints. It is known to cause cancer in animals.
    - b propane,  $\text{C}_3\text{H}_8$ , the main component in liquefied petroleum gas (LPG or LP gas), which is used as fuel in barbecues, portable stoves and motor vehicles.
    - c tetrachloroethylene, or tetrachloroethene,  $\text{C}_2\text{Cl}_4$ , which is the most widely used solvent for the drycleaning of clothes.
    - d formic acid or methanoic acid,  $\text{HCOOH}$ .
  - 7 Describe how carbon–carbon single, double, and triple bonds differ in terms of the number of shared electrons pairs, the bond length, and the bond strength.

## 16.2 From crude oil to petrol

The amount of carbon on Earth is fixed. For the most part, the carbon atoms now present on Earth have been here for billions of years but, their location is not fixed. The various changes in the way in which carbon can move around in the atmosphere, oceans, crust and biosphere (the places on Earth where living things are found) is summarised in the carbon cycle, Figure 16.3.

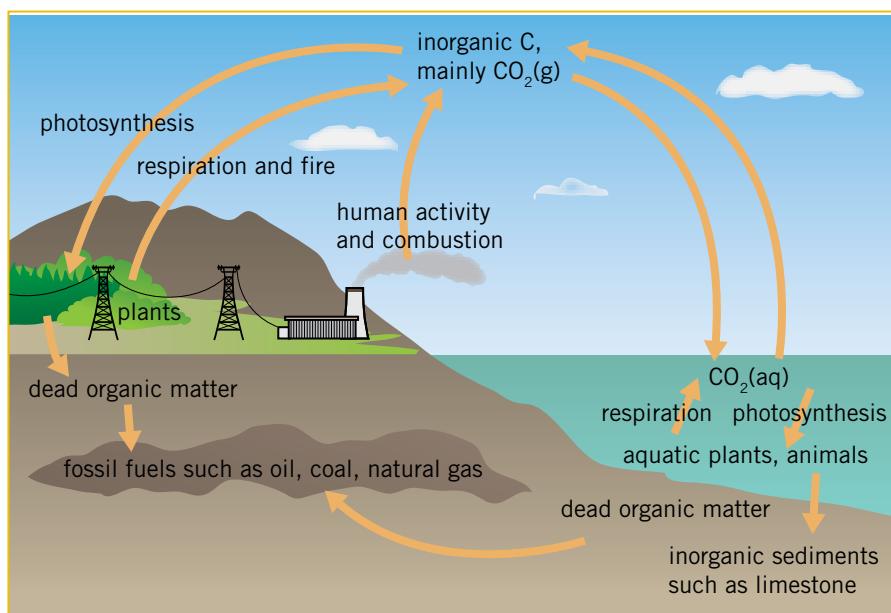


Figure 16.3 A simplified carbon cycle.

While the various carbon exchanges involving carbon dioxide, carbonates, glucose, starch and cellulose take place on a regular basis, some of the carbon trapped in the biosphere was withdrawn from general circulation millions of years ago as dead animals and plants were buried between tonnes of sediment. Subjected to heat and pressure in the absence of oxygen, these deposits ultimately produced coal (mainly carbon), crude oil and natural gas, the latter two being composed mainly of compounds containing carbon and hydrogen—the hydrocarbons.

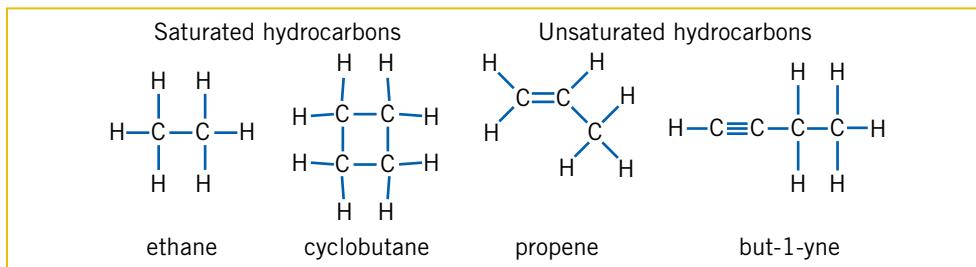
### Introduction to hydrocarbons

The study of the complex area of organic chemistry is made simpler by classifying compounds into families or groups with similar structural features. These features include the types of bonds between the carbon atoms and the presence of other atoms or groups of atoms apart from carbon. Because the physical and chemical properties of an organic compound are determined by its structural features, compounds within the same family have similar physical properties and undergo similar reactions. The group of hydrocarbons, characterised by the presence only of carbon and hydrogen in the compound, can be subdivided into families such as alkanes, alkenes, alkynes and aromatic hydrocarbons.

Hydrocarbons are also sometimes grouped into two major classes, saturated and unsaturated hydrocarbons. The saturated hydrocarbons contain only carbon–carbon single bonds, while the unsaturated hydrocarbons have at least one multiple (double or triple) bond present, as shown in Figure 16.4

**TABLE 16.8 THE 'STEM' NAMES USED FOR THE CONTINUOUS CHAINS IN HYDROCARBONS**

| Number of carbon atoms in chain | 'Stem' name |
|---------------------------------|-------------|
| 1                               | meth-       |
| 2                               | eth-        |
| 3                               | prop-       |
| 4                               | but-        |
| 5                               | pent-       |
| 6                               | hex-        |
| 7                               | hept-       |
| 8                               | oct-        |
| 9                               | non-        |
| 10                              | dec-        |



**Figure 16.4 Examples of saturated and unsaturated hydrocarbons.**

When naming a hydrocarbon, attention must be given to two characteristics of the compound. These are the number of carbon atoms in the hydrocarbon chain and the presence, or absence, of multiple bonds. The number of carbon atoms in the longest continuous carbon chain determines the 'stem' name of the hydrocarbon. Table 16.8 indicates the 'stem' names used for different numbers of carbon atoms in the chain. The suffixes of 'ane', 'ene' or 'yne' are added to the 'stem' name depending on whether the hydrocarbon is an alkane, alkene or alkyne, respectively.

### Alkanes

Alkanes are hydrocarbons having only single carbon–carbon bonds. Table 16.9 lists the first eight members of the alkane family together with their melting points, boiling points and states under normal conditions.

**TABLE 16.9 THE FIRST EIGHT MEMBERS OF THE FAMILY OF ALKANES**

| Name    | Formula                                                                                           | C atoms in chain | Melting point (°C) | Boiling point (°C) | State under normal atmospheric conditions |
|---------|---------------------------------------------------------------------------------------------------|------------------|--------------------|--------------------|-------------------------------------------|
| methane | $\text{CH}_4$                                                                                     | 1                | -182               | -162               | gas                                       |
| ethane  | $\text{CH}_3\text{-CH}_3$                                                                         | 2                | -183               | -89                | gas                                       |
| propane | $\text{CH}_3\text{-CH}_2\text{-CH}_3$                                                             | 3                | -188               | -42                | gas                                       |
| butane  | $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$                                                 | 4                | -138               | 0                  | gas                                       |
| pentane | $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$                                     | 5                | -130               | 36                 | liquid                                    |
| hexane  | $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$                         | 6                | -95                | 69                 | liquid                                    |
| heptane | $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$             | 7                | -91                | 98                 | liquid                                    |
| octane  | $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ | 8                | -57                | 126                | liquid                                    |

The general molecular formula for any alkane is  $\text{C}_n\text{H}_{2n+2}$ , where  $n = 1, 2, 3, 4 \dots$ . For example, the molecular formula of butane with four carbon atoms is  $\text{C}_4\text{H}_{10}$  and the molecular formula for octane with eight carbon atoms is  $\text{C}_8\text{H}_{18}$ .

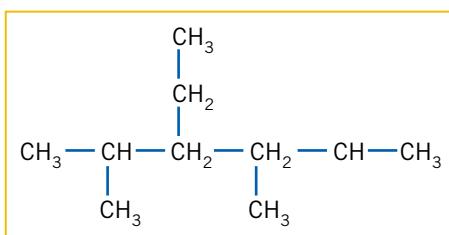
In the alkanes shown in Table 16.9 the carbon atoms are said to be arranged in a continuous straight chain. The carbon atoms in an alkane can also be arranged in a branched chain or in a ring. Examples of these different ways in which carbon atoms can be arranged in alkanes are shown in Table 16.10.

**TABLE 16.10 A RANGE OF ALKANES—STRAIGHT CHAIN, BRANCHED CHAIN AND CYCLIC**

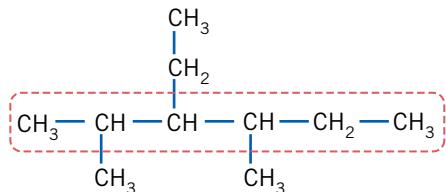
| Carbon atoms arranged in a straight chain                                           | Carbon atoms arranged in branched chains                                                                          | Carbon atoms arranged in a ring                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                     |
|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$<br>hexane | $\begin{array}{c} \text{CH}_3 & \text{CH} & \text{CH}_3 \\ &   & \\ & \text{CH}_3 & \end{array}$<br>methylpropane | $\begin{array}{ccccccccc} & & \text{CH}_3 & & & & & & \\ & &   & & & & & & \\ & & \text{CH}_2 & & & & & & \\ & &   & & & & & & \\ \text{CH}_3 & \text{CH} & \text{CH} & \text{CH}_2 & \text{CH}_2 & \text{CH}_2 & \text{CH}_3 & \\ &   &   &   & & & & \\ & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & & & & \end{array}$<br>3-ethyl-2-methylhexane | $\begin{array}{ccccc} \text{CH}_2 & & \text{CH}_2 & & \\ & \swarrow & & \searrow & \\ & \text{CH}_2 & & \text{CH}_2 & \\ &   & &   & \\ & \text{CH}_2 & & \text{CH}_2 & \end{array}$<br>cyclohexane |

As mentioned earlier, the huge number of possible hydrocarbons demands some systematic way of naming them. The IUPAC rules used to name alkanes are captured in the example in Figure 16.5.

**Figure 16.5 What is the name of this compound?**

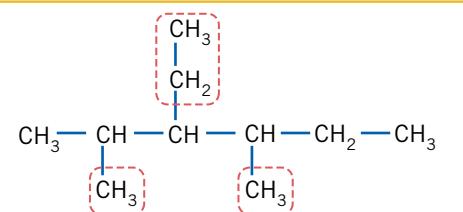


- 1 Identify the longest continuous carbon chain in the alkane. This longest carbon chain is regarded as the parent chain. It is given the stem name associated with the number of carbon atoms in this chain and the suffix for alkanes, that is **-ane**.



The longest chain has six carbons, i.e. **hex-**, and because the compound is an alkane, the parent chain is called **hexane**.

- 2 Name the side chains that branch off the longest chain. The names of these hydrocarbon side chains (alkyl groups) are derived by adding **-yl** to the appropriate hydrocarbon stem names. See Table 16.11 for examples of these names. Write the names of these side chains in alphabetical order before the name of the parent chain.

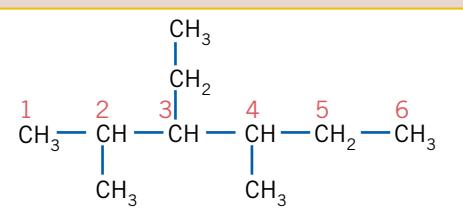


There are three side chains, one ethyl group and two methyl groups.

- 3 If more than one of a particular side chain appears in the molecule, use the prefixes di-, tri-, tetra-, penta- or hexa- to indicate the presence of two, three, four, five or six, respectively, identical groups.

Including the alkyl groups, the name becomes **ethyldimethylhexane**.

- 4 To show the positions of the side chains, number the longest carbon chain consecutively from one end to the other, starting at the end closer to the side chains (to achieve the lowest possible numbers for the side chains). Allocate a number to each side chain and show these numbers before the name of the respective side chains. A hyphen is placed between any word and number, while a comma is placed between two consecutive numbers.



The two methyl groups are on carbons 2 and 4, and the ethyl group on carbon 3. The name becomes **3-ethyl-2,4-dimethylhexane**.

TABLE 16.11 THE NAMES OF HYDROCARBON SIDE CHAIN (ALKYL GROUPS)

| Formula of side chain                           | Name   |
|-------------------------------------------------|--------|
| $\text{CH}_3-$                                  | methyl |
| $\text{CH}_3\text{CH}_2-$                       | ethyl  |
| $\text{CH}_3\text{CH}_2\text{CH}_2-$            | propyl |
| $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$ | butyl  |

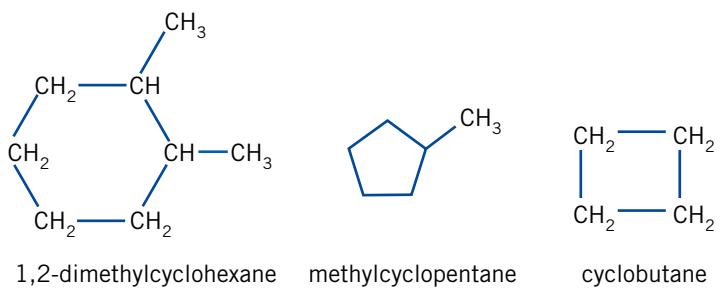


Figure 16.6 Representations of cycloalkanes.

For cyclic alkanes, or cycloalkanes, the same naming rules are followed except the prefix *cyclo*- is used to show that the parent chain is a ring. Examples of cycloalkanes and their names are shown in Figure 16.6. At times, the carbon and hydrogen atoms in the ring of a cycloalkane are not shown in the structural formula, instead, just single lines are used to represent the single bonds between the carbon atoms in the ring, as shown for methylcyclopentane in Figure 16.6.

The properties and reactions of alkanes will be examined further in Section 16.3

### Crude oil as a source of hydrocarbons

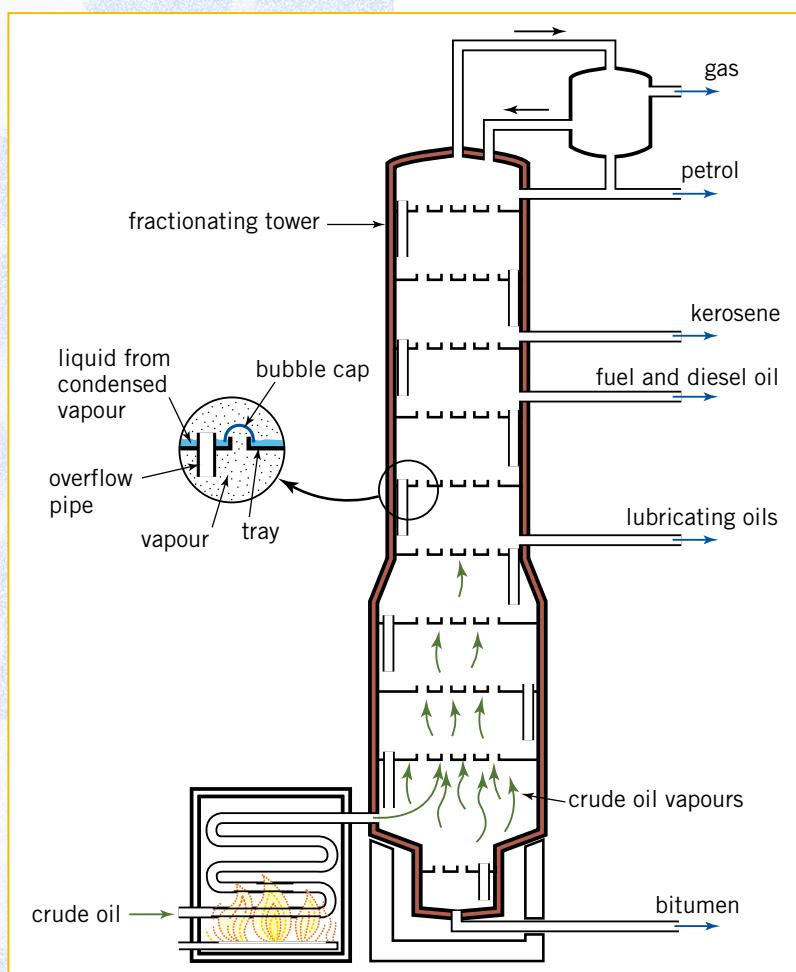


Figure 16.7 A fractionating tower used in the refining of crude oil.

Society makes extensive use of hydrocarbons, for example as fuel for cars and as a source of heat for cooking, heating and running electrical generators. Crude oil is society's major source of hydrocarbons. Because crude oil is a mixture, its composition varies. For instance, Australian crude oil is generally of the 'light crude' type, having more of the lower molecular mass hydrocarbons. Most of the hydrocarbons in crude oil are alkanes, so crude oil is essentially a mixture of many different alkanes.

To make crude oil more commercially useful, it is separated into various components (fractions) in a refining process called fractional distillation. Each fraction obtained in this process contains hydrocarbons with similar boiling points. As indicated by the data in Table 16.9, the boiling points of alkanes are related to their molecular mass—the larger the molecular mass of the alkane, the higher its boiling point. (It is actually the number of electrons in a molecule that is significant in determining the strength of the weak forces between the molecules. This relationship between number of electrons and bonding strength will be discussed further in Unit 3). Fractional distillation therefore allows the crude oil to be separated into components (fractions) of similar molecular mass on the basis of boiling point.

The fractional distillation process begins with the crude oil being heated to around 400°C, at which stage most of it vaporises. This vapour enters a tall fractionating tower similar to that shown in Figure 16.7. The liquid that collects at the bottom is called the residue and it consists of hydrocarbons with forty or more carbon atoms. Much of this residue is used as bitumen for road making.

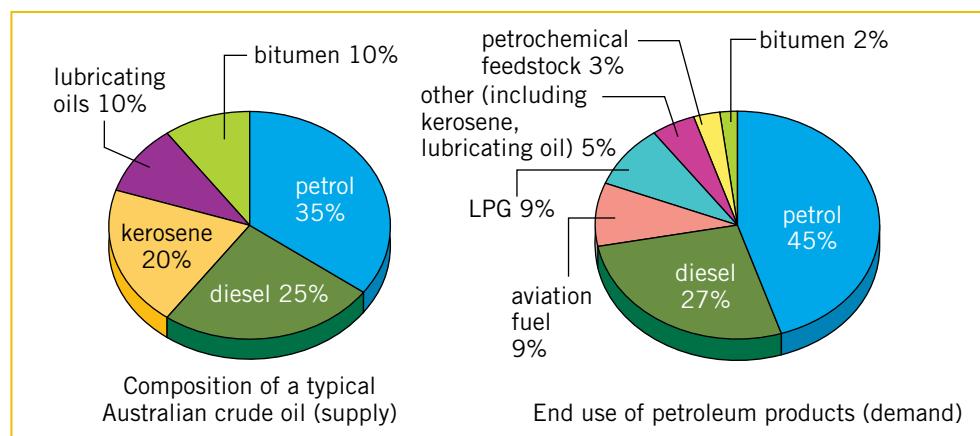
As the mixture of hot gaseous hydrocarbons rises up the fractionating tower, it cools and, if the temperature is low enough, some of it liquefies. Inside the tower are a series of horizontal trays at various heights, as shown in Figure 16.7. Each tray has a number of bubble traps that force the vapour to pass through any liquid that has previously collected in the tray, achieving a more efficient separation.

The higher boiling point components of the crude oil mixture will collect as a liquid first, while the more volatile hydrocarbons will continue to rise up the tower. Lower molecular mass hydrocarbons, with low boiling points, will therefore collect near the top of the tower. The heavier, higher boiling point hydrocarbons will collect further down the tower. Table 16.12 provides a summary of the typical fractions obtained from the fractional distillation of the crude oil.

**TABLE 16.12 THE MAJOR FRACTIONS OBTAINED FROM CRUDE OIL, AND THEIR USES**

| Fraction              | Composition                      | Boiling range °C   | Uses                                                 |
|-----------------------|----------------------------------|--------------------|------------------------------------------------------|
| gas                   | C <sub>1</sub> -C <sub>4</sub>   | below 30           | heating fuel, LPG                                    |
| petrol (straight-run) | C <sub>5</sub> -C <sub>12</sub>  | 30–120             | motor fuel/gasoline                                  |
| kerosene              | C <sub>12</sub> -C <sub>16</sub> | 180–300            | jet and diesel fuel                                  |
| heating fuel oils     | C <sub>16</sub> -C <sub>18</sub> | above 300          | diesel fuel, heating fuel oil, material for cracking |
| lubricating oils      | C <sub>18</sub> -C <sub>20</sub> | above 350          | lubrication, material for cracking                   |
| paraffin waxes        | C <sub>20</sub> -C <sub>40</sub> | low-melting solids | candles, wax                                         |
| bitumen               | above C <sub>40</sub>            | residues, gums     | roofing tar, road surfaces                           |

The composition of the crude oil rarely matches the requirements of the marketplace. As shown in the second pie chart in Figure 16.8, approximately 70% of petroleum products obtained from crude oil are used as petrol or diesel fuels, yet only around 60% of Australian crude oil consists of these particular fuel fractions.



**Figure 16.8 Supply versus demand for different fractions produced by the fractional distillation of crude petroleum.**

The fractions obtained from the distillation of crude petroleum are generally straight chain hydrocarbons with little branching. Straight chain alkanes are not very suitable for use in petrol for automobiles because they ignite too readily—

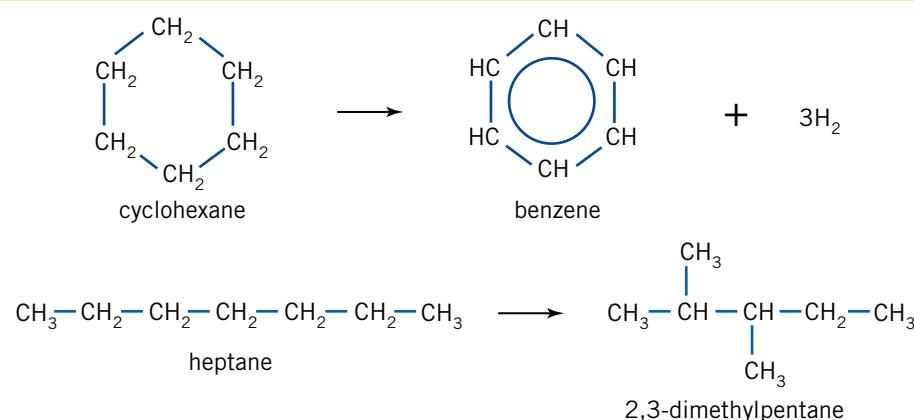
they have a low octane number. As a result, they tend to undergo combustion reactions when they come into contact with the hot walls of the cylinder in which the mixture of fuel and air is being compressed. This means that the mixture of alkanes and air will explode before the spark plug fires. This in turn means that the engine loses efficiency as the mixture ignites before it has undergone complete compression.



**Figure 16.9** Ignition of a mixture of fuel and air in a petrol engine.

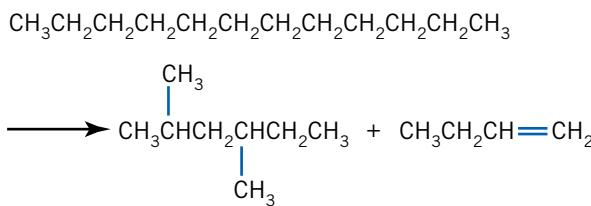
Figure 16.9 shows that the exploding gases, triggered by the spark plug, push the metal cylinder (called a piston) in the bottom-right of the picture down. This provides the power to rotate the wheels. If the mixture ignites before the piston has provided maximum compression (that is, the piston is still moving up when the mixture ignites), power to the wheels will be lost. In some cases this may also damage the engine.

Branched chain alkanes, however, ignite at a higher temperature compared to the straight chain alkanes containing a similar number of carbon atoms. As a result, the process of **reforming** is carried out on the petrol fraction obtained from the distillation of crude oil. Reforming involves the use of heat, pressure, and a catalyst to convert the fractions that do not have the high octane number necessary for combustion in modern automobile engines, into fractions that do not burn as readily. These new fractions, with higher octane numbers, include aromatic compounds (hydrocarbons with a benzene ring present) and more highly branched alkanes. Both aromatic hydrocarbons and branched alkanes burn less readily and so have higher octane numbers.



**Fig 16.10** Some of the reaction types that take place during reforming.

To meet the demand for the fractions with six to twelve carbon atoms, the heavier fractions are subjected to a process known as '**cracking**' in which larger hydrocarbon molecules are broken down into smaller hydrocarbons. Different methods of cracking are used, with the most important being thermal cracking and catalytic cracking. During cracking, enough energy must be provided to break the strong C–C and C–H bonds, and while the mechanism for the thermal process and the catalytic process may differ, the outcome is a smaller molecular mass hydrocarbon and an alkene. For example, a typical cracking reaction is shown in Figure 16.11.



**Figure 16.11** Cracking of a long chain hydrocarbon to produce a smaller alkane and an alkene.



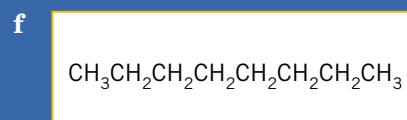
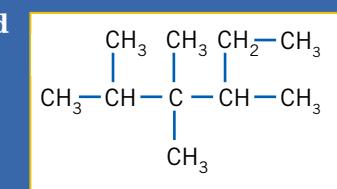
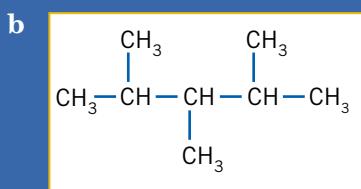
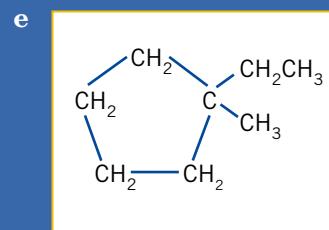
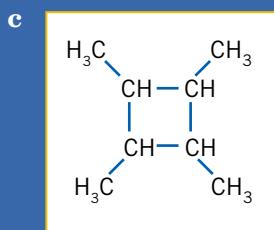
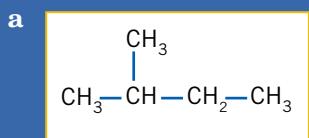
In addition to the production of the more useful, lower molecular mass (and more volatile) alkane, the reaction produces an alkene and as such provides raw materials for the petrochemical industry.

### \* Review exercise 16.2

1 Draw the structural formulas for the following organic compounds:

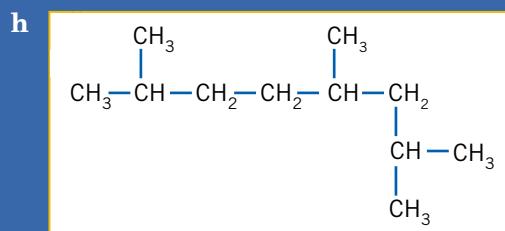
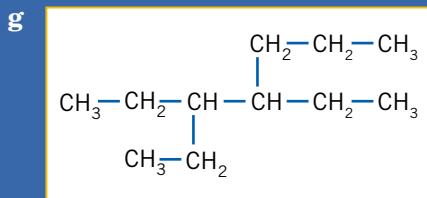
- |                          |                            |
|--------------------------|----------------------------|
| a ethane                 | e 1,4-diethylcyclohexane   |
| b methylpropane          | f ethylpentane             |
| c 2,3-dimethylhexane     | g 1,3-dimethylcyclopentane |
| d 3-ethyl-4-methyloctane | h tetramethylbutane.       |

2 Name each of the following organic compounds.

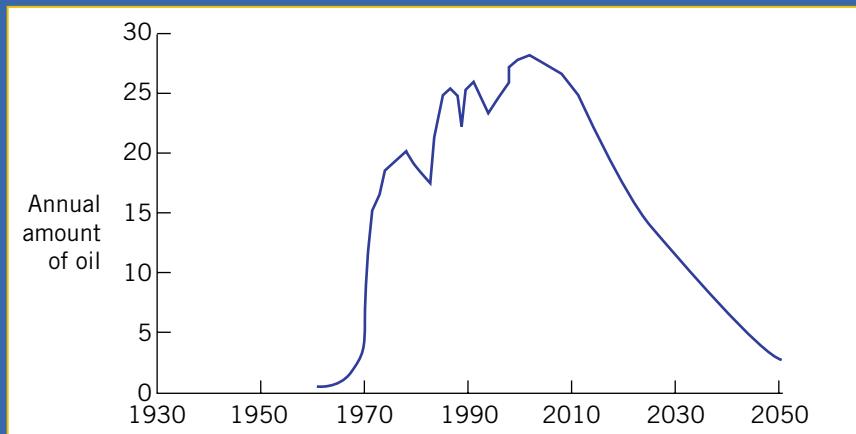


*continued*

**Review exercise 16.2 — *continued***



- 3 The boiling temperature of a hydrocarbon depends on the length of the carbon chain and how close the individual molecules can get to one another in the liquid state.
  - a Explain briefly why a fractionating tower produces hydrocarbons that have different numbers of carbon atoms in the fractions produced near the top of the tower compared to those produced closer to the bottom.
  - b The molecules in two different hydrocarbon samples have approximately the same molecular mass. However, one sample is made up of straight chain alkane molecules whereas the other sample is made up of branched chain alkane molecules. Predict which of the two hydrocarbon samples would have the higher boiling point. Explain your answer.
- 4 **RESEARCH** The graph in Figure 16.12 shows how the amount of oil produced annually in Australia has changed over past decades and how it is projected to change in the future. Similar graphs exist for total world production of crude oil, suggesting what is termed the ‘big rollover’ when demand for oil will outstrip supply at some stage in the next 5–10 years.



**Figure 16.12**

What measures are needed to ensure that our quality of life is sustained during this ‘big rollover’ period? What alternative technologies seem to offer possible solutions?

## 16.3 Properties and reactions of alkanes and cycloalkanes

### Physical properties

The alkanes generally have low melting points and low boiling points, consistent with their covalent molecular character. Because of the weak bonding between the alkane molecules, very little heat is required to disrupt this bonding and so cause the alkane to change state. As seen in the data presented in Table 16.9, the melting and boiling points of the alkanes increase with the addition of an extra CH<sub>2</sub> group to each successive member of the series. The weak forces between the molecules with higher molecular masses (or more correctly, with the larger number of electrons) must therefore be stronger than the weak forces between the molecules of smaller molecular mass. As a consequence, at room temperature, alkanes with one to four carbon atoms are gases, alkanes with up to about nineteen carbon atoms are liquids and alkanes with more than about nineteen carbon atoms are solids with low melting points.

In addition to the relatively low melting and boiling points, alkanes and cycloalkanes are insoluble in water but will dissolve in non-polar solvents such as kerosene. When mixed with polar water molecules, the non-polar alkane, which is usually less dense than water, forms a separate layer on top of the water. Environmentally, this property can have both a negative and positive impact. Oil spills from tankers and refineries are not only unsightly, but they also affect aquatic and bird life. When an animal tries to clean the oil off its fur, or a bird tries to clean its feathers, they ingest the oil and are slowly poisoned. The bird may also become too heavy to fly, or the oil may affect its flight feathers. On the other hand, if petrol starts to leak from the bottom of an underground storage tank, for instance at a petrol station, water can be added to the tank to a level that covers the leak. The upper layer of petrol can then be transferred to another tank, avoiding environmental problems and saving a valuable resource.

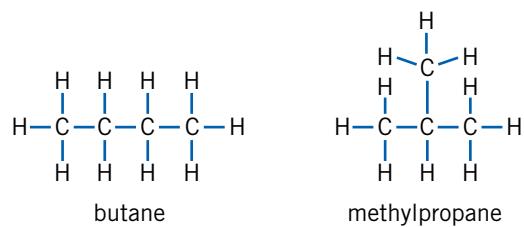
Liquid alkanes serve as excellent solvents for oil-based paints, varnishes, wax-based polishes, insecticides, and as cleaning agents for the removal of oil, fat and grease stains. In addition, alkanes are the major component of commonly used lubricants such as petroleum jelly, engine oil, and grease. Their lubricating properties are in part due to the weak bonds between the alkane molecules. This allows the molecules to easily slip past one another, thus ensuring that the surfaces they are applied to are able to move smoothly against one another. In addition, their lack of solubility in water means that the alkanes are not likely to be washed away from machinery that is exposed to rain or water.

### Isomerism

While there is only one way the carbon and hydrogen atoms can be arranged in the first three alkanes, there are two possible arrangements for the four carbon atoms in an alkane with the formula of C<sub>4</sub>H<sub>10</sub>. Figure 16.14 shows these two possibilities, butane and methylpropane. These two forms of C<sub>4</sub>H<sub>10</sub>, where the atoms are arranged differently, are called **structural isomers**. That is, structural isomers are compounds with the same molecular formula but different structural formulas.

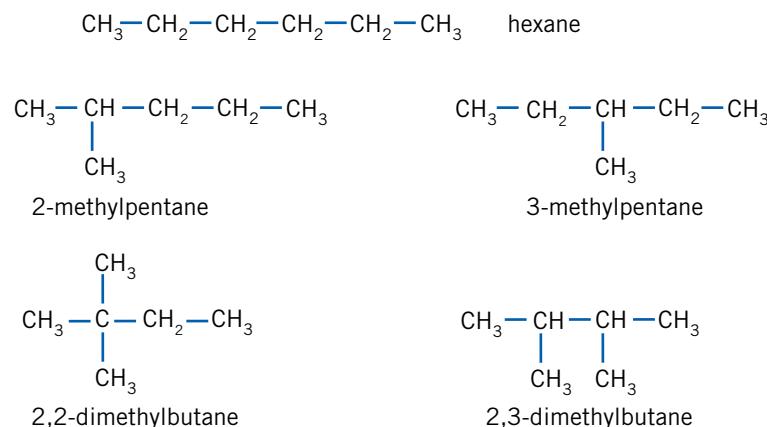


Figure 16.13 Products containing alkane or hydrocarbon solvents.



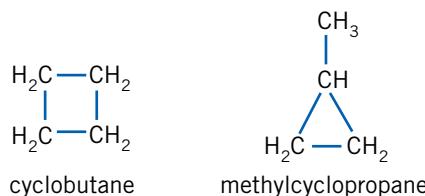
**Figure 16.14** Butane and methylpropane—isomers of  $C_4H_{10}$ .

As the number of carbon atoms in the chain increases, so also does the number of isomers that can exist. For example, hexane,  $C_6H_{14}$ , has five isomers as depicted in Figure 16.15.



**Figure 16.15** The isomers of  $C_6H_{14}$ .

Isomerism also exists in the cycloalkanes. The cycloalkane with the formula  $C_4H_8$  could be either cyclobutane or methylcyclopropane (Figure 16.16).



**Figure 16.16** Cyclic isomers of  $C_4H_8$ .

## Reactions

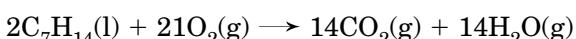
### Combustion

Alkanes undergo combustion reactions in the presence of air or oxygen. These reactions have a ‘high’ activation energy, so they generally require ignition. However, because combustion reactions are also highly exothermic, once started sufficient heat energy is generated to ‘supply’ the required activation energy. The exothermic nature of the combustion reaction is one of the reasons why alkanes are used as fuels for a variety of purposes.

In the presence of excess air or oxygen the products of combustion of an alkane are carbon dioxide and water. For example, the combustion reactions of methane and octane are represented in the following equations:



Similarly, cycloalkanes also undergo combustion reactions. The equation for the combustion of cycloheptane is



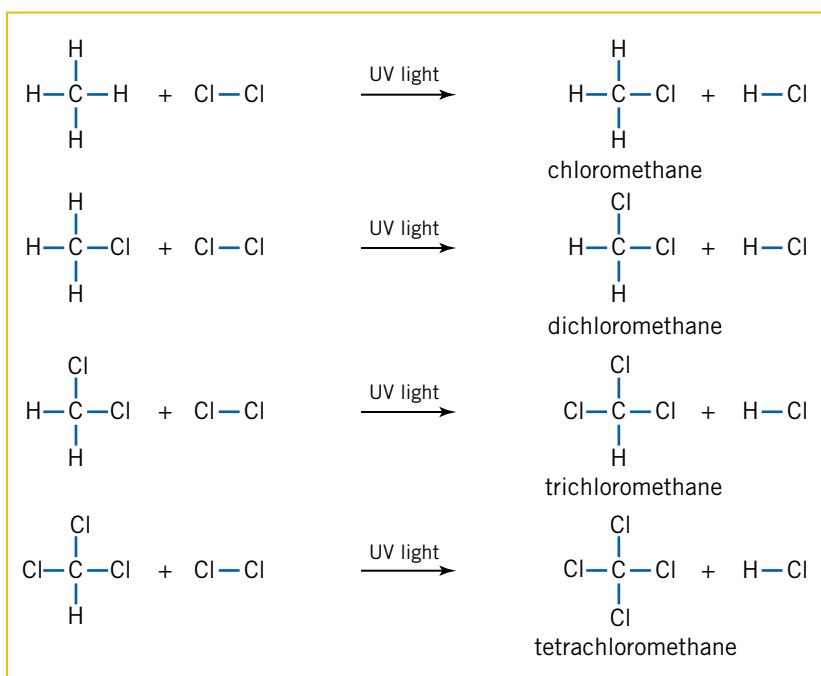
When oxygen is present in limited amounts during the combustion reaction, such as in a car engine, carbon monoxide may form instead of carbon dioxide. The combustion of octane in a limited supply of oxygen, for instance, can be represented by the equation



### Reactions with halogens

In the presence of ultraviolet light, alkanes react with the halogens, fluorine,  $\text{F}_2$ , chlorine,  $\text{Cl}_2$ , bromine,  $\text{Br}_2$ , and iodine,  $\text{I}_2$ . In these relatively slow reactions, C–H bonds in the alkane are broken and new bonds are formed between the carbon and halogen atoms. This type of reaction is called a **substitution reaction**.

Methane, for example, can undergo the following series of substitution reactions with chlorine, in the presence of ultraviolet light, to produce a mixture of haloalkanes:



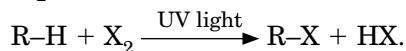
Essentially, in each of these reactions a hydrogen atom in the organic molecule is replaced, or substituted, by a chlorine atom. This ‘displaced’ hydrogen atom then bonds with the second chlorine atom from the chlorine molecule ( $\text{Cl}_2$ ) to form a hydrogen chloride molecule ( $\text{HCl}$ ).



The composition of the resulting product mixture depends on the relative amounts of methane and chlorine originally mixed together. If the methane and chlorine are mixed in a 1:1 mole ratio, the major organic product formed will be chloromethane,  $\text{CH}_3\text{Cl}$ , but if an excess of chlorine is used, the major product will be carbon tetrachloride,  $\text{CCl}_4$ .

Substitution reactions of alkanes with halogens are used industrially to make haloalkanes, but the product mixture usually needs to be fractionally distilled to separate it into its individual components.

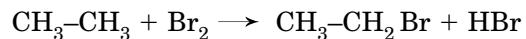
If an alkane is represented by the general formula  $\text{R}-\text{H}$ , where  $\text{R}$  is an alkyl group (see Table 16.11), then the first step in the reaction of any alkane with any halogen (represented as  $\text{X}_2$ ) would be:



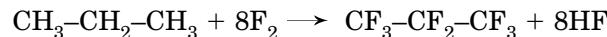
The  $\text{HX}$  in this equation represents the hydrogen halide that is always formed in this reaction together with the haloalkane.

Several examples of substitution reactions are given below:

- i reaction of an excess of ethane with bromine, in the presence of ultraviolet light:



- ii reaction of propane with an excess of fluorine in the presence of ultraviolet light

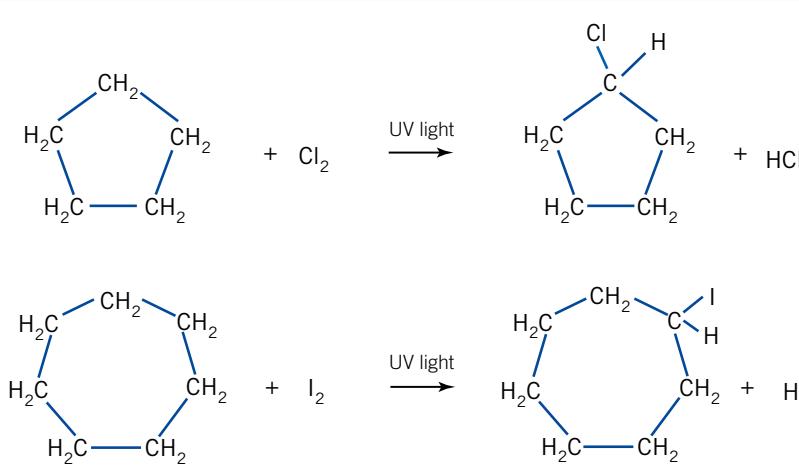
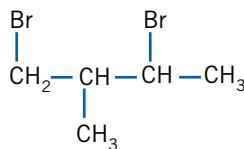


According to the IUPAC convention, the names of the haloalkanes are derived by using the abbreviated name of the halogen (fluoro-, chloro-, bromo-, iodo-) in front of the alkane name, for example, chloromethane. In haloalkanes with more than two carbon atoms it is necessary to designate the position of the halogen substituent using a number, in a similar method used for alkyl side chains. For example, the name of the compound shown on the left is 1,3-dibromo-2-methylbutane.

The haloalkanes generally have low melting and boiling points, although not as low as the parent alkane. The liquid haloalkanes are usually good solvents for fats, oils and greases, and some were previously used as drycleaning solvents. Chlorofluorocarbons (CFCs), such as dichlorodifluoromethane, were once used in refrigerators and air conditioners. Since CFCs are chemically stable, non-toxic and non-flammable they also have been used as the blowing agents in making foams, as well as the propellants for many aerosols. However, their role in the

depletion of stratospheric ozone has resulted in them being banned for such uses in many countries, even though older refrigerators and air conditioners still contain these environmentally damaging chemicals.

Under conditions similar to those required for alkanes, the cycloalkanes will also undergo substitution reactions. Figure 16.17 shows the substitution reactions of several cycloalkanes. Only a mono-halogenated compound is shown, although, like the alkanes, in practice a mixture of products is formed.



**Figure 16.17** Substitution reactions of several cycloalkanes.

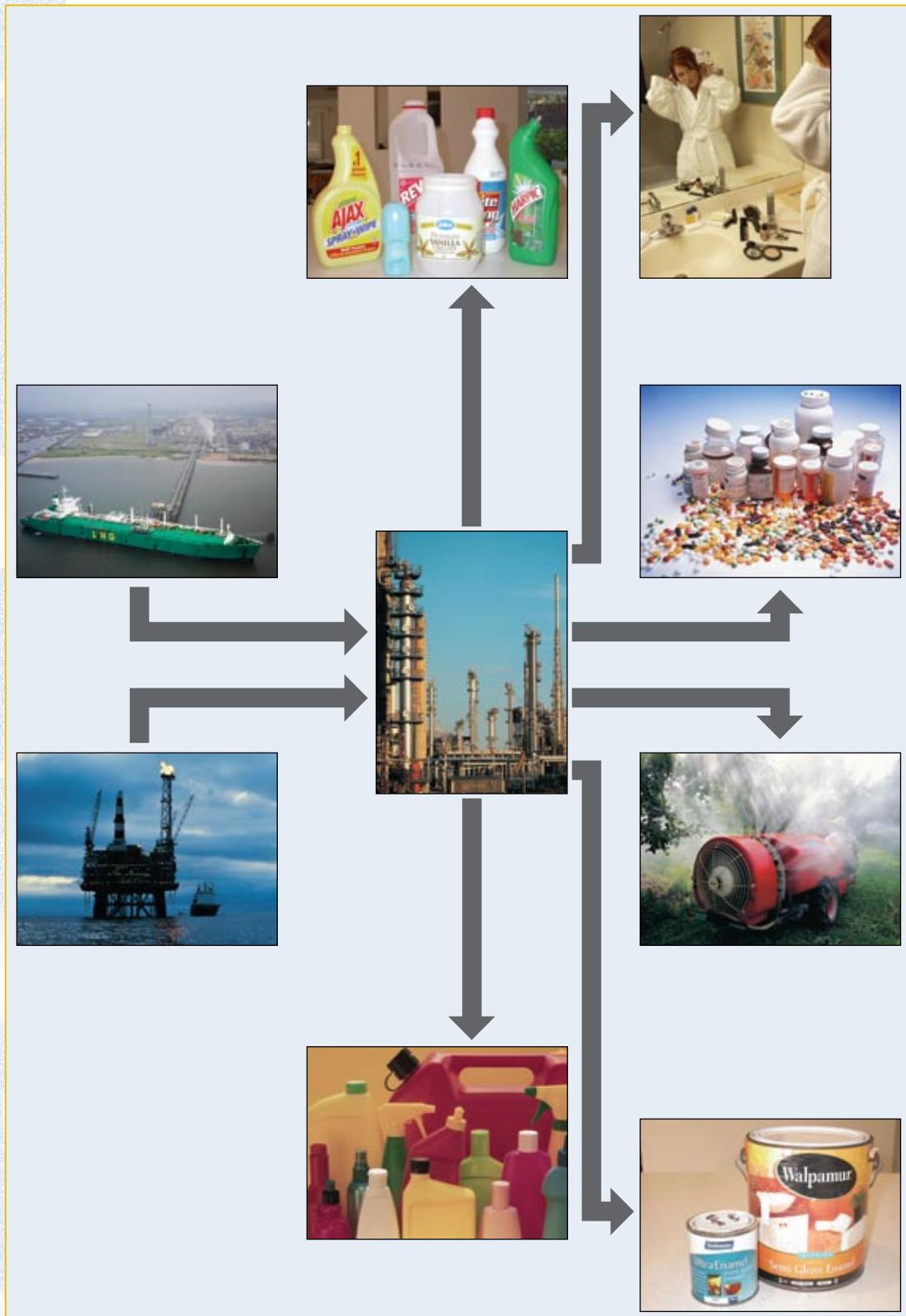
### \* Review exercise 16.3

- 1 Draw and name the structural isomers of:
  - a  $\text{C}_5\text{H}_{12}$
  - b cycloalkanes with a formula  $\text{C}_5\text{H}_{10}$ .
- 2 a Write the equation for the complete combustion of:
  - i hexane
  - ii cyclopentane.  
b Write the formula of the major organic product of the reaction of 1 mole of ethane with 1 mole of bromine in the presence of UV light.  
  
c Write the equation for the reaction of 1 mole of butane with 1 mole of chlorine in the presence of UV light.  
  
d Draw the structures of three different monochlorocycloalkanes formed in the reaction of methylcyclopropane with chlorine. What is the general name given to these three compounds with the same formula?
- 3 ↗ RESEARCH Many action movies show cars exploding during crashes. In fact, the chances of an explosion during a car crash are very small. What are the conditions necessary for a mixture of petrol and air to explode? Why, then, is it unlikely that these conditions will be achieved in a car crash?

## 16.4 Unsaturated hydrocarbons—alkenes and cycloalkenes

As introduced in Section 16.2, cracking of a long-chain alkane produces a shorter chain alkane and an alkene. While the alkene is of little use as a fuel, it is important for the chemical industry because the unsaturated molecules are more reactive than alkanes. As a result it is relatively easy to put different atoms or groups of atoms onto the carbon chain and so provide pathways to a large number of commercially important chemicals. Included in the list of important chemicals prepared from alkenes are plastics and polymers, pharmaceuticals, paints, dyes, textiles, detergents, pesticides, perfumes, flavourings, and solvents.

As long ago as 1872, Dimitri Mendeleev remarked that crude oil was too valuable to burn as a fuel and should be used as a source of organic chemicals. Times have obviously changed since then, but it is still true that the organic chemicals produced from crude oil are now an essential part of our life and lifestyle.



**Figure 16.18** The petrochemical industry—input and output.

Like alkanes, alkenes are also hydrocarbons because they are composed of carbon and hydrogen atoms. However, in alkenes at least two carbon atoms are joined by a double bond. It is this double bond that introduces a chemical reactivity not present in the alkanes, and that opens up pathways to a vast range of organic compounds.

Examples of some low molecular mass alkenes are given in Table 16.13.

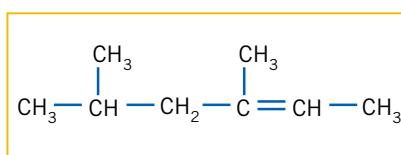
**TABLE 16.13 FORMULAS AND PROPERTIES OF SOME ALKENES**

| Name            | Formula                                                 | C atoms in chain | Melting point (°C) | Boiling point (°C) | State under normal atmospheric conditions |
|-----------------|---------------------------------------------------------|------------------|--------------------|--------------------|-------------------------------------------|
| ethene          | $\text{CH}_2=\text{CH}_2$                               | 2                | -169               | -104               | gas                                       |
| propene         | $\text{CH}_2=\text{CH}-\text{CH}_3$                     | 3                | -185               | -48                | gas                                       |
| but-1-ene       | $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$         | 4                | -185               | -6                 | gas                                       |
| cis-but-2-ene   | $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$           | 4                | -139               | 4                  | gas                                       |
| penta-1,3-diene | $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$ | 5                | -87                | 42                 | liquid                                    |

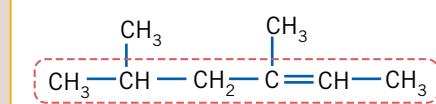
### Naming of alkenes and cycloalkenes

Alkenes are named in a similar way to alkanes but rather than the parent name ending in '-ane', it ends in '-ene' for alkenes. The IUPAC rules for naming alkenes are explained in the example in Figure 16.19.

**Figure 16.19** What is the name of this alkene?

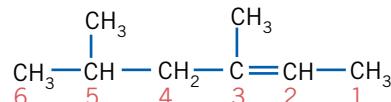


- 1 Identify the longest continuous carbon chain containing the double bond. This is the parent chain. It is given the stem name associated with the number of carbon atoms in this chain and the suffix for alkenes, that is **-ene**.



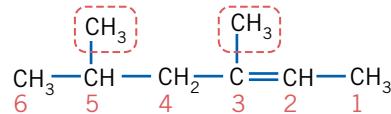
The longest chain has six carbons, that is, **hex-**, and because the compound is an alkene, the parent chain is called **hexene**.

- 2 Number the parent chain from the end that will give the lowest number to the double bond. The position of the double bond is described by the lowest numbered double bonded carbon.



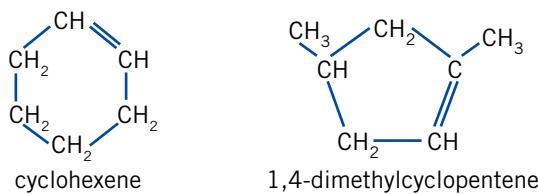
In this example, the chain is numbered from right to left to give double bonded carbons the smallest number. The lowest number for the double bond, that is, 2, is used in the name, and is placed just before suffix **-ene**, to give **hex-2-ene**. Hyphens are used between words and numbers.

- 3 Name the side chains in the same way as with alkanes.



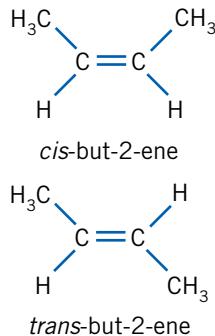
There are two methyl side chains, one on carbon 3 and the other on carbon 5. So the name is **3,5-dimethylhex-2-ene**.

In a similar fashion, the cycloalkenes are named in such a way as to ensure that, when there are other substituents on the ring, the double bond in the ring is given the smallest number. When there are no substituents on the ring, a number indicating the position of the double bond is not required in the name.



**Figure 16.20** Structural formulas and names for several cycloalkenes.

### Isomerism in alkenes



**Figure 16.21** *Cis*- and *trans*- isomers of but-2-ene.

In addition to structural isomerism, the alkenes also exhibit another form of isomerism because, unlike the single carbon–carbon bond, there is no rotation possible about a double bond. This means there is the possibility of forming two different molecules in which the position of the double bond in the chain is the same, but the spatial arrangement of the atoms across the double bond is different. Figure 16.21 shows two molecules of but-2-ene, but in one the CH<sub>3</sub> groups are on the same side of the double bond (the *cis* isomer), and in the other they are on opposite sides (the *trans* isomer). This type of isomerism is called geometrical isomerism.

Two geometrical isomers have different physical properties but chemically they usually behave in a similar fashion. For example the melting points of *cis*-but-2-ene and *trans*-but-2-ene are  $-139^{\circ}\text{C}$  and  $-106^{\circ}\text{C}$  respectively, yet they both react readily with bromine to form haloalkanes.

Alkenes also exhibit structural isomerism. For example, but-1-ene and but-2-ene (Figure 16.22) are structural isomers. In but-1-ene the double bond is between carbon atoms 1 and 2. In but-2-ene the double bond is between carbon atoms 2 and 3.

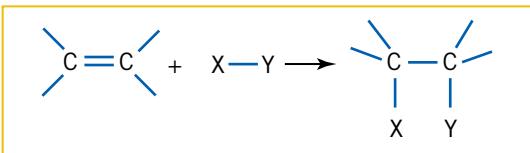


**Figure 16.22** Examples of structural isomers.

### Addition reactions of alkenes and cycloalkenes

Like all hydrocarbons, alkenes and cycloalkenes undergo combustion reactions, but it is the reactivity of the double bond that provides the avenue for the rich diversity of organic molecules that are derived from crude oil. The key reaction that alkenes undergo is known as addition.

In an addition reaction two new atoms or groups of atoms are added to the carbon atoms on either side of the double bond. In the reaction the double bond becomes a single bond, but two new bonds are formed, one to each of the carbon atoms formerly joined by the double bond.



The most important alkene produced in the cracking of the heavier fractions from the distillation of crude oil is ethene,  $\text{H}_2\text{C}=\text{CH}_2$ . Figure 16.23 summarises some of the addition reactions ethene undergoes and the important materials produced as a result of these addition reactions.

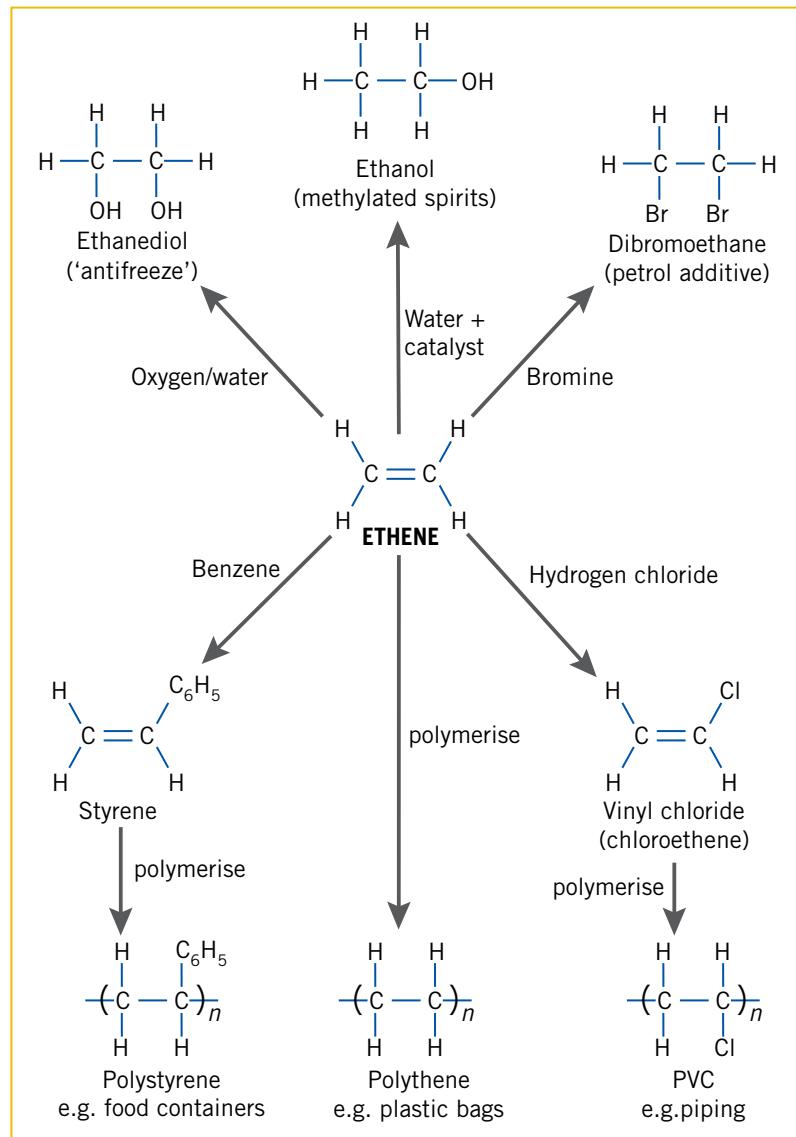
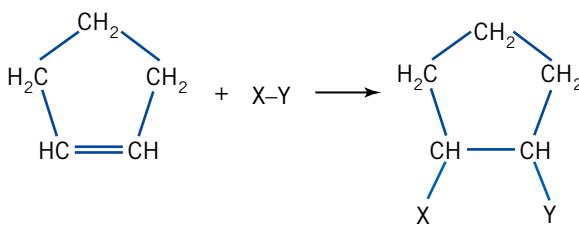


Figure 16.23 Some of the compounds produced from ethene in the petrochemical industry.

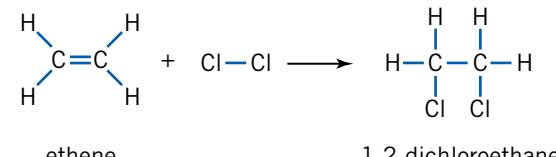
The double bond in cycloalkenes, like that in the alkenes, provides an electron-rich region for attack by a number of molecules such as halogens, hydrogen halides and water. Addition reactions are therefore also the dominant reactions of the cycloalkenes (Figure 16.24).



**Figure 16.24** Addition reaction in cycloalkenes.

### Addition of halogens—halogenation

Alkenes readily undergo addition reactions with the halogens to form haloalkanes. For example, ethene readily reacts with chlorine according to the following equation:



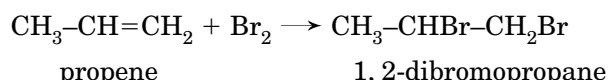
The use of a coloured halogen such as red-brown bromine is a useful test for the presence of a double bond. When bromine, or a dilute solution of bromine in water, is mixed with an alkane the red-brown colour fades very slowly in the presence of ultraviolet light. However, in the presence of an unsaturated hydrocarbon the colour disappears very quickly as the alkene reacts with the bromine.



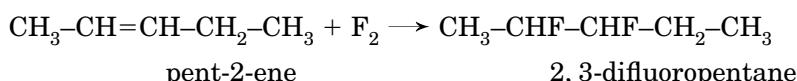
**Figure 16.25** Reaction of an aqueous solution of bromine (lower layer) with an alkene (upper layer in right-hand test tube) and with an alkane (upper layer in left-hand test tube).

Several more examples of addition reactions between alkenes and halogens are given below:

- ### i. the reaction of propene with bromine

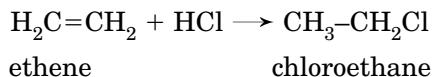


- ## ii the reaction of pent-2-ene with fluorine



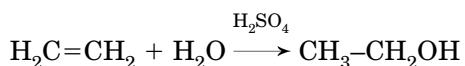
## Addition of hydrogen halides

The hydrogen halides, such as hydrogen chloride or hydrogen bromide, will undergo an addition reaction with an alkene to produce a haloalkane. For example, ethene reacts with hydrogen chloride according to the following equation:



### Addition of water—hydration

Perhaps the most important reaction of ethene is the reaction with water in the presence of sulfuric or phosphoric acid as a catalyst to produce ethanol (an alcohol).



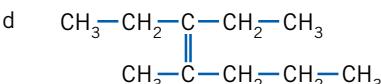
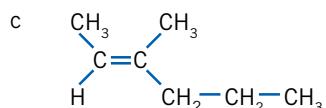
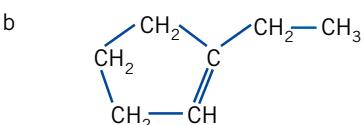
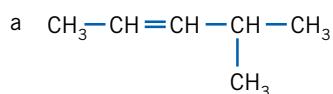
Other alkenes also undergo similar addition reactions with water in the presence of either catalyst.

### \* Review exercise 16.4

- 1** Draw the structural formulas for the following:

**a** 2,3-dimethylhex-1-ene      **c** 3-ethylcyclohexene  
**b** *cis*-5-dimethylhex-2-ene      **d** *trans*-5,5,6-trimethylhept-2-ene.

**2** Give the names of the following:



- 3** Write equations (with structural formulas) for the following addition reactions:

  - a** propene + iodine →
  - b** *cis*-pent-2-ene + hydrogen in the presence of a catalyst →
  - c** 2,3-dimethylpent-1-ene + hydrogen bromide →
  - d** methylcyclopentene + chlorine →
  - e** 1-cycloheptene + steam in the presence of sulfuric acid →

**4** Compare and contrast structural and geometrical isomerism.

**5** Why is geometrical isomerism not possible in propene, or pent-1-ene, but is possible in pent-2-ene?

**6** **a** What is the difference between polyunsaturated, monounsaturated and saturated fats in butter, margarine and edible oils?

**b** In recent years concern has been expressed about the existence of *trans* fatty acids in our diets. These *trans* fatty acids are claimed to behave more like saturated fats. Considering the arrangement of groups around the double bond in a *cis* alkene as opposed to a *trans* alkene, explain why a *trans* fatty acid behaves like a saturated fat.

**c** ↗ RESEARCH How are *trans* fatty acids manufactured?

**d** Why, at room temperature, are *trans* fatty acids more likely to be solid and *cis* fatty acids liquid? Is this consistent with the melting point data given on page 394 for *cis* and *trans*-but-2-ene?

## 16.5 Aromatic hydrocarbons—benzene

First isolated by Michael Faraday in 1825, benzene is the basic unit of the group of organic compounds often referred to as aromatic. While some of the first aromatic substances isolated and identified did have a distinct smell, the name ‘aromatic’ is actually a misnomer, as many of this group of compounds have no particular smell.

The base unit of aromatic compounds, benzene, has the formula C<sub>6</sub>H<sub>6</sub>. The structure of the molecule baffled scientists for some time, as its chemistry is not easily explained in terms of the bonding ideas that were used in the nineteenth century. In 1865, August Kekulé published a ring structure based on cyclohexane with three double bonds (see Figure 16.26a).

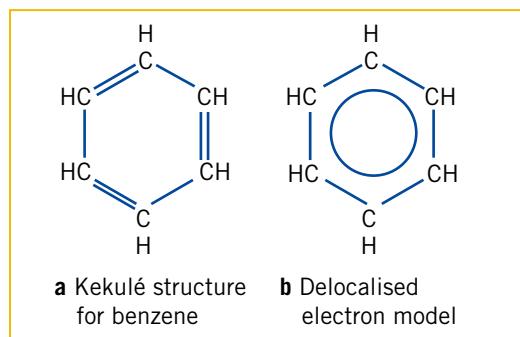


Figure 16.26 Proposed structures for benzene.

However, benzene does not behave as if it has three single and three double bonds. It does not readily undergo addition reactions, even though the structure suggests that it should be very reactive. Spectroscopic and other studies show that the carbon–carbon bonds in benzene are all the same, with a bond length between that of a single and a double bond. While the nature of the bonding in benzene is beyond the scope of this text book, the representation in Figure 16.26b is that understood by many chemists today. The circle represents six delocalised electrons, one from each carbon atom, that are not fixed to any one atom. In this respect the structure of benzene has similarities to that of graphite, in which each carbon atom forms three covalent bonds, and also has a share of a group of delocalised electrons.

Benzene and similar aromatic molecules are obtained during the distillation of crude oil and also from the heating of coal in the absence of air. The importance of aromatic compounds cannot be underestimated as they are not only present in many of the biologically important molecules in living things, but also in pharmaceuticals, dyes, plastics, detergents, textiles, perfumes, insecticides, pesticides and explosives.

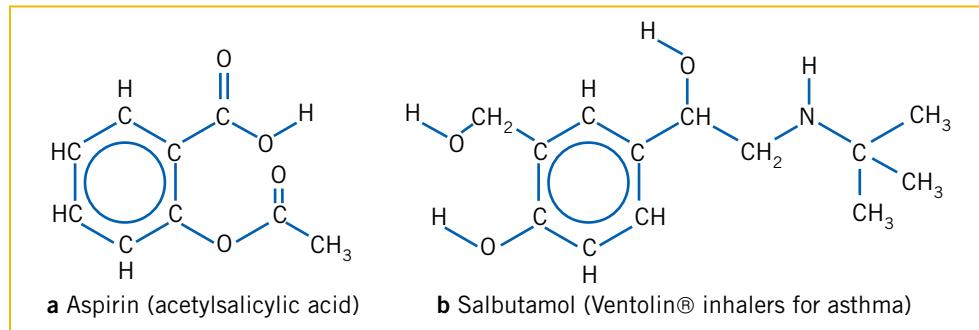
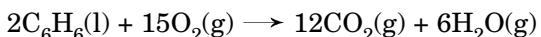


Figure 16.27 Two commonly used aromatic compounds.

## Reactions of benzene

Typical of all hydrocarbons, benzene and other aromatic hydrocarbons will burn in excess air or oxygen to produce carbon dioxide and water. The equation below shows the combustion of benzene.



Further evidence for the special nature of the bonds in benzene is found in its reactivity. Rather than undergoing an addition reaction, which would be expected if double bonds were present, the major reaction is substitution.

Halogenation of benzene can take place at room temperature in the presence of a suitable catalyst such as an aluminium halide. The overall reaction involves the substitution or replacement of a hydrogen atom with a halogen atom.

The bromination of benzene is depicted in Figure 16.28.

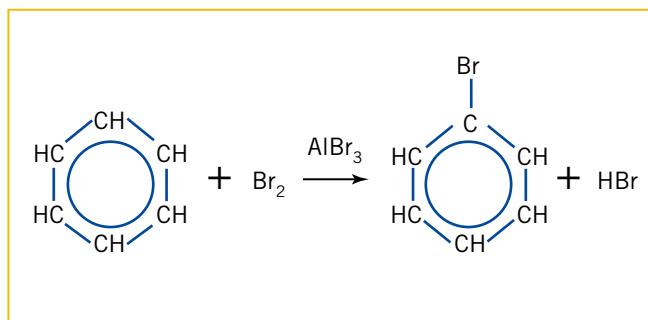
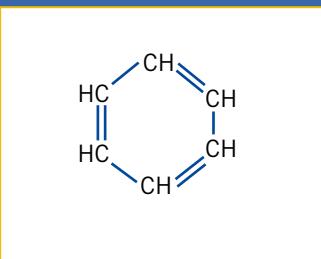


Figure 16.28 Bromination of benzene.

### \* Review exercise 16.5

- 1 'Given that benzene and graphite both have delocalised electrons, both must be good conductors of electricity.' Discuss the truth or otherwise of this statement.
- 2 The classical structure of benzene was represented as



- a What is the experimental evidence that indicates that this structure is not correct?
- b What is the generally accepted structure of benzene that accounts for its properties?
- 3 Write an equation, using structural formulas, for the reaction of benzene with iodine in the presence of aluminium iodide.

## 16.6 Empirical formulas of organic compounds

The empirical formula of a compound gives the simplest whole number ratio of the atoms present in the compound. As explained in Section 12.4, an empirical formula of a compound can be determined by measuring the mass or percentage by mass of each element present and converting this data into a whole number mole ratio.

The empirical formulas of hydrocarbons can also be determined by making use of the combustion reaction which, in the presence of excess air, forms carbon dioxide and water. The solutions to the following examples illustrate these calculations.

### → Example 16.1

A particular hydrocarbon on complete combustion produces 2.641 g of carbon dioxide and 1.441 g of water. Use this information to calculate the empirical formula of the hydrocarbon.

### → Solution

We are told that all the carbon in the hydrocarbon has reacted to form carbon dioxide, and all the hydrogen has formed water.

$$\text{mole of CO}_2 \text{ formed during combustion} = \frac{2.641}{44.01} = 0.06001$$

= mole of C originally present in the hydrocarbon

$$\text{mole of H}_2\text{O formed} = \frac{1.441}{18.016} = 0.07998$$

because in every 1 mole of  $\text{H}_2\text{O}$  there are 2 moles of H

$$\text{mole of H originally in the hydrocarbon} = 2 \times 0.07998 = 0.1600$$

|                                             | C                         | H                        |
|---------------------------------------------|---------------------------|--------------------------|
| Amount, in mole, of elements in hydrocarbon | 0.06001                   | 0.1600                   |
| Divide by smallest number                   | $\frac{0.06001}{0.06001}$ | $\frac{0.1600}{0.06001}$ |
|                                             | = 1                       | = 2.666                  |
| Multiply both numbers by 3                  | = 3                       | = 7.998                  |
| Round off to whole numbers                  | = 3                       | = 8                      |

The empirical formula is therefore  $\text{C}_3\text{H}_8$ .

### → Example 16.2

Complete combustion of 19.4 g of a hydrocarbon was found to produce 58.7 g of carbon dioxide. If the molar mass of this hydrocarbon is  $58.1 \text{ g mol}^{-1}$ , calculate its molecular formula.

### → Solution

i Calculation of the empirical formula:

$$\text{mole of CO}_2 = \frac{58.7}{44.01} = 1.334$$

= mole of C present in the hydrocarbon

$$\text{mass of C present in the hydrocarbon} = 1.334 \times 12.01 = 16.02 \text{ g}$$

mass of H present in the hydrocarbon must therefore be

$$19.4 - 16.02 = 3.38 \text{ g}$$

$$\text{mol of H present in hydrocarbon} = \frac{3.38}{1.008} = 3.353$$

|                                             | C                     | H                     |
|---------------------------------------------|-----------------------|-----------------------|
| Amount, in mole, of elements in hydrocarbon | 1.334                 | 3.353                 |
| Divide by smallest number                   | $\frac{1.334}{1.334}$ | $\frac{3.353}{1.334}$ |
|                                             | = 1                   | = 2.513               |
| Multiply both numbers by 2                  | = 2                   | = 5.027               |
| Round off to whole numbers                  | = 2                   | = 5                   |

The empirical formula is therefore  $C_2H_5$

## ii Calculation of the molecular formula

$$(C_2H_5)_n = \text{molecular formula} \quad (\text{where } n \text{ is a whole number})$$

$$29.06 \times n = 58.1$$

$$n = \frac{58.1}{29.06} = 1.999 \approx 2$$

The molecular formula must be  $(C_2H_5)_2$  or  $C_4H_{10}$ .

It is also possible to determine empirical and molecular formulas from data involving the volumes of gaseous reactants and products. This calculation uses Avogadro's hypothesis which states that equal volumes of gases, at the same temperature and pressure, contain equal amounts, in mole, of the gases. For the following reaction, for example,



1 L of methane would react with 2 L of oxygen to form 1 L of carbon dioxide and 2 L of gaseous water, when all the volumes are measured at the same temperature and pressure.

### → Example 16.3

If 20.0 mL of an unknown hydrocarbon requires 50.0 mL of oxygen for complete combustion, and produces 40.0 mL of carbon dioxide, what is the molecular formula of the hydrocarbon? (Assume all the volumes were measured at the same temperature and pressure.)

### → Solution

A general equation for the combustion reaction of an alkane can be written as



where  $x$  and  $y$  represent the mole ratio of C and H in the molecular formula of the hydrocarbon. This general equation can be used to determine the molecular formula from the volume data:



volumes of gases in reaction: 20.0 mL    50.0 mL    40.0 mL

mole ratio of reactants/products: 1                  2.5                  2

$x$  must therefore equal 2

and  $x + \frac{y}{4} = 2.5$

$\frac{y}{4} = 2.5 - 2 = 0.5$ , so  $y$  must equal  $0.5 \times 4 = 2$

That is, the molecular formula is  $C_2H_2$ .

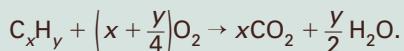
### \* Review exercise 16.6

- 1 A hydrocarbon is found to contain 81.7% carbon by mass. What is the empirical formula of the hydrocarbon?
- 2 1.500 g of a hydrocarbon produced 5.076 g of carbon dioxide on complete combustion. Determine the empirical formula of the hydrocarbon. If the molar mass of the hydrocarbon is around  $78 \text{ g mol}^{-1}$  what is its molecular formula?
- 3 On complete combustion a hydrocarbon is found to produce 1.201 g of water and 2.934 g of carbon dioxide. What is the empirical formula of the hydrocarbon?
- 4 When 30.0 mL of a particular gaseous hydrocarbon was mixed with 100 mL of oxygen and the mixture exploded, the remaining gases occupied a volume of 70.0 mL, and further analysis of the mixture established that 10.0 mL of this was unreacted oxygen. If all volumes are measured at  $15^\circ\text{C}$  and the same pressure, what is the empirical formula of the hydrocarbon?

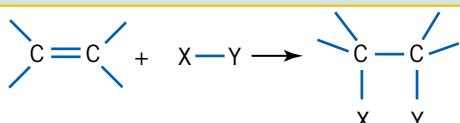


## MAJOR IDEAS

- Hydrocarbons are compounds that contain just carbon and hydrogen. Hydrocarbons can be classified into a number of categories, some of which are alkanes, cycloalkanes, alkene and cycloalkenes.
- Organic chemistry is the study of carbon compounds, particularly those involving carbon bonded to hydrogen.
- Carbon's capacity to form four covalent bonds, to form chains and rings, to bond with many other elements, and to form multiple bonds makes it unique among the elements.
- Molecular formulas of organic compounds can be written as structural formulas, giving information about the order in which the atoms are arranged.
- Some of the carbon in the carbon cycle, particularly the carbon associated with plants and animals, has been locked away over millions of years as the fossil fuels—natural gas, crude oil and coal.
- Hydrocarbons, particularly the alkanes, are the major constituent of crude oil.
- Useful hydrocarbons can be obtained from crude petroleum by a process called fractional distillation.
- The IUPAC has developed a set of systematic rules for naming hydrocarbons.
- Useful hydrocarbons undergo combustion in excess air to produce carbon dioxide and oxygen according to



- Saturated hydrocarbons include alkanes and cycloalkanes.
  - In the presence of ultraviolet light, alkanes and cycloalkanes undergo substitution reactions to produce a range of haloalkanes or halocycloalkanes according to the general equation
- $$R-H + X_2 + \text{UV light} \rightarrow R-X + H-X$$
- Alkanes and cycloalkanes and their halogenated derivatives exhibit structural isomerism—same molecular formula but with a different arrangement of atoms.
  - Alkenes undergo addition reactions in the presence of hydrogen halides, halogens, hydrogen and water.



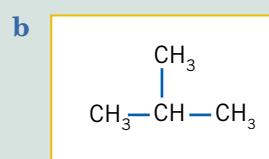
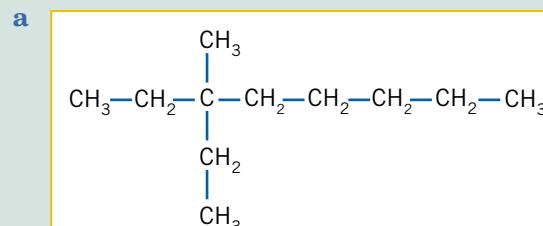
- Alkenes exhibit structural isomerism, and in some cases, geometrical isomerism.
- Aromatic compounds are compounds that contain a benzene ring.

- Benzene contains delocalised electrons and the carbon–carbon bond is intermediate between a single and a double bond.
- Benzene and other aromatic hydrocarbons undergo combustion and substitution reactions.
- In the presence of a halogen and a suitable catalyst, benzene produces a halo-substituted compound.
- The empirical formula of a hydrocarbon gives the simplest whole number ratio of carbon to hydrogen atoms in the molecule.
- Empirical formulas can be determined from percentage composition by mass, mass composition, or from information about the amounts of carbon dioxide and/or water produced in combustion.

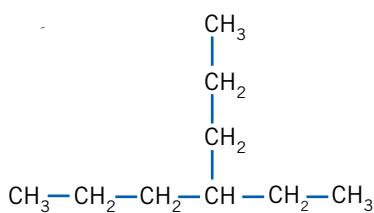
## QUESTIONS

- Explain why the formula  $CH_3CHCHCH_2CH_2CH_3$  is superior to the formula  $C_6H_{12}$ .
- Draw structural formulas for the following.
  - 2,2,5-trimethylheptane
  - 1,2-dibromoethene
  - 1,2-dichlorocyclopropane
  - 3-methyl-4-propyloctane
  - trans*-but-2-ene
  - 2,3-diiodoprop-1-ene
  - 2,3,4,5-tetramethylhex-2-ene
  - diethylpentane
  - 1,2-dibromo-3-methylcyclohexene
  - cis*-2,5-dimethylhex-3-ene
  - 3-bromo-2-methylcycloheptene
  - methylbenzene
  - bromobenzene
  - trans*-1-bromo-2-chloroethene.

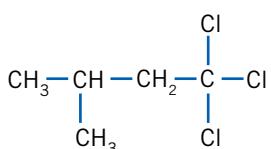
- Write the correct IUPAC name for each of the following.



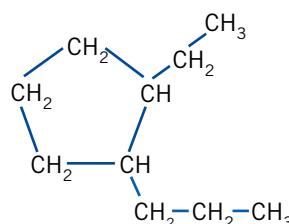
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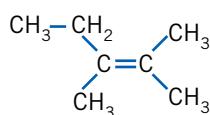
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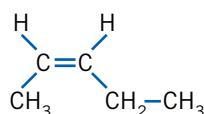
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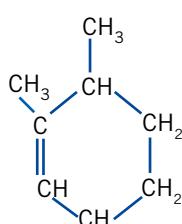
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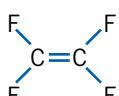
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h



i



- 4 A compound has the formula  $C_4H_8$ . Draw and name five possible structures for hydrocarbons having this formula.

- 5 a Using pent-2-ene and pentane as examples, explain why it is that *cis/trans* isomerism is observed in alkenes but not in alkanes.

- b Considering 1,2-dimethylcyclopentene, discuss whether substituted cycloalkenes can exhibit geometrical isomerism.

- 6 Alkanes have the general formula  $C_nH_{2n+2}$ .

- a Write a balanced equation for the general reaction of an alkane with oxygen in terms of n.

- b The volume of one mole of any gas at STP is 22.4 L. If y grams of a particular alkane produces x litres of carbon dioxide, measured at STP, on complete combustion with oxygen, derive an expression that links x, y, and n.

- 7 Ethane and ethene can both be converted into chloroethane. Write equations for the formation of chloroethane from each hydrocarbon and explain why one method of preparation is superior to the other.

- 8 a A particular hydrocarbon was analysed and found to contain 85.6% carbon by mass. What is the empirical formula of the compound?

- b Could the empirical formula you have determined also be the molecular formula? Why or why not?

- c To what group or groups of the hydrocarbons could the compound in a belong?

- 9 There are many structural isomers with the molecular formula of  $C_6H_{12}$ .

- a Give the structural formulas and names of three isomers (of  $C_6H_{12}$ ) that are alkenes.

- b Give the structural formulas and names of two isomers (of  $C_6H_{12}$ ) that are cycloalkanes.

- 10 Which of the following substances exhibit geometrical isomerism?

- a propane

- b propene

- c 1,2-difluoroethene

- d 1,2-dichloroethane

- e 1,1-dichloroethene

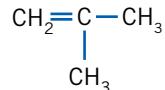
- f 1-chloro-2-bromoethene

- g 1,1-dibromo-2,2-difluoroethene

- h methylpropene

- i 2-bromobut-2-ene

- j 2-methylbut-2-ene  
 k 1,2-dibromo-1,2-dichloroethene  
 l hex-3-ene.
- 11 Write balanced equations for the following if there is a reaction. Draw the organic compounds in the equations as structural formulas.
- 1 mole of bromine is reacted with 1 mole of methane in the presence of ultraviolet light.
  - 1 mole of fluorine is shaken with 1 mole of propane in the presence of sunlight.
  - 1 mole of chlorine is mixed with 1 mole of pentane and the mixture is placed in a dark cupboard.
  - Methane is shaken with an excess of iodine in the presence of ultraviolet light.
  - Chlorine gas (in excess) is mixed with butane and the mixture is exposed to ultraviolet light for several hours.
  - Bromine and ethane are mixed in a 1:1 mole ratio. The mixture is then exposed to ultraviolet light for several hours.
  - Octane is burnt in air.
- 12 Write equations for the following reactions. Show the formulas of the organic compounds as structural formulas.
- Ethene is reacted with chlorine in the absence of ultraviolet light.
  - Cyclooctene is reacted with iodine in the absence of ultraviolet light.
  - A mixture of ethene and bromine (in excess) is allowed to react in the presence of ultraviolet light for several hours.
- 13 The questions below refer to the following organic compound:



- What is the correct IUPAC name for the compound?
- Give the structural formula of the product formed when the compound reacts with chlorine, in the absence of ultraviolet light.
- Give the balanced equation for the complete combustion of the organic compound.
- Give the structural formulas of a pair of *cis/trans* isomers that have the same molecular formula as the organic compound.

- 14 The reactants, products and reaction conditions for some reactions are summarised in Table 16.14. Complete the gaps in the table by ticking the appropriate reaction conditions columns and giving the structural formulas of the products or the reactants. The first example has been completed.

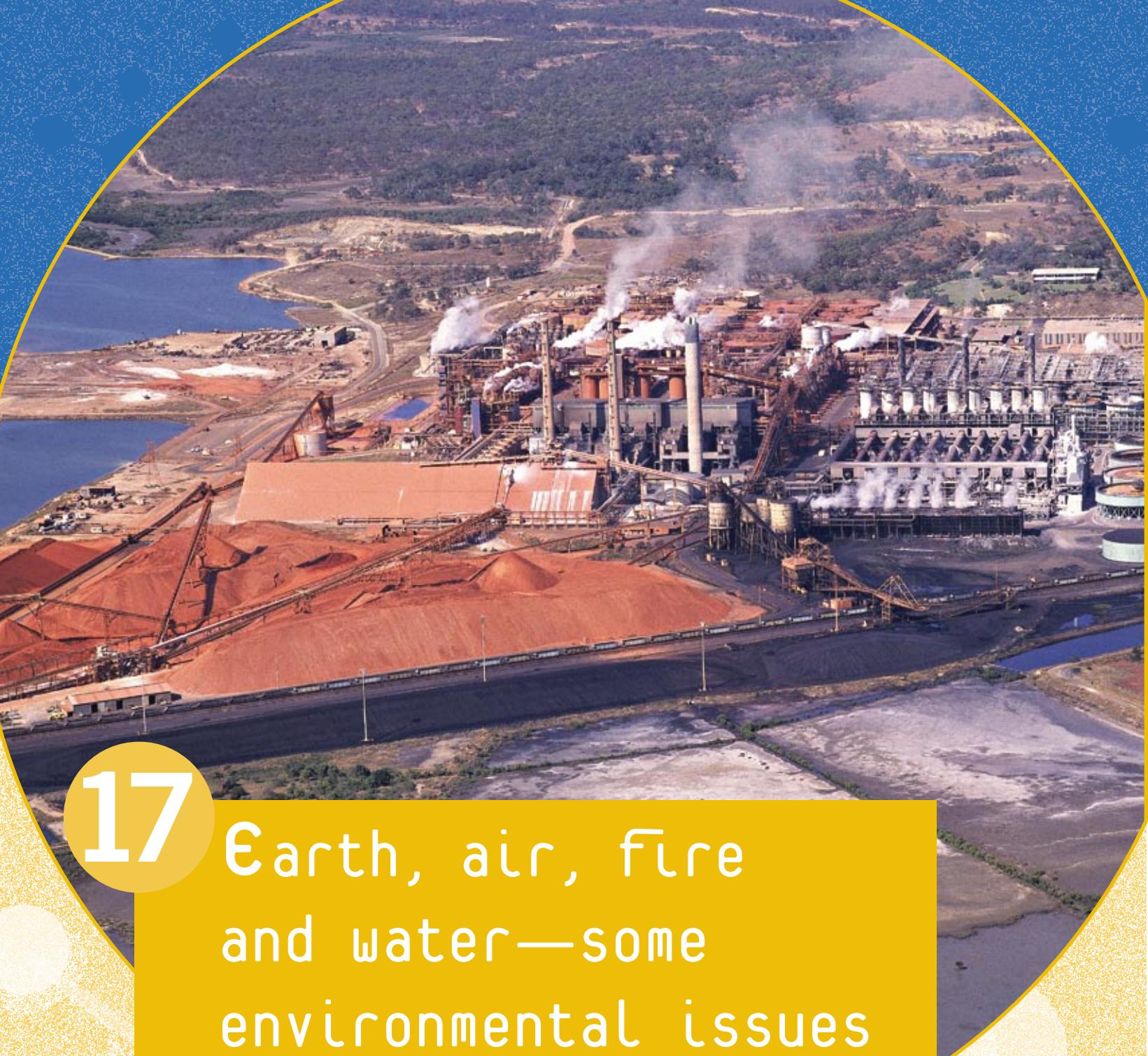
TABLE 16.14 REACTIONS OF ALKANES AND ALKENES

| Reactants                                                                   | Reaction Conditions           |     |     | Product/s |                                                              |
|-----------------------------------------------------------------------------|-------------------------------|-----|-----|-----------|--------------------------------------------------------------|
|                                                                             | Mole ratio (organic: halogen) | 1:1 | 1:2 |           |                                                              |
| $\text{CH}_3-\text{CH}_2-\text{CH}_3 + \text{Cl}_2$                         | ✓                             |     |     | ✓         | $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{Cl} + \text{HCl}$ |
| $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3 + \text{Br}_2$             |                               |     | ✓   | ✓         |                                                              |
| $\text{CH}_2=\text{CH}_2 + \text{F}_2$                                      | ✓                             |     |     | ✓         |                                                              |
|                                                                             | +                             | ✓   |     | ✓         | $\text{CH}_3-\text{CH}-\text{CH}_2-\text{Cl}$<br> <br>Cl     |
| $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 + \text{Cl}_2$ |                               |     | ✓   | ✓         |                                                              |
|                                                                             | +                             |     |     |           | $\text{CBr}_4$                                               |

- 15** A student had two distinct compounds, A and B, which both had the molecular formula  $C_3H_6$ . When added to an aqueous solution of bromine, compound A reacted rapidly, but compound B reacted very slowly. Suggest a structural formula for compound A and for compound B. Name these two compounds.
- 16** Draw and name the structural isomers with the formula  $C_3H_6Cl_2$ .
- 17** Since the banning of CFCs (chlorofluorocarbons), hydrocarbons have become the preferred ‘blowing agents’ for expanding polystyrene. Volatile hydrocarbons injected into the polystyrene mixture vaporise and produce the bubbles (subsequently filled with air) in the polystyrene foam that is used for packing.
- One particular blowing agent is analysed and it is found that 0.360 g of the hydrocarbon, on complete combustion, produced 1.098 g of carbon dioxide and 0.541 g of water. The molar mass of the hydrocarbon is found to be around  $70\text{ g mol}^{-1}$ .
- a** Determine the empirical and molecular formula of the hydrocarbon.
- b** Draw three possible structures for this hydrocarbon and name them.
- 18** LPG (Liquid Petroleum Gas) is a mixture of propane and butane. One particular container of LPG is 50% propane by volume of gas originally compressed into the cylinder. In other words, the gas emerging from this cylinder would contain equal volumes of propane and butane. Avogadro’s hypothesis states that at the same temperature and pressure, equal volumes of all gases contain the same amount in mole.
- a** Write balanced overall equations for the complete reaction of propane and butane with air.
- b** What volume of carbon dioxide would be obtained from the complete reaction of 10.0 L of gas from the container if all volumes are measured at the same temperature and pressure?
- c** Your next-door neighbour is growing tropical plants in a greenhouse. Explain to him why it is better to use a LPG burner rather than an electric heater in the greenhouse during winter.
- 19** A chemist added 100 mL of oxygen to 11.5 mL of a gaseous hydrocarbon. The mixture was exploded and the resulting gas mixture was cooled to the original room temperature conditions ( $25^\circ\text{C}$ ) and was found to occupy a volume of 77.0 mL. When this gas mixture was passed through a solution of sodium hydroxide to dissolve the carbon dioxide the volume of remaining gas dropped to 42.5 mL. This remaining gas reignited a glowing splint. What is the empirical formula of the hydrocarbon?
- 20** Determine the empirical formula of a hydrocarbon that contains 83.3% carbon by mass.
- 21** In Section 16.2 the process of cracking higher molecular mass alkanes from crude petroleum was introduced. In this reaction a single hydrocarbon is split into two simpler hydrocarbons.
- a** Write an equation for the thermal cracking of octane if one of the hydrocarbon fragments contains six carbon atoms.
- b** Why is it that cracking cannot produce two alkanes?
- c** The mixture of hydrocarbons from the cracking process described in part **a**, is treated with iodine vapour in the dark. Write the structural formula of the organic molecule present in the mixture after any reaction has taken place.
- 22** Use the data in Table 16.9 to plot the boiling points of the first eight alkanes.
- a** What do you notice about this graph?
- b** Use your graph to predict the boiling point of nonane and decane (9 and 10 carbons respectively). Look up the boiling points of these alkanes on the Internet and compare these with your predictions.
- 23**  **RESEARCH** Unleaded petrol in Australia has an octane number of around 92. Octane number refers to the percentage (by volume) of 2,2,4-trimethylpentane in a mixture with heptane. Diesel fuels do not use an octane number; they use what is termed a cetane number, based on the percentage of hexadecane in the fuel. Octane and cetane numbers are a measure of the ‘ignitability’ of the fuel. The higher the octane number, the greater is the activation energy for the combustion of the fuel; the higher the cetane number, the lower the activation energy for the combustion.

- a Draw the structural formulas for 2,2,4-trimethylpentane, heptane and hexadecane.
- b Draw energy profile diagrams for the combustion of 2,2,4-trimethylpentane and hexadecane to illustrate the difference in activation energy of the two molecules.
- c 2,2,4-trimethylpentane has a flash point of 4.5°C and an autoignition temperature of 417°C. Hexadecane has a flash point of 135°C and an autoignition temperature of 201°C. What do the terms flash point and autoignition temperature mean and determine which of these fuels would burn most readily:
  - i when a lighted match is applied to an air-fuel mixture
  - ii when an air-fuel mixture is in contact with a hot object at 350°C.
- d Research why the fuels that are optimal for petrol engines are so different from the fuels that are optimal for diesel engines.
- e The hydrocarbons that comprise the fraction that would normally be used to manufacture petrol has an octane rating of around 50–55. How is the octane number of petrol raised to 92?

- 24 RESEARCH** Devise and carry out an experiment to show that a given margarine is unsaturated. Can your experiment be modified to test the degree of unsaturation in a sample of different oils and margarines compared to butter?



# 17

## Earth, air, fire and water—some environmental issues

### BY THE END OF THIS CHAPTER YOU SHOULD BE ABLE TO:

- understand how chemistry plays a vital role in addressing environmental issues in the community with particular focus on
  - mining
  - atmospheric pollution
  - water quality.

When Pythagoras coined the term 'harmony of the spheres' he was referring to the celestial movement of the planets. However, in today's world he could well be talking about the four 'spheres' that define planet Earth and the need for them to exist in harmony for our survival.

The lithosphere includes the rocks, minerals and inorganic matter that make up the outer crust. All the places on Earth where water may be found comprise the hydrosphere and the atmosphere consists of the thin layer of gases and suspended particles that surround the Earth. The biosphere refers to the zone in which life exists, including humankind, whose actions, or lack of them, may compromise the harmony that has developed over time. Linking these four spheres is energy, as the driving force in sustaining or destroying the harmony.

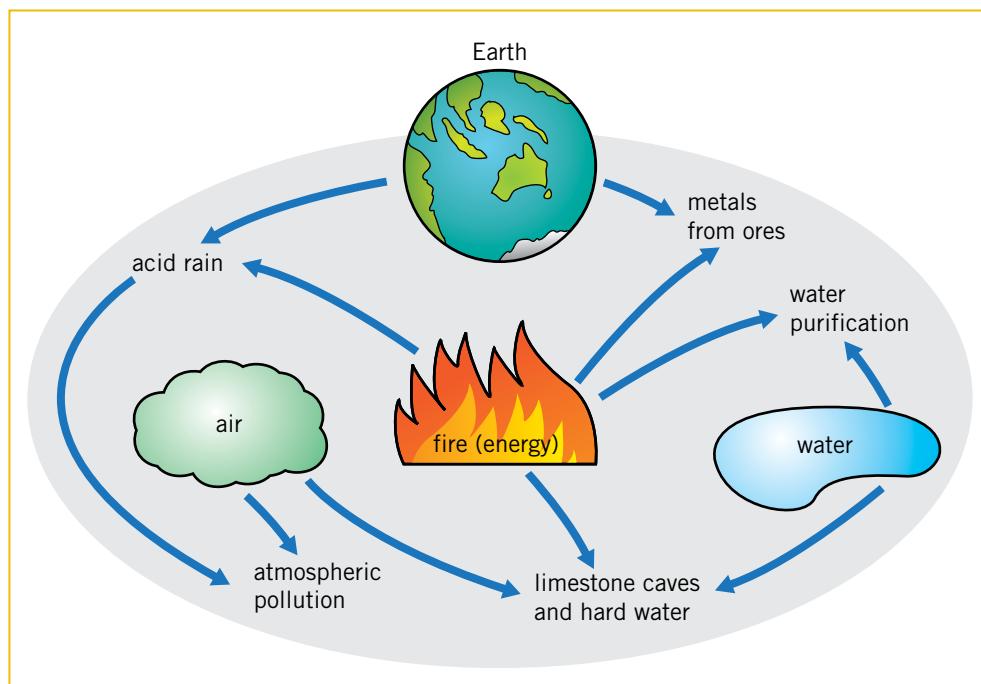


Figure 17.1 Earth, air, fire and water—some connections.

## 17.1 Earth and fire

Just ten elements make up more than 99% of the Earth's crust (Table 17.1). Many of the elements that might be regarded as reasonably 'common' in our lifestyle, such as zinc, copper, tin and nickel, do not appear in this list. Fortunately, these elements tend to be found in concentrated pockets throughout the lithosphere, which allows them to be mined economically. When important but scarce elements such as these and others are naturally concentrated, the name 'ore' is given to the rocks in which they are found.

TABLE 17.1 PERCENTAGE OF ELEMENTS IN THE EARTH'S CRUST

| Element   | Percentage by mass |
|-----------|--------------------|
| oxygen    | 46.6               |
| silicon   | 27.7               |
| aluminium | 8.1                |
| iron      | 5.0                |
| calcium   | 3.6                |
| sodium    | 2.8                |
| potassium | 2.6                |
| magnesium | 2.0                |
| titanium  | 0.56               |
| hydrogen  | 0.14               |

While a small number of elements are found in their native state, such as gold, most elements are found as minerals. These minerals are compounds ranging from simple binary compounds such as bauxite,  $\text{Al}_2\text{O}_3$ , haematite,  $\text{Fe}_2\text{O}_3$ , or quartz,  $\text{SiO}_2$ , through to compounds with very complex structures, and equally complex formulas such as blue asbestos,  $\text{Na}_2\text{Fe}_3\text{Fe}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$ .

Many minerals contain silicon, however there are also some important non-silicate minerals. These include the halides such as sodium chloride ( $\text{NaCl}$ ), oxides such as bauxite ( $\text{Al}_2\text{O}_3$ ), rutile ( $\text{TiO}_2$ ) and haematite ( $\text{Fe}_2\text{O}_3$ ), sulfides such as galena ( $\text{PbS}$ ) and nickel sulfide ( $\text{NiS}$ ), and carbonates such as limestone ( $\text{CaCO}_3$ ) and magnesite ( $\text{MgCO}_3$ ). In Australia, and Western Australia in particular, the mining of these non-silicate minerals provides much of the nation's wealth.

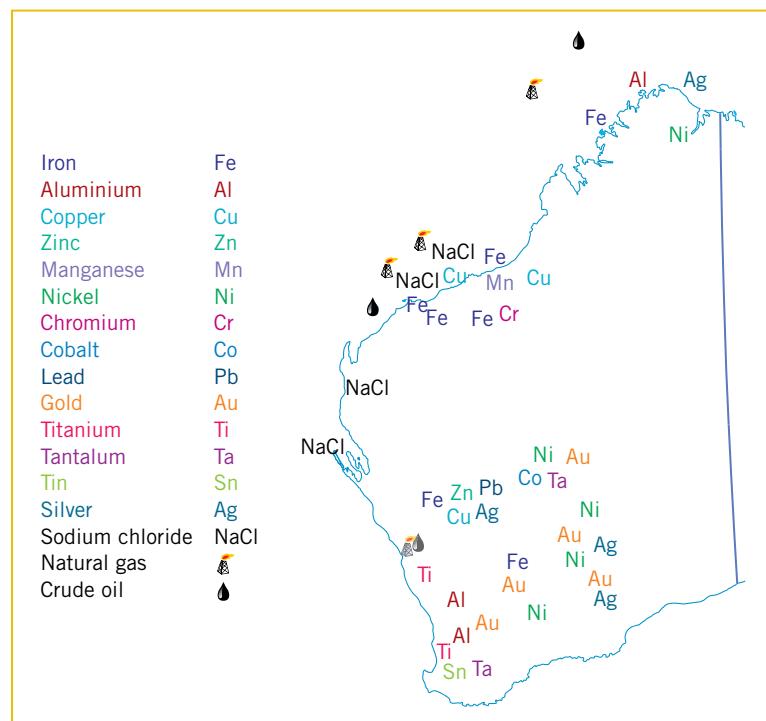


Figure 17.2 Locations of some of the mineral and resource sites in Western Australia.

## From gold to aluminium—a study in redox chemistry

The chemistry of the production of metals from ores is closely related to the reactivity of the metal. Weak reductants such as gold can be found naturally occurring as the element. Iron is a stronger reductant and has to be obtained from its ore by chemical reduction. Aluminium is a particularly strong reductant and can only readily be obtained from its ore in an electrolytic process.

### Gold

Despite the strong oxidising conditions that have existed on Earth for several billion years, gold's lack of reactivity has kept it free from oxidation. As a result gold is found in its elemental form in nature.

Several centuries ago, it was possible to find large nuggets of gold in some locations around Australia, particularly in Western Australia near Kalgoorlie and surrounding areas. Today the discovery of such concentrated gold deposits is rare and the mining industry works on a knife-edge of production costs versus gold value. Various chemical techniques are implemented to make the gold recovery process more economically viable.

Western Australia provides approximately 75% of Australia's gold production, mining around 220 tonnes of gold per year. This is around 10% of the world's gold production. Such is the value of gold that it is economical to mine ore bodies that contain just a few grams of gold per tonne of rock. Total reserves of gold yet to be mined in Australia were put at just over 5200 tonnes at the beginning of 2008.

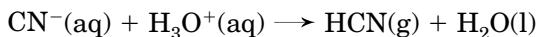
While in theory there is no energy requirement for the production of gold, the fact that it is so thinly spread in the crust, even in regions where gold-bearing ores are found, means that a significant energy input is needed to separate the gold from the remaining material.

In the gold recovery process the gold-containing ore is first crushed to expose as much of the gold at the surface of the lumps of ore as possible. This crushed ore is then mixed and stirred with a dilute solution of sodium cyanide and sufficient calcium oxide or sodium hydroxide to raise the pH of the mixture to around 11. The cyanide ion, in the presence of oxygen from the air that is stirred into the mixture during the agitation process, oxidises the gold from the 0 to +1 oxidation state.



The soluble aurocyanide ion,  $\text{Au(CN)}_2^-$ , is an example of a complex ion, an ion in this case that contains a central gold(I) ion bonded to two cyanide ions. In Unit 3 the nature of the bonding interactions that exist in complex ions will be introduced.

Keeping the pH of the gold mixture between 10.5 and 11 ensures that the cyanide ion does not have enough hydrogen ions to react with to form the volatile and highly toxic hydrogen cyanide. The cyanide anion is a base and can accept a hydrogen ion from hydronium ions to produce hydrogen cyanide.



Given the scale of the mining operation and the need to minimise dangers for workers in the industry, the hydronium ion concentration must be kept as low as possible.

At this stage in the process, the ore mixture is composed of dissolved aurocyanide ions and a pulp or slurry of insoluble crushed rock material. To recover the  $\text{Au(CN)}_2^-$ (aq) ions from the rock pulp, the carbon-in-pulp (CIP) process is now the most commonly used technique.



Figure 17.3 Gold ingots.

Activated carbon is a porous form of carbon that can adsorb ions such as aurocyanide. The carbon used in this recovery process is formed as spherical particles that are larger than the crushed rock particles. When added to the mixture of crushed rock and gold-bearing solution, the activated carbon adsorbs the aurocyanide ions into the huge number of pores in its surface.

Once the carbon has adsorbed most of the aurocyanide ions from solution, the mixture of carbon, crushed rock and spent solution is passed through a wire mesh. This mesh collects the larger carbon particles loaded with the adsorbed aurocyanide ions.

The loaded carbon particles are then placed in a hot concentrated solution of cyanide ions at high pH. The high temperature and cyanide ion concentration increases the rate at which the adsorbed aurocyanide ions are removed from the carbon and put back into the solution. After this process, called desorption, the carbon can be heated to reactivate it, ready to be used again.

Electrolysis of the solution of aurocyanide ions is then undertaken to reduce the gold from the +1 oxidation state to the element. Since reduction involves electron gain, it takes place at the negative (cathode) in an electrolytic cell. Steel wool cathodes are used as a surface onto which the gold can be electrolytically deposited when the current flows. The cathodes are then washed in acid to react with any residual iron leaving the unreacted gold. Finally, this crude gold is smelted into bars.

Figure 17.4 summarises the steps and key chemistry associated with the refining of gold from its ore to the final product.

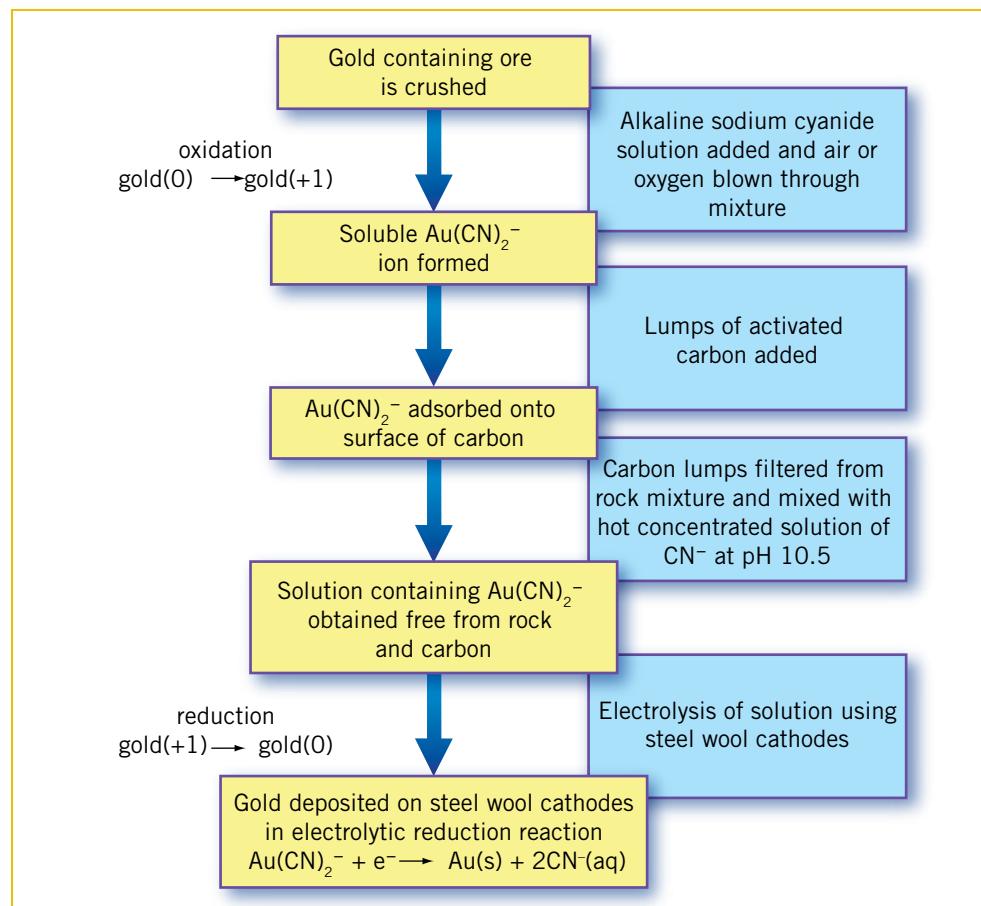


Figure 17.4 Stages in the extraction of gold from its ore.

Unlike gold, most metals are found naturally as compounds in mineral deposits. Since the metals are present as positive ions, that is, in an oxidised form, a reduction process is necessary to produce the metal from its ore.

### Iron

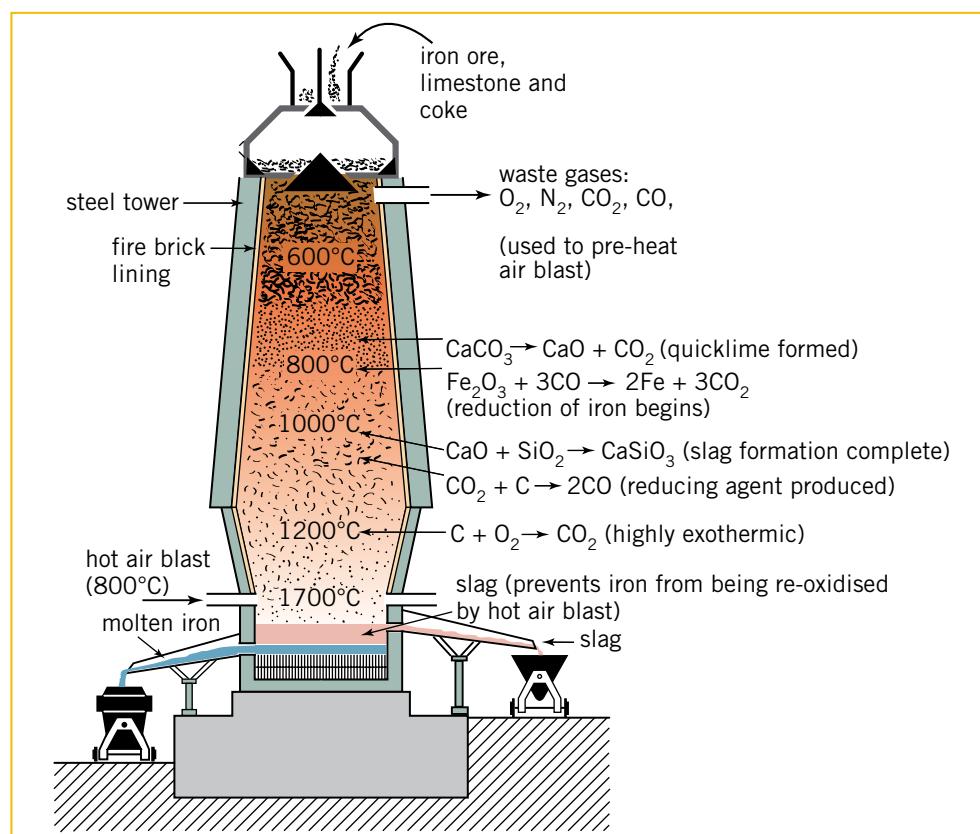
Our world has been transformed by iron and steel. While making up only 5% of the Earth's crust, iron is commercially the most important metal in the world, with around a billion tonnes of its ore mined annually. In 2006, Australia produced around 275 million tonnes of iron ore, third only to China and Brazil in world production. Of the iron ore produced in Australia, 98% comes from the open cut mines in the Pilbara region of Western Australia.

In general, there are four main stages involved in the conversion of an ore to the metal in a state of high purity. Overall, the process is called extractive metallurgy:

- mining—removing the ore from the ground
- milling and concentrating—a variety of techniques that produce the ore in a higher state of purity
- smelting—extracting the crude metal from the treated ore
- refining—producing the metal in a high state of purity.

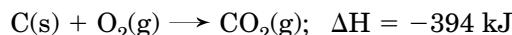
The chemistry of the production of iron from its ore is dominated by redox and energy considerations. In most metal ores the metal is found in its highest oxidation state, and this is true for iron, with most of the ore mined in Western Australia being relatively high purity  $\text{Fe}_2\text{O}_3$ . As a consequence, the mineral has to be reduced and this requires energy.

A cross-section of a typical blast furnace used for the production of iron is shown in Figure 17.5.



**Figure 17.5** Section through a blast furnace used for the production of iron from iron ore.

A mixture of the iron ore (mainly  $\text{Fe}_2\text{O}_3$ ), coke (a form of carbon), and limestone ( $\text{CaCO}_3$ ) is fed into the top of the furnace using a system of valves to minimise the loss of heat energy and gases from the furnace. A blast of hot air at around  $750\text{--}800^\circ\text{C}$  enters the furnace part-way up the tower where it combines with the coke in an exothermic reaction to form carbon dioxide.

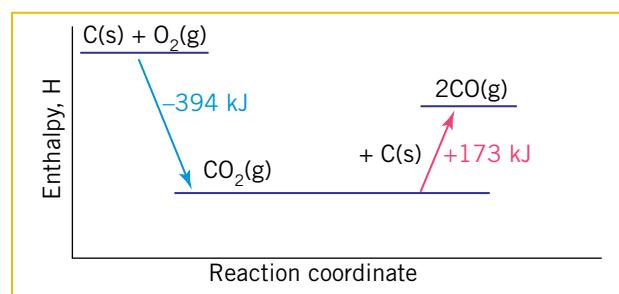


This reaction produces temperatures close to  $2000^\circ\text{C}$ .

In the presence of excess coke, the carbon dioxide reacts in an endothermic process to produce carbon monoxide.

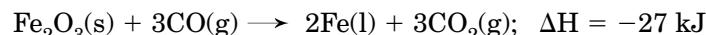


This reaction will tend to lower the temperature of the gases in the furnace. Overall, however, these two reactions produce an exothermic process as shown in Figure 17.6.



**Figure 17.6** The conversion of carbon to carbon monoxide.

The carbon monoxide acts as the reducing agent for the conversion of the iron oxide to iron.



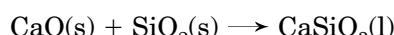
The exothermic reversible reaction can be made to favour the formation of iron by ensuring an excess of carbon monoxide is available for the reaction. The reaction begins near the top of the furnace and is complete closer to the bottom where the temperature is in excess of the melting point of iron ( $1540^\circ\text{C}$ ). The liquid iron then percolates to the bottom of the furnace where, from time to time, it is tapped off. In the journey to the bottom of the furnace the iron dissolves some impurities such as carbon, that have to be removed in the refining process.

The limestone is added to the blast furnace to react with silicate rocks and silicon dioxide (impurities in the iron ore) to form calcium silicate, which, being less dense than iron, forms a liquid 'slag' on the surface of the molten iron. This slag is removed periodically, but it also protects the molten iron from the blast of hot air.

The first step in this process of removing the impurities is the thermal decomposition of calcium carbonate into calcium oxide.



This is followed by reaction with, for example, silicon dioxide (sand) to produce molten calcium silicate (slag).



The hot gases that exit the blast furnace may contain a significant amount of carbon monoxide that can be burned to provide more energy and, with the other hot gases, used to preheat the incoming air. The slag is used for road making, insulation (the molten material is 'frothed up' with air to produce a rockwool-type material) and cement.

The blast furnace is a continuous process, which means the iron and slag are tapped off and more raw materials are added without shutting down the furnace.

The molten iron that is run off may contain up to 5% carbon together with other impurities that make the impure solid iron brittle and not very strong. Most of this crude iron is converted to steel using a blast of pure oxygen to oxidise the impurities such as carbon, sulfur and silicon.

The relatively large amount of energy required to convert iron oxide to iron hints at the ease with which iron reverts to the more stable iron oxide. The rusting of iron is a serious problem for society. Fortunately, the direct reaction between iron and atmospheric oxygen is a relatively slow process because the activation energy for this reaction is high. However, an alternative redox reaction involving oxygen, water and iron takes place more readily, particularly where the water contains dissolved electrolytes. The electrochemical processes involved in the rusting of iron will be covered in more detail in Unit 3.

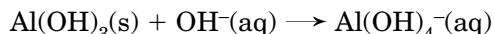
### Aluminium

Aluminium is the third most abundant element in the Earth's crust and the most abundant metal, but until the late 1800s it was more expensive than gold. The reason for such a common element being so expensive lies in part with its reactivity. Once oxidised to the  $\text{Al}^{3+}$  ion, the reduction back to aluminium requires a considerable amount of energy. A commercially viable method of preparation of the metal was established only when electrolysis was applied to the production in 1886.

Aluminium is widely spread in compounds throughout the environment, but for the metal extraction process to be cost effective the aluminium needs to be concentrated as an ore. The main ore of aluminium is bauxite that contains the mineral gibbsite or aluminium hydroxide,  $\text{Al}(\text{OH})_3$ . Aluminium hydroxide may also be represented as  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ .

The extraction of aluminium from the bauxite ore involves two stages. First the production, in the Bayer process, of pure aluminium oxide (alumina) from bauxite followed by the electrolysis of the aluminium oxide to form aluminium.

Aluminium oxide and aluminium hydroxide are amphoteric. This means they react with both acids and bases. The major impurities present in the bauxite ore are iron(III) oxide, which is basic, reacting only with acids, and silicon dioxide,  $\text{SiO}_2$ , which will only react with very hot concentrated solutions of a base. As a result, treatment of the bauxite ore with a hot sodium hydroxide solution, in the Bayer process, results in the formation of a solution of sodium aluminate.



The aluminate ion,  $\text{Al}(\text{OH})_4^-$ , is another example of a complex ion with a central metal ion surrounded by four negative hydroxide ions.

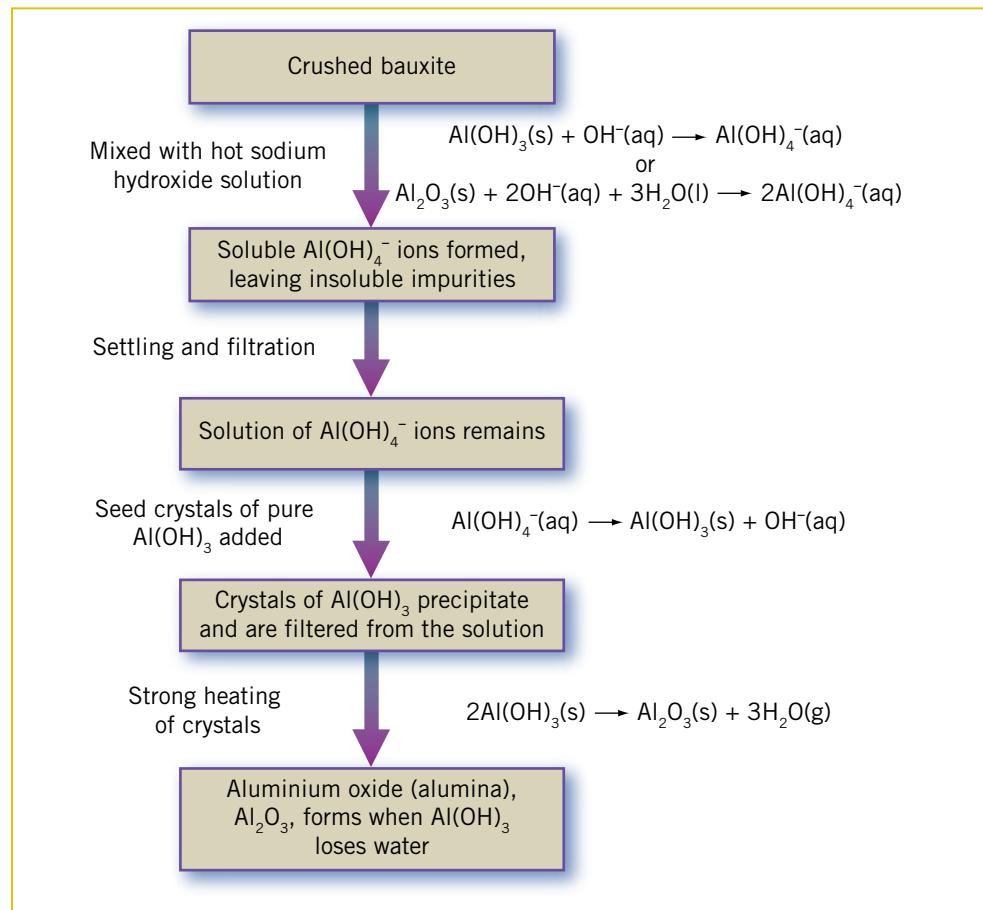
Following this digestion process to dissolve the aluminium-containing minerals, the mixture is allowed to settle, during which time a red mud of insoluble material containing silicon dioxide, complex silicates and iron oxide precipitates.

The clear liquid obtained from this settling or clarification process is a supersaturated solution of sodium aluminate. The solution is removed from the red mud and in a carefully controlled process involving adding crystals of pure  $\text{Al}(\text{OH})_3$ , a process called seeding, aluminium hydroxide precipitates.



The solid is collected by filtration and dehydrated at temperatures up to  $1200^\circ\text{C}$  to produce alumina,  $\text{Al}_2\text{O}_3$ .





**Figure 17.7 Flowchart for the production of alumina in the Bayer process.**

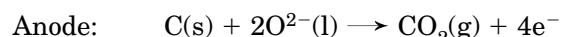
The reduction of alumina to produce aluminium requires a huge amount of energy, making chemical reduction extremely difficult, and as a result, expensive.



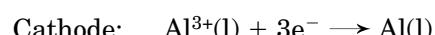
Use of carbon monoxide at high temperature was possible for the reduction of iron(III) oxide, but this method is economically impractical for the production of the more reactive aluminium.

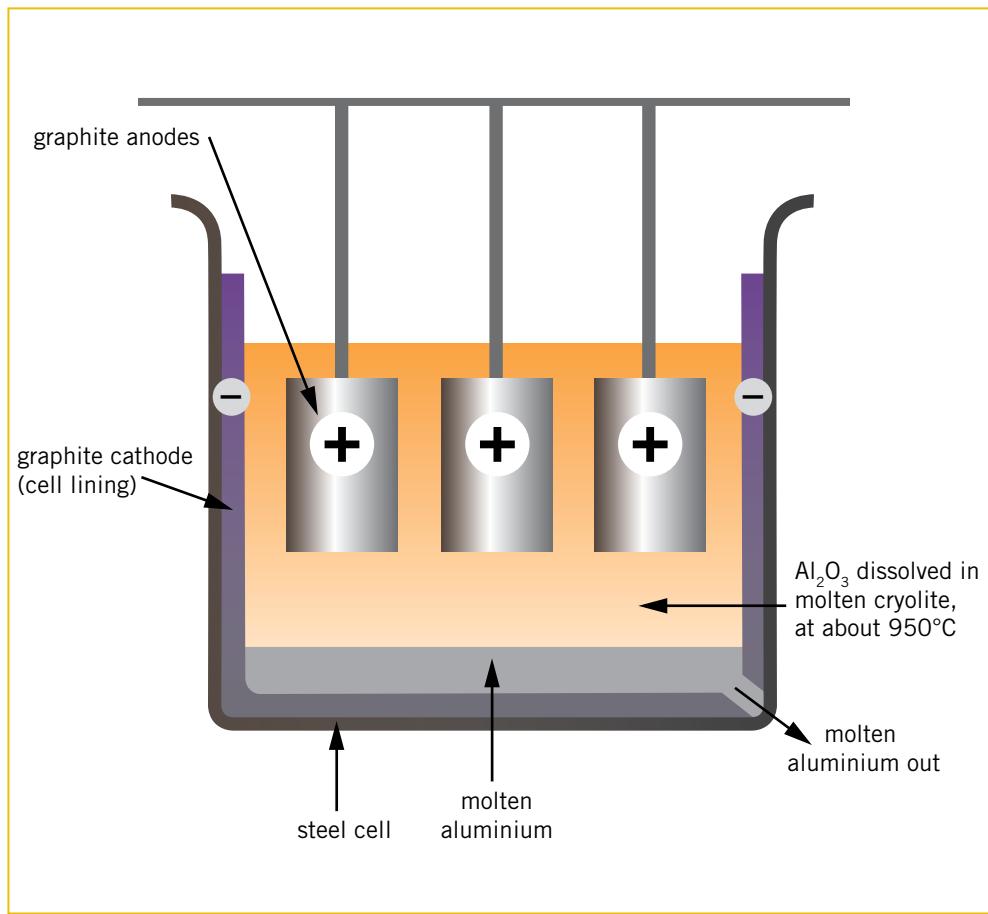
In 1886, Charles Hall and Paul Héroult independently found that alumina,  $\text{Al}_2\text{O}_3$ , could be dissolved in cryolite,  $\text{Na}_3\text{AlF}_6$ , at around  $950^\circ\text{C}$  to produce a solution that can be made to undergo electrolysis to produce aluminium. Electrolytic reduction of alumina in the Hall–Héroult process must be achieved in the absence of water, as the aluminium ion is a weaker oxidant than water. Cryolite is used as the solvent because the melting temperature of alumina is around  $2054^\circ\text{C}$ , making the energy requirement for producing a molten electrolyte of pure alumina prohibitive.

Using steel surrounded by carbon as the cathode, and carbon as the anode, and employing extremely high currents (100,000 amps or more) at around 3 to 5 volts DC, the alumina is electrolysed according to the following half-equations.



The carbon in this equation is the anode material itself. At the temperatures employed in the cell, the oxygen that might have been produced at the anode from the oxide ion alone reacts with the carbon to produce carbon dioxide.





**Figure 17.8** The Hall–Héroult cell for the electrolytic production of aluminium.

The molten aluminium that collects at the bottom of the cell is tapped off.

Uses of aluminium are varied, particularly in the form of various alloys. However, major uses include in the building and construction industry, for containers and packaging, as electrical cables and wires, in the transport industry, and in consumer products.

### \* Review exercise 17.1

- 1 Account for the fact that in ores most metals exist in their oxidised state rather than as the element.
- 2 Iron is less abundant in the Earth's crust than aluminium, yet it is significantly cheaper. Why is this so?
- 3 What are the differences between ores, rocks and minerals?
- 4 Outline the role played by coke, air and limestone in the production of iron from iron oxide in the blast furnace.
- 5 a In the production of iron from iron oxide, the coke, limestone and iron ore are ground together prior to being poured into the blast furnace. What is the purpose of this?

*continued*

### Review exercise 17.1 — *continued*

- b** Instead of using the powder obtained from this grinding process, the mixture is gently heated to produce pellets. What is the advantage of using pellets over powder?
- 6** The production of iron from iron oxide,  $\text{Fe}_2\text{O}_3$ , requires that the oxide be reduced to molten iron by carbon monoxide.
- Write a balanced equation for the reduction of iron(III) oxide to iron with carbon monoxide.
  - RESEARCH** Pure oxygen is fed into the molten iron from the blast furnace in the formation of steel. It seems odd that having taken care to reduce the iron oxide, the molten product is then treated with a powerful oxidising agent. Research the production of steel from molten iron, showing how the oxygen is used in transforming iron to steel.
- 7** In the gold extraction process, why is the elemental gold found in ores oxidised before being electrolytically reduced?
- 8** **a** Why is it not possible to obtain aluminium from the electrolysis of an aqueous solution of a salt such as aluminium sulfate?
- b** Combining the anode and cathode half-equations for the electrolysis of aluminium oxide, in a Hall–Héroult cell, produces the following overall redox equation
- $$2\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Al} + 3\text{CO}_2$$
- Why then is it not reasonable to describe the Hall–Héroult process as an example of carbon reduction similar to that for iron?
- 9** **RESEARCH** Why doesn't the cryolite itself undergo electrolysis rather than the dissolved aluminium oxide in the Hall–Héroult cell?
- 10** The chemical engineer at a mine site that carries out the smelting of copper pyrites is required to determine how much calcium oxide will be needed to treat the sulfur dioxide emitted from the plant each day. Copper pyrites has the formula  $\text{CuFeS}_2$  and is converted to crude copper in a two-step process during smelting. In the first step, the pyrites is heated strongly with oxygen from the air, in the presence of sand,  $\text{SiO}_2$ , to form copper(I) sulfide, iron(II) silicate,  $\text{FeSiO}_3$  and sulfur dioxide gas. The copper(I) sulfide is then roasted with another blast of air to convert it to copper and more sulfur dioxide.
- The copper containing ore averages 9.85%, by mass, of copper pyrites and the particular plant smelts 100 tonnes of ore each day.
- Write the equation for the reaction of copper pyrites with sand and oxygen to produce copper(I) sulfide, iron(II) silicate and sulfur dioxide, and also the equation for the reaction of copper(I) sulfide with oxygen to produce copper and sulfur dioxide.
  - Determine the mass of copper pyrites in 100 tonne of the ore.
  - Calculate the total amount of sulfur dioxide, in mole, that would be produced at the mine per day if the processes are all 100% efficient.
  - Write the equation for the reaction of sulfur dioxide with calcium oxide to produce calcium sulfite,  $\text{CaSO}_3$ .
  - Determine the mass of calcium oxide necessary to react with all of the sulfur dioxide produced at the mine each day.
  - What is the percentage, by mass, of copper in the ore smelted at the mine?

- 11** In August 2006 *New Scientist* reported that iron could be made from iron oxide by electrolysis of the ore dissolved in a mixture of silicon dioxide and calcium oxide at 1600°C. The research claimed to cut down on the emission of carbon dioxide that occurs in the production of iron from iron ore in the blast furnace.

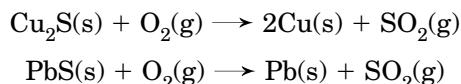
The process suggested is very similar to that used for the production of aluminium by electrolysis of aluminium oxide dissolved in a molten electrolyte.

- a** Write the half-equations for the anode and cathode reactions assuming this article is correct. Identify the oxidant and reductant in the cell.
- b** The procedure described uses carbon electrodes. From your answer to part **a**, suggest what might happen to the carbon anode under the conditions of the experiment and comment on the claim made about gaseous emissions from the electrolysis.
- c** Suggest how the problem identified in part **b** with respect to gaseous emissions might be addressed.
- d** Even if the issue of gaseous emissions is resolved in your answer to part **c**, explain why environmentalists argue that the electrolysis of iron oxide to produce iron still has a significant carbon pollution problem.

## 17.2 Pollutants in the atmosphere

The production of carbon dioxide during the extraction of iron and aluminium from their ores hints at the atmosphere as a ‘dumping ground’ for the by-products of the metal refining industry.

Many of the metals important to our society are produced from sulfide minerals that are roasted (heated) to produce sulfur dioxide as well as the metal during the refining process. For example, the equations for the roasting of copper and lead sulfides can be summarised as



It is gases such as sulfur dioxide that contribute globally to air pollution.

Air pollution arises from the presence in the atmosphere of gases, or particulate matter, that could be harmful to our health or that of other animals, cause discomfort, or damage the built or natural environment. All human activity produces waste products. As populations grow and lifestyles change, the effects of some of the atmospheric wastes become so significant that they create major concerns, particularly if they are concentrated in certain regions, such as cities.

There are two types of atmospheric pollutants. Those that are mixed directly into the atmosphere, such as carbon monoxide, nitrogen oxides, hydrocarbons and particulate matter, are called primary pollutants. Secondary pollutants are those formed when primary pollutants undergo chemical changes. Photochemical smog is an example of secondary pollution.

Table 17.2 overviews the source and effect of some of the significant contributors to pollution in the atmosphere.

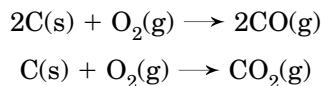
**TABLE 17.2 PRIMARY POLLUTANTS IN THE ATMOSPHERE**

| Primary pollutant                 | Source                                                                                                                                                                    | Effect                                                                                                                                                                                                                               |
|-----------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| carbon monoxide                   | incomplete combustion of carbon-based fuels                                                                                                                               | <ul style="list-style-type: none"> <li>• prevents blood from carrying oxygen by attaching to haemoglobin</li> </ul>                                                                                                                  |
| carbon dioxide                    | produced in any combustion process of carbon-based fuels                                                                                                                  | <ul style="list-style-type: none"> <li>• significant greenhouse gas i.e. contributes to global warming</li> </ul>                                                                                                                    |
| nitrogen oxides ( $\text{NO}_x$ ) | any high temperature combustion process involving air (the source of the nitrogen)                                                                                        | <ul style="list-style-type: none"> <li>• acid rain</li> <li>• may trigger asthma attacks</li> <li>• part of photochemical smog formation</li> <li>• <math>\text{NO}_2</math> is a significant contributor to 'brown haze'</li> </ul> |
| hydrocarbons                      | unburnt fuel from vehicle exhaust                                                                                                                                         | <ul style="list-style-type: none"> <li>• part of photochemical smog formation</li> </ul>                                                                                                                                             |
| sulfur dioxide                    | by-product of combustion of sulfur-containing fuels; often produced by coal-fired power stations as well as from some mineral smelters processing sulfide containing ores | <ul style="list-style-type: none"> <li>• triggers asthma attacks and other respiratory problems</li> <li>• acid rain</li> </ul>                                                                                                      |
| particulates                      | while also produced by natural sources such as volcanoes, or from wind-blown dust and sea salt, the major city source is from vehicle exhausts and industry               | <ul style="list-style-type: none"> <li>• respiratory problems</li> <li>• significant contributor to 'brown haze'</li> </ul>                                                                                                          |
| methane                           | decomposition of organic matter in the absence of oxygen (anaerobic), seepage from natural gas sources, waste product of digestion of ruminants e.g. cows, sheep          | <ul style="list-style-type: none"> <li>• greenhouse gas</li> </ul>                                                                                                                                                                   |
| CFCs (chlorofluorocarbons)        | once used as the refrigerant in air-conditioners and the propellant in spray cans                                                                                         | <ul style="list-style-type: none"> <li>• stratospheric ozone depletion</li> </ul>                                                                                                                                                    |

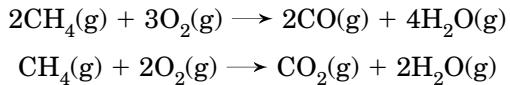


Each of the oxides in Table 17.2 is formed during a combustion process. Carbon monoxide and carbon dioxide are the products of the reaction of carbon or carbon-containing fuels, with the oxygen from air.

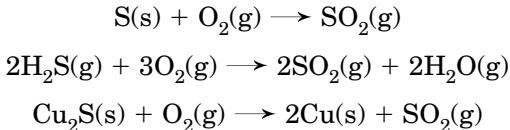
Coal is a complex mixture of substances but on the assumption that it is essentially carbon, the formation of carbon monoxide and carbon dioxide, during combustion, can be represented as:



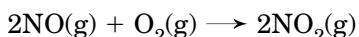
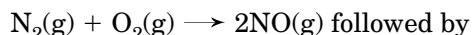
The burning of natural gas or methane,  $\text{CH}_4$ , can also give rise to these two gases:



Sulfur dioxide is a product of the combustion of elemental sulfur impurities in coal and of hydrogen sulfide in some natural gas supplies. It is also produced during the smelting of sulfur-containing minerals.



Nitrogen oxides ( $\text{NO}$  and  $\text{NO}_2$ , collectively known as  $\text{NO}_x$ ) are produced from the high temperature reaction of nitrogen with oxygen.



Each of these combustion reactions involves the conversion of elemental oxygen into a molecular oxide in a redox reaction. In the examples above, the carbon, sulfur and nitrogen are oxidised while the oxygen is reduced.

### Secondary pollution—acid rain, photochemical smog and stratospheric ozone depletion

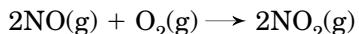
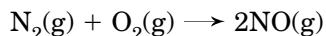
#### Acid rain

Acids react with metals and some rocks and minerals, for example, limestone, corroding their surfaces and creating structural or aesthetic problems. Substances that are acids produce aqueous solutions whose pH (a measure of acidity) is less than 7. The lower the pH of the solution, the more acidic the solution. While acids are everywhere in the environment, problems arise when they move into places in which they do not normally exist. For example, the acid in our stomach would seriously affect our health if placed anywhere else inside the body.

Acid rain, then, is the production of an acidic solution that is misplaced in the environment. A dilute solution of nitric acid has been raining on Earth for millions of years as a result of lightning during thunderstorms. Various estimates put the number of lightning flashes occurring across the Earth each day in excess of three million. There is some uncertainty associated with the measurement of the nitric acid formed exclusively from thunderstorms as bushfires and microbial activity in the soil also convert atmospheric nitrogen into nitric acid (a process known as nitrogen fixation). However, figures ranging from 30 million to 60 million tonnes of nitric acid per year have been published.

Normal rainwater contains dissolved carbon dioxide, which makes it slightly acidic. However, when this is added to the nitric acid and sulfuric acid that come from nitrogen oxides and sulfur oxides respectively, the pH of rainwater in polluted areas can drop as low as 1. In Australia, the situation with acid rain is not as extreme as in Europe and North America, but the pH of rainwater in Sydney is around 4.3. With the extensive deposits of limestone around Perth, the environmental impact of acid rain is largely neutralised as limestone reacts with acid.

Any high temperature combustion process will produce a small amount of nitrogen monoxide,  $\text{NO}$ , which can then be oxidised further to nitrogen dioxide,  $\text{NO}_2$ .



Only about 1% of the original nitrogen in the volume of air involved in the combustion is converted in this process (which is fortunate, as oxygen supplies in the atmosphere would very quickly be depleted if this oxidation were any more efficient). While this does not sound like much, in cities with a large number of cars, each burning hydrocarbon fuels in the presence of air, the accompanying reaction of nitrogen with oxygen at the high temperature of the engine produces significant amounts of the nitrogen oxides.

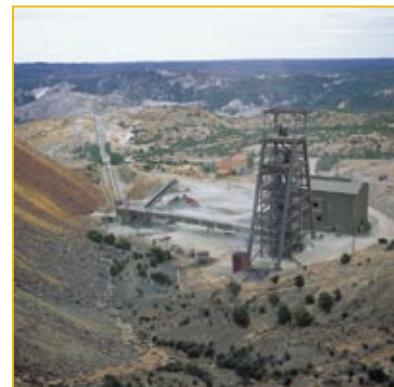


Figure 17.9 Copper mining in Queenstown, Tasmania, produced acid rain in the form of sulfuric acid that killed vegetation in the region and changed the landscape.



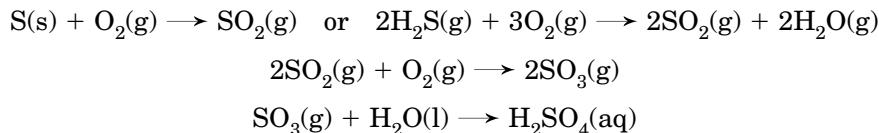
Figure 17.10 A stone statue showing the effect of acid rain.

In the presence of water, nitrogen dioxide dissolves to form a solution of nitrous and nitric acids.



If this acidic solution is deposited as rain in a city landscape with an abundance of metals and stonework, the acid will cause the surface of both to pit (form holes) and corrode. The corrosion of iron will be covered in more detail in Unit 3, but it is a significant economic problem for society. Corrosion or rusting of iron is enhanced in an acidic environment.

Adding to the production of nitric acid in rainwater is the contribution of sulfuric acid,  $\text{H}_2\text{SO}_4$ , from the burning of sulfur-containing fuels. The sulfur dioxide that forms in the initial oxidation reaction is further oxidised to sulfur trioxide in the atmosphere and, in the presence of moisture or rain, becomes a solution of sulfuric acid.



While this process occurs naturally during volcanic eruptions, the amount of sulfur dioxide produced by human-made emissions is sufficient to cause environmental problems. In addition, the gas is more likely to be concentrated in urban environments where there are, for example, power stations burning sulfur-containing coal.

Figure 17.10 shows an example of the effect of acid rain on a stone statue. This extreme has not been reached in Australia as yet. Strategies to reduce the amount of nitrogen oxides coming from car exhausts through the use of catalytic converters, as well as the use of sulfur dioxide scrubbers in the exhaust stacks of power stations, will hopefully ensure that this does not become commonplace.

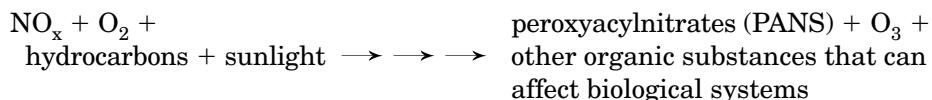
In addition to causing problems through corrosion of metal and stone in urban environments, acid rain is also capable of damaging and possibly killing plants and changing the pH of rivers and lakes to such an extent that fish and other aquatic life are killed. Figure 17.9, at the beginning of this section, shows the effect of sulfur dioxide and sulfuric acid rain in Queenstown, Tasmania, during the first half of the last century. The Mount Lyall copper smelter was set up to smelt the copper sulfide-containing ore in a process that converts the sulfide in the ore to sulfur dioxide. This sulfur dioxide gas was discharged directly into the atmosphere and when it rained, it did so as a dilute solution of sulfuric acid. The forest region around Queenstown was denuded by the corrosive rain as well as by logging to provide the timbers to fire the smelters. Since smelting on the site ended in 1969, some vegetation has grown back, providing an indication that the damage can possibly be reversed.

### Photochemical smog

The nitrogen oxides that contribute to acid rain also play an integral role in the formation of photochemical smog—a complex mix of ozone, organic molecules and nitrogen dioxide that contribute to respiratory problems, eye irritation, headache and fatigue.

In the hot, dry summer weather that characterises much of Western Australia, nitrogen dioxide, sunlight, oxygen and unburned hydrocarbons from vehicle exhausts combine to produce the chemical cocktail referred to as photochemical smog. The chemistry is complex and involves the formation of atoms and molecules called free radicals (or just radicals). Radicals, such as oxygen atoms and  $\text{CH}_3\text{CH}_2\cdot$ , have unpaired electrons and as a result are very reactive.

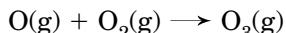
In simple terms, the chemistry of the production of photochemical smog may be summarised as



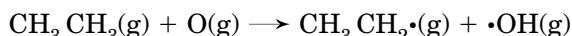
To begin the process, the nitrogen monoxide, NO, from car exhausts is oxidised in the air to form nitrogen dioxide, a brown poisonous gas. In the presence of sunlight, the nitrogen dioxide splits into nitrogen monoxide and an oxygen atom



The reactive oxygen atom then combines with oxygen to produce ozone,

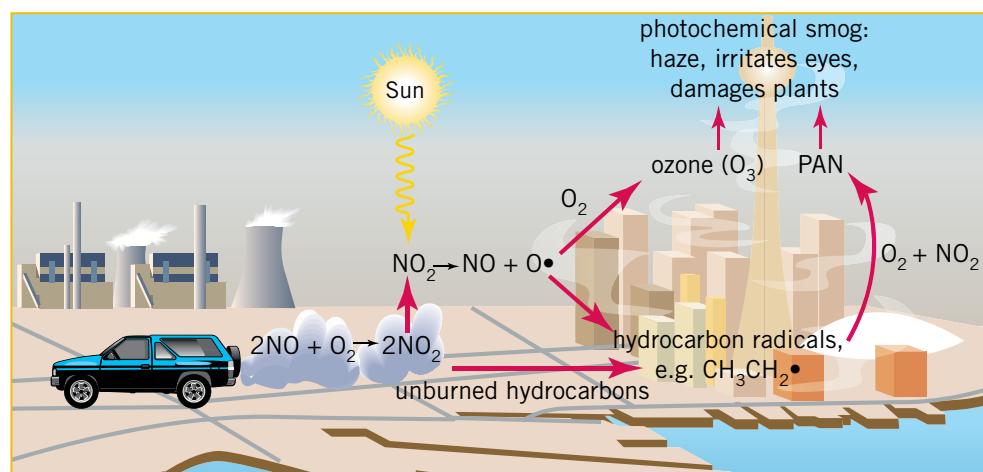


In addition, these reactive oxygen atoms react with the unburnt hydrocarbons coming from the vehicle exhausts to produce hydrocarbon radicals, for example



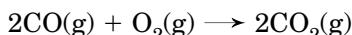
This is followed by a complex series of reactions between  $\text{NO}_2$ ,  $\text{O}_2$ , and the hydrocarbon radicals leading to the production of peroxyacetyl nitrates (PANs). An example of a PAN is peroxyacetyl nitrate,  $\text{CH}_3\text{COOONO}_2$ .

Where weather conditions permit the dispersal of the oxides of nitrogen and hydrocarbons, photochemical smog is not a particular concern. However, in strong sunlight and in the absence of a breeze it does not take long for this chemistry to produce a brown, choking combination of products that can cause serious problems for plants and animals. Peroxyacetyl nitrates and ozone are powerful oxidants that, in part, explains their effect on living organisms.



**Figure 17.11** Simplified overview of photochemical smog formation.

Catalytic converters in cars have gone some way to reducing the amount of nitrogen oxides that come from vehicle exhausts. One of the catalysts is responsible for reducing the nitrogen monoxide back to nitrogen and oxygen, then using the oxygen produced to convert carbon monoxide to carbon dioxide.

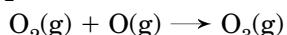
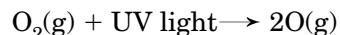


In addition, modern automotive emission control systems circulate some of the exhaust gases back through the air intake in an effort to oxidise some of the unburned hydrocarbons.

## Stratospheric ozone depletion

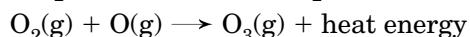
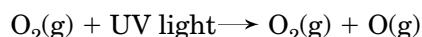
Having just established that the presence of ozone in the lower regions of the atmosphere (the troposphere) creates significant environmental problems, it is ironic, that its presence higher in the atmosphere, in the stratosphere, is vital for life. There are, however, significant concerns about the extent to which particular pollutants are affecting the amount of ozone in the stratosphere.

The ozone layer in the stratosphere is a region of relatively high concentration of ozone,  $O_3$ , (2–8 parts per million) about 15–40 kilometres above the surface of the Earth. Here oxygen molecules absorb ultraviolet light from the Sun and break into individual atoms. An atom of oxygen can then combine with a molecule of oxygen molecules and to form ozone.



The formation of ozone in this process is relatively slow.

While the breaking of oxygen molecules into individual atoms in the stratosphere protects the Earth from some of the harmful ultraviolet radiation from the sun, the absorption of ultraviolet radiation by ozone also contributes to this protective effect. When an ozone molecule absorbs ultraviolet radiation, it rapidly decomposes to form an oxygen molecule and an oxygen atom. These oxygen molecules and atoms then recombine to reform ozone molecules:



Heat is also formed in the recombination reaction.

Ozone molecules can be lost from the ozone layer by reactions with oxygen atoms, another ozone molecule or other trace gases that may be present in the stratosphere. For example:

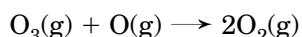
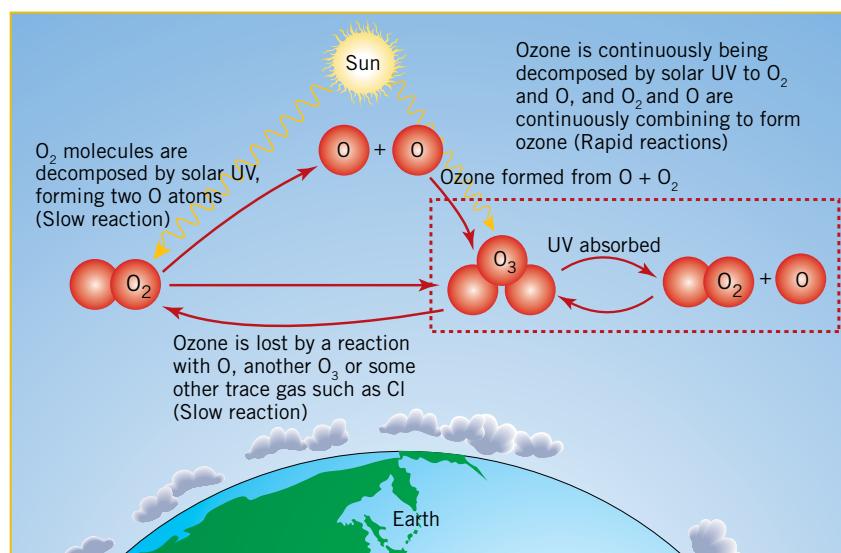


Figure 17.12 depicts the balance that needs to occur between the formation and decomposition of ozone to keep the concentration of ozone in the stratosphere unchanged.

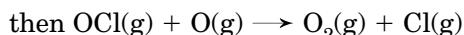
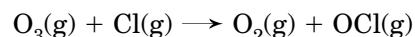


**Figure 17.12** The set of balanced reactions in the stratosphere that form and decompose ozone.

DNA, the genetic material of life, can be damaged by the ultraviolet light that is absorbed by ozone in the stratosphere. As a consequence, without the ozone layer

the chances of damage to the genetic material of living things would increase substantially. In addition to the genetic damage, the increase in cancer rates, particularly skin cancers, would be significant. Consequently, it is a concern that over the past forty or so years, the thickness of the ozone layer over some parts of the Earth has decreased significantly.

Molecules such as nitrogen monoxide and atoms such as chlorine or bromine are known to catalyse the decomposition of ozone. For example, with chlorine atoms, the following sequence of reactions can take place:



The catalytic effect of the chlorine atom can be seen in its regeneration in the second step. A single chlorine atom can continue to decompose ozone for years before it is moved out of the stratosphere by various dispersion mechanisms.

The source of the chlorine and bromine is almost certainly due to human activity. Chlorofluorocarbons (CFCs), used extensively as refrigerants and the propellant for aerosol sprays prior to the 1990s, together with haloalkanes (such as methyl bromide,  $\text{CH}_3\text{Br}$ , used as a fumigant) have spread into the stratosphere where they decompose in the presence of the high energy ultraviolet radiation to produce free halogen atoms.

International agreements, introduced in 1987, have led to the phasing out of CFC use, with Australia banning the use of such gases totally in the 1990s. Evidence is growing that the banning of CFCs and restrictions on the use of haloalkanes is allowing ozone levels to be replenished, though it is not likely that these levels will return to normal before about 2050.

### \* Review exercise 17.2

- 1 Discuss the changes in the oxidation number of nitrogen and sulfur during the formation of acid rain.
- 2 Which of the primary pollutants listed in Table 17.2 would be present in the exhaust gases of cars?
- 3 It is proposed that one method of reducing the amount of carbon monoxide formed in the internal combustion engine is to make sure that the fuel is mixed with an excess of air.
  - a Write two equations for the combustion of octane,  $\text{C}_8\text{H}_{18}$ , one producing carbon monoxide and the other producing carbon dioxide. Explain, in terms of these equations, why the statement above is correct.
  - b Unfortunately, there is another consequence of using an excess of air. What is the pollution problem associated with using an excess of air in the internal combustion engine?
- 4 A 1000-megawatt coal-fired power station consumes about 3 million tonnes of coal each year. On the assumption that this coal contains 0.5% by mass of sulfur, determine:
  - a the mass of sulfur dioxide produced by such a power station each year
  - b the mass of calcium oxide,  $\text{CaO}$ , required to react with this sulfur dioxide in order to convert it into the environmentally less sensitive calcium sulfite,  $\text{CaSO}_3$ .
- 5 a Some who argued about the link between CFCs, such as  $\text{CCl}_2\text{F}_2$ , and stratospheric ozone depletion proposed that CFCs could not get into the stratosphere because they are such heavy gases. What is the flaw in this argument?

*continued*

### Review exercise 17.2 — *continued*

- b** Others suggested that more chlorine is produced from volcanic eruptions in the form of  $\text{HCl(g)}$  than was ever introduced by CFCs, and it was therefore this natural chlorine that was causing the effect. There are at least two counter arguments to this proposal. What are they?
- 6** Two of the CFCs used as refrigerants were dichlorodifluoromethane and trichlorofluoromethane. Draw the electron dot diagrams of these two molecules.
- 7** Oxygen and ozone are called allotropes.
- What does the term allotrope mean?
  - Draw electron dot diagrams for oxygen and ozone molecules
  - An alternative representation of an ozone molecule is shown in Figure 17.13. However, this is actually not the structure of ozone. What evidence would be required to show that it is not a valid structure?
  - The ozone molecule can be drawn in two equivalent ways. Draw the structures of each of these.
- 8** Carbon monoxide is a poison that interferes with oxygen ( $\text{O}_2$ ) transport in the body.
- Draw electron dot diagrams of oxygen and carbon monoxide. What similarities are present?
  - How does carbon monoxide interfere with oxygen transport in the bloodstream?
- 9** Nitrous oxide,  $\text{N}_2\text{O}$ , also called ‘laughing gas’, is sometimes added to racing car fuel to give the car better acceleration.
- What is the oxidation number of nitrogen in nitrous oxide?
  - RESEARCH There are three reasons why the added  $\text{N}_2\text{O}$  assists the engine. By first writing the equation for the decomposition of nitrous oxide to nitrogen and oxygen, suggest what these three reasons are.
- 10** RESEARCH Outline the key points you would make in an essay titled: ‘Ozone—friend at a distance, enemy at home’.
- 11** RESEARCH In the 1990s eight people were ‘locked away’ in a giant bubble in the Arizona desert known as Biosphere II. The chamber was set up to test whether it was possible to produce the same equilibrium between carbon dioxide and oxygen via respiration and photosynthesis as exists in the Earth’s biosphere, as a precursor to using such strategies for self-supporting colonies on the Moon or Mars. Two years into the experiment, with oxygen levels dropping and carbon dioxide levels rising, the project was interrupted through provision of additional oxygen. The puzzle of the missing oxygen baffled scientists for some time.
- Write equations for the photosynthesis and respiration reactions. Label the oxidants and reductants in these equations.
  - The overall equation for photosynthesis is the reverse of the equation for respiration. Does the fact that one equation is the reverse of another mean that the reaction pathways are also the reverse of one another? Explain your answer.
  - Research the Biosphere II project and describe some of the suggestions that were proposed to account for the missing oxygen.
  - One of the suggestions seems to be inconsistent with the amount of carbon dioxide also present in the chamber, yet this is regarded as the most likely answer to the missing oxygen. How was the carbon dioxide/oxygen puzzle resolved?

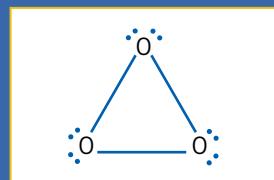


Figure 17.13

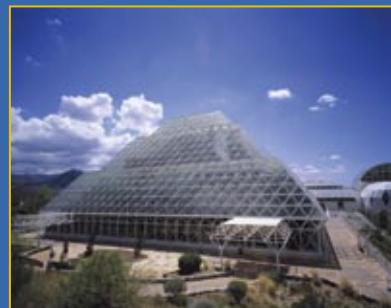


Figure 17.14 Biosphere II in the Arizona desert.

## 17.3 Water and fire

With over 70% of the Earth's surface covered by water, it plays a critical role in our lives. Depending on age and gender, the human body is around 65%, by mass, of water. It is the solvent for much of the complex biochemistry that regulates our life and also that of the other animals and plants around us. Elsewhere, water is found in oceans, lakes, rivers, underground aquifers, the atmosphere, glaciers, polar ice caps, as well as the sand and soil.

The path of water through the environment is described by the water cycle (see Figure 17.15). Solar radiation causes water in the oceans to evaporate. The water vapour forms clouds that are blown by the wind across land. Water in the clouds may precipitate as rain, hail or snow. This is particularly the case if clouds are forced to rise (and cool) by hills or mountains. The water reaching the ground may evaporate immediately, or form runoff and return to the ocean via rivers or streams. It may also collect in low-lying areas, lakes or dams, or be absorbed by plants via the roots, later to be released back into the atmosphere as the plant transpires. Some of the water, particularly in Western Australia, with its abundance of sand over less permeable rock, flows into underground aquifers. Liquid water in the water cycle carries the ingredients that are essential to life—dissolved oxygen, carbon dioxide, nitrogen in the form of nitrates and ammonium ions, and phosphorus in the form of the dihydrogenphosphate ion, as well as an abundance of other ions and trace elements.

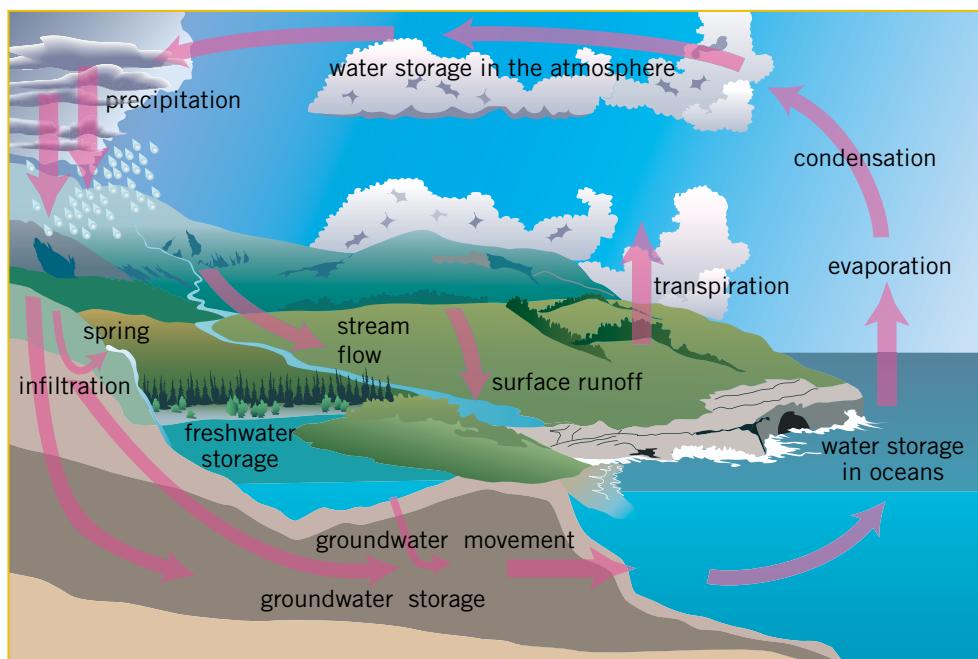
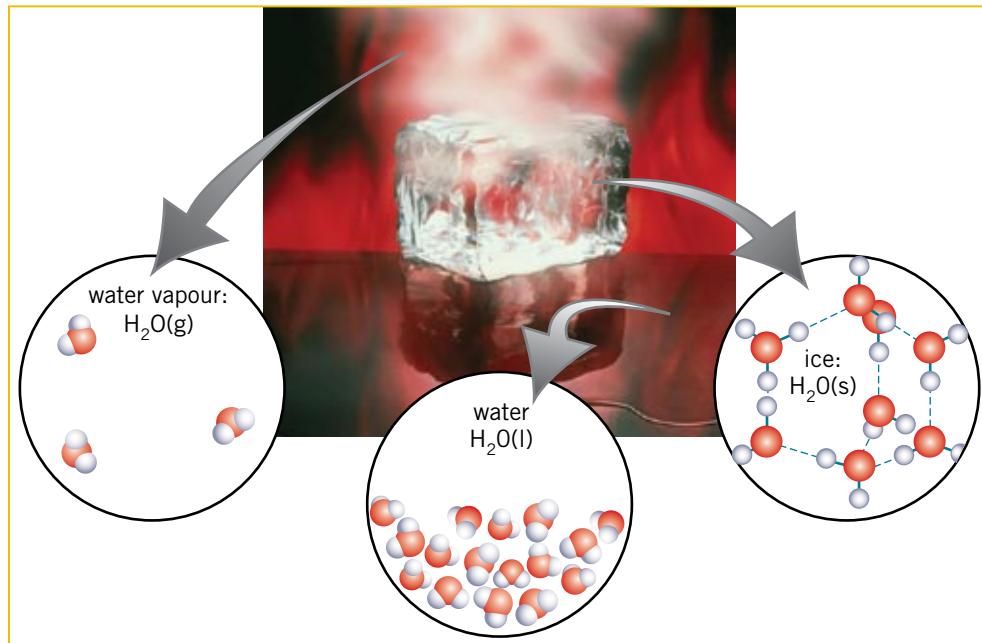


Figure 17.15 The water cycle.

In the water cycle, water can exist in all three states—solid ice, liquid and gas (water vapour), as depicted in Figure 17.16. The ability to exist in all three states on Earth is, in part, one of the reasons for water's importance.



**Figure 17.16 Water in its three physical states—a macro and a micro view.**

### Properties of water

Water has a range of important properties that, when combined, give this compound a powerful role in the environment. Table 17.3 summarises some of these properties and their significance.

**TABLE 17.3 IMPORTANT PROPERTIES OF WATER**

| Property                                                           | Significance and overview                                                                                                                                                                                                                                                                         |
|--------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| An excellent solvent                                               | Much of the chemistry of living things takes place in water. In addition to its ability to dissolve many solids, gases such as oxygen, carbon dioxide and nitrogen also dissolve in water (to a small extent).                                                                                    |
| The density of ice at 0°C is less than the density of liquid water | Water is one of the few substances whose solid form floats on the liquid form. As a result, even when the surface of a body of water has frozen, in cold climates, aquatic life can continue to exist underneath.                                                                                 |
| Transparent to visible light                                       | Water allows light to penetrate into oceans and other waterways so that plants can continue to photosynthesise.                                                                                                                                                                                   |
| High latent heat of fusion and vaporisation                        | This means that it takes a relatively large amount of energy to change a given amount of ice into water (fusion, or melting) as well as water into steam (vaporisation). As a result, ice does not melt easily, nor does liquid water evaporate easily. This has an effect on Earth's climate.    |
| High specific heat capacity                                        | It takes 4.18 joules of energy to raise the temperature of 1 gram of water by 1°C. Not only is this important for the climate, but it also means that living things, whose chemistry is dependent on water, do not exhibit huge changes in temperature as climatic conditions change around them. |
| High surface tension                                               | This is a measure of water's tendency to be attracted to itself—cohesion. In addition, water has a tendency to stick (adhere) to some other substances. These cohesive and adhesive forces are particularly important in biological systems such as plants.                                       |

## Groundwater, acidity and cave formation

Carbon dioxide is a product of the respiration reaction carried out by all living things. In addition, it is produced in the combustion of fuels and other substances containing organic molecules. Rainwater absorbs and reacts with carbon dioxide in the atmosphere to produce a solution that is slightly acidic.

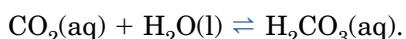
As explained in Section 13.3, according to the Brønsted–Lowry theory, acids are hydrogen ion,  $\text{H}^+$ , donors and bases are hydrogen ion acceptors. Carbon dioxide,  $\text{CO}_2$ , does not have a hydrogen ion to donate, so how is it possible that carbon dioxide dissolves in water to produce an acidic solution? The set of equations below provides the answer to this question.

First, some of the carbon dioxide dissolves in the water:



The double arrow,  $\rightleftharpoons$ , depicts a reaction that can proceed in forward and reverse directions.

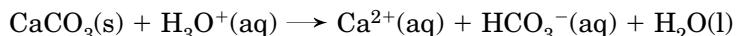
Next, the dissolved carbon dioxide combines with water to form a very dilute solution of carbonic acid ( $\text{H}_2\text{CO}_3$ ):



The carbonic acid can now behave as an acid and donate a hydrogen ion to water:

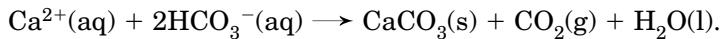


The rainwater, the acidity of which is explained in the set of equations above, may then percolate through an area that is rich in limestone,  $\text{CaCO}_3$ . Over millions of years, underground limestone deposits have reacted according to the equation:



In this reaction, the insoluble limestone is converted into a water-soluble compound that is washed away, leaving behind spectacular caves.

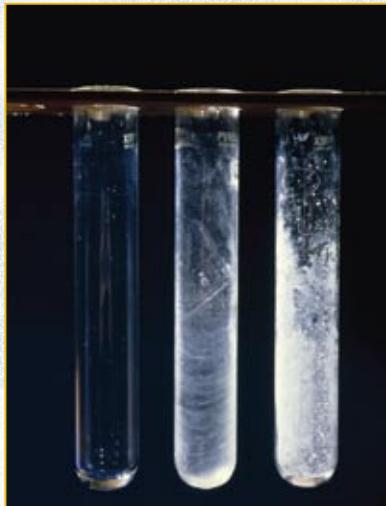
These caves are often even more spectacular as a result of one more chemical reaction. As water containing dissolved calcium hydrogencarbonate drips from the top of the cave, a reaction can occur that is the reverse of the one that formed the caves:



As the carbon dioxide gas is ‘lost’ to the atmosphere of the cave, the solid calcium carbonate may build up in the cave. Over time, spectacular formations of stalactites and stalagmites form.



Figure 17.17 Limestone cave and stalactite/stalagmite formation at Lake Cave, Margaret River.



**Figure 17.18** Three test tubes with deposits remaining after boiling dry: pure water, temporary hard water and permanently hard water. Permanent hard water usually leaves more solid deposits.

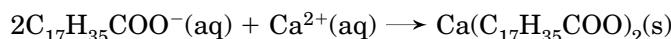
## Hard water

Hardness in water is caused by dissolved cations such as calcium ions,  $\text{Ca}^{2+}$ , and magnesium ions,  $\text{Mg}^{2+}$ , that are produced from underground deposits of limestone and magnesite (magnesium carbonate) when water containing dissolved carbon dioxide percolates through them. The insoluble carbonates react with the acidic rainwater to form the soluble hydrogencarbonates. Anions such as sulfate and chloride ions may also be present. Where the hardness of the water is due to calcium ions and hydrogencarbonate ions, the hardness is termed temporary. When calcium ions and sulfate or chloride ions are present or where magnesium ions are involved, the hardness is referred to as permanent. There are some problems associated with hard water as described below.

### Soap precipitates in hard water

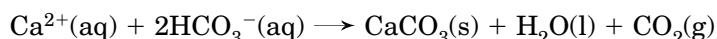
Dissolved calcium ions and magnesium ions form a precipitate or ‘scum’ with conventional soaps. As a result the water will not lather and the cleaning effect of the soap is reduced. Also, the insoluble soap scum leaves a residue on showers, baths and clothes.

Soap is a sodium or potassium salt of a long carbon chain fatty acid (see Unit 3). For example, the soap sodium stearate has the formula  $\text{NaC}_{17}\text{H}_{35}\text{COO}$ . In the presence of positive calcium or magnesium ions, the stearate ion forms an insoluble substance that precipitates from solution. As a solid the stearate ion cannot perform its cleaning function.



### Solids form when hard water is heated

When temporary hard water is heated, the dissolved calcium hydrogencarbonate decomposes to produce insoluble calcium carbonate and carbon dioxide:

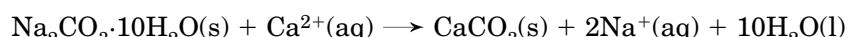


This decomposition reaction is the same as the one that forms stalactites and stalagmites in limestone caves. While this is a simple method of removing the hardness from the water, if it takes place in kettles, boilers, furnaces or hot-water pipes, it can produce a deposit of a solid (called scale) that reduces the efficiency of heat transfer or may block pipes.

Calcium sulfate is less soluble in hot water than in cold water, so where the hardness in the water is due to dissolved calcium sulfate, the problem of scale formation in industries that use hot water is a significant cost and safety issue.

### Softening water

It is possible to soften hard water by removing the calcium and magnesium ions from the water. Obviously, boiling water that is temporarily hard is one way to remove the hardness. The softened water can be simply poured off the precipitated calcium carbonate. If a soluble carbonate such as sodium carbonate is added to water containing dissolved calcium ions, then calcium carbonate will precipitate. The remaining dissolved sodium ions do not affect the hardness of the water. Washing soda, hydrated sodium carbonate, is used for this purpose:



For water that contains either calcium ions or magnesium ions, a complex phosphate-containing salt can be used to form soluble complex ions from the cations. These complex ions remain in solution and do not interfere with the cleaning action of the soap.

Ion-exchange resins, as the name suggests, replace the ions that cause hardness in water with ions, such as  $\text{Na}^+(\text{aq})$ , that do not contribute to hardness. When it is necessary to remove all the positive and negative ions, the cations are replaced by  $\text{H}^+(\text{aq})$  and the anions by  $\text{OH}^-(\text{aq})$ . These two ions combine to produce water.

The alternative to removing the ions from the water is to remove the water from the ions. For example, distillation ensures that the water obtained is free of ionic impurities, but is a very expensive solution to the hard water problem.

## Water treatment and supply

Good-quality water is almost taken for granted in Australia. However, assuring such water supply requires a significant infrastructure of monitoring and testing, quality control and research.

Only 2.5% of the water on Earth is freshwater, and over 75% of this is locked up in ice caps and glaciers. As the driest continent on Earth, Australia has a limited freshwater supply. Just 1% of the freshwater available on Earth is found in Australia, with much of this being in underground aquifers. Should these underground supplies become polluted, the task of cleaning it up would be immense.

Around 70% of water used in Australia is for agriculture, predominantly irrigation, with just under 10% used for household purposes. In the home, only 1% of the water used is actually for drinking. The largest consumer of water in the home is the garden, averaging around 35%, with this sometimes going as high as 90%.

The National Health and Medical Research Council, supported by the Natural Resource Management Ministerial Council, monitors Australian drinking-water standards. Together with other local and state government infrastructures, such as the Water Corporation and Health Department in Western Australia, drinking-water supplies are monitored and treated, not only to safeguard human health but also to monitor aesthetic qualities such as colour, texture and taste.

With water being such an excellent solvent for a range of substances, it is virtually impossible to obtain drinking water that is free from impurities. The issue then becomes one of ensuring that these impurities do not compromise health. The limits that are set for the amount of an impurity in our drinking water are generally 10% to 100% below what bodies such as the World Health Organisation consider safe for consumption.

Some of the impurities in drinking water are actually desirable, such as calcium and magnesium ions (in small quantities from weathering of soils and rocks), which are good for health and improve the taste of the water.

Ensuring the safety of our water supplies requires the testing and treatment of the supply. The range of micro-organisms that may contaminate water supplies is too large to monitor. Particular organisms that are quick and easy to detect, and are also generally found when harmful micro-organisms are present, are monitored on a regular basis. *Escherichia coli* (*E. Coli*), a bacterium found in the human gut, is the organism that is most often used as an indicator of other problems associated with microbes in the water supply.

The simplest tests that are carried out on water supplies include the turbidity or cloudiness of the water. Such suspended particles often provide a rich source of nutrient for harmful micro-organisms. Colour, pH and residues from chlorination procedures (see later) are also included in these simple tests.



Figure 17.19 Typical water use in the home.

Since underground water contributes about 50% of Perth's water supply, it is especially important to maintain this testing regime to monitor pollution from livestock waste, fertilisers and pesticides used for agriculture and forestry, hazardous waste storage by industry, human waste from housing areas, leakage from landfill sites and runoff from mining.

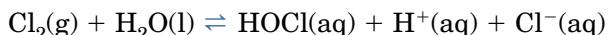
Table 17.4 provides an overview of the various treatments that may be necessary for water supplies and the rationale for each treatment.

**TABLE 17.4 WATER-SUPPLY TREATMENTS**

| Treatment                                                             | Source                                                                                                                                                                                                                   | Rationale for treatment                                                                                                                                                                                                                                                                                                                                                                                            |
|-----------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Remove colour                                                         | Presence of iron(III) ions, $\text{Fe}^{3+}$ , dissolved from rocks and minerals into underground water supplies. Tannins from trees and other vegetation—this gives some water supplies the appearance of 'dilute tea'. | Removal is generally for aesthetic reasons. The process of coagulation and flocculation may help to remove some colour. The water may also be passed over fine filters whose large surface area adsorbs some of these ions and molecules. Filters for water supplies in the home often contain activated charcoal which has a very large adsorbing surface area.                                                   |
| Remove dissolved gases such as $\text{CO}_2$ and $\text{H}_2\text{S}$ | Not a particular problem with dam water, but often present in underground water supplies that may be associated with sulfide minerals.                                                                                   | Generally, the water is extensively aerated (stirred) to provide a large surface area via which the dissolved gases can escape. This aerated water is then mixed with the general water supply. Aeration also oxidises $\text{Fe}^{2+}$ dissolved in the water to $\text{Fe}^{3+}$ , which is more easily removed as insoluble iron oxide.                                                                         |
| Water softening—removal of calcium ions                               | Much of Perth's water supply is obtained from areas rich in limestone, $\text{CaCO}_3$ . Dissolved carbon dioxide in rainwater will slowly dissolve some of this limestone.                                              | Sodium carbonate can be added to convert the dissolved calcium ions to insoluble calcium carbonate. Some Perth water is treated with calcium hydroxide while passing the water over beds of garnet-containing minerals (complex silicates containing calcium, aluminium, magnesium ions and more). The solid calcium carbonate collects on the fine sand, presumably by another adsorption process.                |
| Remove suspended matter                                               | Often due to small particles of clay minerals held in suspension as a colloid.                                                                                                                                           | The clay-containing mineral suspension consists of negatively charged ions that stay in solution due to their mutual repulsion. Highly charged cations such as $\text{Al}^{3+}$ can neutralise this charge and cause the particles to coagulate and precipitate. Concerns about the presence of aluminium ions in water and possible links to Alzheimer's disease are bringing this process under closer scrutiny. |
| Removal of micro-organisms                                            | Often from animal and human waste.                                                                                                                                                                                       | Chlorine gas or sodium hypochlorite solutions are added early in the water-processing treatment. Ammonia is also added to Mundaring Weir near Perth to convert the chlorine into more stable chloramines for the long journey to Kalgoorlie.                                                                                                                                                                       |
| Dental-cavity protection                                              | Sources of fluoride ions are added to water supplies to assist in the prevention of dental decay, particularly in young children.                                                                                        | Small amounts of $\text{Na}_2\text{SiF}_6$ , or $\text{NaF}$ , are added to water supplies. These convert the natural enamel on teeth to the more acid-resistant fluoroapatite (as $\text{OH}^-$ in the complex material is replaced by $\text{F}^-$ ). There is still some controversy about such treatment of water supplies and this can be tracked via articles readily available on the Internet.             |

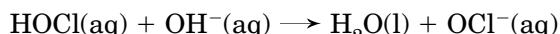
The chlorine that is added to water supplies is usually in one of two forms, as elemental chlorine gas or as a solution of sodium hypochlorite ( $\text{NaOCl}$ ). In home swimming pools it is usually added as solid calcium hypochlorite or a concentrated solution of sodium hypochlorite. Some home swimming pools also generate chlorine by the electrolysis of salt water. (Solid salt is added to the pool and a small electric current is used to convert the chloride ion to chlorine.)

The killing effect of chlorine is believed to be due to hypochlorous acid ( $\text{HOCl}$ ) or the hypochlorite ion ( $\text{OCl}^-$ ), formed when chlorine reacts with water.

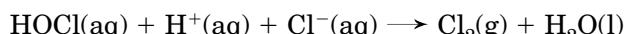


At a concentration of around 1–2 parts per million the hypochlorous acid attacks the cell walls of bacteria and reacts with some of the enzymes that are responsible for the biochemistry of the bacterial cell.

In swimming pools the concentration of hypochlorous acid depends on the pH. If the pH is around 7.4 then the concentration of the hypochlorous acid is at its optimum value. At higher pH values, the acid reacts with the excess hydroxide ions to produce the hypochlorite ion. Hypochlorous acid oxidises bacteria in a matter of seconds, while the hypochlorite ion may take up to an hour to achieve the same effect.



If the pH is too low, the hypochlorous acid reacts with the excess  $\text{H}^+$  to generate chlorine that may irritate eyes and skin, and also produces the unpleasant ‘chlorine smell’ in the pool.



### Drinking water from salty water

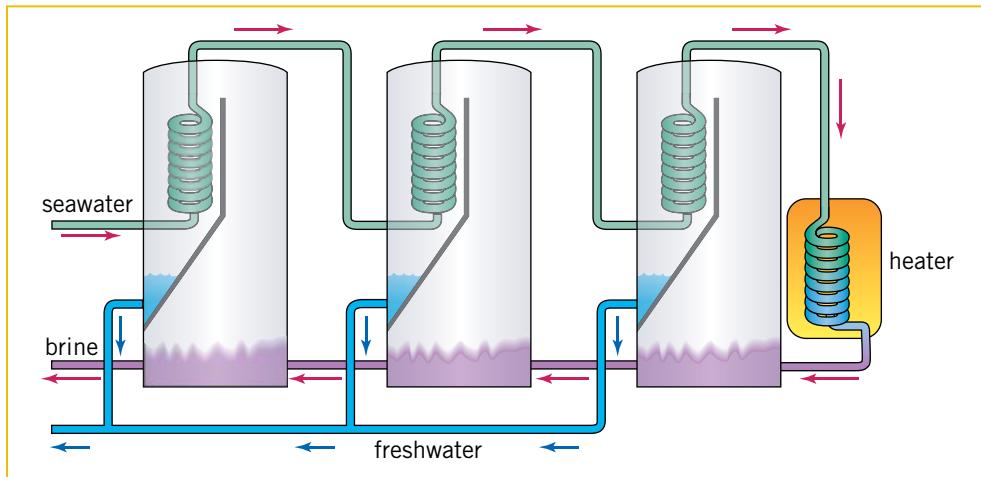
With such a small amount of available fresh water on a planet with such a vast supply of water, it is obvious that attempts will be made to convert salty water to water of drinking quality (or water suitable for agriculture, where most of the freshwater supply is presently used). The properties of water that make it such a good solvent also work to ensure that removing these dissolved materials will not be easy.

Essentially, there are two ways of removing dissolved impurities in water:

- remove the water from the impurity
- remove the impurity from the water.

### Removing water from the impurity

Distillation is the simplest way of separating water from dissolved salts. While this technique is simple in a school laboratory, the energy cost is large on a commercial scale. Some countries in the Middle East have been using a process called flash evaporation for many years. Seawater is heated in tubes before it is passed into a chamber in which the atmospheric pressure is lower than in the heating tubes. The liquid quickly evaporates to provide water vapour and leaves the salts behind to exit with the remaining water. The water that has vaporised is then condensed on the outside of the tubes that are carrying the incoming seawater. The energy released in the condensation process is used as a heat source for the seawater. Flash-distillation plants have been modified to provide multiple ‘flash chambers’. Where one flash chamber is used the temperature of the water may drop from  $100^\circ\text{C}$  to  $60^\circ\text{C}$  in the first evaporation stage. If this water is simply discharged back into the ocean, much of the energy used is ‘lost’. Consequently, modern flash-distillation plants (Figure 17.20) use several chambers at successively lower and lower pressures so that the water that ultimately leaves the plant is only about  $30^\circ\text{C}$ .



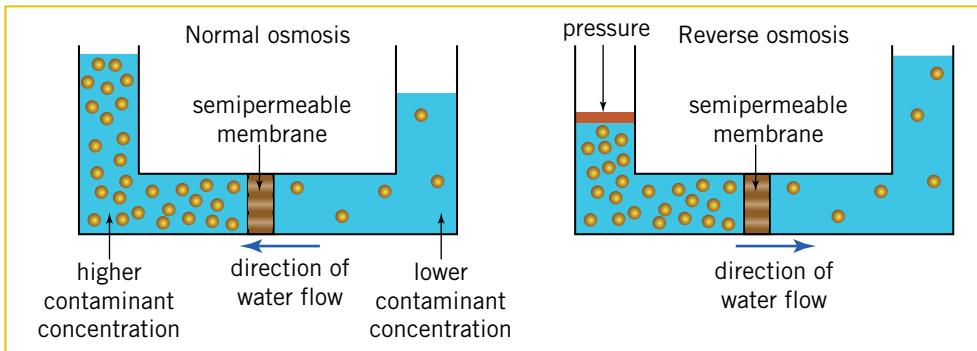
**Figure 17.20 Multi-stage flash evaporation to convert seawater to drinking water.**

Perth has chosen to build a desalination plant at Kwinana to produce drinking water using reverse osmosis rather than distillation. Like distillation, reverse osmosis removes the water from the impurity, but it does so at a much lower temperature. The Kwinana plant can provide an extra 45 gigalitres of water for Perth each year.

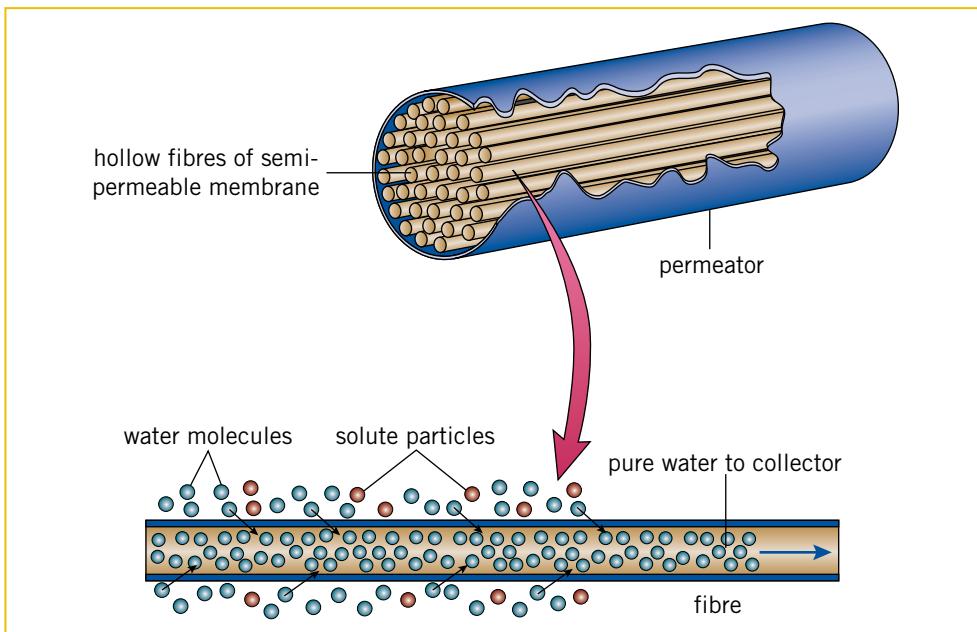
A smaller-scale reverse osmosis plant was recently opened at Kwinana to treat the water from the effluent at the Woodman's Point wastewater treatment plant that would normally be discharged into Cockburn Sound, south of Perth. The wastewater is treated with sodium hypochlorite to remove bacteria and other micro-organisms. To remove as much of the particulate matter as possible, the water then passes through a very fine filter. This improves the quality of the water that will undergo reverse osmosis and protects the membranes that are the key part of the reverse-osmosis process.

Osmosis is a process in which water moves from a region of low concentration of dissolved salt, through a semipermeable membrane (a barrier that allows small molecules such as water to pass through, but restricts the movement of larger ions or other particles) to a region of higher ion concentration. This is a significant mechanism for the transport of water in plants. The difference in concentrations between the two sides of the cell wall produces what is known as an osmotic pressure. Figure 17.21 shows how the flow of water through the membrane in normal osmosis pushes the level of the water higher on the more concentrated side—this is the osmotic pressure. As a result, the water outside the plant seems to be pushed through the cell walls into the plant.

The natural process of osmosis involves water moving through a semipermeable membrane from a region of low salt concentration to a region of high salt concentration. In reverse osmosis, however, water moves through the membrane, away from a region of high salt concentration. This occurs when a pressure (greater than the normal osmotic pressure) is applied to the saltwater side of the membrane, resulting in the water molecules being pushed through the membrane against the natural flow. The ions are not able to move through the membrane and so the saltwater becomes more concentrated.



**Figure 17.21** How do osmosis and reverse osmosis work?



**Figure 17.22** Cross-section of a reverse-osmosis membrane.

A desalination plant requires a continuous feed of salty water to provide the pressure on the semipermeable membrane. Water from which much of the salt has been removed emerges from the other side of the membrane while the more highly concentrated by-product of the process is pumped out into the sea.

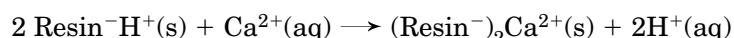
### Removing the impurity from the water

The production of deionised water (water from which the ions have been removed) involves the passage of water through an ion exchange resin. There are two types of ion exchange resin, those that exchange cations (called cation exchange resins) and those that exchange anions (anion exchange resins). The cation exchange resin replaces cations such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with hydrogen ions,  $\text{H}^+$ . The anion exchange resin replaces anions such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$  with hydroxide ions,  $\text{OH}^-$ .

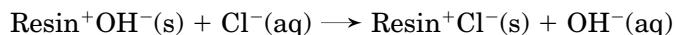
Each of the resins is made from large organic molecules to which have been attached charged groups. The cation exchange resins have negatively charged groups of atoms on the resin to which  $\text{H}^+$  ions have been attached (often represented as  $\text{Resin}^-\text{H}^+(\text{s})$ ). The anion exchange resins have positively charged groups of atoms to which  $\text{OH}^-$  ions have been attached (represented as  $\text{Resin}^+\text{OH}^-(\text{s})$ ).

The action of the resins can be summarised in the following equations.

Cation exchange resin: The resin containing H<sup>+</sup> ions removes ions such as Ca<sup>2+</sup>(responsible for hardness in water) and replaces them with hydrogen ions in solution.



Anion exchange resin: The resin containing OH<sup>-</sup> ions removes ions such as chloride (from salty water) and replaces them with hydroxide ions in solution.



The hydrogen ions and hydroxide ion in solution then combine to form water. In other words, water has been produced in exchange for the cations and anions that were present in the original water supply.

When the resins have lost their capacity for exchange, that is, when most of the H<sup>+</sup> and OH<sup>-</sup> on the resin has been exchanged, they can be regenerated by washing the cation resin with acid solution and the anion resin with a solution of a base.

Some of the water purifiers used in the home are based on the use of cationic and anionic exchange resins. The use of these resins also takes place on a larger scale in some industrial plants. However, the resins are not suitable for seawater because of the high concentration of ions present. In addition, the cost of the acid and base to replenish the resin makes large-scale water production in this way uneconomic.

### Recycling water—environmental and emotional

Figure 17.15 showed how water is recycled naturally in our environment. For the most part, the water molecules in the next glass of water you drink will have been in oceans, rivers, plants, animals (including humans), and will have been associated with many other inorganic and organic chemicals.

We have no say in whether or not to drink recycled water—we already do. A key question for society is whether to drink water that has been recycled with the assistance of various chemical and biological treatments.

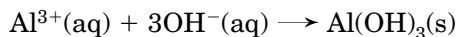
Wastewater treatment generally involves three stages: separation of solids, removal of organic material and bacteria, and, if necessary, removal of heavy metal ions, phosphates and residual organic compounds.



Figure 17.23 Aerial view of a sewage treatment facility.

### **Primary treatment**

Screens and filters are used to separate much of the solid material present in the wastewater. After this coarse filtration, the water may pass into a settling tank where more sludge, sand and grit will deposit. At this stage, a mixture of aluminium sulfate and calcium hydroxide may be added. These two chemicals react to produce aluminium hydroxide, which is a flocculation agent.



As the aluminium hydroxide precipitates, it carries suspended dirt particles because the highly charged aluminium ion is strongly attracted to the negatively charged silicates in the dirt. Any grease or other insoluble material less dense than water is skimmed off the surface during this primary treatment. Some of the organic sludge can be used to decompose in an oxygen-poor environment to produce methane and other small-chain hydrocarbons that can provide fuel to supplement the running costs of the treatment plant. Gas storage tanks can be seen in the upper left of the plant in Figure 17.23.

### **Secondary treatment**

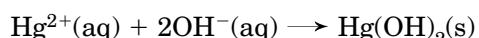
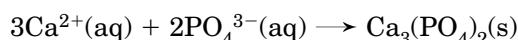
This is perhaps the most important stage, as most of the organic material is oxidised and dangerous bacteria are removed. The waste is allowed to trickle over various filters and rock beds, similar to the natural filtration that would take place as water passed through soil or sand. In some cases, pure oxygen or oxygenated air is passed into the wastewater as it passes through these filtration beds, aeration tanks and sedimentation tanks. Various micro-organisms thrive in this environment as they break down the impurities into harmless oxidation products such as carbon dioxide and more water.

If necessary the water emerging from this treatment is chlorinated. In some recycling operations, the water is treated with ozone to avoid giving the water a 'chlorine' taste. In both cases, the treatment kills any residual bacteria.

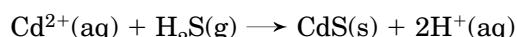
### **Tertiary treatment**

Water treatment at this stage can be very expensive as the material that remains in the water after the first two treatments is obviously not easy to remove. The major impurities at this stage are heavy metal ions such as mercury, lead and cadmium, phosphates, nitrates and residual organic material.

Application of the solubility rules from earlier in this course would suggest that the metal ions and phosphates could be removed by precipitation. Adding calcium hydroxide solution would lead to the formation of calcium phosphate and may precipitate insoluble hydroxides of some of the heavy metals.



It is also possible to precipitate some of the metal cations as sulfides by passing hydrogen sulfide gas through the water.



The solubility of nitrates makes it impossible to use a chemical treatment to remove the nitrate ions from water supplies. Instead, denitrifying bacteria, similar to those found naturally in soil, can be used to convert the nitrates into nitrogen gas.

Finally, any organic material that has not been oxidised in the primary or secondary treatment can be removed by passing the water over activated charcoal. The large surface area of the carbon in this material adsorbs the more complex organic molecules but not the smaller water molecules. The adsorbed organic molecules are oxidised by removing the carbon and heating it to high temperatures, after which the carbon is re-activated.

### \* Review exercise 17.3

- 1 Table 17.3 summarised some of the important properties of water. Not all of these properties are beneficial. Consider these properties again, but this time, tabulate the positive and negative aspects of each property.
- 2 Specific heat capacity is the amount of energy necessary to change the temperature of 1 kg of material by  $1^{\circ}\text{C}$ . The specific heat capacity of water is about  $4200 \text{ J kg}^{-1} \text{ }^{\circ}\text{C}^{-1}$ , while that of land is around  $1300 \text{ J kg}^{-1} \text{ }^{\circ}\text{C}^{-1}$ . Depending on the conditions of measurement the specific heat capacity of air varies from 700 to  $1000 \text{ J kg}^{-1} \text{ }^{\circ}\text{C}^{-1}$ . Use this data to explain how a large body of water such as the Indian Ocean can stabilise the temperature of the land and the atmosphere.
- 3 It has been proposed that waterways containing high concentrations of phosphate from fertilisers be treated with calcium hydroxide to precipitate the phosphate as calcium phosphate. What questions would you want answered before considering this as a treatment?
- 4 A website for a particular water filter technology makes the following statement:

... achieves what many other water filter technologies can only dream of—naturally energised water that is up to twice as ‘wet’ as ordinary water. Wetter water is better for hydration ...

<http://www.wellness.com.au/>

Comment on the scientific accuracy of this claim.
- 5 a Outline the relationship between limestone cave formation and the hardness of water.  
b In what way is temporary hardness different from permanent hardness in water?
- 6 If the formation of stalactites and stalagmites is simply the reverse of the formation of the cave in the first place, why doesn't the cave fill up with limestone as fast as it forms?
- 7 What are the problems that industries face when they use supplies of hard water?
- 8 Carbon dioxide, sulfur dioxide and nitrogen dioxide are associated with the acidity of rainwater. Write equations to explain how each can behave as an acid in water.
- 9 Those who champion the use of water filters do so on the basis of their capacity to remove bacteria, sediment, chlorine and other chemicals—natural and added. Those who champion bottled water promote a product that contains dissolved ions that are not present in higher concentrations in general drinking water. Is it possible that both are right? How?
- 10 List some of the properties of water that make it so difficult to obtain large quantities of drinking-quality water.
- 11 **RESEARCH** What factors would have been considered in the decision to locate a reverse osmosis rather than a multistage flash distillation plant at Kwinana?
- 12 It has been argued that the production of large-scale supplies of good-quality water will be achieved by physical rather than chemical means. What is it that supports such a statement?

- 13** Table 17.5 provides a comparison of the chemical composition of seawater, three commercial bottled mineral waters (brands X, Y and Z) and reservoir water from an Australian city. All measurements are in  $\text{mg L}^{-1}$ .

**TABLE 17.5** CHEMICAL COMPOSITION OF SOME WATER SOURCES

| Ion                | Seawater | Brand X | Brand Y | Brand Z | City |
|--------------------|----------|---------|---------|---------|------|
| $\text{Ca}^{2+}$   | 411      | 35      | 0.16    | 86      | 16.5 |
| $\text{Mg}^{2+}$   | 1 250    | 3.2     | 1.33    | 9       | 1.4  |
| $\text{Na}^+$      | 10 800   | 3.3     | 9.9     | 35      | 3.5  |
| $\text{K}^+$       | 392      | 0.43    | 0.22    | 0.2     | 0.65 |
| $\text{Cl}^-$      | 19 400   | 3.7     | 4.26    | 70      | 3.9  |
| $\text{SO}_4^{2-}$ | 2 690    | 3.3     | 2.2     | 28      | 6.7  |
| $\text{HCO}_3^-$   | 146      | —       | 2.0     | 260     | —    |
| $\text{F}^-$       | 13       | —       | —       | 0.2     | 0.9  |

- a** If people drink seawater they are likely to die from dehydration. Account for this observation.
- b** Comment on the chemical composition of brand Y and indicate, with justification, the nature of the environment from which it was obtained.
- c** From the chemical analysis of brand Z state, with justification, whether it is likely to be acidic, neutral or basic.
- d** On the assumption that the ion has the same molar mass as the atom or group of atoms of which it is composed, it is possible to convert the data in  $\text{mg L}^{-1}$  to  $\text{mol L}^{-1}$ . From this it is then possible to determine whether the amount of positive charge in the sample balances the amount of negative charge.  
Convert the data for brand Z to  $\text{mol L}^{-1}$  and then determine whether the sample has a charge balance (total positive charge = total negative charge). If not, account for the difference.
- e** The water supply from the city reservoir is checked regularly and the pH has been found to vary from 7.8 to 8.5. What is the likely composition of the soils and rocks in the catchment area for this reservoir?
- f** Brand X can be purchased for \$2.10 per litre. City water can be purchased for 0.035¢ per litre. What chemical reasons, if any, are there for purchasing brand X?

- 14**  **RESEARCH** Concern has been expressed by some that allowing people to visit limestone cave formations risks damaging the delicate equilibrium that is set up in the cave. What do these people mean by ‘delicate equilibrium’? In what way(s) would human access to the cave disturb this equilibrium?

- 15**  **RESEARCH** The costs associated with the production of water suitable for drinking are as follows:

|                    |                      |
|--------------------|----------------------|
| Groundwater        | 30–50¢ per kilolitre |
| Surface water      | 35–45¢ per kilolitre |
| Desalination       | 150¢ per kilolitre   |
| Kimberley pipeline | 400¢ per kilolitre   |
| Rainwater tanks    | 750¢ per kilolitre.  |

With such an abundance of underground water (groundwater) in Western Australia why don’t we simply use it to supply all our water needs?

*continued*

**Review exercise 17.3 — *continued***

- 16**  **RESEARCH** If changing the state of water from liquid to gas can remove the water from impurities then presumably changing the state of water from liquid to solid can achieve the same thing.
- a** Are icebergs ‘pure water’?
  - b** What is freeze desalination and how is it achieved?
- 17**  **RESEARCH** When the issue of recycling ‘black water’, which is water obtained from sources such as sewage, is raised there is often community concern that such water should not be used again as it is already ‘tainted’. Use your understanding of the water cycle to provide an argument to refute the claim that appropriately recycled ‘black water’ is ‘tainted’.
- 18**  **RESEARCH** In 2000, *Fortune* magazine made the comment: ‘Water promises to be to the 21st century what oil was for the 20th century’. Discuss this statement in terms of the technologies used in the purification of water supplies.



## MAJOR IDEAS

- While gold can be found naturally as the free element, many commercially important metals are extracted from ores that contain the element bound to oxygen or sulfur. These ores have to be reduced to convert them to the metal.
- Gold is separated from rock and other material by oxidising it in the presence of cyanide ion and oxygen to form the aurocyanide ion.
- The aurocyanide ion is adsorbed onto a form of activated charcoal in the carbon-in-pulp process.
- The gold-containing complex ion is then electrolytically reduced to metallic gold using steel wool cathodes.
- The raw materials for the extraction of iron from iron oxide are  $\text{Fe}_2\text{O}_3$ , calcium carbonate and coke.
- The reduction of iron ore takes place in a blast furnace.
- The reducing agent in the blast furnace is carbon monoxide, made from the oxidation of carbon with hot air in an overall exothermic reaction.
- Aluminium is obtained from bauxite in a two-step process.
- Aluminium oxide is removed from other impurities by making use of the amphoteric nature of the aluminium oxide and dissolving it in a hot concentrated sodium hydroxide solution.
- The purified aluminium oxide is dissolved in molten cryolite and electrolysed to produce aluminium by the reduction of the aluminium ion.
- Atmospheric pollution arises from the localisation of gases that can be detrimental to health, or cause environmental problems, particularly in urban areas.
- Particular pollution concerns arise from atmospheric carbon dioxide, carbon monoxide, hydrocarbons, sulfur dioxide, ozone, and various oxides of nitrogen.
- Carbon monoxide is a product of inefficient combustion of fossil fuels and causes respiratory problems by blocking oxygen transport via haemoglobin.
- Nitrogen oxides contribute to atmospheric haze, acid rain and photochemical smog.
- Nitric acid produced in thunderstorms, and the nitrates and ammonium salts produced by soil bacteria are important for plant growth.
- Nitrogen dioxide, formed from the oxidation of nitrogen monoxide, dissolves in rainwater to produce a mixture of dilute nitric acid and nitrous acid.
- Sulfur dioxide is produced from the oxidation of sulfur containing fossil fuels, mineral sulfides, or hydrogen sulfide. In the presence of air it is oxidised further to sulfur trioxide, which produces a dilute solution of sulfuric acid in rainwater.
- Acid rain is a problem in regions where the sulfuric acid and nitric acid can concentrate in the atmosphere and significantly alter the pH of rainwater.
- Ozone in the stratosphere absorbs some of the harmful ultraviolet radiation that would otherwise reach Earth.
- A range of chemicals, particularly CFCs, cause this ozone to be depleted.
- The water cycle describes the transport of water through the environment, reinforcing the idea that all water is recycled.
- Water has a range of physical and chemical properties that are important in explaining and understanding the path that water takes through the water cycle:
  - excellent solvent
  - solid less dense than liquid
  - high heat of vaporisation, fusion and specific heat capacity
  - transparent
  - high surface tension.
- Dissolved carbon dioxide plays an essential role in the formation of limestone caves and in the production of hard water.
- Carbon dioxide dissolved in water reacts to produce an acidic solution.
- Water can be separated from its dissolved impurities by distillation, multi-flash distillation and reverse osmosis:
  - Multi-flash distillation boils water at pressures below atmospheric.
  - Reverse osmosis uses pressure and a semi-permeable membrane to push water away from the dissolved impurities.
- Dissolved impurities can be separated from water by the use of ion exchange resins:
  - cations are exchanged for  $\text{H}^+$
  - anions are exchanged for  $\text{OH}^-$
  - $\text{H}^+$  and  $\text{OH}^-$  combine to form water.

## Unit 2B Review Questions

### \*PART A: MULTIPLE-CHOICE QUESTIONS

**1** According to the Arrhenius theory of acids and bases, what is a base?

- A** It produces hydrogen ions in aqueous solution.
- B** It produces a neutral solution when dissolved in water.
- C** It forms hydroxide ions in aqueous solution.
- D** It turns blue litmus red in aqueous solution.

**2** According to the Brønsted–Lowry theory of acids and bases, which of the following best describes an acid?

- A** It produces hydrogen ions in aqueous solution.
- B** It produces a solution that turns litmus blue.
- C** It donates a proton to a base.
- D** It reacts with metals to form hydrogen gas.

**3** Which of the following is the best definition of a weak acid?

- A** It is only partially ionised in aqueous solution.
- B** It does not have a pH value that can be measured.
- C** It does not react completely with a solution of a base like sodium hydroxide.
- D** It dissolves in water to form only OH<sup>−</sup> ions and no H<sup>+</sup> ions.

**4** Which one of the following substances is a multiprotic acid?

- |                                         |                                         |
|-----------------------------------------|-----------------------------------------|
| <b>A</b> CH <sub>3</sub> COOH           | <b>B</b> Ba(OH) <sub>2</sub>            |
| <b>C</b> H <sub>3</sub> PO <sub>4</sub> | <b>D</b> HCO <sub>3</sub> <sup>2−</sup> |

**5** A 17 mol L<sup>−1</sup> solution of acetic acid has a low electrical conductivity. Which of the following is correct?

- A** It is a concentrated solution of a strong acid.
- B** It is a concentrated solution of a weak acid.
- C** It is a strong solution of a dilute acid.
- D** It is a dilute solution of a concentrated acid.

**6** X, Y and Z are elements belonging to the same period of the periodic table. The oxide of X dissolves in water, forming a solution that changes red litmus to blue. Y reacts with water, forming a solution that changes blue litmus to pink. The oxide of Z reacts with both acid and alkali.

Which of the following is correct if the elements are arranged in order of increasing atomic number?

**A** X, Y, Z

**C** Y, Z, X

**B** X, Z, Y

**D** Z, Y, X

**7** The sourness of a substance can be a guide to its acidity—sourness increases with increasing acidity (although it is not recommended that unfamiliar chemicals be tasted).

Which of the following is most likely to be true if solution P tastes sourer than solution Q?

- A** Solution P was at a higher pH than solution Q.
- B** Solution P has more OH<sup>−</sup>(aq) ions in solution than solution Q.
- C** Solution P would turn red litmus blue, while solution Q would have no effect on litmus.
- D** Solution P has a higher concentration of H<sub>3</sub>O<sup>+</sup>(aq) ions than solution Q.
- E** Solution Q was a stronger acid than solution P.

**8** Which one of the following statements contains two correct descriptions of oxidation?

- A** addition of electrons, decrease in oxidation number
- B** removal of electrons, decrease in oxidation number
- C** addition of electrons, increase in oxidation number
- D** removal of electrons, increase in oxidation number

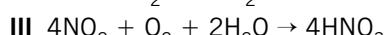
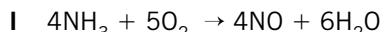
**9** Which one of the following is the best definition of an oxidant?

- A** An oxidant always contains oxygen.
- B** An oxidant causes the oxidation of another substance.
- C** An oxidant is oxidised during reactions.
- D** An oxidant donates electrons to another substance.

**10** In which one of the following does nitrogen (N) have an oxidation number of −3?

- |                             |                                        |
|-----------------------------|----------------------------------------|
| <b>A</b> HNO <sub>2</sub>   | <b>B</b> N <sub>2</sub> O <sub>5</sub> |
| <b>C</b> NH <sub>4</sub> Cl | <b>D</b> N <sub>2</sub>                |

**11** Nitric acid can be prepared in the Ostwald process using NH<sub>3</sub> and O<sub>2</sub> as the initial reactants. Some of the reactions which occur are represented by the following equations:



In which of the above steps is the oxidation number of oxygen reduced?

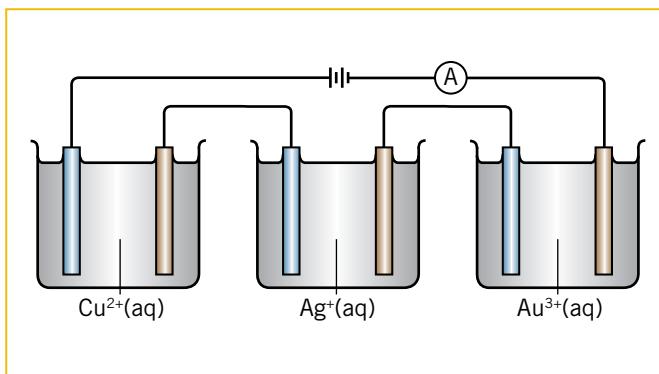
- A** I only
- B** II and III only
- C** none of them
- D** all of them.

**12** During the electrolysis of molten KCl, which one of the following statements is true?

- A** The mass of potassium metal deposited equals the mass of chlorine gas liberated.
- B** Two atoms of potassium are deposited for each molecule of chlorine liberated.
- C** Chlorine gas is liberated at the cathode.
- D** Hydrogen gas is liberated at the cathode.

Questions 13 and 14 refer to the following information.

The diagram below represents a circuit for electroplating copper, silver and gold in three separate cells connected in series.



A current of 1.00 amp flows through the circuit for 1 hour.

**13** Which of the following lists the metals in increasing order of amount in mole deposited?

- |                     |                     |
|---------------------|---------------------|
| <b>A</b> Cu, Au, Ag | <b>B</b> Ag, Cu, Au |
| <b>C</b> Cu, Ag, Au | <b>D</b> Au, Cu, Ag |

**14** Which of the following lists the metals in increasing order of mass deposited?

- |                     |                     |
|---------------------|---------------------|
| <b>A</b> Cu, Au, Ag | <b>B</b> Ag, Cu, Au |
| <b>C</b> Cu, Ag, Au | <b>D</b> Au, Cu, Ag |

**15** A compound has the formula C<sub>6</sub>H<sub>12</sub>. Which one of the following could it be?

- A** a straight chain alkane
- B** a cycloalkene with one double bond
- C** an alkene with one double bond
- D** an aromatic hydrocarbon

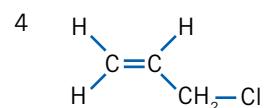
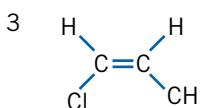
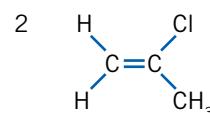
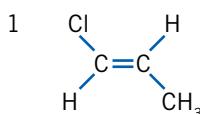
**16** Which of the following formulas could represent a cycloalkane?

- |                                         |                                         |
|-----------------------------------------|-----------------------------------------|
| <b>A</b> C <sub>2</sub> H <sub>4</sub>  | <b>B</b> C <sub>3</sub> H <sub>8</sub>  |
| <b>C</b> C <sub>4</sub> H <sub>8</sub>  | <b>D</b> C <sub>5</sub> H <sub>12</sub> |
| <b>E</b> C <sub>6</sub> H <sub>14</sub> |                                         |

**17** Which one of the following compounds does not exhibit geometrical isomerism (i.e. form *cis* and *trans* isomers)?

- A** CH<sub>3</sub>CH<sub>2</sub>CH=CHCH<sub>2</sub>CH<sub>3</sub>
- B** Br<sub>2</sub>C=CHBr
- C** CH<sub>3</sub>CH=CHBr
- D** CH<sub>3</sub>CH=CHCH<sub>2</sub>CH<sub>3</sub>

**18** Consider the following structures:



Which are isomers?

- A** (1) and (3) only
- B** (1), (2) and (3) only
- C** (2), (3) and (4) only
- D** (1) and (2) only
- E** (1), (2), (3) and (4).

**19** Which one of the following compounds readily undergoes an addition reaction?

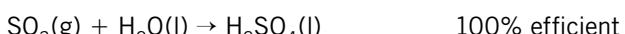
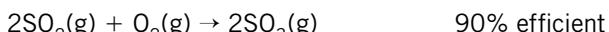
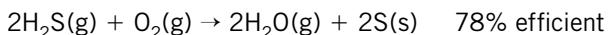
- A** propene
- B** ethane
- C** benzene
- D** cyclopentane
- E** 3-methylhexane

**20** Which of the following reactions are substitution reactions?

- |                                                                                                                                                                                                                                                                                                                                    |                                                                |                                       |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------|---------------------------------------|
| <b>I</b> CH <sub>4</sub> + I <sub>2</sub> → CH <sub>3</sub> I + HI<br><b>II</b> HC≡CH + HBr → CH <sub>2</sub> =CHBr<br><b>III</b> CH <sub>2</sub> =CH <sub>2</sub> + Br <sub>2</sub> → CH <sub>2</sub> Br—CH <sub>2</sub> Br<br><b>IV</b> C <sub>6</sub> H <sub>6</sub> + Cl <sub>2</sub> → C <sub>6</sub> H <sub>5</sub> Cl + HCl | <b>A</b> I and II<br><b>C</b> II and III<br><b>E</b> I and IV. | <b>B</b> II and IV<br><b>D</b> I only |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------|---------------------------------------|

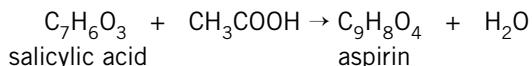
## \*PART B: SHORT-ANSWER QUESTIONS

**1** In some natural gas supplies, an impurity is hydrogen sulfide. This impurity can be converted into the commercially useful sulfuric acid according to the following steps:



What mass of  $\text{H}_2\text{S}$  is required to prepare 100 kg of sulfuric acid?

**2** Aspirin can be made by treating salicylic acid with acetic acid in the presence of a small amount of concentrated sulfuric acid.



A chemist combines 200 g of salicylic acid with 100 g of acetic acid in order to produce aspirin. Assuming that the reaction is 100% efficient, what mass of aspirin will be obtained?

**3** Consider  $0.100 \text{ mol L}^{-1}$  solutions of the following; ammonia, sulfuric acid, barium hydroxide and acetic acid.

a Certain combinations, in the correct stoichiometric ratio for complete reaction, of these solutions are made. Place the resulting solutions in increasing order of conductivity and explain your choice.

ammonia + acetic acid

ammonia + sulfuric acid

barium hydroxide + sulfuric acid

b Which of the original four solutions would have the highest pH? Explain your answer. (Refer to all four substances in your response.)

**4** Write ionic equations for the following reactions:

a Marble chips (calcium carbonate) are added to excess dilute nitric acid.

b Aluminium nitrate solution is added to a solution of lithium carbonate.

c Dilute sulfuric acid is added to solid magnesium oxide.

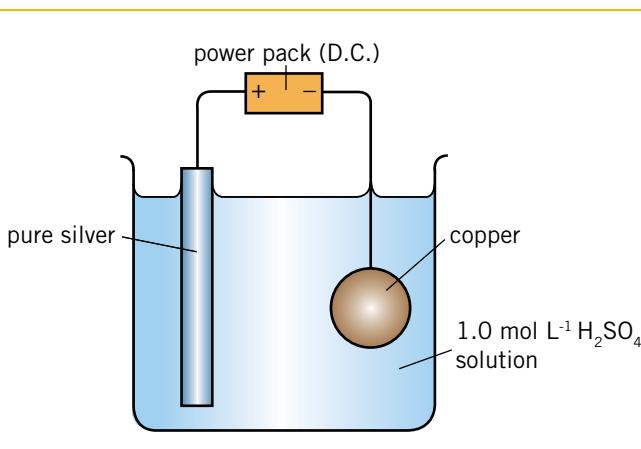
d Sodium carbonate solution is added to solid calcium iodide.

e Lead nitrate solution is acidified with dilute sulfuric acid.

**f** Dilute sulfuric acid is added to copper(II) hydroxide.

**g** Dilute hydrochloric acid is added to a solution of silver nitrate.

**5** A student wanting to electroplate a copper disc with silver makes the disk the negative electrode in an electrolytic cell. The anode is a piece of 99.9% silver and the two metals are placed in a solution of sulfuric acid as shown.



**a** When the power pack is turned on and a steady current is flowing the student notes that the change at the negative electrode is not what she expected. What is observed forming at the negative electrode when the electrolysis is first started? Explain your answer.

**b** If the experiment were left for some time what will eventually form at the negative electrode? Write an equation for this observation.

**c** Identify which metal is the anode and which forms the cathode.

**d** What is the equation for the reaction at the anode? Is this an oxidation or a reduction reaction?

**e** A friend of the student suggests that she repeat the experiment using hydrochloric acid rather than sulfuric acid. Explain why you regard this suggestion as reasonable or otherwise.

**6** Identify the following as true or false. In each case explain how you reached your answer.

Comparing 1 L of  $0.1 \text{ mol L}^{-1}$  acetic acid and 1 L of  $0.1 \text{ mol L}^{-1}$  hydrochloric acid:

**a** Both solutions would have the same pH.

**b** The acetic acid solution would contain fewer hydrogen ions than the hydrochloric acid solution.

**c** Both solutions could be prepared by dissolving 0.1 mole of the respective acid in 1 L of solution.

- d** The pH of the acetic acid solution would be greater than 7 and the pH of the hydrochloric acid solution would be less than 7.
- e** The hydrochloric acid would be a better conductor of electricity than the acetic acid.
- f** Both solutions contain the same mass of acid.
- g** Both solutions would require the same volume of  $0.1 \text{ mol L}^{-1}$  sodium hydroxide for complete reaction.

**7** Outline a chemical test that would distinguish between cyclohexane and cyclohexene. What observations would be made? Write equations for any reactions that occur.

**8** Write an equation for each of the following reactions:

- a** Methane is reacted with excess chlorine in the presence of UV light.
- b** Propene is reacted with hydrogen gas, in the presence of a catalyst.
- c** *Cis*-but-2-ene is reacted with bromine gas.
- d** Cyclopropane is burnt in excess air.

**9** Draw and name the following:

- a** two cycloalkanes containing four carbon atoms per molecule
- b** an aromatic hydrocarbon containing seven carbon atoms per molecule
- c** a pair of geometrical isomers containing five carbon atoms per molecule.

**10** A sample of a hydrocarbon with a mass of 5.94 g is burned and produces 18.64 g of carbon dioxide. Further analysis revealed that a molecule of the substance contained four carbon atoms. However, this analysis also revealed that the substance was in fact a mixture of three different compounds, A, B and C.

A and B both reacted with bromine at room temperature and produced the same compound. C did not react with bromine under the conditions used in the experiment. Determine the empirical formula of the hydrocarbon and then identify, providing reasoning, the possible identity of compounds A, B and C.

**11** Western Australia is a major producer of titanium dioxide, the most widely used white pigment for paints, coatings, paper, fibres, foods and cosmetics. More recently, interest has focused on the use of titanium dioxide in the solar-powered splitting of water into hydrogen and oxygen.

One of the ores mined in Western Australia is ilmenite,  $\text{FeTiO}_3$ . This can be considered as an ore based on the combination of  $\text{TiO}_2$  with  $\text{FeO}$ . The separation of titanium dioxide from ilmenite takes place via the Becher process and involves the smelting of ilmenite with coal to produce iron. The mixture of iron and titanium dioxide is then aerated to convert the iron to iron(III) oxide. Finally, the mixture of titanium dioxide and iron oxide is combined with dilute sulfuric acid to dissolve the iron and leave the enriched titanium dioxide.

- a** Assume that the coal used in the first stage of the Becher process is carbon and that the chemistry associated with the reduction of iron ore to iron in the blast furnace is also the chemistry involved in this smelting process. Write the three equations that summarise the conversion of ilmenite to soluble iron(III) sulfate and titanium oxide.
- b** What volume of  $2.00 \text{ mol L}^{-1}$  sulfuric acid is required to react with the iron(III) oxide produced from the smelting and aeration of 100 tonnes of an ore that is 98.0% by mass of ilmenite?

The production of titanium metal involves the conversion of titanium oxide to the volatile titanium tetrachloride which is then heated in the presence of magnesium metal to form titanium.

- c** Write the balanced equation for the conversion of titanium tetrachloride to titanium by magnesium. What general type of reaction is this? Explain how you reached this conclusion.
- d** What mass of magnesium metal is required to convert 150 kg of titanium chloride gas to titanium?

**12** Limestone caves are produced as a result of the reaction of underground limestone deposits with a solution of a dilute acid.

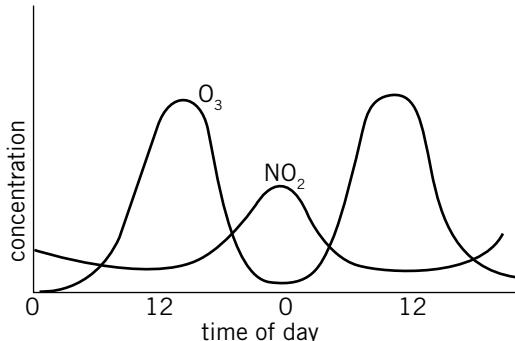
- a** Write the equation for the formation of the cave from the original limestone rock.

Increased atmospheric pollution results in the formation of acid rain. Such rain is regarded as a threat to limestone caves.

- b** What are the major acids present in acid rain? How did they get into the atmosphere?
- c** Given that the formation of the caves in the first place involved the reaction of limestone with a dilute acid solution, why is it that there is so much concern about acid rain and limestone caves?
- d** Water supplies are usually hard in regions where there are limestone caves. Why is this so?

- e Is the water in a region where there are limestone caves more likely to be permanently hard or temporarily hard? What is the difference between these two forms of hardness?
- f Water that exhibits temporary hardness is also slightly basic. Write an equation to explain why the pH of this water is greater than 7.

13 Environmental organisations in large cities regularly monitor the atmosphere to determine the concentration of pollutants. The graph below shows how the concentration of ozone,  $O_3$  and nitrogen dioxide,  $NO_2$ , changes with time over a two-day period in a particular city.



- a Describe how the concentrations of ozone and nitrogen dioxide change as a function of the time of day.  
The reactions that take place in the atmosphere that involve  $O_3$  and  $NO_2$  are summarised below.  
 $N_2 + O_2 \rightleftharpoons 2NO$   
 $2NO + O_2 \rightleftharpoons 2NO_2$   
 $UV\ light$   
 $NO_2 + O_2 \rightleftharpoons NO + O_3$
- b What are the oxidation numbers of oxygen and nitrogen in each of the molecules depicted above?
- c What is the most likely source of the nitrogen dioxide in a large city?
- d Why do the ozone levels peak around midday?
- e Why do the nitrogen dioxide levels not peak until the evening?

# APPENDICES

## Appendix 1 Commonly used physical constants and units

### Physical constants

The Avogadro Constant,  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Magnitude of the electronic charge,  
 $q_e = 1.602 \times 10^{-19} \text{ coulomb (C)}$

Magnitude of the charge carried by one mole of electrons = 1 faraday ( $F$ ) =  $9.649 \times 10^4 \text{ C}$

Universal Gas Constant,  $R = 8.315 \text{ J K}^{-1} \text{ mol}^{-1}$

Volume of 1.000 mol of an ideal gas at  $0.0^\circ\text{C}$  and 101.3 kPa is 22.41 L (STP is  $0.0^\circ\text{C}$  and 101.3 kPa)

### Commonly used units:

|               |                                                                                                                                                      |
|---------------|------------------------------------------------------------------------------------------------------------------------------------------------------|
| Volume        | litres (L), or millilitres (mL)<br>( $1 \text{ cm}^3 = 1 \text{ mL}$ ,<br>$1 \text{ dm}^3 = 1 \text{ L} = 1000 \text{ mL}$ )                         |
| Temperature   | degrees Celsius ( $^\circ\text{C}$ ) or Kelvin (K).<br>( $0.0^\circ\text{C} = 273.1 \text{ K}$ )                                                     |
| Energy change | kilojoule (kJ)                                                                                                                                       |
| Pressure      | kilopascal (kPa), atmospheres (atm),<br>or in millimetres of mercury (mmHg)<br>( $1.000 \text{ atm} = 101.3 \text{ kPa} =$<br>$760.0 \text{ mmHg}$ ) |

### Symbols for units

|                |                  |
|----------------|------------------|
| ampere         | A                |
| coulomb        | C                |
| degree Celsius | $^\circ\text{C}$ |
| gram           | g                |
| joule          | J                |
| kelvin         | K                |
| litre          | L                |
| metre          | m                |
| mole           | mol              |
| pascal         | Pa               |
| second         | s                |

### Prefixes

| Multiple   | Prefix | Symbol |
|------------|--------|--------|
| $10^6$     | mega   | M      |
| $10^3$     | kilo   | k      |
| $10^{-1}$  | deci   | d      |
| $10^{-2}$  | centi  | c      |
| $10^{-3}$  | milli  | m      |
| $10^{-6}$  | micro  | $\mu$  |
| $10^{-9}$  | nano   | n      |
| $10^{-12}$ | pico   | p      |

## Appendix 2 Exponential notation and significant figures

### Exponential or scientific notation

Very large and very small numbers are often written in an abbreviated form using powers of ten. Numbers represented this way are said to be expressed in scientific or exponential notation. Using this system the numbers are written as a number between 1 and 10 multiplied by the appropriate power of 10.

As it is necessary to deal with both very large and very small numbers it is often convenient to write them in scientific or exponential notation. For example:

$$5\ 430\ 000 = 5.43 \times 1\ 000\ 000 = 5.43 \times 10^6$$

$$0.000101 = 1.01 \times 0.0001 = 1.01 \times 10^{-4}$$

### Significant figures

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

The following points need to be considered when determining the number of significant figures quoted in a measurement:

- non-zero digits always count as significant figures, for example, 54.7 g is quoted to 3 significant figures
- zeros that precede non-zero digits do not count as significant figures, for example, 0.0016 mL is quoted to 2 significant figures
- zeros between non-zero digits always count as significant figures, for example, 38.02 g is quoted to 4 significant figures
- zeros at the end of a number that contains a decimal point are always significant, for example, 4.2100 mL is quoted to 5 significant figures
- zeros at the end of a whole number may or may not be significant, for example, 3400 L may represent a number expressed to 2, 3 or 4 significant figures
- exact numbers have an infinite number of significant figures
- it is more easy to show the number of significant figures if the number is expressed in exponential notation, for example, if the measurement 3400 L was expressed as  $3.400 \times 10^3 \text{ L}$  then it was quoted to 4 significant figures

For example:

3.890 g is quoted to 4 significant figures  
 12.089 mL is quoted to 5 significant figures  
 0.025 mg is quoted to 2 significant figures  
 $6.000 \times 10^{-5}$  kg is quoted to 4 significant figures  
 300 g is quoted to 1, 2 or 3 significant figures (it is not known whether the zeros are accurate measurements or used to show the value of the number i.e. hundreds)

### Rounding numbers

At times, a number must be rounded off to a certain number of significant figures. In this procedure, the last digit written should give the best approximation of the number as it was before rounding.

If the number before rounding is as close to one number as another, the one ending with an even digit is chosen, zero being regarded as even.

For example: 0.3826 g rounded off to three significant figures is 0.383 g

12.45 g rounded off to three significant figures is 12.4 g

12.451 g rounded off to three significant figures is 12.5 g

12.442 g rounded off to three significant figures is 12.4 g

1209.75 g rounded off to three significant figures is  $1.21 \times 10^3$  g

### Significant figures in calculations

In all calculations involving measurements, the number of significant figures in the original measurements must be taken into consideration when deciding the number of significant figures that should be quoted in the final answer.

When adding or subtracting numbers, the answer should be quoted to the same number of decimal places as the least accurate measurement used in the calculation.

For example: for the sum (0.34 cm + 21.6 cm), the least accurate number is 21.6, and it is quoted to only one decimal place. Consequently, the answer must be rounded off to one decimal place, to give 21.9 cm and not 21.94 cm.

When multiplying or dividing numbers, the answer should be quoted to the same number of significant figures as the measurement with the smallest number of significant figures.

For example: for the calculation ( $0.23 \text{ cm} \times 5.715 \text{ cm}$ ), 0.23 cm is quoted to the smallest number of significant figures, and so the answer must be rounded off to two significant figures to give 1.3 cm<sup>2</sup>.

## Appendix 3 Table of relative atomic masses (Atomic weights)

| Name        | Symbol | Atomic number | Relative atomic mass |
|-------------|--------|---------------|----------------------|
| Actinium    | Ac     | 89            | (227)                |
| Aluminium   | Al     | 13            | 26.98                |
| Americium   | Am     | 95            | (243)                |
| Antimony    | Sb     | 51            | 121.8                |
| Argon       | Ar     | 18            | 39.95                |
| Arsenic     | As     | 33            | 74.92                |
| Astatine    | At     | 85            | (210)                |
| Barium      | Ba     | 56            | 137.3                |
| Berkelium   | Bk     | 97            | (247)                |
| Beryllium   | Be     | 4             | 9.012                |
| Bismuth     | Bi     | 83            | 209.0                |
| Boron       | B      | 5             | 10.81                |
| Bromine     | Br     | 35            | 79.90                |
| Cadmium     | Cd     | 48            | 112.4                |
| Caesium     | Cs     | 55            | 132.9                |
| Calcium     | Ca     | 20            | 40.08                |
| Californium | Cf     | 98            | (251)                |
| Carbon      | C      | 6             | 12.01                |
| Cerium      | Ce     | 58            | 140.1                |
| Chlorine    | Cl     | 17            | 35.45                |
| Chromium    | Cr     | 24            | 52.00                |
| Cobalt      | Co     | 27            | 58.93                |
| Copper      | Cu     | 29            | 63.55                |
| Curium      | Cm     | 96            | (247)                |
| Dysprosium  | Dy     | 66            | 162.5                |
| Einsteinium | Es     | 99            | (252)                |
| Erbium      | Er     | 68            | 167.3                |
| Europium    | Eu     | 63            | 152.0                |
| Fermium     | Fm     | 100           | (257)                |
| Fluorine    | F      | 9             | 19.00                |
| Francium    | Fr     | 87            | (223)                |
| Gadolinium  | Gd     | 64            | 157.2                |
| Gallium     | Ga     | 31            | 69.72                |
| Germanium   | Ge     | 32            | 72.61                |
| Gold        | Au     | 79            | 197.0                |
| Hafnium     | Hf     | 72            | 178.5                |
| Helium      | He     | 2             | 4.003                |
| Holmium     | Ho     | 67            | 164.9                |
| Hydrogen    | H      | 1             | 1.008                |
| Indium      | In     | 49            | 114.8                |
| Iodine      | I      | 53            | 126.9                |

|              |    |     |       |           |    |    |       |
|--------------|----|-----|-------|-----------|----|----|-------|
| Iridium      | Ir | 77  | 192.2 | Tellurium | Te | 52 | 127.6 |
| Iron         | Fe | 26  | 55.85 | Terbium   | Tb | 65 | 158.9 |
| Krypton      | Kr | 36  | 83.80 | Thallium  | Tl | 81 | 204.4 |
| Lanthanum    | La | 57  | 138.9 | Thorium   | Th | 90 | 232.0 |
| Lawrencium   | Lr | 103 | (260) | Thulium   | Tm | 69 | 168.9 |
| Lead         | Pb | 82  | 207.2 | Tin       | Sn | 50 | 118.7 |
| Lithium      | Li | 3   | 6.941 | Titanium  | Ti | 22 | 47.88 |
| Lutetium     | Lu | 71  | 175.0 | Tungsten  | W  | 74 | 183.8 |
| Magnesium    | Mg | 12  | 24.31 | Uranium   | U  | 92 | 238.0 |
| Manganese    | Mn | 25  | 54.94 | Vanadium  | V  | 23 | 50.94 |
| Mendelevium  | Md | 101 | (258) | Xenon     | Xe | 54 | 131.3 |
| Mercury      | Hg | 80  | 200.6 | Ytterbium | Yb | 70 | 173.0 |
| Molybdenum   | Mo | 42  | 95.94 | Yttrium   | Y  | 39 | 88.91 |
| Neodymium    | Nd | 60  | 144.2 | Zinc      | Zn | 30 | 65.38 |
| Neon         | Ne | 10  | 20.18 | Zirconium | Zr | 40 | 91.22 |
| Neptunium    | Np | 93  | (237) |           |    |    |       |
| Nickel       | Ni | 28  | 58.69 |           |    |    |       |
| Niobium      | Nb | 41  | 92.91 |           |    |    |       |
| Nitrogen     | N  | 7   | 14.01 |           |    |    |       |
| Nobelium     | No | 102 | (259) |           |    |    |       |
| Osmium       | Os | 76  | 190.2 |           |    |    |       |
| Oxygen       | O  | 8   | 16.00 |           |    |    |       |
| Palladium    | Pd | 46  | 106.4 |           |    |    |       |
| Phosphorus   | P  | 15  | 30.97 |           |    |    |       |
| Platinum     | Pt | 78  | 195.1 |           |    |    |       |
| Plutonium    | Pu | 94  | (244) |           |    |    |       |
| Polonium     | Po | 84  | (209) |           |    |    |       |
| Potassium    | K  | 19  | 39.10 |           |    |    |       |
| Praseodymium | Pr | 59  | 140.9 |           |    |    |       |
| Promethium   | Pm | 61  | (145) |           |    |    |       |
| Protactinium | Pa | 91  | 231.0 |           |    |    |       |
| Radium       | Ra | 88  | 226.0 |           |    |    |       |
| Radon        | Rn | 86  | (222) |           |    |    |       |
| Rhenium      | Re | 75  | 186.2 |           |    |    |       |
| Rhodium      | Rh | 45  | 102.9 |           |    |    |       |
| Rubidium     | Rb | 37  | 85.47 |           |    |    |       |
| Ruthenium    | Ru | 44  | 101.1 |           |    |    |       |
| Samarium     | Sm | 62  | 150.4 |           |    |    |       |
| Scandium     | Sc | 21  | 44.96 |           |    |    |       |
| Selenium     | Se | 34  | 78.96 |           |    |    |       |
| Silicon      | Si | 14  | 28.09 |           |    |    |       |
| Silver       | Ag | 47  | 107.9 |           |    |    |       |
| Sodium       | Na | 11  | 22.99 |           |    |    |       |
| Strontium    | Sr | 38  | 87.62 |           |    |    |       |
| Sulfur       | S  | 16  | 32.06 |           |    |    |       |
| Tantalum     | Ta | 73  | 180.9 |           |    |    |       |
| Technetium   | Tc | 43  | (98)  |           |    |    |       |

## Appendix 4 Standard Reduction Potentials at 25°C

| <b>Half-reaction</b>                                                                    | <b><math>E^\circ</math>(volts)</b> |
|-----------------------------------------------------------------------------------------|------------------------------------|
| $F_2(g) + 2 e^- \rightleftharpoons 2 F^-(aq)$                                           | + 2.87                             |
| $H_2O_2(aq) + 2 H^+(aq) + 2 e^- \rightleftharpoons 2 H_2O(l)$                           | + 1.78                             |
| $PbO_2(s) + SO_4^{2-}(aq) + 4 H^+(aq) + 2 e^- \rightleftharpoons PbSO_4(s) + 2 H_2O(l)$ | + 1.69                             |
| $2 HClO(aq) + 2 H^+(aq) + 2 e^- \rightleftharpoons Cl_2(g) + 2 H_2O(l)$                 | + 1.61                             |
| $MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \rightleftharpoons Mn^{2+}(aq) + 4 H_2O(l)$            | + 1.51                             |
| $Au^{3+}(aq) + 3 e^- \rightleftharpoons Au(s)$                                          | + 1.50                             |
| $HClO(aq) + H^+(aq) + 2 e^- \rightleftharpoons Cl^-(aq) + H_2O(l)$                      | + 1.48                             |
| $PbO_2(s) + 4 H^+(aq) + 2 e^- \rightleftharpoons Pb^{2+}(aq) + 2 H_2O(l)$               | + 1.46                             |
| $Cl_2(g) + 2 e^- \rightleftharpoons 2 Cl^-(aq)$                                         | + 1.36                             |
| $Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^- \rightleftharpoons 2 Cr^{3+}(aq) + 7 H_2O(l)$    | + 1.23                             |
| $O_2(g) + 4 H^+(aq) + 4 e^- \rightleftharpoons 2 H_2O(l)$                               | + 1.23                             |
| $Br_2(l) + 2 e^- \rightleftharpoons 2 Br^-(aq)$                                         | + 1.07                             |
| $NO_3^-(aq) + 4 H^+(aq) + 3 e^- \rightleftharpoons NO(g) + 2 H_2O(l)$                   | + 0.96                             |
| $NO_3^-(aq) + 2 H^+(aq) + e^- \rightleftharpoons NO_2(g) + H_2O(l)$                     | + 0.80                             |
| $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$                                               | + 0.80                             |
| $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$                                      | + 0.77                             |
| $O_2(g) + 2 H^+(aq) + 2 e^- \rightleftharpoons H_2O_2(aq)$                              | + 0.68                             |
| $I_2(s) + 2 e^- \rightleftharpoons 2 I^-(aq)$                                           | + 0.54                             |
| $O_2(g) + 2 H_2O(l) + 4 e^- \rightleftharpoons 4 OH^-(aq)$                              | + 0.40                             |
| $Cu^{2+}(aq) + 2 e^- \rightleftharpoons Cu(s)$                                          | + 0.34                             |
| $Sn^{4+}(aq) + 2 e^- \rightleftharpoons Sn^{2+}(aq)$                                    | + 0.15                             |
| $S(s) + 2 H^+(aq) + 2 e^- \rightleftharpoons H_2S(aq)$                                  | + 0.14                             |
| $2 H^+(aq) + 2 e^- \rightleftharpoons H_2(g)$                                           | 0 exactly                          |
| $Pb^{2+}(aq) + 2 e^- \rightleftharpoons Pb(s)$                                          | - 0.13                             |
| $Sn^{2+}(aq) + 2 e^- \rightleftharpoons Sn(s)$                                          | - 0.14                             |
| $Ni^{2+}(aq) + 2 e^- \rightleftharpoons Ni(s)$                                          | - 0.26                             |
| $Co^{2+}(aq) + 2 e^- \rightleftharpoons Co(s)$                                          | - 0.28                             |
| $PbSO_4(s) + 2 e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$                            | - 0.36                             |
| $Cd^{2+}(aq) + 2 e^- \rightleftharpoons Cd(s)$                                          | - 0.40                             |
| $2 CO_2(g) + 2 H^+(aq) + 2 e^- \rightleftharpoons HOOCCOOH(aq)$                         | - 0.43                             |
| $Fe^{2+}(aq) + 2 e^- \rightleftharpoons Fe(s)$                                          | - 0.44                             |
| $Au(CN)_2^-(aq) + e^- \rightleftharpoons Au(s) + 2 CN^-(aq)$                            | - 0.60                             |
| $Cr^{3+}(aq) + 3 e^- \rightleftharpoons Cr(s)$                                          | - 0.73                             |
| $Zn^{2+}(aq) + 2 e^- \rightleftharpoons Zn(s)$                                          | - 0.76                             |
| $2 H_2O(l) + 2 e^- \rightleftharpoons H_2(g) + 2 OH^-(aq)$                              | - 0.83                             |
| $Mn^{2+}(aq) + 2 e^- \rightleftharpoons Mn(s)$                                          | - 1.18                             |
| $Al^{3+}(aq) + 3 e^- \rightleftharpoons Al(s)$                                          | - 1.66                             |
| $Mg^{2+}(aq) + 2 e^- \rightleftharpoons Mg(s)$                                          | - 2.37                             |
| $Na^+(aq) + e^- \rightleftharpoons Na(s)$                                               | - 2.71                             |
| $Ca^{2+}(aq) + 2 e^- \rightleftharpoons Ca(s)$                                          | - 2.76                             |
| $Sr^{2+}(aq) + 2 e^- \rightleftharpoons Sr(s)$                                          | - 2.89                             |
| $Ba^{2+}(aq) + 2 e^- \rightleftharpoons Ba(s)$                                          | - 2.91                             |
| $K^+(aq) + e^- \rightleftharpoons K(s)$                                                 | - 2.93                             |

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