

# Chemistry for WWA 2

Stage 3:  
Units 3A and 3B

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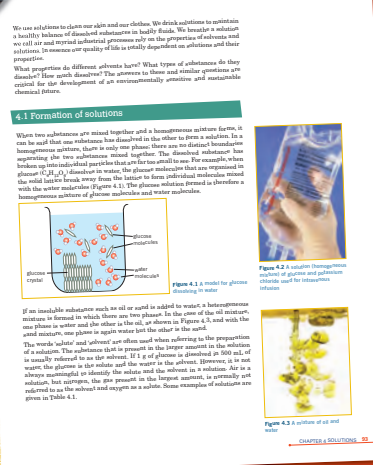
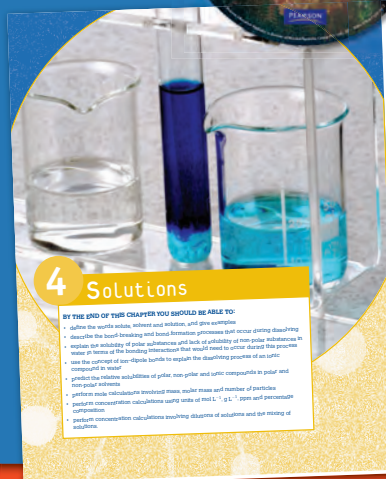
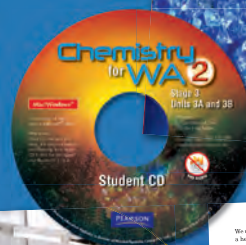
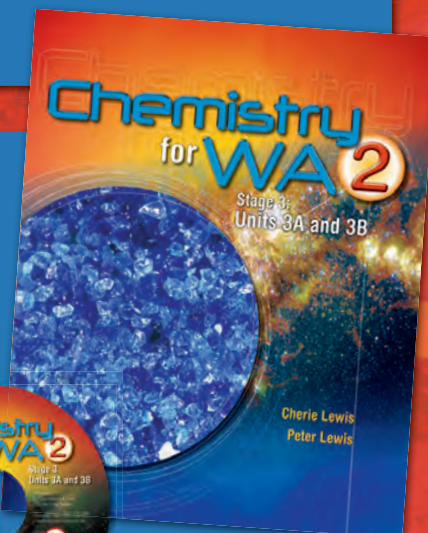
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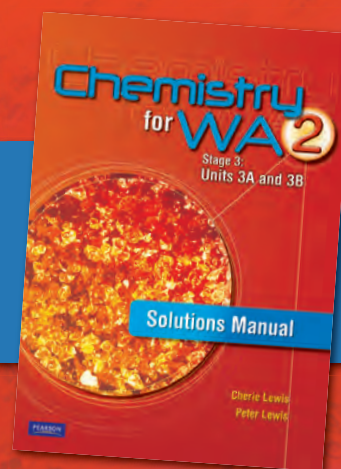
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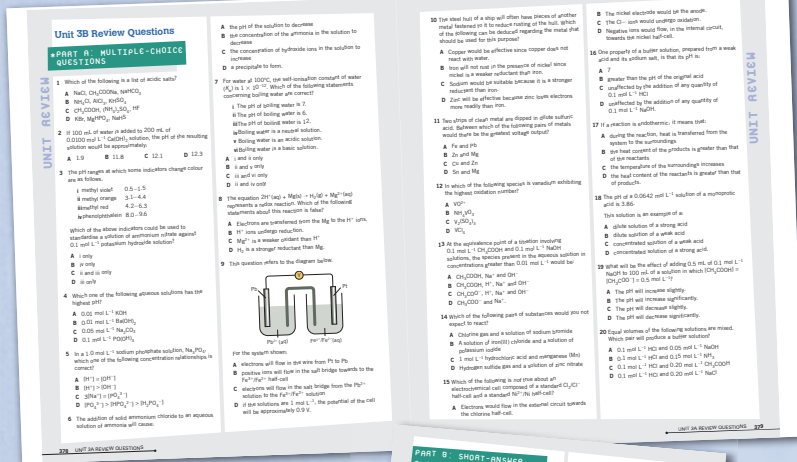
To help students consolidate knowledge and encourage independent learning, each chapter ends with a comprehensive review including:

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- **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.

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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 2 Student Book*.

## UNIT 3A

	1	2	3	4	5	6	7	8	9	10	11	12	13
<b>Macroscopic properties of matter</b>													
Interpreting observations					◆	◆		◆					
Prediction of precipitation reactions					◆			◆					
Concentration calculations, dilution of solutions				◆	◆			◆					
Dilution of solutions & calculations				◆	◆			◆					
<b>Atomic structure and bonding</b>													
Sub-atomic structure of atoms	◆												
Shell model of electron arrangement in atoms	◆												
Trends in ionisation energy, atomic radius and electronegativity	◆	◆	◆										
Physical properties and the structure of ionic, metallic, covalent network and covalent molecular substances		◆	◆	◆									
Shape of molecules and polyatomic ions		◆	◆										
Polarity of molecules			◆										
Comparison of intermolecular and intramolecular forces		◆	◆										
Dispersion forces, dipole-dipole attractions, hydrogen bonds			◆										
Ion-dipole interactions				◆									
Trends in melting and boiling points of molecular substances, including hydrides			◆	◆							◆	◆	
Explanation of solution process in water				◆							◆	◆	
<b>Chemical reactions</b>													
Ionic equations				◆	◆	◆	◆	◆					
Celsius and kelvin temperature scales					◆								
Calculations involving mass, mole, concentration				◆	◆			◆					
$PV = nRT$					◆								
Percentage purity, percentage yield					◆								
Limiting reagent problems					◆								
Rates of reactions, collision theory						◆							
Dynamic chemical equilibrium						◆							
Equilibrium law expressions						◆	◆						
Le Châtelier's principle						◆	◆						
<b>Applied chemistry</b>													
Application of chemical equilibrium in industry						◆	◆						
Investigate real world problems in a laboratory setting				◆	◆			◆					
Biological, environmental and industrial processes						◆							◆

## UNIT 3B

	1	2	3	4	5	6	7	8	9	10	11	12	13
<b>Chemical reactions</b>													
Equations for neutralisation, hydrolysis of salts, redox							♦	♦	♦			♦	
Volumetric analysis using acid–base or redox contexts								♦					
Primary standards and standard solutions								♦					
Indicators, end point and equivalence point								♦					
Empirical and molecular formulas												♦	
<b>Acids and bases in aqueous solutions</b>													
Self-ionisation of water, $K_w$							♦						
Arrhenius and Brønsted–Lowry models of acids and bases							♦						
Calculation of pH							♦						
Hydrolysis of acidic and basic salts							♦						
Buffer solutions							♦						
<b>Oxidation and reduction</b>													
Use of standard reductions potentials to predict reaction tendency									♦	♦			
Oxidation numbers									♦	♦			
Common oxidising and reducing agents									♦				
Electrochemical (galvanic) cell									♦	♦			
Hydrogen half-cell									♦				
<b>Organic chemistry</b>													
Reactions of hydrocarbons											♦	♦	
Structural isomers of alkanes and alkenes, geometric isomers of alkenes											♦		
Functional groups & alcohols, aldehydes, ketones, carboxylic acids and esters											♦	♦	♦
Alcohols & structures, properties and reactions			♦	♦	♦							♦	♦
Oxidation of alcohols to form aldehydes, ketones, carboxylic acids												♦	
Amines – structure												♦	
$\alpha$ -Amino acids – structural formula												♦	
<b>Applied chemistry</b>													
Soaps, detergents, amino acids and <i>trans</i> -fatty acids												♦	♦
Polymerisation – polypeptides, silicones and plastics													♦
Investigate real world problems in a laboratory setting				♦	♦			♦				♦	
Commercial electrochemical cells										♦			
Corrosion										♦			
Biological, environmental and industrial processes						♦				♦			♦

# 1

## Atoms and the periodic table

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

- describe the structure of atoms in terms of protons, neutrons and electrons
- relate the atomic number and mass number to the number of protons, electrons and neutrons in neutral atoms and ions
- describe the electronic structure of the atom in terms of electron shells
- explain how ionisation energy data can be used as evidence of electron shells
- outline the broad structure of the periodic table and determine the group and period of a particular element
- describe and explain the change in atomic radius, ionisation energy and electronegativity down a group and across a period in the periodic table.

Over the past 100 years, the way people live has been changed forever through chemistry. Chemistry has played a vital role in the development and production of items and materials that affect our lives in major ways, such as computers, medicines and plastics, to seemingly insignificant items such as sunglasses, swimming pool chemicals and chewing gum.



The contribution of the chemical industry to society is not just in the products it develops and produces, but also in the range and extent of the employment opportunities it presents. In some respects, the wealth of a country is related to the extent of its chemical industry. The role of chemistry and chemicals in our lives and lifestyles cannot be underestimated. The proposal that chemistry has made a critical difference to our standard of living is difficult to dismiss. Some argue that the difference enhances our lives, while others contend that chemicals endanger our quality of life.

The challenge for the chemical industry is to continue to economically provide the materials and items that will benefit society but without causing damaging effects to life and the environment both now and in the future. In other words, the challenge is to create a chemical industry for which sustainable development is its key objective.

What does the term ‘sustainable development’ mean? According to a United Nations Commission on Environment and Development in 1987, sustainable development can be defined as progress that meets ‘the needs of the present without compromising the ability of future generations to meet their own needs’.

One direction taken by the chemical industry to help create a sustainable future is through the development of a new ‘genre’ of chemistry, called green chemistry. Conceived by the US Environmental Protection Agency (EPA) in the early 1990s, the term ‘green chemistry’ means ‘to promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture and use of chemical products’.

An understanding of chemical models and principles, such as atomic structure, bonding, reactions, quantitative methods, reaction rates and equilibrium, is a prerequisite for people wanting to be involved, either actively or by having informed opinions, in the establishment of a sustainable future.

## 1.1 Atomic structure

The fundamental building block of matter is the atom. Atoms are thought to be made up of protons, neutrons and electrons. The position of these subatomic particles and their relative masses and charges are summarised in Table 1.1.

**TABLE 1.1 PROTONS, NEUTRONS AND ELECTRONS**

Subatomic particle	Position in the atom	Relative charge	Relative mass	Actual mass of particle (g)
Proton	In the nucleus of the atom	+1	1	$1.6726 \times 10^{-27}$
Neutron	In the nucleus of the atom	0	1	$1.6749 \times 10^{-27}$
Electron	Moving rapidly around the nucleus	-1	$\frac{1}{1836}$	$9.1094 \times 10^{-31}$

The atom is therefore pictured as being composed of the protons and neutrons in the nucleus with electrons moving rapidly in regions of space around the nucleus, as shown in Figure 1.1.

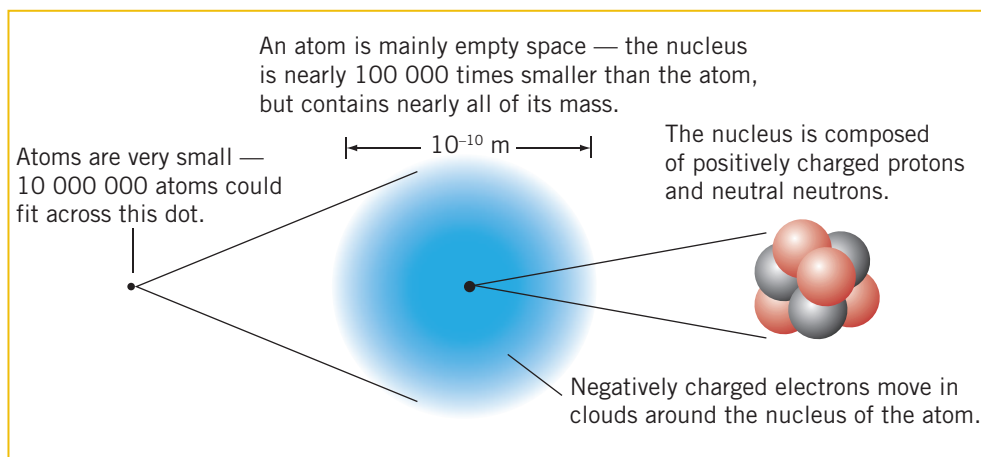


Figure 1.1 The structure of an atom

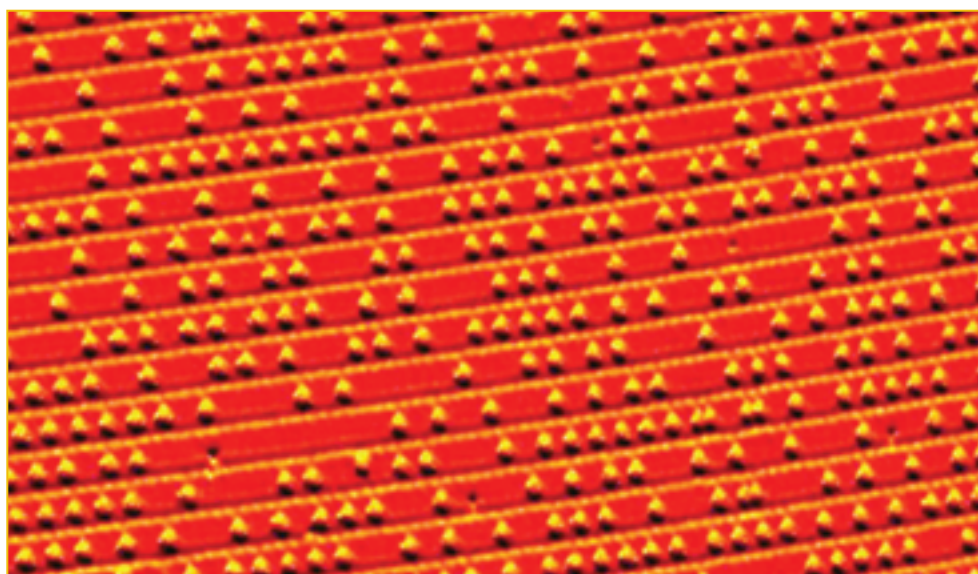


Figure 1.2 Coloured scanning tunnelling microscope image of the surface of a storage medium that uses single atoms to represent data. The yellow dots are individual silicon atoms. These atoms hold data in the same way as the pits on a CD-ROM disc.

The nucleus contains most of the mass of the atom, yet this mass is confined to a very small volume. The diameter of a typical atom is about 100 000 times larger than the diameter of its nucleus. As a consequence, most of an atom is empty space.

All the atoms of a particular element have the same number of protons. Atoms of different elements contain a different number of protons. For example, all carbon atoms have 6 protons and all iron atoms have 26 protons. The number of protons in each atom of an element is called the atomic number ( $Z$ ). The atomic number of carbon is 6 and the atomic number of iron is 26. The atomic number of the atoms for each of the known elements is shown in the periodic table in Figure 1.8.

Atoms of the same element do not necessarily have the same number of neutrons. These atoms of the same element with a different number of neutrons are called

isotopes. For example, carbon atoms with 6 neutrons and carbon atoms with 7 neutrons are isotopes of carbon. The number of protons and neutrons in the nucleus of an atom is called the mass number ( $A$ ). The two isotopes of carbon mentioned earlier would have mass numbers of  $(6 + 6) = 12$  and  $(6 + 7) = 13$ , respectively.

The following formula is sometimes used to represent a particular isotope:



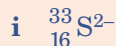
where  $A$  is the mass number,  $Z$  is the atomic number and  $X$  is the symbol of the particular isotope. The two carbon isotopes previously referred to can be represented as  ${}^{12}_6\text{C}$  and  ${}^{13}_6\text{C}$ .

In a neutral atom, the number of protons equals the number of electrons. The number of protons can be determined from the atomic number of the atom. Neutral carbon atoms, for example, have 6 protons and 6 electrons. If an atom gains or loses one or more electrons, it becomes positively or negatively charged. Charged atoms are called ions. In the formula of an ion, the charge on the ion is written as a superscript after the symbol of the atom. Magnesium ions have a formula of  $\text{Mg}^{2+}$ , which means they have 2 more protons than electrons; that is, 12 protons and 10 electrons. Nitride ions, with a formula of  $\text{N}^{3-}$ , have 7 protons and 10 electrons.



### → Example 1.1

**a** How many protons, neutrons and electrons are in the following species?



**ii**  $\text{Al}^{3+}$  with a mass number of 27

**b** Give the formula, similar to that shown in part **a i**, for an ion with 28 protons, 30 neutrons and 26 electrons.

### → Solution

**a i** Protons: the atomic number is 16, so the number of **protons** is **16**.

Neutrons: the mass number is 33, which equals protons + neutrons, so number of **neutrons** is  $(33 - 16) = 17$ .

Electrons: the ion has a charge of  $-2$ , which means it has 2 more electrons than protons, so number of **electrons** =  $16 + 2 = 18$ .

**ii** Protons: aluminium has an atomic number of 13, so number of **protons** is **13**.

Neutrons: the mass number is 27, so number of **neutrons** is  $(27 - 13) = 14$ .

Electrons: the ion has a charge of  $+3$ , which means it has 3 more protons than electrons, so number of **electrons** =  $13 - 3 = 10$ .

**b** Atomic number: equals the number of protons, i.e. 28.

Symbol of atom: the atom with an atomic number of 28 is Ni.

Mass number:  $(\text{protons} + \text{neutrons}) = (28 + 30) = 58$

Charge on the ion: the ion has 2 more positively charged protons than negatively charged electrons, so the charge is  $+2$ .

The formula is therefore  ${}^{58}_{28}\text{Ni}^{2+}$ .

## \* Review exercise 1.1

- 1 Nuclear power can come from the fission of uranium, plutonium or thorium, or the fusion of hydrogen into helium. In most nuclear power plants today, uranium-235 is the main fuel used. Uranium-235 undergoes fission, when it absorbs an additional neutron, according to the following equations:



The neutrons produced in this process can then be absorbed by other uranium-235 atoms to cause more fission reactions. Other nuclear reactions also occur when the neutrons bombard the other kinds of atoms present in the nuclear fuel (which is usually only about 3% uranium-235). The heat produced from these fission reactions is used to form steam that then drives the turbines and finally the electrical generators. Control rods, containing a material that is able to absorb neutrons, limit the rate of these nuclear reactions.



**Figure 1.3** Nuclear fuel pellets made from uranium dioxide. The pellets will be loaded into fuel rods and then used in a nuclear reactor to create a controlled nuclear reaction and generate electricity.

The fission of an atom of uranium-235 produces 10 million times the energy produced by the combustion of an atom of carbon from coal. So can nuclear energy be regarded as a more sustainable alternative to coal and other fossil fuels in Australian power plants? The answer to this question depends on two safety issues: the safe operation of nuclear power plants, and the safe disposal of the highly radioactive by-products produced by the plants.

- ${}_{92}^{235}\text{U}$  and  ${}_{92}^{236}\text{U}$  are isotopes of uranium. What is meant by this statement?
- Determine the number of protons and neutrons in the four different atoms given in the nuclear equations at the beginning of the question.
- During the fusion reaction of hydrogen, four hydrogen-1 atoms combine to form a helium atom with two neutrons, together with positrons (positively charged electrons). This fusion reaction is a possible source of energy for nuclear power stations and it is the reaction that produces most of the sun's energy. Write an equation, like the one given for the fission of uranium, to represent the fusion reaction for hydrogen.

- 2 Copy and complete the following table.

Formula	Atomic number	Mass number	Number of protons	Number of electrons	Number of neutrons
Cs		133			
$\text{Sn}^{2+}$					70
	35	81		36	
			24	21	28

- If the diameter of a typical atom is  $1 \times 10^{-10}$  m, how many atoms would fit across a 10-cent coin with a diameter of 2.3 cm?
  - If you were going to make a scale model of a typical atom, and you made the nucleus in your model the same size as the nucleus shown on the right of Figure 1.1, what would the diameter of your model atom be?

## 1.2 Electronic structure of atoms

### Electron arrangement in shells



Since the electrons are the outermost part of every atom, the unique chemical properties of each element can be traced to the number of these electrons and their arrangement. The shell model of electron arrangement proposes that electrons in atoms are only able to possess discrete amounts of energy. Depending on this energy, the electrons occupy regions of space, called shells or energy levels, around the nucleus. These shells are, on average, different distances from the nucleus and each can contain a specific maximum number of electrons, as shown in Table 1.2.

**TABLE 1.2 CHARACTERISTICS OF ELECTRON SHELLS (ENERGY LEVELS) IN ATOMS (RANGING OUT FROM THE NUCLEUS)**

Shell number	Shell letter	Maximum number of electrons in the shell
1	K	2
2	L	8
3	M	18
4	N	32
$n$ th shell		$2n^2$

Electrons in an atom occupy the shells that are closest to the nucleus. The first shell is filled before the second shell, which is filled before the third shell. For example, for an aluminium atom that has 13 electrons in total, 2 electrons are in the first shell, 8 electrons in the second shell and 3 electrons in the third shell. This electron arrangement can be written as 2, 8, 3.

For the larger shells, the order in which electrons occupy shells is not as simple. For example, when filling the third shell, once 8 electrons are in this shell, the next 2 electrons occupy part of the fourth shell. As a result, the calcium atom with 20 electrons has an electron configuration of 2, 8, 8, 2 and not 2, 8, 10. Examples of the electron configurations of other atoms and ions are shown in Table 1.3.

**TABLE 1.3 EXAMPLES OF ELECTRON CONFIGURATIONS**

Species	Number of protons	Number of electrons	Number of electrons in each shell				Electron configuration
			1	2	3	4	
C	6	6	2	4			2, 4
O <sup>2-</sup>	8	10	2	8			2, 8
Cl	17	17	2	8	7		2, 8, 7
P <sup>3-</sup>	15	18	2	8	8		2, 8, 8
K	19	19	2	8	8	1	2, 8, 8, 1
Ca <sup>2+</sup>	20	18	2	8	8		2, 8, 8

For the sake of simplicity, the electron arrangement of a particular atom or ion is sometimes represented by the Bohr model of the atom. In this model, circles are used to represent shells and dots or crosses show how many electrons are in each shell, as shown in Figure 1.4. This pictorial representation inaccurately suggests that the electrons travel along specific circular paths. However, according to more recent ideas about electron arrangement, it is not possible to specify the



exact location or path of an electron around the nucleus. Only the probability of locating an electron in a given region in space can be predicted.

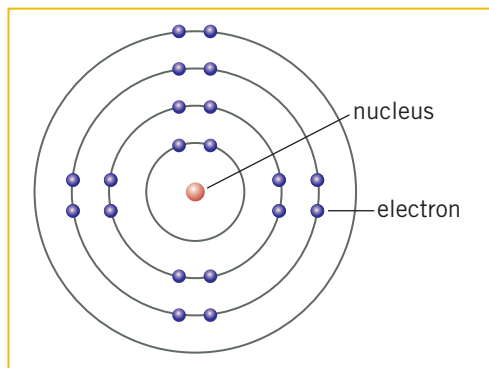
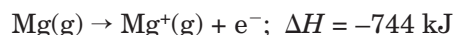


Figure 1.4 A Bohr model representation of the electron configuration of calcium, 2, 8, 8, 2

## Ionisation energy

Evidence for the existence of electron shells in atoms is provided by examining ionisation energy data. At sufficiently high temperatures, it is possible for one or more electrons in an atom to gain enough energy to break away from the atom. The energy required to remove an electron from an atom or ion is referred to as the ionisation energy.

The first ionisation energy of an element is defined as the energy required to remove the outermost, or first, electron from 1 mole of atoms of the element in its gaseous state. For example, magnesium has a first ionisation energy of  $744 \text{ kJ mol}^{-1}$ . This means that  $744 \text{ kJ}$  of energy is required to remove the outermost electron from 1 mole or  $6.022 \times 10^{23}$  atoms of gaseous magnesium, as shown in the following equation:



Energy is required to remove electrons from atoms because the negatively charged electrons are attracted to the positively charged nucleus.

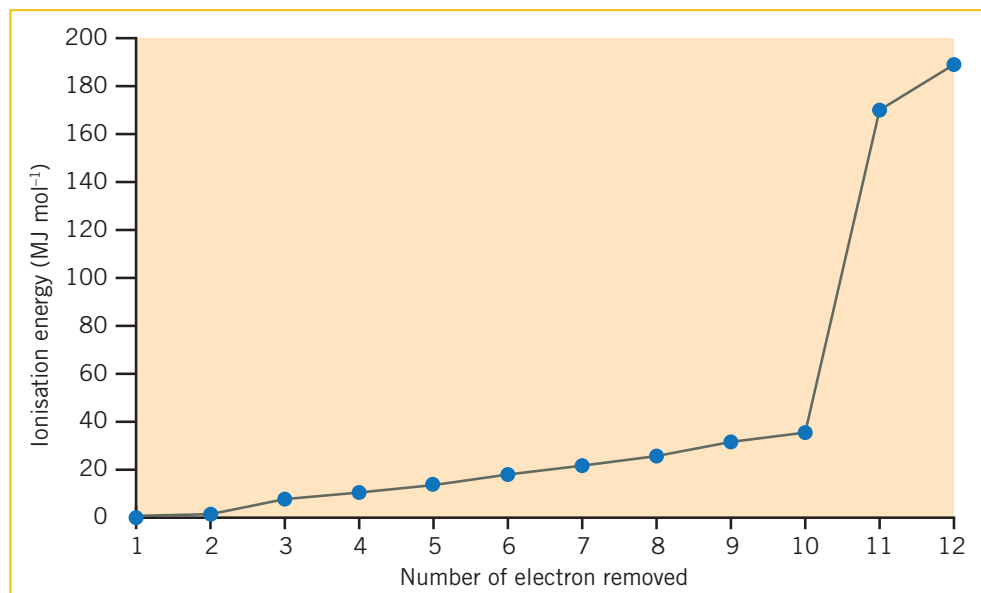
More than one electron can be removed from an atom containing numerous electrons. The second ionisation energy is the energy required to remove the second electron from 1 mole of +1 ions, the third ionisation energy is the energy required to remove the third electron and so on. These are called successive ionisation energies. The successive ionisation energies for magnesium are shown in Table 1.4.

TABLE 1.4 SUCCESSIVE IONISATION ENERGIES FOR MAGNESIUM

Ionisation	Ionisation reaction occurring	Ionisation energy ( $\text{MJ mol}^{-1}$ )
1st	$\text{Mg(g)} \rightarrow \text{Mg}^{\text{+}}(\text{g}) + \text{e}^{-}$	0.744
2nd	$\text{Mg}^{\text{+}}(\text{g}) \rightarrow \text{Mg}^{\text{2+}}(\text{g}) + \text{e}^{-}$	1.46
3rd	$\text{Mg}^{\text{2+}}(\text{g}) \rightarrow \text{Mg}^{\text{3+}}(\text{g}) + \text{e}^{-}$	7.74
4th	$\text{Mg}^{\text{3+}}(\text{g}) \rightarrow \text{Mg}^{\text{4+}}(\text{g}) + \text{e}^{-}$	10.5
5th	$\text{Mg}^{\text{4+}}(\text{g}) \rightarrow \text{Mg}^{\text{5+}}(\text{g}) + \text{e}^{-}$	13.6
6th	$\text{Mg}^{\text{5+}}(\text{g}) \rightarrow \text{Mg}^{\text{6+}}(\text{g}) + \text{e}^{-}$	18.0
7th	$\text{Mg}^{\text{6+}}(\text{g}) \rightarrow \text{Mg}^{\text{7+}}(\text{g}) + \text{e}^{-}$	21.7
8th	$\text{Mg}^{\text{7+}}(\text{g}) \rightarrow \text{Mg}^{\text{8+}}(\text{g}) + \text{e}^{-}$	25.7
9th	$\text{Mg}^{\text{8+}}(\text{g}) \rightarrow \text{Mg}^{\text{9+}}(\text{g}) + \text{e}^{-}$	31.6
10th	$\text{Mg}^{\text{9+}}(\text{g}) \rightarrow \text{Mg}^{\text{10+}}(\text{g}) + \text{e}^{-}$	35.5
11th	$\text{Mg}^{\text{10+}}(\text{g}) \rightarrow \text{Mg}^{\text{11+}}(\text{g}) + \text{e}^{-}$	170.0
12th	$\text{Mg}^{\text{11+}}(\text{g}) \rightarrow \text{Mg}^{\text{12+}}(\text{g}) + \text{e}^{-}$	189.0

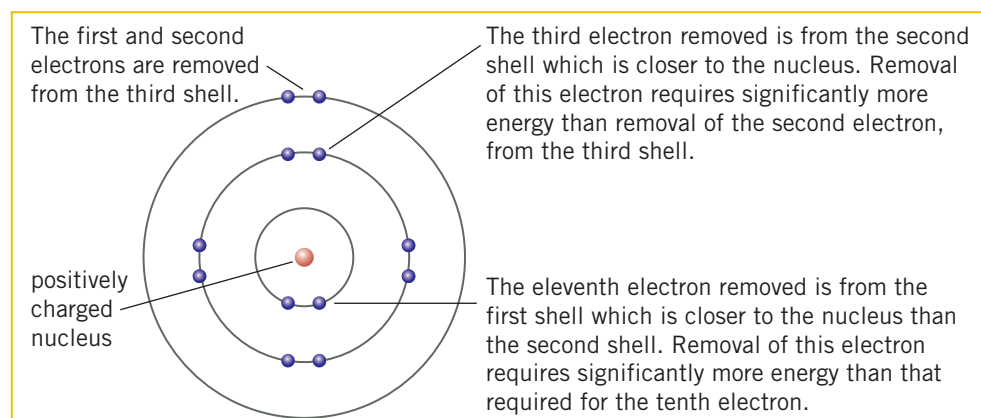
For a particular atom, successive ionisation energies become larger in value because the electrons are being removed from ions with progressively larger positive charges. For the first ionisation energy, the electron is removed from a developing single positive ion, for the second ionisation energy from a developing double positive ion and so on. This can be seen in the ionisation energy data for magnesium (Table 1.4), which show that an increasing amount of energy is required to remove each successive electron.

A steady increase in successive ionisation energies would be expected if the electrons in atoms were 'allowed' to have any amount of energy; that is, if there were no restrictions on where around the nucleus the electrons are most likely to be found. However, when a graph of the successive ionisation energies of magnesium (Figure 1.5) is examined, it can be seen that the amount of energy required to remove each successive electron does not increase steadily. There are several instances where the amount of energy required to remove an electron is substantially more than the previous value.



**Figure 1.5** Graph of the successive ionisation energies of magnesium

These considerable increases in ionisation energy for magnesium can be explained in the following way. For magnesium, with an electron configuration of 2, 8, 2, the first two electrons removed in the ionisation process will be from the third shell, as shown in Figure 1.6. The third electron to be removed will be from the second shell. The electrons in this second shell are significantly closer to the nucleus than the electrons in the third shell. As a result, the second-shell electrons are attracted more strongly to the nucleus, and so require significantly more energy for removal than the electrons in the third shell.



**Figure 1.6** The Bohr model of a magnesium atom can be used to illustrate the removal of electrons for each successive ionisation.

As successive electrons are removed from the second shell, the ionisation energies gradually increase due to these electrons being removed from ions with progressively larger positive charges. However, again there is another sudden increase in the energy required to remove the eleventh electron from magnesium. This electron is in the first shell and so is much closer to the nucleus and attracted more strongly than the electrons in the second shell. The amount of energy required to remove the final twelfth electron is then only a little more than the eleventh ionisation energy. This is because both electrons are in the same first shell.

The same patterns observed in the successive ionisation energies of magnesium are also seen in the ionisation energy data for other elements. These patterns can be summarised as follows:

- Successive ionisation energies gradually increase for an atom as the charge on the ion being formed increases.
- Successive ionisation energies markedly increase when the electron is removed from a shell closer to the nucleus.

### → Example 1.2

Which of the elements, sodium, aluminium or silicon, would you expect to have the following first seven successive ionisation energies?

584 1823 2751 11 584 14 837 18 384 23 302 kJ mol<sup>-1</sup>

### → Solution

The electron configurations of the three elements are:

- sodium (11 electrons) 2, 8, 1
- aluminium (13 electrons) 2, 8, 3
- silicon (14 electrons) 2, 8, 4

Examination of the increase in the value of each ionisation energy compared to the next one shows:

584      1823      2751      11 584      14 837      18 384      23 302

approx. 3×    approx. 1.5×    approx. 4×    approx. 1.3×    approx. 1.2×    approx. 1.3×

The largest increase in the successive ionisation energies appears to be between the third and the fourth ionisation energies. Significantly more energy is required to remove the fourth outermost electron than the third outermost electron. This suggests that the fourth outermost electron is in a shell closer to the nucleus than the shell containing the first three electrons. The substance therefore has three electrons in its outermost shell, which means it is **aluminium**.

### → Example 1.3

The first six successive ionisation energies of an element are:

596 1152 4918 6480 8150 10 502 kJ mol<sup>-1</sup>

How many valence electrons, i.e. electrons in the outermost shell, would you expect atoms of this element to have?

### → Solution

Examination of the ionisation energies shows:

596      1152      4918      6480      8150      10 502

approx. 2×    approx. 4×    approx. 1.2×    approx. 1.2×    approx. 1.2×

The first two electrons are relatively easy to remove, but the third electron requires significantly more energy. This suggests that the third electron is in a shell closer to the nucleus than the shell of the second electron. Consequently, the atoms must have **two electrons** in their outermost shell or two valence electrons.

## \* Review exercise 1.2

- 1 Give the electron configurations of the following atoms and ions.
  - a beryllium
  - b silicon
  - c potassium ion,  $K^+$
  - d nitride ion,  $N^{3-}$
  - e calcium
  - f lithium ion,  $Li^+$
- 2 Give the formula of an example of an atom or ion for each of the following descriptions:
  - a A neutral atom that has 6 electrons in its second shell
  - b Another negative ion that has the same electron configuration as  $F^-$
  - c A positive ion that has the same electron configuration as  $F^-$
  - d A neutral atom that has a 'full' second shell
  - e An atom with electrons in only one shell
  - f An ion composed of one proton and no electrons
- 3 For boron, the five successive ionisation energies are as follows.  
807    2433    3666    25 033    32 834  $\text{kJ mol}^{-1}$ 
  - a Why is the second ionisation energy larger than the first ionisation energy?
  - b Explain why the difference between the third and fourth ionisation energies is much larger than the difference between the second and third ionisation energies.
- 4 The first six successive ionisation energies, in  $\text{MJ mol}^{-1}$ , of several elements are given below. Predict how many electrons there would be in the outermost shell of the atoms of each element.
  - a 0.793, 1.583, 3.238, 4.362, 16.098, 19.791
  - b 0.502, 4.569, 6.919, 9.550, 13.356, 16.616
- 5 The graph in Figure 1.7 shows the successive ionisation energies for neon.

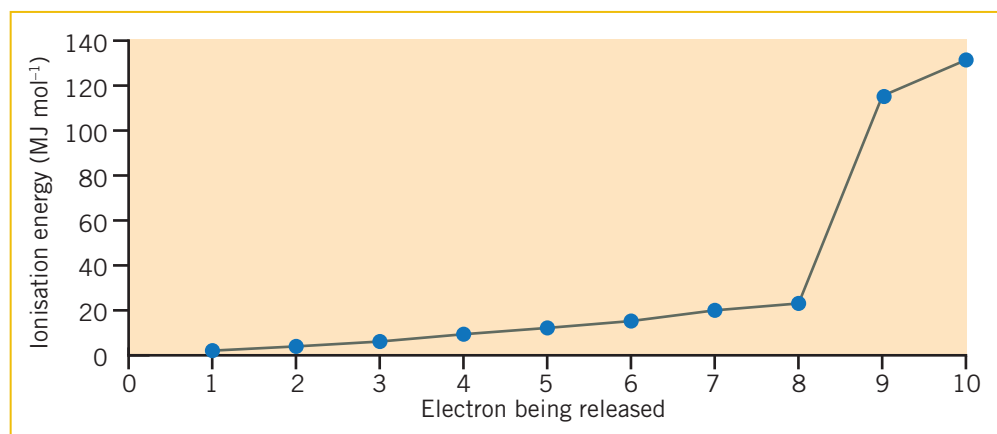


Figure 1.7 Successive ionisation energies for neon

*continued*

### Review exercise 1.2 — continued

- a What is the electron configuration of neon?
- b Explain the shape of the graph shown in Figure 1.7.
- c
  - i Write the electron configuration of argon.
  - ii Make a sketch of the graph of successive ionisation energies, like that drawn in Figure 1.7, you would expect for argon. Include figures on the horizontal axis, but not on the vertical axis.

## 1.3 The periodic table

Controlling our material world requires an understanding of how matter behaves. Throughout recorded history, we find various anecdotes of the endeavours of first alchemists and later chemists to categorise and classify matter. During the 19th century, some researchers recognised that there were recurring or periodic patterns in the properties of the known elements, and they suggested schemes to organise these elements according to their similarities. In 1869, the Russian chemist Dmitri Mendeleev published a tabulation that not only described the behaviour of the known elements, but importantly pointed to the existence of unknown ones. The periodic table—a powerful descriptive and predictive tool—was born.

Group		1	2											13	14	15	16	17	18	
	1	<div style="border: 1px solid black; padding: 2px; display: inline-block;">                     1 — atomic number                      H — symbol                 </div>															2	He		
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 1.8** The modern periodic table showing the groups and periods. The shading indicates the metallic and non-metallic character of the elements. Yellow shading represents the metals and blue the non-metals.

In the modern periodic table, shown in Figure 1.8, the elements are arranged horizontally in order of increasing atomic number and vertically according to their outer-shell electron configuration. This organisation gives a periodic table that comprises periods, the horizontal rows, and groups, the vertical columns.

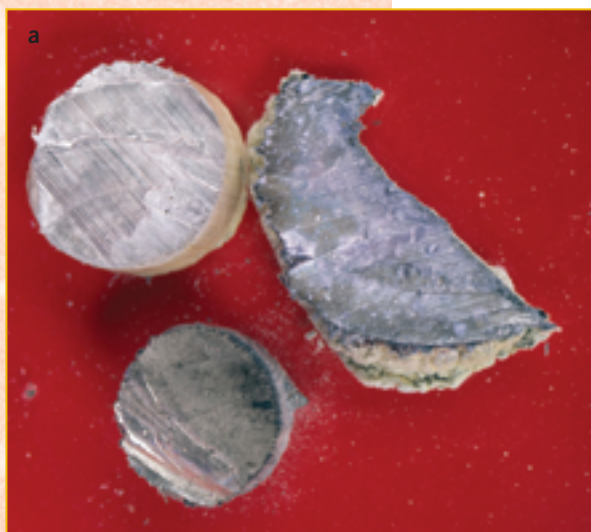
Elements in the same period have their outermost electrons in the same shell. For instance, elements in the fourth period all have their outermost electrons in the fourth shell. Elements in the same group have the same number of electrons in their outermost shell. Group 14 elements, for example, all have 4 electrons in their outer shell.

When the elements are organised in this way in the periodic table, the metallic elements lie on the left-hand side of the table and the non-metallic elements on the upper right-hand side. The elements in between, shaded green in Figure 1.8, exhibit both metallic and non-metallic properties.

The properties of the elements are, for the most part, determined by the number of outer-shell or valence electrons. Since elements in the same vertical column (group), have the same number of outer-shell electrons, these groups identify in general terms the type of chemistry likely to be exhibited by an element. To illustrate this, some properties of the elements in two groups of the periodic table are described in Table 1.5.

**TABLE 1.5 SOME CHEMISTRY OF GROUP 1 AND GROUP 17 ELEMENTS**

	Melting point (°C)	Boiling point (°C)	Electrical conductivity at 25°C (MS m <sup>-1</sup> )	First ionisation energy (MJ mol <sup>-1</sup> )	Reaction with non-metals	Reaction with metals
<b>Group 1 — Alkali metals</b>						
Li	180	1342	10.5	0.526	React to form ionic compounds	Do not react
Na	98	883	21	0.502		
K	63	760	14	0.425		
Rb	39	686	8.1	0.409		
Cs	28	669	5.0	0.382		
<b>Group 17 — Halogens</b>						
F	-220	-188	–	1.687	React to form molecular compounds	React to form ionic compounds
Cl	-101	-35	–	1.257		
Br	-7	59	10 <sup>-16</sup>	1.146		
I	114	184	10 <sup>-13</sup>	1.015		



**Figure 1.9** (a) Group 1 elements—lithium, sodium and potassium (clockwise from the bottom). (b) Group 17 elements—chlorine, bromine and iodine (left to right)

#### → Example 1.4

For the two elements barium and selenium, answer the following questions.

- How many protons and electrons are in their neutral atoms?
- What is the group number and period of each element?
- How many electrons do they have in their outermost shells?
- Which shell contains the outermost electrons?
- Name another element that would have similar properties to each of the two elements.

#### → Solution

##### **Barium:**

- The atomic number of barium, Ba, is 56. The neutral atoms therefore contain 56 protons and 56 electrons.
- Group 2, period 6
- Elements in group 2 have 2 electrons in their outermost shell.
- Because barium is in period 6, its 2 outermost electrons will be in the sixth shell.
- Any element in group 2, such as calcium, will have similar properties to barium.

##### **Selenium:**

- The atomic number of selenium, Se, is 34. The neutral atoms therefore contain 34 protons and 34 electrons.
- Group 16, period 4
- Elements in group 16 have 6 electrons in their outermost shell.
- Because selenium is in period 4, its 6 outermost electrons will be in the fourth shell.
- Any element in group 16, such as sulfur, will have similar properties to selenium.

At times it is convenient to think of the periodic table as consisting of several main blocks of elements, as shown in Figure 1.10.

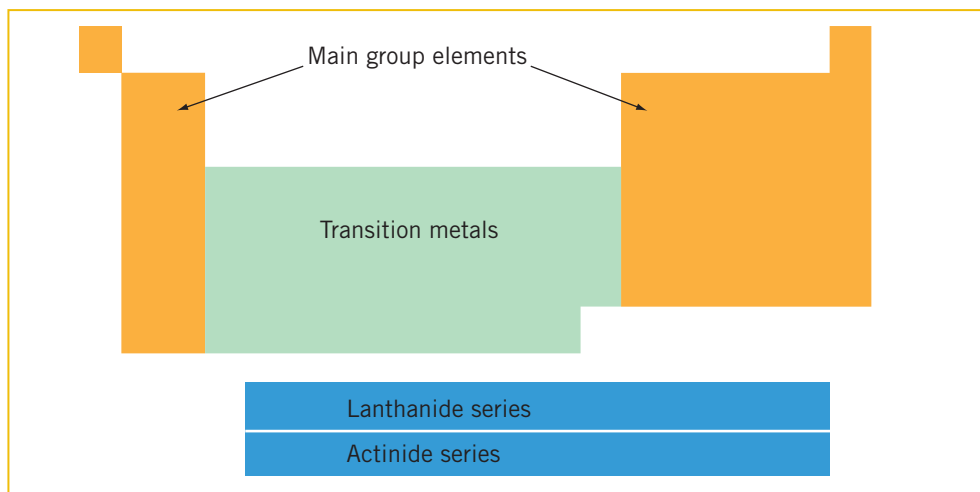


Figure 1.10 The main blocks of the periodic table

The elements in groups 1, 2 and 13 to 18 are sometimes referred to as the main group elements. Groups 3 to 12 are referred to as the transition metals. Many of the metals in this block tend to behave in similar ways; for example, most form coloured ionic compounds. The two rows at the bottom of the periodic table are referred to as the lanthanides (upper row) and the actinides. Most of these metals also have similar properties to one another.

### \* Review exercise 1.3

- 1 Give the name of:
  - a gaseous element, at room temperature, in period 3 of the periodic table
  - a group 14 element that is a non-metal
  - the group 2, period 2 element
  - a transition metal that forms blue-coloured compounds
  - the period 4 element with 7 electrons in its outermost shell
  - a group 2 element whose atoms have more protons in their nuclei than calcium atoms.
- 2 The first six successive ionisation energies of element X are listed below (in  $\text{kJ mol}^{-1}$ ).

580	1820	2750	11 600	14 800	18 400
-----	------	------	--------	--------	--------

  - To which group of the periodic table does this element belong?
  - What evidence given in the ionisation energy data establishes that X cannot be a period 2 element?
- 3 Compare the properties of the group 1 and group 17 elements listed in Table 1.5.



## 1.4 Periodic table trends

Most, if not all, of the properties of elements depend on the number of protons and electrons, and the electron arrangement, in their atoms. As a result, when these elements are organised according to their atomic number and electron arrangement, trends in the properties of the elements can be recognised. The trends of three properties, atomic radius, ionisation energy and electronegativity, are discussed in this section; other trends are summarised in Chapter 3.

The atomic radius, ionisation energy and electronegativity of an element each depend on two opposing influences:

- the number of electrons in an atom and the shells occupied by these electrons. The more shells occupied by electrons, the further the outermost electrons will be from the nucleus of the atom
- the positive charge (due to the presence of protons) of the nucleus. The larger the positive charge of the nucleus; that is, the larger the number of protons in the nucleus, the stronger the attractive force between the nucleus and the electrons of the atom. However, the outer-shell electrons in an atom do not usually 'feel' the attraction of the full nuclear charge of the atom; instead they experience a weaker attraction. The concept of core charge or effective nuclear charge can be used to explain this reduction in attractive forces between the outermost electrons and the nucleus.

The core charge of an atom can be regarded as the effective positive charge experienced by the valence or outer-shell electrons in the atom. The electrons in the inner shells of an atom are thought to have a shielding or cancelling effect of the positive charge on the nucleus. The approximate core charge experienced by the outer electrons is calculated by subtracting the shielding effect of the negative inner-shell electrons from the number of protons in the nucleus:

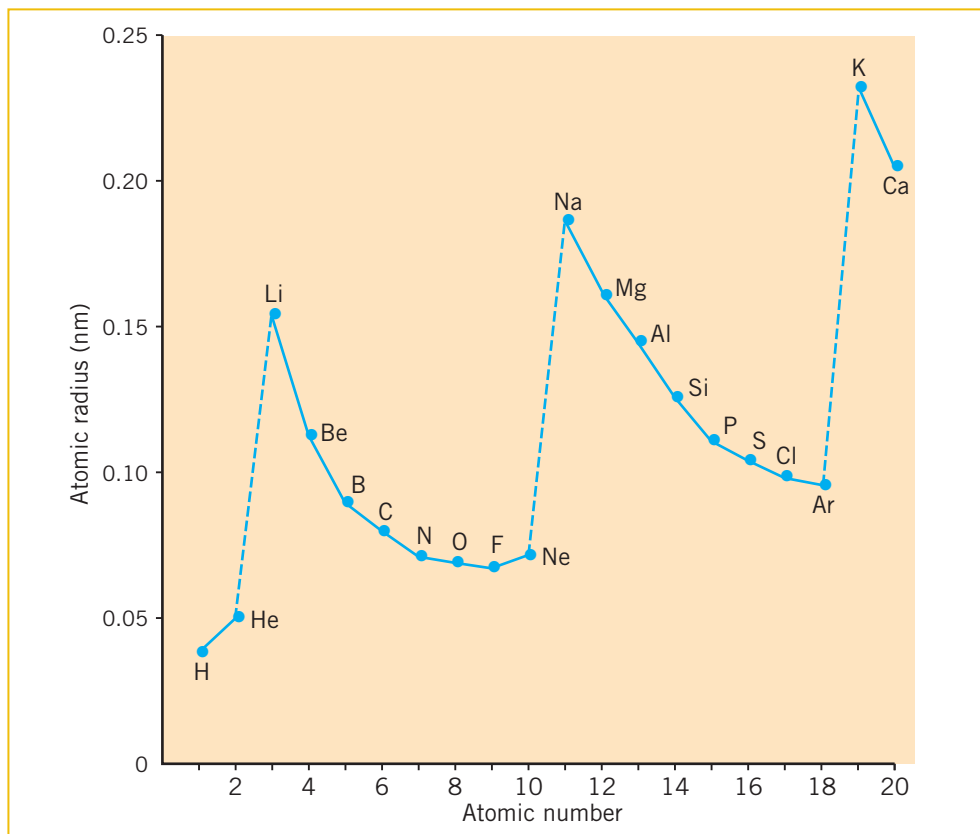
$$\text{core charge} = \text{number of protons in the nucleus} - \text{number of inner-shell electrons}$$

For example, sodium, a group 1 element, has 11 protons in its nucleus and, with an electron configuration of 2, 8, 1, it has 10 electrons in its inner shells. The core charge or effective nuclear charge experienced by the outer-shell electron of sodium is therefore approximately  $11 - 10 = +1$ . Indeed, for each of the elements in group 1, the core charge attracting the single outer-shell electron will be approximately +1.

### Atomic radius

The size (or atomic radius) of an atom or ion is dependent on the number of electrons in the atom, the shells in which these electrons are located and the charge on the nucleus of the atom.

The range of atomic radii of the first 20 elements is shown graphically in Figure 1.11.

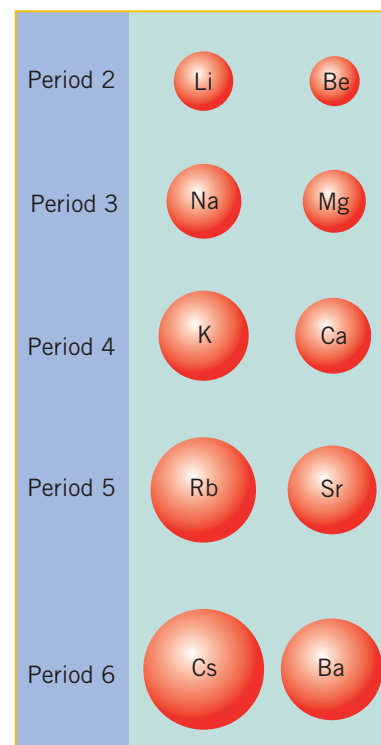


**Figure 1.11** Atomic radii of the first 20 elements in the periodic table

In the periodic table, the elements are arranged in the same vertical column or group on the basis of the number of outer-shell electrons. This means that on going down a group, these outer-shell electrons are in shells that are progressively further from the nucleus. Consequently, the atomic size (often referred to as the atomic radius) increases going down a group of elements (Figure 1.12).

Going down a group, the number of protons in the nuclei of the atoms of each successive element increases. It might therefore be expected that this increased positive nuclear charge would ‘pull’ the electrons closer to the nucleus, making the atomic size smaller. However, within a group, because the positive nuclear charges are partially shielded by electrons in inner shells, the nuclear charge experienced by the outer-shell electrons is approximately the same for the atoms of each element. For example, the outer-shell electrons in the atoms of all the group 2 elements experience an effective nuclear charge of approximately +2.

Except for period 1, going across any period of the periodic table the atomic radii decrease. This trend can be seen for periods 2 and 3 in the graph in Figure 1.11. The number of protons in the nuclei of the atoms increases across a period, and the outermost electrons are in the same shell for each successive element. This means the effective nuclear charge ‘felt’ by the outermost electrons in the atoms will increase across a particular period. The electrons in the atoms of each successive element will therefore experience a stronger attractive force, pulling them closer to the nucleus. This will result in the atoms becoming smaller moving from left to right across the period. The relative sizes of the atoms of the elements in periods 3 and 4 are shown in Figure 1.13.



**Figure 1.12** Relative sizes of metal atoms going down group 1 and group 2

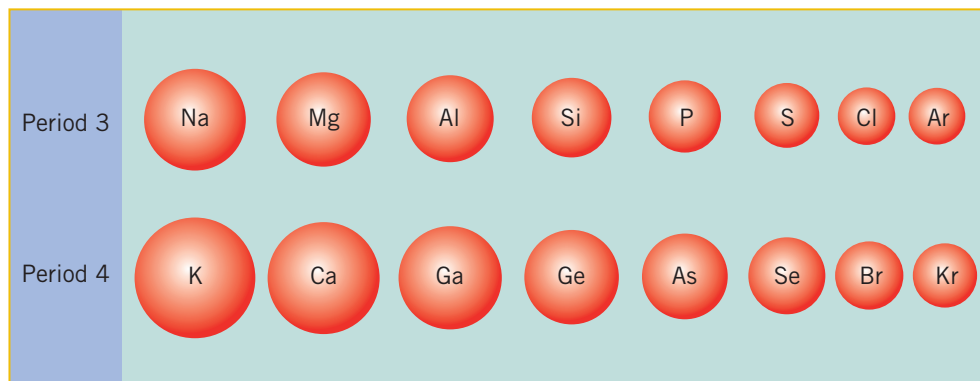


Figure 1.13 The empirically measured relative atomic radii of elements in periods 3 and 4

### → Example 1.5

The atomic radii of three atoms are given below.

Atom	Atomic radius (nm)
Magnesium	0.160
Aluminium	0.143
Calcium	0.197

- Explain why the atomic radius of aluminium is smaller than the atomic radius of magnesium.
- Why is the atomic radius of calcium larger than that of magnesium?
- Which ion,  $\text{Mg}^{2+}$  or  $\text{Al}^{3+}$ , would you expect to have the larger radius?

### → Solution

- The electron configuration of magnesium is 2, 8, 2 and of aluminium is 2, 8, 3. Their outermost electrons are therefore in the same shell—the third shell. Their difference in size must therefore be due to the positive charge on their respective nuclei. Magnesium has 12 protons in its nucleus (a core charge of +2), but aluminium has 13 protons (a core charge of +3). The attractive force between the nucleus and the electrons will be larger for aluminium than for magnesium. As a result, aluminium's electrons will be pulled closer to its nucleus, giving it a smaller radius, compared to magnesium.
- The electron configuration of magnesium is 2, 8, 2 and of calcium is 2, 8, 8, 2. The outermost electrons in calcium are in the fourth shell and those in magnesium are in the third shell (the core charge for both atoms is approximately +2). The outermost electrons in calcium are therefore, on average, further from the nucleus than those of magnesium, resulting in calcium having the larger atomic radius.
- The  $\text{Mg}^{2+}$  ion has 12 protons and an electron configuration of 2, 8. The  $\text{Al}^{3+}$  ion has 13 protons and an electron configuration of 2, 8. The outermost electrons for both of these ions are in the same second shell, but the two ions have a different nuclear charge. Because the nuclear charge is larger for the  $\text{Al}^{3+}$  ion, its electrons will be attracted more strongly to the nucleus. The radius of the  $\text{Al}^{3+}$  ion will therefore be smaller than the radius of the  $\text{Mg}^{2+}$  ion.

## First ionisation energy

The first ionisation energies of the elements decrease down a group, as can be seen for the elements in groups 1 and 17 in Table 1.6.

TABLE 1.6 FIRST IONISATION ENERGY OF GROUP 1 AND 17 ELEMENTS

Group 1 elements	Ionisation energy (MJ mol <sup>-1</sup> )	Group 17 elements	Ionisation energy (MJ mol <sup>-1</sup> )
Lithium	0.526	Fluorine	1.687
Sodium	0.502	Chlorine	1.257
Potassium	0.425	Bromine	1.146
Rubidium	0.409	Iodine	1.015
Caesium	0.382		



This decrease in the first ionisation energy down a group can be explained in terms of the distance from the nucleus of the electron being removed. For a larger atom, the outermost electron (the first electron to be removed) is in a shell further from the nucleus, and will not be attracted as strongly to the nucleus, as the outermost electron in a smaller atom. Less energy will therefore be required to remove the outermost electron from a larger atom.

The core charge for all the elements in the one group is approximately the same. The positive charge experienced by the outer electrons, no matter what shells they are in, will be approximately the same for each element. The increase in the number of protons in the nucleus going down the group therefore has little effect on the energy required to remove the outermost electron.

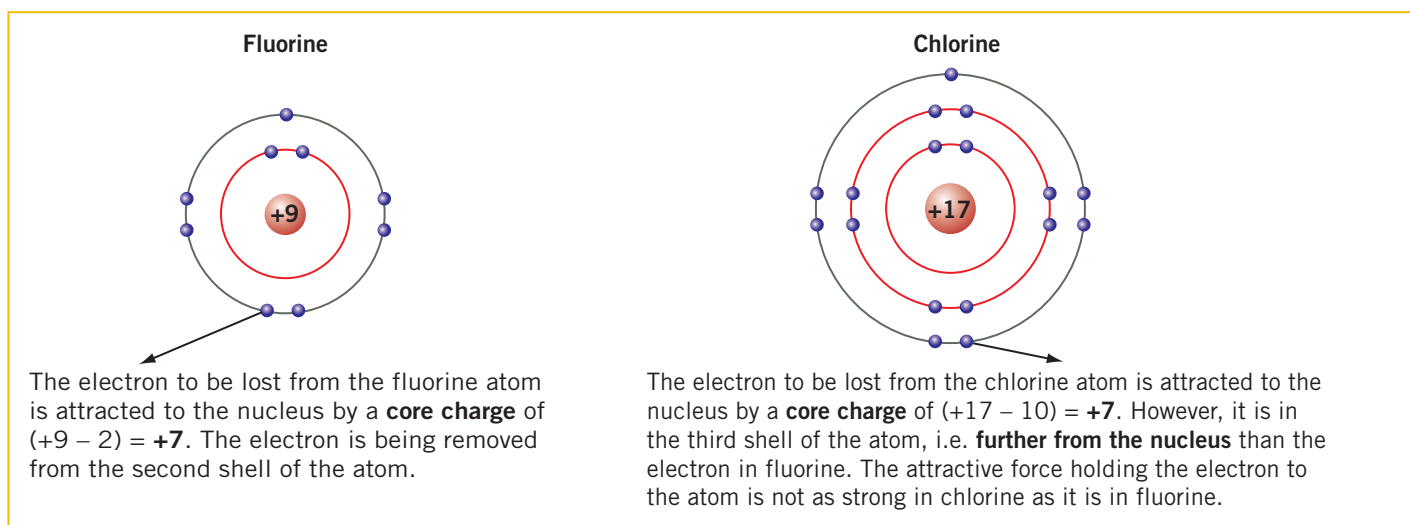
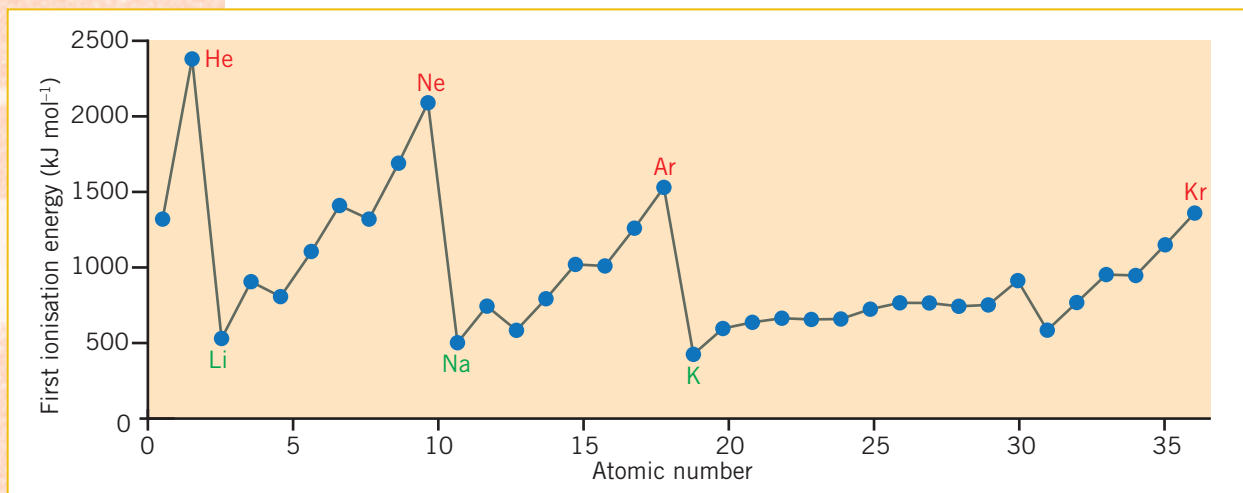


Figure 1.14 Using the Bohr model to explain why chlorine, an element further down group 17, has a smaller first ionisation energy than fluorine

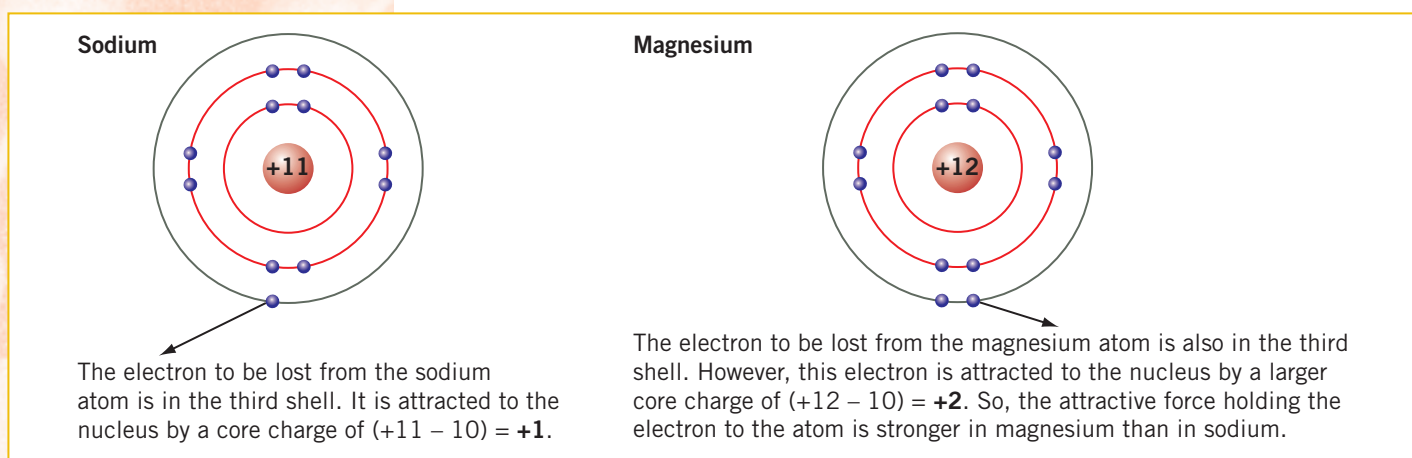
Going down a group, the difference in the first ionisation energies of the elements is therefore due mainly to the different distances between the nucleus and the outermost electron being removed during the ionisation process.

In Figure 1.15, the first ionisation energies of the elements of the first four periods of the periodic table are plotted against atomic number.



**Figure 1.15** The first ionisation energies of elements from the first four periods of the periodic table

From lithium to neon (period 2) and sodium to argon (period 3), the general trend is for the first ionisation energy to increase. The reason for this increase is similar to that given for the decrease in atomic size across a period. Moving from one element to the next across a period, an additional proton is added to the nucleus (increasing the core charge); therefore, the electrons in the outermost shell will be attracted more strongly to the nucleus. As a result, it will be more difficult to remove an electron from the atoms with the larger atomic numbers (or larger core charges) in a particular period. For example, as shown in Figure 1.16, a sodium atom has 11 protons in its nucleus, but the next element in the same period, magnesium, has 12 protons in its nucleus. The outermost electrons in both sodium and magnesium are in the second shell, so they will occupy similar regions around the nucleus. However, the outermost electrons in the magnesium atoms will be attracted more strongly to the nuclei than those in the sodium atoms. As a result, it will require more energy to remove an outermost electron from a magnesium atom than from a sodium atom. Magnesium will have a higher first ionisation energy than sodium.



**Figure 1.16** Using the Bohr model to explain why magnesium has a larger first ionisation energy than sodium, even though both elements are in the same period

As can be seen in the graph of ionisation energies in Figure 1.15, the element with the highest first ionisation energy in each period is the group 18 element, the noble gas. These gases are generally unreactive, with their high ionisation

energies showing that it is most unlikely they will give away electrons during a chemical reaction. These elements have complete outer shells, or 8 electrons in their outer shell. This observation is the basis of the 'octet rule', which proposes that when atoms react, they gain, lose or share electrons so as to achieve a more stable electron configuration of 8 electrons in their outermost shell.



## Electronegativity

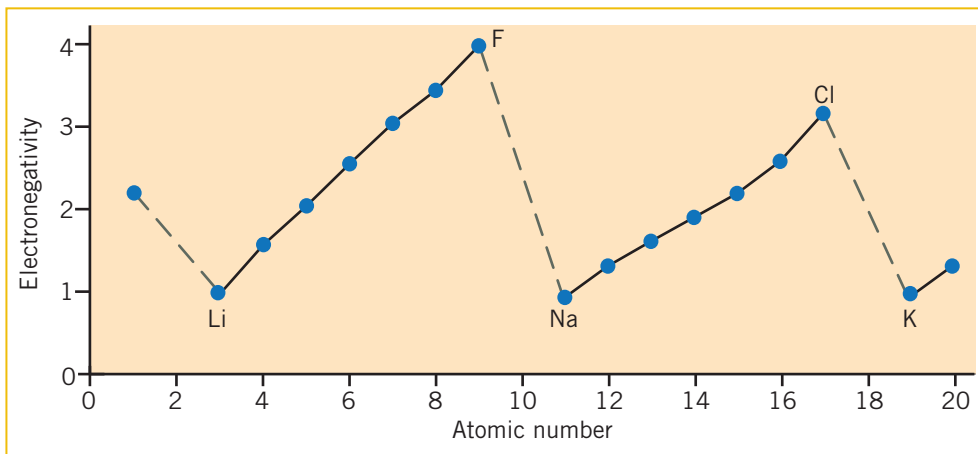
While ionisation energies provide useful data to help explain why some atoms lose electrons to form positive ions, it is not as useful for explaining why some atoms gain or share electrons with other atoms. A measure related to ionisation energy, but applicable to a broader range of elements and compounds, is electronegativity. In simple terms, electronegativity is defined as the electron-attracting power of an atom in a molecule. However, the concept is also applied to ionic compounds and metals where there are no molecules present.

The most commonly used electronegativity scale is that proposed in the early 1930s by Linus Pauling. In Table 1.7 the electronegativities, according to Pauling's scale, of some of the elements are listed.

**TABLE 1.7 ELECTRONEGATIVITIES OF THE MAIN GROUP ELEMENTS**

H	2.20						
Li	0.98	Be	1.57	B	2.04	C	2.55
		N	3.04	O	3.44	F	3.98
Na	0.93	Mg	1.31	Al	1.61	Si	1.90
		P	2.19	S	2.58	Cl	3.16
K	0.82	Ca	1.00	Ga	1.81	Ge	2.01
		As	2.18	Se	2.55	Br	2.96
Rb	0.82	Sr	0.95	In	1.78	Sn	2.96
		Sb	2.05	Te	2.1	I	2.66
Cs	0.79	Ba	0.89	Tl	2.04	Pb	2.33
		Bi	2.02	Po	2.0	At	2.2
Fr	0.7	Ra	0.9				

It is obvious that the metals have low electronegativity values. Having just a few, relatively loosely held valence electrons, it is not surprising that the metals do not have a strong attraction for these electrons when they form compounds with other elements. On the other hand, the non-metals have high electronegativities as they generally have a stronger attraction for electrons. This is observed in the formation of negative ions such as  $O^{2-}$ ,  $Cl^-$  and  $Br^-$ .



**Figure 1.17** Electronegativity values of the first 20 elements in the periodic table

As can be seen in Figure 1.17, electronegativities increase across a period in the periodic table. Moving across a period, the atoms become smaller and their core charge increases, which would lead to an increase in the electron-attracting power of the atoms. The extra electron in the outer shell for each successive element does not 'shield' the progressive increase in the positive nuclear charge. For example, considering the following two successive elements in the second period:

Nitrogen: 7 protons, electron configuration of 2, 5, core charge of  $(7 - 2) = +5$

Oxygen: 8 protons, electron configuration of 2, 6, core charge of  $(8 - 2) = +6$

Because oxygen has a greater core charge and it is a smaller atom, an incoming electron will be able to approach the larger nuclear charge more closely and so it will be attracted more strongly by oxygen than it would be by nitrogen. Oxygen is therefore more electronegative than nitrogen.

Electronegativities decrease down a group in the periodic table. This occurs because there is a greater distance between the nucleus and an incoming electron, as the atoms become larger. The increasing nuclear charge is 'cancelled out' by the increasing number of complete shells; that is, the core charge is approximately the same for all the elements within the one group. Comparing the following two elements in group 16:

Oxygen: 8 protons, electron configuration of 2, 6, core charge of  $(8 - 2) = +6$

Sulfur: 16 protons, electron configuration of 2, 8, 6, core charge of  $(16 - 10) = +6$

For both elements, an incoming electron will experience an attractive force from a charge of approximately +6, but because oxygen has electrons in fewer shells, the electron will be able to approach the positive charge more closely and so will be attracted more strongly. Because of this, oxygen is more electronegative than sulfur.

Since electronegativity increases across a period and decreases down a group:

- the elements on the top right-hand side of the periodic table have the highest electronegativities, with fluorine being the highest (4.0)
- the elements on the bottom left-hand corner have the lowest electronegativities; francium is 0.7.

A summary of the periodic table trends in ionisation energy, atomic radius and electronegativity is shown in Figure 1.18.

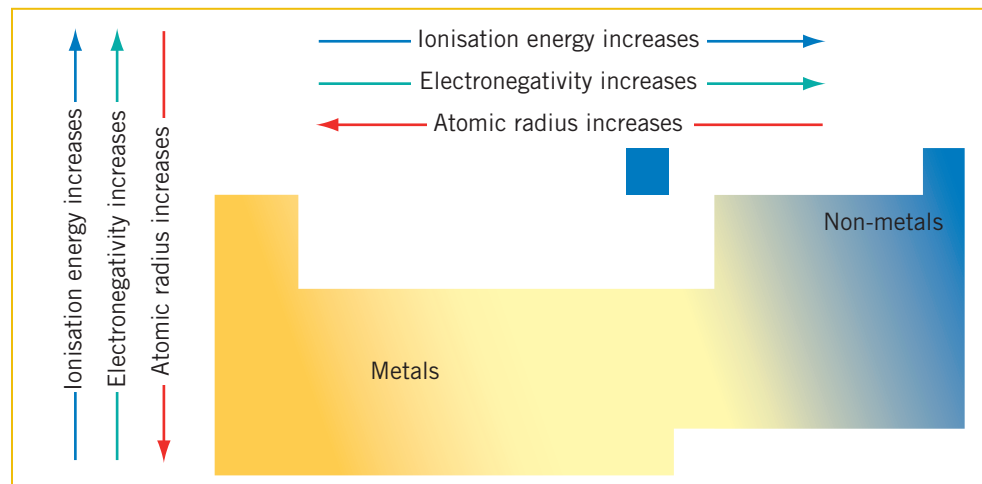


Figure 1.18 Periodic table trends in atomic radius, ionisation energy and electronegativity

Trends in other properties both across periods and down groups will be discussed in section 3.9.

## \* Review exercise 1.4

1 The following diagram is a representation of part of the periodic table.

								a
e				m			b	
				h			i	
	g	Transition metals						
							d	l
f								

Choose the letter that best represents the position of each of the elements described below.

- a The metal with the largest atomic radius
  - b The group 17 element with the higher electronegativity
  - c A non-metal with 6 electrons in its outermost shell
  - d An element in group 13
  - e The element with a core charge of +4
  - f The period 2 element with the highest first ionisation energy
  - g An element in group 2
  - h A metal in period 3
  - i The element with the highest first ionisation energy
  - j The element with the lowest electronegativity
  - k The element with the highest electronegativity
- 2 Explain why, going down a group, the atomic radius increases even though the number of protons in the nucleus that can attract the electrons increases.
- 3
- a Would a sodium ion,  $\text{Na}^+$ , have a larger or smaller atomic radius than a sodium atom? Explain your answer.
  - b The ionic radii of the phosphide ion ( $\text{P}^{3-}$ ), sulfide ion ( $\text{S}^{2-}$ ) and chloride ion ( $\text{Cl}^-$ ) are respectively 212, 190 and 181 pm ( $1 \text{ pm} = 10^{-12} \text{ m}$ ). Explain this trend.
- 4 How does the concept of core charge help to explain:
- a the change in atomic radii of the elements across period 2 of the periodic table?
  - b the change in first ionisation energy of the elements down group 17?
- 5
- a What is the first ionisation energy a measure of?
  - b Define the word 'electronegativity'.
  - c Explain why both the first ionisation energies and the electronegativities increase across a period.
  - d Explain why both the first ionisation energies and the electronegativities decrease down a group.



## 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.
- 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 number of protons and neutrons in the nucleus of that atom.
- The structure of an atom can be represented as  ${}^A_ZX$  where  $X$  is the element's symbol.
- Isotopes are atoms of the same element that have different numbers of neutrons in the nucleus.
- 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 only in certain allowed energy levels or shells.
- Electron configurations can be written showing the number of electrons in each shell; for example, an atom with 20 electrons has a configuration of 2, 8, 8, 2.
- Valence electrons are electrons in the outermost shell of an atom.
- In the periodic table, the elements are arranged in order of 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.
- The behaviour of substances within and around us can be predicted and understood from knowledge of the periodic table.
- Ionisation energy is the energy required to remove the most loosely bound electron from an atom, in the gaseous phase.
- Successive ionisation energies increase for an atom:
  - gradually as the charge on the ion being formed increases
  - markedly when the electron is removed from a shell closer to the nucleus.
- Core charge is determined by subtracting the number of inner-shell electrons from the number of protons in the nucleus.
- The atomic radius, ionisation energy and electronegativity of an element depend on the core charge experienced by the outermost electrons and the average distance of these outermost electrons from the nucleus.

- Atomic radius increases down a group and decreases across a period.
- First ionisation energy decreases down a group and increases across a period.
- Electronegativity is a measure of the electron-attracting power of an atom in a molecule.
- Electronegativity decreases down a group and increases across a period.

## QUESTIONS

- 1 Identify each of the following as true or false:

In all neutral atoms made up of protons, electrons and neutrons:

- a the number of neutrons minus the number of electrons is zero
  - b the number of protons equals the number of electrons
  - c the number of protons plus the number of neutrons equals the number of electrons
  - d the number of neutrons equals the number of protons
  - e the mass number minus the atomic number equals the number of neutrons
  - f the atomic number equals the number of electrons
  - g the number of protons plus the number of electrons equals the mass number.
- 2 For the questions below, choose your answers from the following species (the symbols are fictitious):
- $${}^{70}_{31}Z^{3+} \quad {}^{74}_{33}Y \quad {}^{73}_{32}X \quad {}^{80}_{34}T \quad {}^{65}_{30}R^{2+} \quad {}^{76}_{33}Q \quad {}^{79}_{35}M$$
- a Which of the species are isotopes of the same element?
  - b Which two have the same number of electrons?
  - c Which have the same number of neutrons?
  - d Which is a group 17 element?
  - e Which would have similar properties to sulfur?
- 3 Which of the following entities have an electron configuration of 2, 8, 8?
- $$\text{Ne} \quad \text{Cl}^- \quad \text{Sr}^{2+} \quad \text{Ca}^{2+} \quad \text{Ar} \quad \text{Al}^{3+} \quad \text{S}^{2-} \quad \text{K}^+$$
- 4 Write the electron configuration for:
- a the sodium atom
  - b the element in group 16, period 3
  - c the  $\text{Al}^{3+}$  ion
  - d the -3 ion of the element in group 15, period 3

e a halogen with electrons in only two shells.

- 5 Water in which both hydrogen atoms in each molecule are the isotope deuterium is called heavy water. Its formula is often written as  $D_2O$ , where D stands for the isotope  $^2_1H$ . Heavy water is commonly used in nuclear power stations to slow down the neutrons that will cause the fission reaction in uranium. Normal water and heavy water have very similar chemical properties; however, some of their physical properties differ slightly. For example, at  $20^\circ C$ , the density of  $H_2O$  is  $1.00 \text{ g mL}^{-1}$  but the density of  $D_2O$  is  $1.11 \text{ g mL}^{-1}$ . Propose an explanation for the difference in the density of these two forms of water.
- 6 Describe and explain the trend in first ionisation energy down a group in the periodic table.
- 7 The chloride ion,  $Cl^-$ , is isoelectronic (has the same number of electrons) with the argon atom. How does the radius of a chloride ion compare with that of an argon atom? Explain your answer.
- 8 Explain why the successive ionisation energies of a given element increase.
- 9 The successive ionisation energies, in  $\text{MJ mol}^{-1}$ , for carbon are 1.093, 2.359, 4.627, 6.229, 37.838 and 47.285. What does the dramatic increase between the fourth and fifth ionisation energies tell you about the reality of the electron shell model of the atom?
- 10 Consider the following first eight successive ionisation energies, in  $\text{MJ mol}^{-1}$ , for elements X, Y and Z.

X	Y	Z
0.509	1.15	0.79
0.969	2.11	1.58
3.43	3.5	3.23
4.7	4.57	4.36
6.0	5.77	16.1
7.7	8.56	19.8
9.0	9.94	23.8
10.7	18.6	29.2

- a Using these data, determine the group in the periodic table to which each element belongs.
- b Use the following information about these elements to identify X, Y and Z.  
One element is the second most abundant in the Earth's crust, another is a dark red liquid at room temperature, and the name of the

remaining one comes from the Greek 'barys', meaning heavy.

- 11 The electronegativities of three elements are: carbon 2.5, nitrogen 3.0, phosphorus 2.2.
- a Explain why the electronegativity of carbon is less than that of nitrogen.
- b Explain why the electronegativity of nitrogen is larger than that of phosphorus.
- 12 Account for the following observations.
- a The second ionisation energy of lithium is higher than the first ionisation energy of helium even though  $Li^+$  and He have the same number of electrons.
- b The second ionisation energy of sodium is much higher than the second ionisation energy of magnesium.
- 13 What is the relationship between first ionisation energy and electronegativity?
- 14 The first three elements of period 3 are sodium, magnesium and aluminium. The first ionisation energies (in  $\text{kJ mol}^{-1}$ ) of these three elements, in no particular order, are 736, 494 and 576, while the ionic radii (in pm), again in no particular order, are 68, 100 and 50. Match these values to each of the three elements and explain how you reached this conclusion.
- 15 a Determine the electron configuration and core charge (effective nuclear charge) of the following period 3 ions:  
 $Na^+$     $Mg^{2+}$     $Al^{3+}$     $P^{3-}$     $S^{2-}$     $Cl^-$
- b Sketch a graph showing the trend you would expect in the radii of these common ions formed by period 3 elements (except for Si) going across the period.
- c Explain your reasoning in estimating the relative ionic sizes.

16 Consider the graphs shown in Figure 1.19.

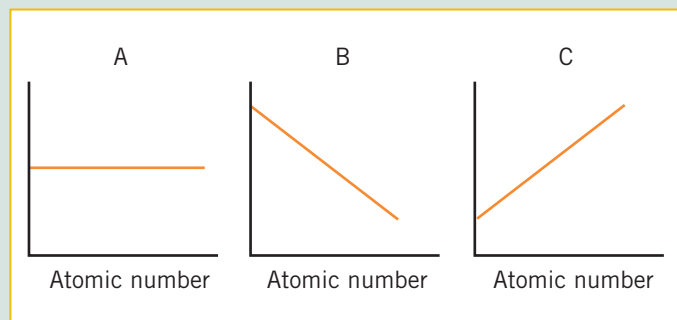


Figure 1.19

Which of these graphs could approximately represent each of the following descriptions?

- a The plot of first ionisation energy for As, Se and Br in that order
  - b The plot of atomic radius for Al, Si and P in that order
  - c The plot of number of outer-shell electrons for  $\text{Cl}^-$ , Ar and  $\text{K}^+$
  - d The plot of ionic radius for  $\text{N}^{3-}$ ,  $\text{O}^{2-}$ , and  $\text{F}^-$  in that order
  - e The plot of core charge of O, S and Se
  - f The plot of electronegativity of Cl, Br and I
- 17 Lithium salts are toxic, but in controlled doses they have proved to be remarkably effective in the treatment of certain depressive illnesses. In the human body, the most commonly found group 1 and 2 elements (in the form of ions) include sodium, potassium, magnesium and calcium. The following table provides some data relating to the atomic and ionic radii of these elements.

Element	Atomic radius (pm)	Ionic radius (pm)
Lithium	152	60
Sodium	186	95
Potassium	227	133
Magnesium	160	65
Calcium	197	99

- a Account for the difference in atomic and ionic radii for lithium, sodium and potassium.
- b Why are the ionic radii of these elements smaller than the atomic radii?
- c Why is the ionic radius of a calcium ion so much smaller than the ionic radius of a potassium ion?

d From the information provided suggest which one of these elements lithium might be replacing in its biological action. Justify your answer.

- 18 Of the elements whose atomic radii have been measured, the atom with the largest atomic radius is caesium, Cs. Its atomic radius is determined to be between 260 and 273 pm.
- a Why does caesium have such a large atomic radius?
  - b Your answer to part a suggests that there should be another element with a larger atomic radius. What is this element?



# 2

## Review of strong bonding

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

- distinguish between ionic, covalent and metallic bonding
- relate the properties of substances to the nature of the bonding present
- recall that all bonding is electrostatic in nature
- draw electron dot diagrams for ionic and molecular substances and polyatomic ions
- distinguish between covalent molecular and covalent network substances
- use a periodic table to make general predictions about the properties and behaviours of individual elements.



**Figure 2.1** Sparks flying in a foundry during copper smelting

The behaviour of matter is intimately linked to the way the particles of matter interact and bond together. The bonding and structure of ionic, metallic, covalent molecular and covalent network substances, introduced in Stage 2, determine not only their physical properties, but also influence their chemical behaviour. These bonding ideas are central to the understanding of chemical processes and lifestyle chemistry and they will be summarised in this chapter.

## 2.1 Metallic bonding

Whether they are elements or alloys, substances that exhibit metallic bonding possess a unique set of properties, such as conduction of electricity and heat, strength, malleability and ductility. Because of these properties, metallic substances are used extensively in society. However, most of these metallic substances are not found naturally in their metallic form on Earth. As a result, many industrial processes are involved in either extracting the metals from their ores or converting the extracted metal to a more useful alloyed form.

### Bonding and structure of metals

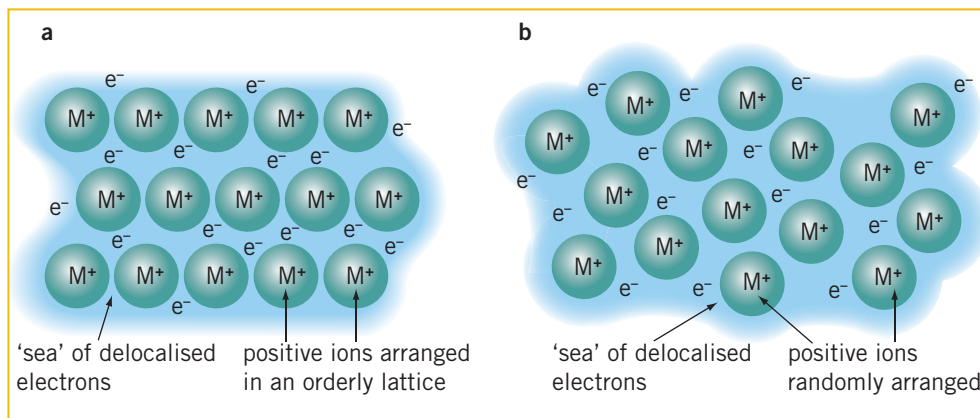
Metal elements have low first ionisation energies compared to non-metal elements, as shown in Table 2.1.

**TABLE 2.1** IONISATION ENERGIES OF SOME TYPICAL METALS AND NON-METALS

Element	Metal or non-metal	First four ionisation energies ( $\text{MJ mol}^{-1}$ )			
		1st	2nd	3rd	4th
Sodium	Metal	0.502	4.569	6.919	9.550
Calcium	Metal	0.596	1.152	4.918	6.480
Iron	Metal	0.766	1.567	2.964	5.29
Nitrogen	Non-metal	1.407	2.862	4.585	7.482
Chlorine	Non-metal	1.257	2.303	3.828	5.164

In the solid and liquid states, the metal atoms release their outer shell or valence electrons so they are free to move among the positive ions produced in this ionisation process. In the solid state, the positive ions are arranged in an orderly lattice, but in the liquid state, they are randomly arranged, as represented in Figure 2.2.

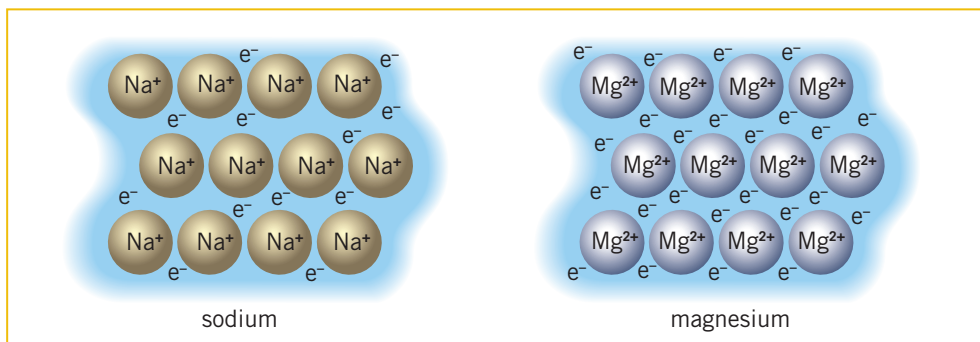




**Figure 2.2** Metals, in both the (a) solid and (b) liquid states, are composed of positive ions in a 'sea' of delocalised electrons.

In metals, it is the electrostatic attraction between positive ions and a 'sea' of delocalised electrons that holds the positive ions together. These attractive forces are referred to as metallic bonding. Because the electrons in the metallic lattice are delocalised and are not attracted to just one particular positive ion, the metallic bonds are said to be non-directional.

For a particular metal, the charge on the positive ions in the metallic lattice and the number of delocalised electrons per positive ion are related to the number of valence electrons in the metal atoms. The valence electrons are the electrons in the outer shell of an atom. With metals, only a relatively small amount of energy is required for these valence electrons to be 'donated' by the metal atoms. In potassium, with an electron configuration of 2, 8, 8, 1, each atom forms an ion with a +1 charge and contributes one electron to the delocalised electron cloud. The metallic lattice of potassium would therefore be composed of  $K^+$  ions surrounded by the delocalised electrons. Because magnesium has a configuration of 2, 8, 2, its lattice is composed of  $Mg^{2+}$  ions surrounded by a sea of electrons comprising two electrons for every positive ion.



**Figure 2.3** Metals are composed of positive ions and delocalised electrons. However, for different metals the positive charge on the ions and the number of delocalised electrons per positive ion may vary.

The strength of the metallic bonding depends to some extent on the charge of the positive ions and the number of delocalised electrons. For example, sodium is composed of  $Na^+$  ions and one delocalised electron per positive ion, and magnesium is composed of  $Mg^{2+}$  ions and two delocalised electrons per positive ion. Sodium would therefore be expected to have weaker metallic bonding than magnesium. The strength of the metallic bond is also dependent on the size of the positive ions and the way in which the positive ions are organised in their lattice.

## Physical properties of metals

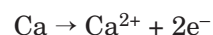
The delocalised electron model of metallic bonding can be used to explain many of the properties exhibited by metals. Table 2.2 summarises some of these properties and explanations.

TABLE 2.2 TYPICAL PROPERTIES OF METALS

Property	Explanation
High electrical conductivity in solid and liquid states	The delocalised electrons are free to move under the influence of an electric field. When one end of the piece of metal is made positive and the other end made negative (e.g. when they are connected to the terminals of a battery), the electrons flow away from the negative end of the metal towards the positive end.
Good heat conductivity in solid and liquid states	Heat conduction is a result of kinetic energy being transferred when one particle collides with a neighbouring particle and so on through the lattice. In the case of metals, because the delocalised electrons are free to move through the lattice of positive ions, they can transfer kinetic energy with ease.
Malleability and ductility	When metals are bent or stretched, layers of positive ions are forced to move relative to one another. However, no matter where the positive ions are shifted, the delocalised electrons are free to move into the region between the ions, keeping the structure together by ensuring that the electrostatic attractions (metallic bonds) are maximised.
High lustre (shiny surface)	The interaction between photons of light from an external light source and the mobile 'electron sea' on the surface of the metal lattice creates the typical metallic reflection or shininess.
Generally high melting points, although there are variations	A solid melts when sufficient energy has been provided to disrupt the crystal lattice. In a metal, this corresponds to the energy necessary to break the positive ions away from the regular lattice. The more strongly bound the positive ions are to the lattice by the electrostatic forces of attraction with the mobile valence electrons, the higher the temperature at which the metal melts. Metallic lattices made up of positive ions with larger charges and a larger number of delocalised electrons will tend to have stronger metallic bonds and, as a consequence, higher melting points. Going down a group in the periodic table, the melting points decrease because the positive ions increase in size. While the charge on each positive ion stays the same (and the number of delocalised electrons per positive ion), the ion's surface area over which this positive charge is spread becomes larger. For example, in group 1, caesium will have a weaker attraction for its mobile electrons than will sodium. Caesium will have a lower melting point than sodium.
Most are hard materials	To break or dent a metal, the attractive forces (metallic bonds) between the positive ions and the delocalised electrons must be disrupted. Because metallic bonds are strong, much energy will usually be required to disrupt them. However, for similar reasons given for the variation in melting points between metals, some metals will be softer than others. For example, sodium is softer than magnesium.

## Chemical properties of metals

When a metal reacts with a non-metal, because the metal has the smaller ionisation energy, it loses its valence (outer-shell) electrons to form positive ions. In this type of reaction, the metal is oxidised and so acts as a reductant. For example, when sodium and calcium reduce a non-metal such as oxygen, the reactions these two metals undergo can be represented by the following half-equations:



The number of electrons a metal loses in oxidation reactions, such as these two reactions, can be explained in terms of the metal's successive ionisation energies. As shown in Table 2.1, sodium has a relatively small first ionisation energy, but a significantly larger second ionisation energy. This means that in a reaction, sodium readily loses one electron, but not two electrons, to form ions with a +1 charge. On the other hand, the first and second ionisation energies of calcium are

relatively small, but its third ionisation is significantly larger. As a consequence, when calcium reacts, it readily gives up two electrons, but not three. Calcium therefore forms  $\text{Ca}^{2+}$  ions in reactions.



**Figure 2.4** Because of their properties, considerable use is made of metals in the construction of industrial plants such as the oil refinery shown in this photo.

## Main group metals and transition metals

Metals in groups 1, 2 and 13 to 16 in the periodic table are often referred to as main group metals. The remaining metals are identified as transition metals (groups 3 to 12), lanthanides and actinides, as shown in the periodic table in Figure 2.5.



Groups												13	14	15	16	17	18
1	2	Transition metals															
Li	Be											B	C	N	O	F	He
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	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							
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 green exhibit both metallic and non-metallic properties. The blue-shaded elements are non-metals.



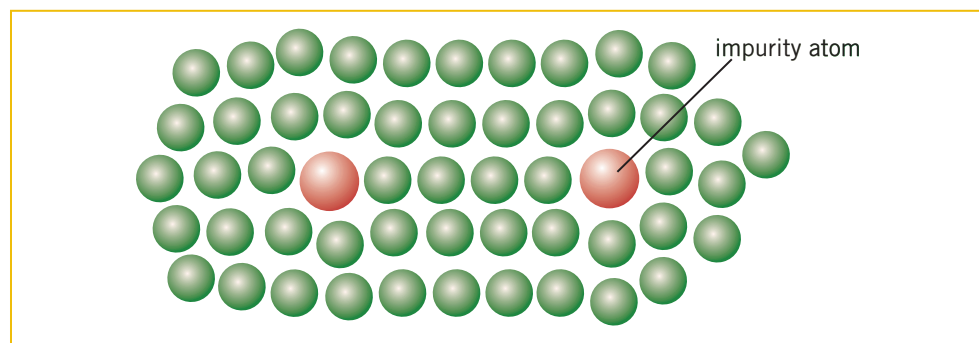
The properties common to all metals were listed in Table 2.2, but some of the properties of the main group metals, particularly for groups 1 and 2, vary from those of the other metals. These metals are compared in Table 2.3.

**TABLE 2.3** COMPARISON OF THE PROPERTIES OF METALS FROM GROUP 1 AND GROUP 2 AND TRANSITION METALS

Group 1 and 2 metals	Transition metals
Good conductors of electricity and heat	
Malleable and ductile	
Moderate melting and boiling points	High melting and boiling points
Relatively soft metals	Hard metals
Form +1 and +2 ions, respectively	Form positive ions of variable charge
Form white or colourless compounds	Form compounds that are often coloured

### Alloys

Scientists have discovered that by mixing a metal with other metals or non-metals, the properties of the metal can be altered to make it more suitable for a particular use. For example, pure iron is relatively soft and bends easily. However, if a small amount of carbon is dissolved in it, the iron becomes stronger and harder. This alloy of iron is called steel. If chromium is also added to the mixture of iron and carbon, the stainless steel alloy formed is resistant to rusting. Alloys have the same basic metallic structure as pure metals. They are composed of a lattice of positive ions surrounded by a sea of electrons, with the atoms of the impurity usually being incorporated into this lattice (Figure 2.6). These atoms of the impurity tend to disrupt the orderly nature of the metallic lattice and make it more difficult for the layers of positive ions to slide over one another if the metal is bent. Alloys therefore tend to be harder and stronger (less prone to bending) than the pure metal.



**Figure 2.6** Impurity atoms in an alloy disrupt the orderly arrangement of the metallic lattice and so make it more difficult for layers to slip over one another when the metal is bent or hit.

## \* Review exercise 2.1

- 1 In terms of the valence electrons, what distinguishes metals from non-metals?
- 2
  - a When sodium reacts with a non-metal, it only forms ions with a +1 charge, but iron forms two different ions with +2 or +3 charges. Use the ionisation energy data given in Table 2.1 to propose a reason for this difference in behaviour of the two metals.
  - b A chunk of sodium can be easily cut with a knife and yet a bar of iron is much harder. Suggest a reason for the difference in hardness of these two metals.
- 3
  - a The melting and boiling points of three metals are listed in Table 2.4. Suggest an explanation for the trends in these values.

TABLE 2.4

Element	Melting point (°C)	Boiling point (°C)
Calcium	839	1484
Strontium	764	1384
Barium	725	1140

- b Table 2.5 lists the boiling points of the group 1, 2 and 13 metals of period 4. Explain the trend in these values.

TABLE 2.5

Element	Boiling point (°C)
Potassium	774
Calcium	1484
Gallium	2403

- 4 What properties would you look for in a metal used for the following items?
  - a A water tank for collecting rainwater from the roof for use in the garden
  - b A fuel tank for a car
  - c Electrical transmission lines from a power plant to the city
  - d A saucepan for cooking food
  - e The body of a space shuttle
- 5 The following passage is a description of thallium.

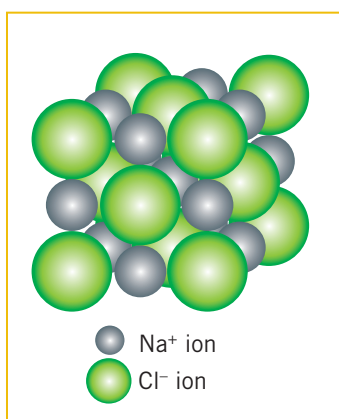
*Thallium is a blue-white metal. It is soft enough to be cut with a knife and is also very malleable. Being quite reactive, thallium readily reacts with oxygen in the air to produce a dark grey oxide. Thallium is highly toxic and has been used in murders. It has the nickname of 'the poisoner's poison'. However, now that its effects are well known and an antidote for it has been found, thallium has lost its popularity as the 'poison-of-choice' for murderers.*

  - a How many valence electrons would you expect thallium to have in its neutral atoms?
  - b Describe the bonding and structure of thallium. In your answer, include a simplified sketch of the particles present and their arrangement.
  - c Explain why thallium is malleable.
  - d Many metals are hard, but thallium is a soft metal. Propose an explanation for why thallium is a soft metal.
  - e Would you expect thallium to conduct electricity? Explain your answer in terms of the bonding and structure of thallium.
  - f Suggest why thallium reacts so readily with oxygen.

## 2.2 Ionic bonding

The production of the metals whose properties were described in the previous section is generally achieved by reactions involving ionic compounds. In addition, the raw materials for the industrial production of non-metals like chlorine are usually ionic compounds. Chemical processes that involve ionic compounds are associated with agriculture, cleaning, cooking and building construction. These processes can be better understood from knowledge of the bonding involved in these ionic compounds.

Compounds composed of positive and negative ions are called ionic compounds. Ionic bonding is the strong electrostatic attraction that occurs between the positive ions and negative ions in these compounds. In the solid state these oppositely charged ions are arranged in an orderly lattice so that each positive ion is surrounded by negative ions and each negative ion is surrounded by positive ions, as shown in the sodium chloride example in Figure 2.7.



**Figure 2.7** Ionic lattice of sodium chloride. The smaller sodium ions are surrounded by six chloride ions and each chloride ion is, in turn, surrounded by six sodium ions.

### Formulas of ionic compounds

A selection of positive and negative ions that exist in ionic compounds is listed in Table 2.6.

**TABLE 2.6** NAMES AND FORMULAS OF SOME POSITIVE AND NEGATIVE IONS

Positive ions		
+1	+2	+3
Caesium ion, Cs <sup>+</sup>	Barium ion, Ba <sup>2+</sup>	Aluminium ion, Al <sup>3+</sup>
Lithium ion, Li <sup>+</sup>	Calcium ion, Ca <sup>2+</sup>	Chromium(III) ion, Cr <sup>3+</sup>
Potassium ion, K <sup>+</sup>	Cobalt(II) ion, Co <sup>2+</sup>	Iron(III) ion, Fe <sup>3+</sup>
Rubidium ion, Rb <sup>+</sup>	Copper(II) ion, Cu <sup>2+</sup>	
Silver ion, Ag <sup>+</sup>	Iron(II) ion, Fe <sup>2+</sup>	
Sodium ion, Na <sup>+</sup>	Lead(II) ion, Pb <sup>2+</sup>	
Ammonium ion, NH <sub>4</sub> <sup>+</sup>	Magnesium ion, Mg <sup>2+</sup>	
	Manganese(II) ion, Mn <sup>2+</sup>	
	Nickel(II) ion, Ni <sup>2+</sup>	
	Strontium ion, Sr <sup>2+</sup>	
	Zinc ion, Zn <sup>2+</sup>	

Negative ions		
-1	-2	-3
Acetate (ethanoate) ion, $\text{CH}_3\text{COO}^-$	Carbonate ion, $\text{CO}_3^{2-}$	Nitride ion, $\text{N}^{3-}$
Bromide ion, $\text{Br}^-$	Chromate ion, $\text{CrO}_4^{2-}$	Phosphate ion, $\text{PO}_4^{3-}$
Chloride ion, $\text{Cl}^-$	Dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$	Phosphide ion, $\text{P}^{3-}$
Cyanide ion, $\text{CN}^-$	Hydrogenphosphate ion, $\text{HPO}_4^{2-}$	
Dihydrogenphosphate ion, $\text{H}_2\text{PO}_4^-$	Oxalate ion, $\text{C}_2\text{O}_4^{2-}$	
Fluoride ion, $\text{F}^-$	Oxide ion, $\text{O}^{2-}$	
Hydrogencarbonate ion, $\text{HCO}_3^-$	Sulfate ion, $\text{SO}_4^{2-}$	
Hydrogensulfate ion, $\text{HSO}_4^-$	Sulfide ion, $\text{S}^{2-}$	
Hydroxide ion, $\text{OH}^-$	Sulfite ion, $\text{SO}_3^{2-}$	
Iodide ion, $\text{I}^-$		
Nitrate ion, $\text{NO}_3^-$		
Nitrite ion, $\text{NO}_2^-$		
Permanganate ion, $\text{MnO}_4^-$		
Hypochlorite ion, $\text{ClO}^-$		
Chlorite ion, $\text{ClO}_2^-$		
Chlorate ion, $\text{ClO}_3^-$		
Perchlorate ion, $\text{ClO}_4^-$		

Some of these ions are monatomic (composed of only one atom) but others such as the carbonate ion,  $\text{CO}_3^{2-}$ , are polyatomic (composed of more than one atom). In the polyatomic ions, the atoms are held together by covalent bonds.

When positive ions and negative ions combine to form an ionic compound, they do so in a ratio that ensures the compound is neutral. This observation is reflected in the formula of the ionic compound. When writing the formula, the ions are shown in the simplest whole-number ratio that indicates an equal number of positive charges and negative charges. In this formula, the positive ion is always written first. Examples of the formulas of some ionic compounds are shown in Table 2.7.

**TABLE 2.7 FORMULAS OF SOME IONIC COMPOUNDS**

Name of ionic compound	Positive ion in compound	Negative ion in compound	Formula of ionic compound
Potassium oxide	Potassium ion, $\text{K}^+$	Oxide ion, $\text{O}^{2-}$	$\text{K}_2\text{O}$
Aluminium sulfide	Aluminium ion, $\text{Al}^{3+}$	Sulfide ion, $\text{S}^{2-}$	$\text{Al}_2\text{S}_3$
Silver sulfate	Silver ion, $\text{Ag}^+$	Sulfate, $\text{SO}_4^{2-}$	$\text{Ag}_2\text{SO}_4$
Calcium nitrate	Calcium ion, $\text{Ca}^{2+}$	Nitrate ion, $\text{NO}_3^-$	$\text{Ca}(\text{NO}_3)_2$
Iron(III) hydroxide	Iron(III) ion, $\text{Fe}^{3+}$	Hydroxide, $\text{OH}^-$	$\text{Fe}(\text{OH})_3$

As can be seen in the last two examples in this table, when it is necessary to indicate more than one polyatomic ion in the formula, the formula of the polyatomic ion is enclosed in brackets, for example in the formula of magnesium cyanide,  $\text{Mg}(\text{CN})_2$ .

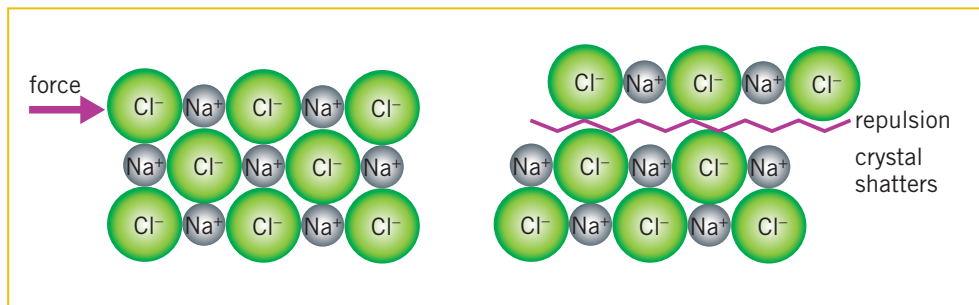
When naming ions and ionic compounds, the conventions listed below are usually followed.

- The name of the positive ion is the same as the element's name from which it was formed.
- When there are two or more positive ions derived from the same element, the charge on the ion is put in brackets after the name; for example  $\text{Fe}^{2+}$  is called the iron(II) ion.



**Figure 2.8** The gemstones of ruby (red), sapphire (blue) and emerald (darker green) are ionic compounds. Ruby and sapphire are impure forms of aluminium oxide,  $\text{Al}_2\text{O}_3$ , and emerald has the formula  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ .





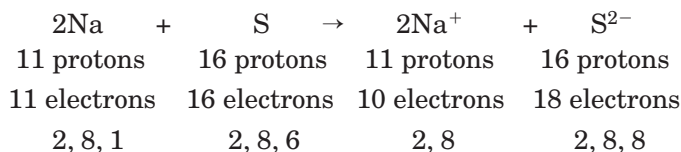
**Figure 2.9** When a strong force is applied to an ionic crystal, shattering occurs.

- They have high melting and boiling points. The strength of the electrostatic attractions (ionic bonds) in the three dimensional array of ions ensures that much energy is required to overcome these forces in the melting process. Even in the liquid phase, the attractive forces between the positive and negative ions are strong, resulting in a high boiling point.

### Formation of ionic compounds

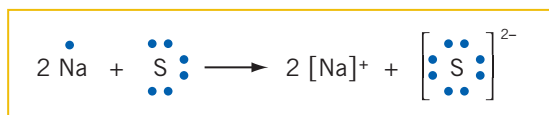
When a metal reacts with a non-metal, there is a transfer of one or more electrons from each of the metal atoms to each of the non-metal atoms. In this way, the atoms can achieve a more stable electron configuration. The electron configurations of the noble gases (group 18) are the most stable. This stable configuration normally entails having eight electrons in the outermost shell (or, for hydrogen, helium or lithium, two electrons in the outermost shell).

For example, when sodium atoms react with sulfur atoms, the following occurs:



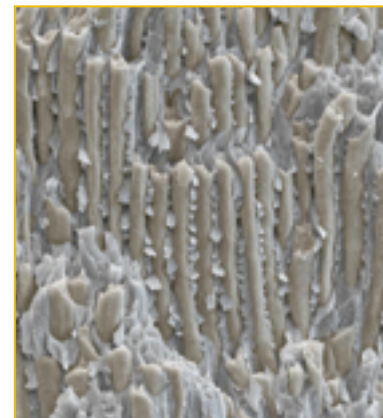
In this reaction, one electron is transferred from each of two sodium atoms to a sulfur atom to produce sodium ions, Na<sup>+</sup>, and sulfide ions, S<sup>2-</sup>. These two different ions have eight electrons in their outermost shell. The formula of the ionic compound formed in this reaction is Na<sub>2</sub>S.

The electron transfer process involved in the formation of ions when a metal reacts with a non-metal can also be represented by electron dot diagrams. In an electron dot diagram, the valence electrons of each atom or ion are shown organised around the chemical symbol of the atom or ion. For example, the electron dot representation of the formation of sodium sulfide can be drawn as shown in Figure 2.11.



**Figure 2.11** The electron dot representation of the formation of sodium sulfide

The electron dot diagram for an ion is drawn in square brackets with the charge written outside the bracket, as shown in Figure 2.11.



**Figure 2.10** A scanning electron micrograph of tooth enamel that is composed of rows of a calcium phosphate ionic compound (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)) (light brown) embedded in a protein matrix (pale grey). Because of their ionic composition, teeth are very hard, but they are also brittle.

## \* Review exercise 2.2

- 1 Explain, in terms of the transfer of electrons, why when potassium reacts with phosphorus the formula of the compound formed is  $K_3P$ . Use an electron dot diagram as part of your answer.
- 2 Propose an explanation for why the melting point of magnesium oxide ( $2850^\circ\text{C}$ ) is much higher than the melting point of sodium fluoride ( $993^\circ\text{C}$ ), despite both substances being ionic compounds.
- 3 Both calcium and calcium chloride are composed of continuous arrays of charged particles.
  - a Compare the types of charged particles present in these two substances.
  - b These continuous arrays of charged particles are held together by bonds. Compare the bonding in the two substances.
  - c Explain the differences and the similarities you would expect in the electrical conductivity of these two substances.
- 4 Why does a crystal of copper sulfate break into many small pieces if hit by a hammer, yet if a piece of copper is hit, only a dent appears in its surface.
- 5 Explain why ionic compounds are solids at room temperature.
- 6 If a normal AA battery or an alkaline battery is cut open, a paste of ionic compounds will be found among the contents. What general property of ionic compounds is being utilised by having this paste inside the battery?
- 7
  - a Name the following ionic compounds.
    - i  $(\text{NH}_4)_2\text{SO}_4$
    - ii  $\text{Ca}(\text{HCO}_3)_2$
    - iii  $\text{Fe}(\text{H}_2\text{PO}_4)_3$
  - b Write the formulas for the following ionic compounds.
    - i magnesium chlorite
    - ii sodium dichromate
    - iii copper(II) phosphide



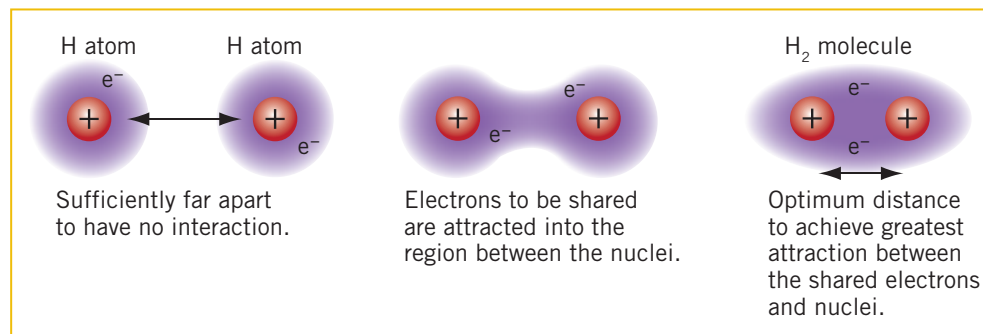
## 2.3 Covalent bonding

Compounds such as ammonia, sulfuric acid and nitric acid are among the most important manufactured chemicals. In each of these substances, covalent bonds hold atoms together. In addition, substances that include cosmetics, pharmaceuticals and fossil fuels, to identify just a few, also have covalent bonds between atoms. As it is for metallic and ionic substances, the chemistry of the production and uses of covalent substances is determined, in part, by the nature of the covalent bonding present.

The third type of strong bonding, the covalent bond, is most commonly observed between non-metal atoms. The formation of a covalent bond between two atoms results from the sharing of electrons between the two atoms.

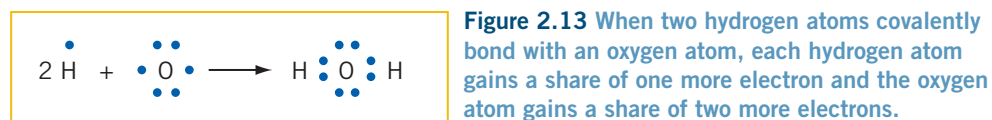
A covalent bond between two atoms forms in the following way. As the two atoms approach one another, the electrons that are to be shared experience an

attraction towards the two nuclei of the atoms. The electron clouds occupied by these electrons shift and combine so that the most probable place to find the shared electrons is between the two nuclei. The attractive force between the shared electrons and the positive nuclei of the atoms holds the two atoms together. This attractive electrostatic force, between the shared electrons and the nuclei, is the covalent bond. The formation of a covalent bond between two hydrogen atoms is illustrated in Figure 2.12.



**Figure 2.12** Hydrogen atoms are composed of one proton and one electron. As the two atoms approach, the two electrons are attracted into the region between the two nuclei. In the molecule formed, the two nuclei are held together by their attraction to the two shared electrons; that is, a covalent bond exists between the hydrogen atoms.

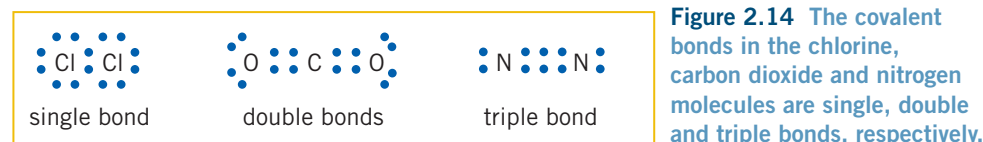
As with ionic compounds, when atoms form covalent bonds they usually gain a share in sufficient electrons to achieve a noble gas electron configuration. For example, when an oxygen atom, with an electron configuration of 2, 6, covalently bonds with another atom or atoms, it gains a share in two more electrons, to achieve a configuration of 2, 8. This is illustrated in the reaction between oxygen and hydrogen atoms to form water, shown using electron dot diagrams in Figure 2.13.



**Figure 2.13** When two hydrogen atoms covalently bond with an oxygen atom, each hydrogen atom gains a share of one more electron and the oxygen atom gains a share of two more electrons.

As explained with ionic compounds, only the valence electrons of each atom are shown in the electron dot diagrams.

Different numbers of electrons can be shared between two atoms. When the two atoms share one pair of electrons, a single covalent bond is formed. If two pairs of electrons (four electrons) are shared between the two atoms, then a double covalent bond is formed, and a triple covalent bond is produced when three pairs of electrons (six electrons) are shared. Examples of electron dot diagrams of molecules with single, double and triple bonds are shown in Figure 2.14.

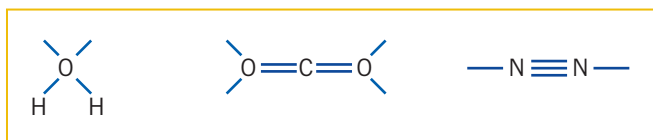


**Figure 2.14** The covalent bonds in the chlorine, carbon dioxide and nitrogen molecules are single, double and triple bonds, respectively.

In many molecules not all the valence electrons are involved in the covalent bonding. These valence electrons that are not part of a covalent bond are called non-bonding electrons, or lone pairs. The electrons involved in a covalent bond are called bonding electrons. For example, in the chlorine molecule shown in Figure 2.14, there are one pair of bonding electrons and six pairs of non-bonding electrons or lone pairs.



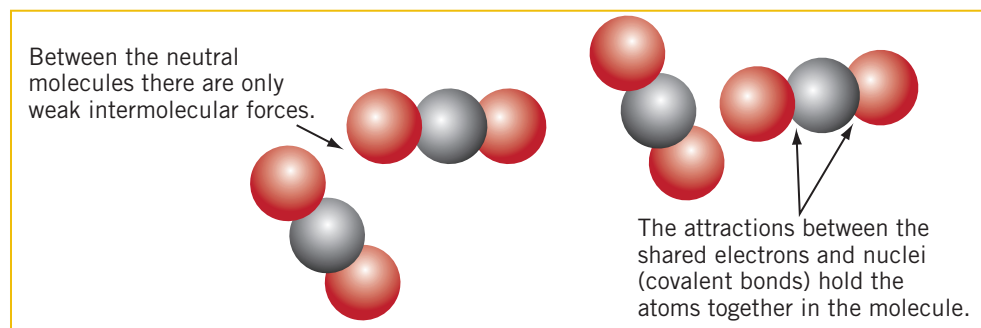
Electron pairs making up covalent bonds and lone pairs are also sometimes shown as lines between and around the atoms. A single line is used for a single bond and for a lone pair, a double line for a double bond and three lines for a triple bond. Figure 2.15 shows examples of formulas where lines have been used to represent the pairs of valence electrons in the molecules.



**Figure 2.15** Line structures of water, carbon dioxide and nitrogen molecules containing single, double and triple covalent bonds, respectively

## Covalent molecular substances

Substances composed of atoms covalently bonded together in small groups (molecules) are identified as covalent molecular substances. Water ( $\text{H}_2\text{O}$ ), carbon dioxide ( $\text{CO}_2$ ), methane ( $\text{CH}_4$ ), glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ), sulfur dioxide ( $\text{SO}_2$ ) and ozone ( $\text{O}_3$ ) are all examples of covalent molecular substances. In each of these substances, the atoms are strongly bonded in the molecules, but between the neutral molecules there are only weak bonds (intermolecular forces) (Figure 2.17).



**Figure 2.17** In carbon dioxide,  $\text{CO}_2$ , there are strong covalent bonds between the carbon and oxygen atoms in the molecules and weak forces between the neutral molecules.



**Figure 2.16** An example of a covalent molecular substance is ethanol. This liquid is a possible renewable fuel for vehicles. It is produced in the fermentation process of plant material such as barley (centre), corn, sugar cane and switch grass (lower right).

## Physical properties

The physical properties of covalent molecular substances tend to be determined by the fact that the particles making up the substances are neutral and as a result are only attracted to one another by weak intermolecular forces. These typical physical properties are:

- they have low melting and boiling points (they are often liquids and gases at room temperature). The covalent bonds between the atoms in the molecules are very strong, but the bonds between the molecules are weak. Not much heat is required to disrupt or break these weak intermolecular bonds, enabling the substance to melt or boil
- the solids are often soft. The bonds between the molecules are weak and so very little force is required to push some molecules past others in the solid
- they do not conduct electricity in solid or liquid states. Conduction of electricity requires the presence of mobile charged particles. The molecules in molecular substances (solids, liquids and gases) are neutral and the electrons and protons are localised within each molecule. Consequently, there are no free charged particles to act as charge carriers to conduct the electricity.

## Drawing electron dot diagrams of molecules

As with ions, molecules can also be represented by electron dot diagrams. Once again, the octet rule can be applied to most cases. When atoms combine, they tend to share electrons to attain an outer shell containing eight electrons (except for hydrogen—it gains a share of two electrons).

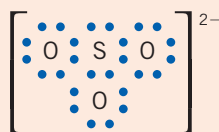
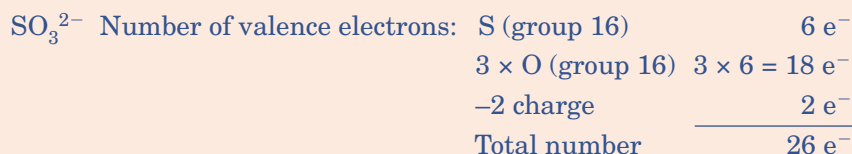
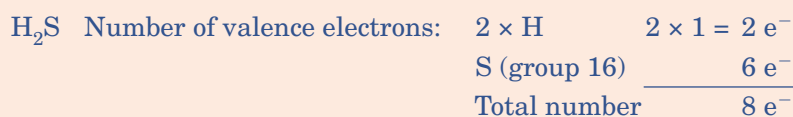
To determine electron dot diagrams of species, the following steps may be helpful:

- i Write down the symbols of the atoms present in their correct arrangement.
  - If there are more than two atoms, the single atom in the molecule is normally the central atom.
  - Atoms tend to be symmetrically arranged.
  - For substances containing O and H atoms, these two atoms are often present as an OH group attached to the central atom, for example in  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HSO}_4^-$  and  $\text{HCO}_3^-$ .
  - For organic molecules, such as  $\text{C}_3\text{H}_8$ , the carbon atoms are normally arranged in a chain.
- ii Determine the total number of valence electrons that should be shown in the diagram.
- iii If the species is a negative ion, add the appropriate number of electrons to the total number of valence electrons. If the ion is positive, subtract the appropriate number of electrons.
- iv Position the electrons around the atoms in the diagram, beginning by showing at least two electrons between each pair of atoms.
- v Rearrange the electrons so that each atom has a share of eight electrons (or two electrons for hydrogen).
- vi If the species is an ion, draw square brackets around the ion and include its charge.

### → Example 2.2

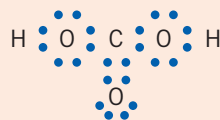
Draw the electron dot diagrams for  $\text{H}_2\text{S}$ ,  $\text{SO}_3^{2-}$ ,  $\text{H}_2\text{CO}_3$  and  $\text{C}_2\text{H}_2$ .

### → Solution



*continued*

$\text{H}_2\text{CO}_3$	Number of valence electrons:	$2 \times \text{H}$	$2 \text{ e}^-$
		$\text{C}$ (group 14)	$4 \text{ e}^-$
		$3 \times \text{O}$ (group 16)	$3 \times 6 = 18 \text{ e}^-$
		Total number	$24 \text{ e}^-$



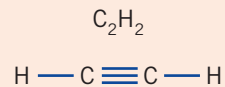
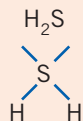
$\text{C}_2\text{H}_2$	Number of valence electrons:	$2 \times \text{C}$ (group 14)	$2 \times 4 = 8 \text{ e}^-$
		$2 \times \text{H}$	$2 \times 1 = 2 \text{ e}^-$
		Total number	$10 \text{ e}^-$



### → Example 2.3

Draw line structures for  $\text{H}_2\text{S}$  and  $\text{C}_2\text{H}_2$ .

### → Solution



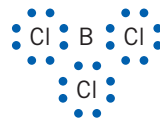
### Non-octet molecular compounds

For many molecules, the sharing of electrons results in each of the atoms having eight electrons in their valence shell (except hydrogen, which has two electrons). In some molecules, however, there may be atoms that do not 'satisfy' the octet rule.

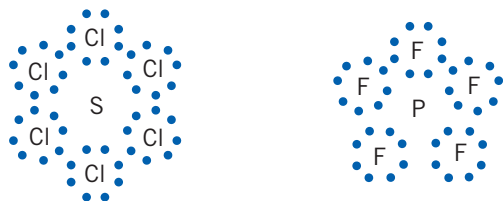
There are some molecules in which atoms have fewer than eight electrons in their outermost shell. In molecules containing beryllium, the beryllium atom has a share of four valence electrons. For example, the electron dot diagram for  $\text{BeF}_2$  is:



Boron also accepts a share of less than eight electrons in molecules. In  $\text{BCl}_3$ , boron has a share of six valence electrons as shown in the electron dot diagram below:



Atoms of elements in period 3 and beyond sometimes have a share of up to 12 electrons in some molecules. Examples of these molecules are  $\text{SCl}_6$  and  $\text{PF}_5$ .



## Covalent network substances

Sharing electrons to form covalent bonds is not confined to molecular substances and polyatomic ions. The covalent network substances such as diamond, graphite, silicon, silicon dioxide and silicon carbide also have their atoms bonded together by shared electron pairs. However, in these substances the atoms covalently bond to one another in vast lattice arrays.

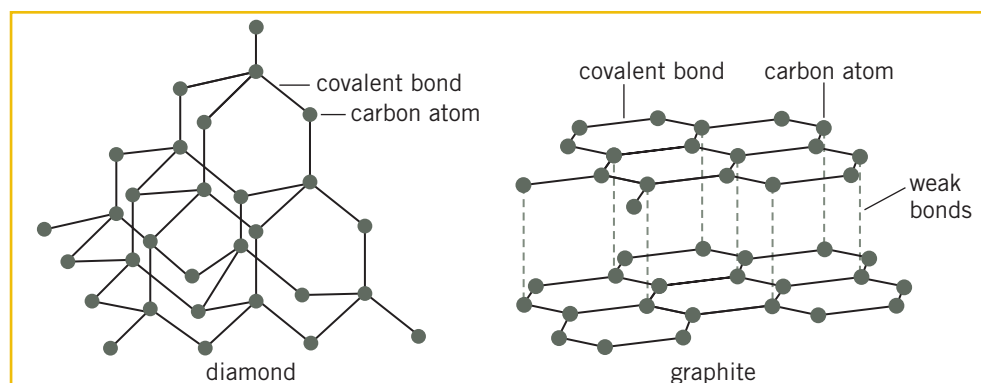


Figure 2.18 Covalent network substances—diamond and graphite

The physical properties of covalent network substances include:

- very hard, but if broken, they are brittle
- very high melting and boiling points
- do not conduct electricity in solid or liquid states (except graphite).

Because each atom in a covalent network substance is held in the lattice by strong covalent bonds, much heat or force is necessary to disrupt this lattice. However, once the lattice is disrupted in one area, this will then put a strain on the rest of the lattice and it will break apart. The substances do not conduct electricity because there are no free charged particles to move throughout the lattice.

Several of the physical properties of graphite are different from those of most other covalent network substances. Graphite's structure is really that of a layer lattice, rather than a three-dimensional lattice. In graphite, the carbon atoms are strongly bonded in two-dimensional layers, but between the layers there are only weak attractive forces. As a result, graphite has a slippery feel because the layers can easily slide over one another. Also within the layers, only three of the valence electrons of each carbon atom are shared in the covalent bonds. The remaining fourth electron from each atom is delocalised between the layers. These delocalised electrons account for graphite being an excellent conductor of electricity.

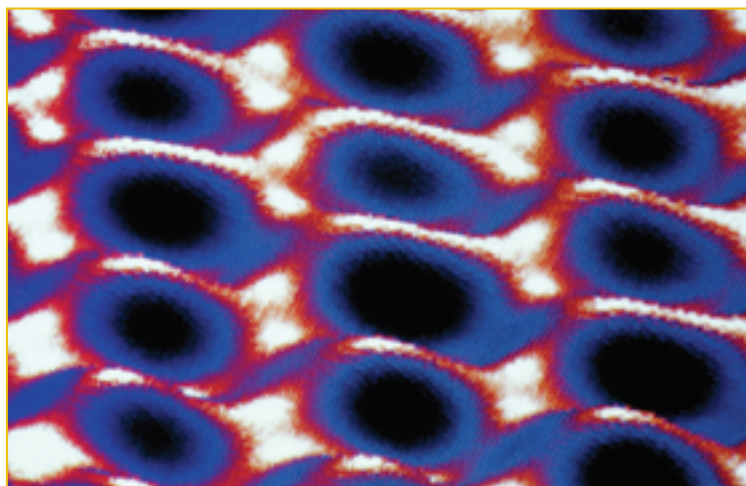


Figure 2.19 The scanning tunnelling microscope image of the surface of graphite shows the regular arrangement of the carbon atoms in a layer.

## \* Review exercise 2.3

- Draw electron dot diagrams for each of the following molecules.
  - $\text{NI}_3$
  - $\text{CClF}_3$
  - $\text{N}_2\text{O}$
  - $\text{HBr}$
  - $\text{CH}_3\text{COOH}$
  - $\text{HCN}$
- Draw line structures for the following molecules and polyatomic ions.
  - $\text{SiH}_4$
  - $\text{NO}_2^-$
  - $\text{PO}_4^{3-}$
  - $\text{PH}_3$
  - $\text{N}_2\text{H}_4$
- Explain the differences in the properties of the following two compounds in terms of their bonding and structure.

	Melting point ( $^{\circ}\text{C}$ )	Hardness of solid
$\text{CO}_2$	-57 (under pressure)	Easily broken into smaller pieces
$\text{SiO}_2$	1710	Very hard

- How many bonding electrons are in a molecule of  $\text{H}_2\text{O}$ ?
  - How many pairs of bonding electrons are in a molecule of  $\text{SiCl}_4$ ?
  - How many lone pairs of electrons are in a molecule of  $\text{NF}_3$ ?
- When water boils, which bonds are broken?
  - When electricity is passed through water (containing a little dissolved salt), hydrogen and oxygen gases are formed. Which bonds are broken in this electrolysis process?
  - When potassium nitrate,  $\text{KNO}_3$ , is melted, which bonds are broken?
- Explain why carbon tetrachloride,  $\text{CCl}_4$ , has a melting point of  $-23^{\circ}\text{C}$  yet calcium chloride,  $\text{CaCl}_2$ , has a melting point of  $772^{\circ}\text{C}$ .
- Why would you not expect liquid hydrogen chloride,  $\text{HCl}$ , to conduct electricity?
  - However, when hydrogen chloride,  $\text{HCl}$ , is dissolved in water, the resulting solution is a good conductor of electricity. Propose an explanation for this observation.
- The hydrocarbons ethane, ethene and ethyne are all gases at room temperature. Despite being composed of the same types of atoms, their C–C bond lengths and bond strengths differ, as shown in Table 2.8.

TABLE 2.8

Hydrocarbon	Molecular formula	C–C bond length (pm)	C–C bond strength ( $\text{kJ mol}^{-1}$ )
Ethane	$\text{C}_2\text{H}_6$	153	347
Ethene	$\text{C}_2\text{H}_4$	134	614
Ethyne	$\text{C}_2\text{H}_2$	120	839

- a Draw electron dot diagrams for ethane, ethene and ethyne.
- b Why are these three compounds gases at room temperature?
- c Explain the differences in the C–C bond lengths of these three compounds.
- d Propose an explanation for why the C–C bond strengths should be different for these three hydrocarbons.

9 Read the following information about silicon carbide, then answer the questions.

### Silicon carbide

*Silicon combines with carbon to form a crystalline compound, silicon carbide, with a rigid diamond-like structure. The arrangement of atoms is similar to that in diamond except alternate carbon atoms are replaced by silicon atoms.*

*Silicon carbide (SiC), known as carborundum, is commonly used as an abrasive in sharpening and grinding tools and on 'sandpaper'. Because it can withstand extreme temperatures, it is used for manufacturing high-performance brake discs in sports cars. Silicon carbide heating elements are used in industrial processes such as the melting of non-ferrous metals and in the production of glass, ceramics and electronic components. A gem-quality synthetic form of silicon carbide is also sold under the tradename of moissanite, as a low-cost alternative to diamond. It is almost as hard as diamond but has a larger index of refraction that gives it more fire and brilliance.*

- a What type of substance is silicon carbide?
- b Describe the type of bonding that exists between the atoms in silicon carbide.
- c Draw a small portion of the crystal lattice of silicon carbide.
- d Discuss the uses of silicon carbide in terms of its properties, bonding and structure.



Figure 2.20 A grinding wheel made from coarse particles of silicon carbide

## 2.4 Summary of strong bonding

### Ionisation energy and types of substances formed

Ionisation energy data can be used to explain the types of substances formed by some elements.

- Metal elements tend to have low first ionisation energies. Consequently, they usually react by losing electrons to form positive ions in ionic substances.

Group 1 elements have reasonably low first ionisation energies; however, much more energy is required to remove a second electron. These elements readily lose one electron to form an ion with a +1 charge, but it is highly unlikely that they would form an ion with a +2 charge.

Group 2 elements have reasonably low first and second ionisation energies; however, their third ionisation energy is much larger. They form ions with a +2 charge, rather than +1 or +3 ions.

- Non-metal elements from groups 14 to 17 have reasonably high first ionisation energies. This means that large amounts of energy are required to remove electrons from these elements. So they tend to react by gaining

electrons to form negative ions or sharing electrons, rather than losing them.

Group 18 elements (He, Ne, Ar etc.) have large first ionisation energies, and so do not lose (or gain) electrons under normal reaction conditions. They are very stable (unreactive) elements.

### Comparison of the properties of the different types of substances

The properties of the four types of substances have been summarised in the flow chart shown in Figure 2.21.

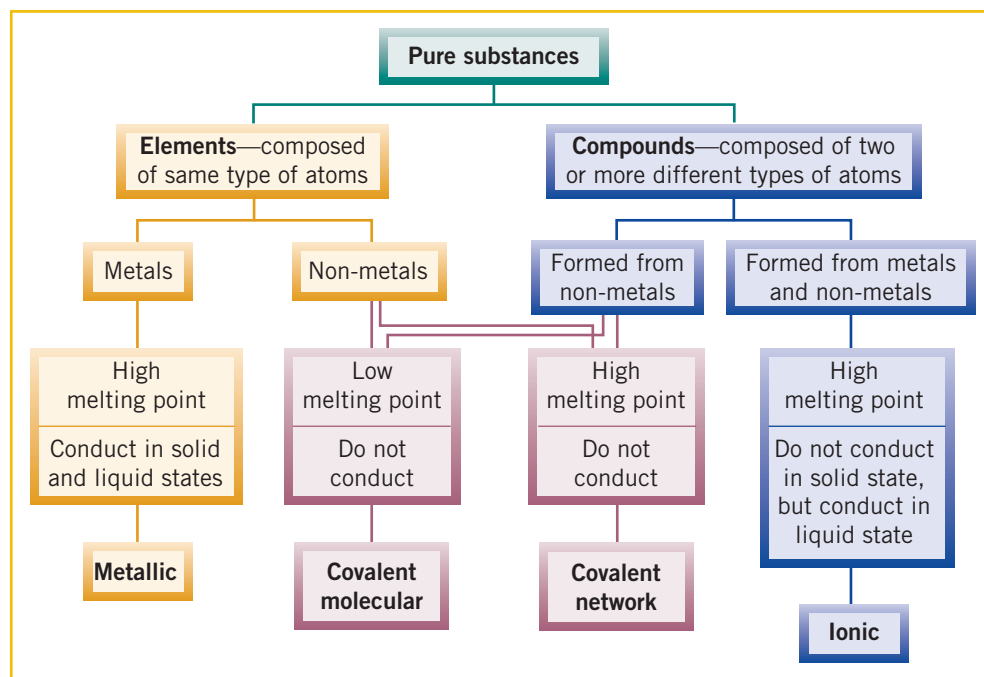


Figure 2.21 Summary of the relationships between the melting point and conductivity properties of the four different types of substances

### \* Review exercise 2.4

- 1 Explain each of the following observations in terms of the bonds or forces present and the types of particles in the substance.
  - a Silver is a malleable element.
  - b Diamond is a very hard substance.
  - c Acetone,  $C_3H_6O$ , is a volatile liquid.
  - d Calcium carbonate is a brittle solid.
  - e Graphite is a good conductor of electricity.
- 2 Consider the following processes.
  - i Sublimation of dry ice (solid  $CO_2$ )
  - ii  $Cl_2(g) \rightarrow 2Cl(g)$
  - iii Bending an iron nail until it breaks in half
  - iv Shattering a crystal of potassium nitrate
  - v Breaking the 'lead' (graphite) of a pencil

For each of these processes, identify the types of:

- a bonds being broken
- b particles (molecules, atoms or ions) being separated.

3 Consider the following substances:

lead(II) bromide  
hydrogen bromide

sodium chloride  
potassium iodide

sulfur  
zinc

ethanol (C<sub>2</sub>H<sub>5</sub>OH)  
silicon carbide

From these substances name those you would expect to:

- a conduct electricity in the solid state
  - b conduct electricity both in the liquid state and as an aqueous solution
  - c not conduct electricity in their pure form at room temperature but produce a conducting liquid when dissolved in water
  - d not readily conduct electricity under any conditions
  - e have a melting point below 120°C.
- 4 Copy and complete the following table to summarise the properties of different types of substances.

Type of substance	Particles present (atoms, ions, electrons, molecules)	Melting point (high or low)	Electrical conductivity	
			of solid	of liquid
Ionic				
Metallic				
Covalent molecular				
Covalent network				

## 2.5 Familiar yet unusual

Many materials in common use today do not fit neatly into one of the categories of ionic, metallic, covalent molecular or covalent network substances. Some of these, like concrete, have been in use for many years, but others, such as liquid crystals, have been more recently developed. The chemistry of most of these substances is quite intricate but, just to serve as an introduction to these intriguing materials, a brief description of their properties, composition and uses is given in this section.

### Glass

Glass is an amorphous substance, meaning that, like a liquid, its particles are not organised in an orderly lattice. However, despite having the structure of a liquid, glass has the properties of a solid. In its formation, the molten glass mixture is cooled rapidly so that there is insufficient time for the particles to become organised in a crystalline pattern. They therefore remain in a distorted jumble in the 'solid' state.

Pure silicon dioxide, or quartz, can be formed into a glass. However, because it needs to be heated to such a high temperature, over 1000°C, to soften it so it can be shaped, it is quite expensive. Glasses do not have definite melting points; instead they slowly soften when heated. Since the late 1980s, silicon dioxide glass, usually mixed with other glasses, has been used for making the optical fibres in



fibre optic cables. Because light can travel large distances along an optical fibre with little or no absorbance, these fibres are used in telecommunication systems for transmitting sound and images in the form of light.



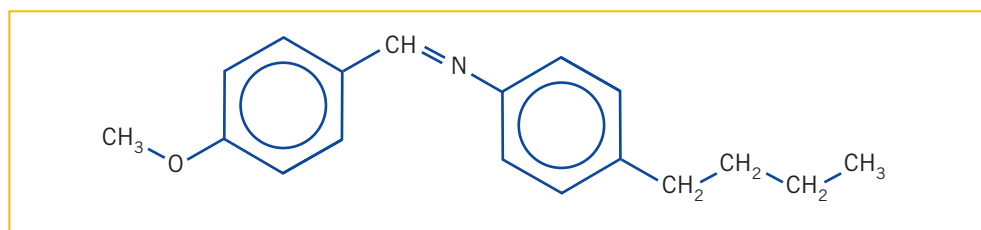
**Figure 2.22** Optical fibres emitting light. These fibres are used for transmitting sound and images in the form of light.

The most familiar glass is soda glass which is used in drinking glasses, bottles and windows. To produce soda glass, a mixture of silicon dioxide (sand), sodium carbonate and calcium carbonate is heated to form a molten mixture of sodium and calcium silicates,  $\text{Na}_2\text{SiO}_3$  and  $\text{CaSiO}_3$ , that is then rapidly cooled. Soda glass can be readily worked and shaped because when it is heated it begins to soften at low temperatures. It can usually be softened in a Bunsen burner flame.

The properties of glass can be varied greatly by adding different substances. For example, optical glass, a hard glass used for spectacles and contact lenses, has potassium oxide,  $\text{K}_2\text{O}$ , added to it. Addition of boron oxide,  $\text{B}_2\text{O}_3$ , to silicon dioxide, together with a few other minor ingredients, produces borosilicate glass. This glass, commonly known by its brand name of Pyrex glass, has a higher softening temperature than soda glass, but more importantly it expands and contracts very little under large temperature changes. As a result, it can be used for cooking and scientific equipment such as baking dishes, test tubes and beakers.

### Liquid crystals

Liquid crystals are more or less the opposite of glass. They have the properties of a liquid yet their structure has some order, like that in a crystalline solid. Liquid crystals consist of polar molecules that in most cases have a long cylindrical shape, and a structure that allows them to weakly attract one another but inhibits their arrangement in a perfectly ordered lattice. One such molecule, 4-methoxybenzylidene-4'-n-butylaniline, MBBA, is shown in Figure 2.23.



**Figure 2.23** 4-Methoxybenzylidene-4'-n-butylaniline—a liquid crystal molecule

Depending on conditions such as temperature, the presence of an electric field, even touch or a scratch mark, the liquid crystals can rearrange in different ways to create a change in one or more of their properties, such as colour.

Liquid crystals are being employed in an increasing number of different ways. For instance, liquid crystal displays (LCD) are used in wristwatches, clocks, calculators, portable computers and various other devices where a low-power display is needed. Liquid crystals whose particle arrangements depend on temperature have been used in liquid crystal thermometers, which are safer than mercury thermometers to use with children, in the charge indicator strip on batteries and for novelty objects like mood rings. They are also important in the formation of super-strength polymers, such as Kevlar, used in bullet-proof vests. Liquid crystals also occur in living systems; for example, the membrane in every cell in the human body is a liquid crystal substance.

## Ceramics

Ceramics are made from clays that consist of tiny thin platelets formed from the breakdown of silicate minerals. Clays have complex compositions, but one clay formed from the weathering of feldspar is kaolinite, which has an empirical formula of  $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$ . Wet clay can easily be moulded into different shapes because the water in between the platelets allows them to slip over one another. But when dry, the clay becomes hard and rigid because the platelets cling together and so can no longer slide past one another. When the clay is fired at high temperatures, the ions present rearrange to form an extended network-type glass. The ceramic product formed is permanently rigid, even in contact with water.

The use of ceramics as containers for food and drink has a very long history. However, their stability at high temperatures and resistance to corrosion has led them to become 'high tech' materials. Some of the new uses made of ceramics include car engine parts, supports or layering materials in electronic microchips, cutting tools, armour-plating reinforcement fibres and surgical implants.

## Composites

A composite material is made by combining two or more materials with very different properties. In the composite material the components remain separate on the macroscopic level. However, the properties of the composite material are a combination of the properties of the components. Composite materials include car tyres, fibreglass, reinforced concrete, plywood and mud bricks.

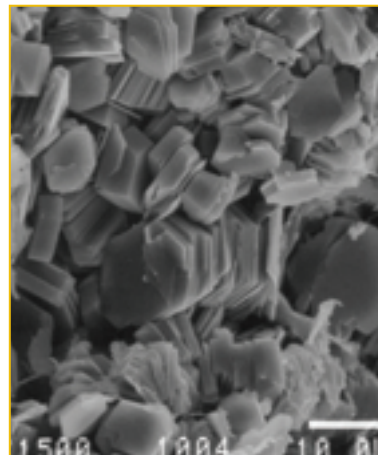


Figure 2.24 Magnified view of kaolinite clay platelets

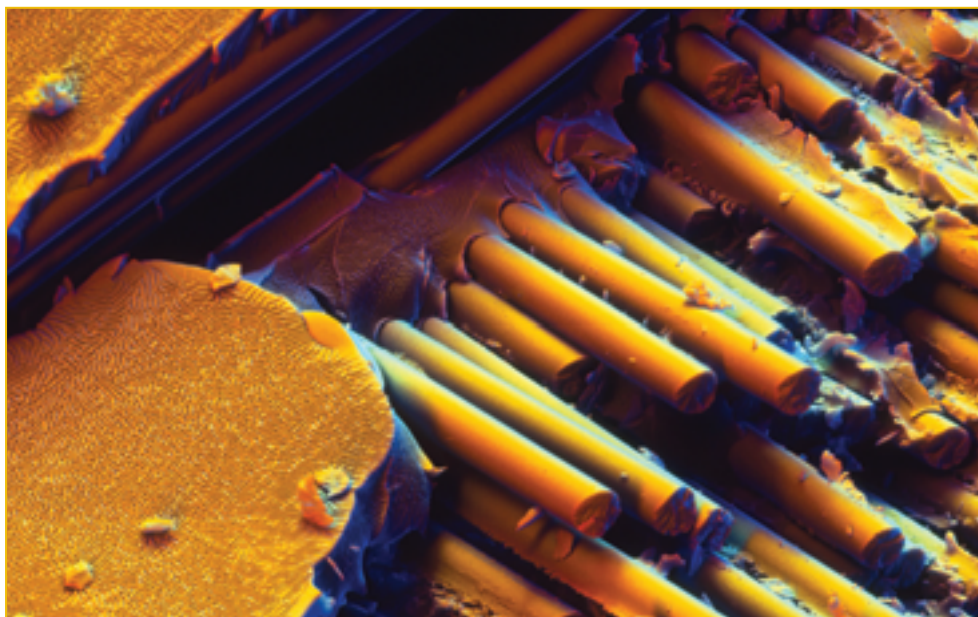


Figure 2.25 Coloured scanning electron micrograph of fibreglass. This material consists of glass fibres (rod shapes) embedded in polyester (a type of plastic). Fibreglass is hard, strong and light, and is used in the construction of aircraft, cars and yachts.

## Concrete

Houses, roads, factories, high-rise buildings, pipes, footpaths and dams are a few things made from concrete. It is the basic building material for modern societies. Concrete is mostly made by mixing Portland cement with sand, gravel and water. Portland cement is a powdered mixture of calcium silicates,  $\text{Ca}_2\text{SiO}_4$  and  $\text{Ca}_3\text{SiO}_5$ ; calcium aluminate,  $\text{Ca}_3\text{Al}_2\text{O}_6$ ; and a trace of calcium iron aluminate,  $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ . It is made by strongly heating a mixture of limestone and clay, then grinding the product with some gypsum (calcium sulfate).

When the powdered cement, sand and gravel mixture is combined with a little water, it becomes a pliable substance that eventually hardens. The hardening process is not due to the evaporation of water but to the water being incorporated into the complex silicate structure that forms during the setting of the cement. The result is a dry hard material. This setting process is not fully understood, but it is known that calcium silicate hydrate forms a three-dimensional network structure that holds the components of the concrete together.

Because concrete deteriorates and cracks over time, research is being carried out to improve its durability and to increase its strength. The addition of superplasticisers and fibres made of steel, glass or carbon-based polymers are being tried.



### \* Review exercise 2.5

- 1   ▷ **RESEARCH**
  - a What are the properties of soda glass?
  - b Discuss the 'pluses and minuses' of using this type of glass, relating these to the properties of the glass.
- 2   ▷ **RESEARCH**
  - a What are optical fibres?
  - b Relate the properties of optical fibres to their uses.
  - c How are optical fibres made?
  - d Discuss the contribution of fibre optic cables to modern society.
- 3   ▷ **RESEARCH**
  - a Give some examples of composite materials.
  - b For each example:
    - i name the materials present in the composite
    - ii compare the properties of these separated materials with the properties of the composite.
- 4   ▷ **RESEARCH**

How are liquid crystals used in calculator displays to provide the black and clear regions when keyboard buttons are pressed? What features of the liquid crystal molecule are important in this process?

## MAJOR IDEAS

- Metallic bonding involves the electrostatic attraction of positive metal ions for delocalised valence electrons.
- Metallic bonding explains properties such as conductivity of heat and electricity, malleability and ductility, lustre and melting points.
- As the charge on the positive ions in the metallic lattice increases, so does the attraction between those ions and the delocalised electrons.
- As the atomic radii of the metal atoms increase down a group, the attraction of the positive ions for the delocalised electrons decreases.
- When metals lose electrons in chemical reactions, they behave as reductants.
- Ionic bonding is the electrostatic attraction between positive ions and negative ions in a crystal lattice.
- In the formation of ionic compounds, metals, with lower ionisation energies, form positive ions or cations, and non-metals form negative ions or anions.
- Ions can include the monatomic metal and non-metal ions as well as a range of polyatomic ions in which individual atoms are covalently bonded, but overall there is an ionic charge.
- The properties of ionic compounds such as high melting and boiling points, non-conductivity in the solid state, but conductivity when molten or dissolved in water, and brittleness can be explained in terms of the arrangement of ions in the solid crystal lattice.
- Covalent bonding results from the electrostatic attraction between atomic nuclei and shared electrons occupying the region of space between these nuclei.
- Single, double and triple covalent bonds can form.
- Electron dot diagrams, in which only the valence electrons around the atoms are shown, can be drawn for molecules and ions.
- Covalent bonding is present in molecular substances as well as in covalent network substances.
- In covalent molecular substances, the covalent bonds within the molecule are strong, but the bonding between the molecules is weak.
- In covalent network substances, the strong covalent bonding extends throughout the lattice.
- Covalent network substances have much higher melting and boiling points, and are usually much harder than covalent molecular substances.

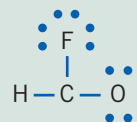
## QUESTIONS

- 1 The following compounds may be found around the home. Draw the electron dot diagrams for each of these.

	Common name	Use	Formula
a	Bicarbonate of soda	In cooking	$\text{NaHCO}_3$
b	Sulfate of ammonia	Fertiliser	$(\text{NH}_4)_2\text{SO}_4$
c	Caustic soda	Drain cleaner	$\text{NaOH}$
d	Sulfuric acid	Car battery acid	$\text{H}_2\text{SO}_4$
e	Ethanol	Wine	$\text{CH}_3\text{CH}_2\text{OH}$
f	Hydrogen peroxide	Teeth whitener	$\text{H}_2\text{O}_2$

- 2 As can be seen in Figure 2.4, which shows the many pipes and towers that are part of an oil refinery, metals are used extensively for these constructions. Suggest reasons why metals are used for this purpose and not ionic, covalent network or covalent molecular substances.

- 3 Consider the structure of fluoromethanal drawn below.



- a Explain what is wrong with this structure.  
b Redraw the structure correctly.
- 4 Why is the boiling point of a metal a better measure of the strength of the metallic bond than the melting point?
- 5 Explain the uses of each of the following materials in terms of their bonding and properties.
- a An alloy of magnesium is used in the wheels of some cars.  
b Aluminium is used for window frames.  
c Silicon carbide is used in sandpaper.  
d Sodium chloride is present in sports drinks, such as Gatorade.  
e Copper is used in electrical wiring.  
f Limestone is used in the construction of buildings, fences and retaining walls.  
g Hydrocarbons are used as propellants in spray cans.  
h Graphite is used in 'lead' pencils.  
i Ammonium nitrate is a better 'fast acting' fertiliser than urea,  $\text{CO}(\text{NH}_2)_2$ .

**TABLE 2.9 IONISATION ENERGIES AND SOME PHYSICAL PROPERTIES OF A VARIETY OF METALS FROM THE SAME PERIOD OF THE PERIODIC TABLE**

Metal	Group	Melting point (°C)	Density (g cm <sup>-3</sup> )	Hardness (Brinell scale, MPa)	Successive ionisation energies (MJ mol <sup>-1</sup> )			
					1st	2nd	3rd	4th
Potassium	1	254	0.86	0.363	0.425	3.058	4.418	5.883
Calcium	2	839	1.55	167	0.596	1.152	4.918	6.480
Scandium	Transition metal	1538	3.0	750	0.637	1.241	2.395	7.095
Titanium	Transition metal	1660	4.50	716	0.664	1.316	2.659	4.181
Iron	Transition metal	1535	7.86	490	0.766	1.567	2.964	5.29

- 6 Use the data given in Table 2.9 to suggest explanations for the following observations.
- Iron has a higher melting point than calcium.
  - Potassium is a softer metal than scandium.
  - Potassium only forms +1 ions, but titanium forms +2 and +3 ions.
  - The density of titanium is greater than the density of calcium.
- 7 Explain why metals are always reductants in oxidation–reduction reactions.
- 8 Propose explanations for the differences in the covalent bond energies (the energy required for  $X_2(g) \rightarrow 2X(g)$ ) given below:

F <sub>2</sub>	160 kJ mol <sup>-1</sup>
O <sub>2</sub>	498 kJ mol <sup>-1</sup>
N <sub>2</sub>	945 kJ mol <sup>-1</sup>

- 9 Lead can be flattened into a thin sheet by an applied force, but lead nitrate shatters. Account for these two observations.
- 10 The atomic radii of the atoms of the period 2 elements are shown in Figure 2.26. Explain the trend shown in this data.

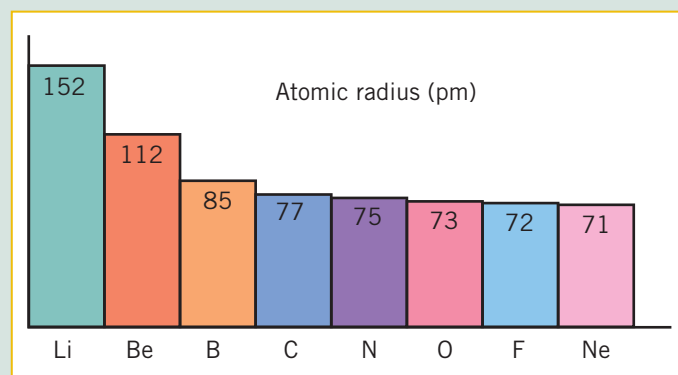


Figure 2.26

- 11 Superconductors are materials through which electricity can flow with little or no resistance. As a consequence, when electricity flows through a superconductor, there should be little or no heating effect. Superconductors offer the promise of benefits such as power transmission without power loss and superfast electronic circuits. However, the few metals that can be superconducting, such as aluminium and mercury, only exhibit this property at extremely low temperatures, just above absolute zero. Research is being carried out to develop superconducting materials that can work at room temperatures.

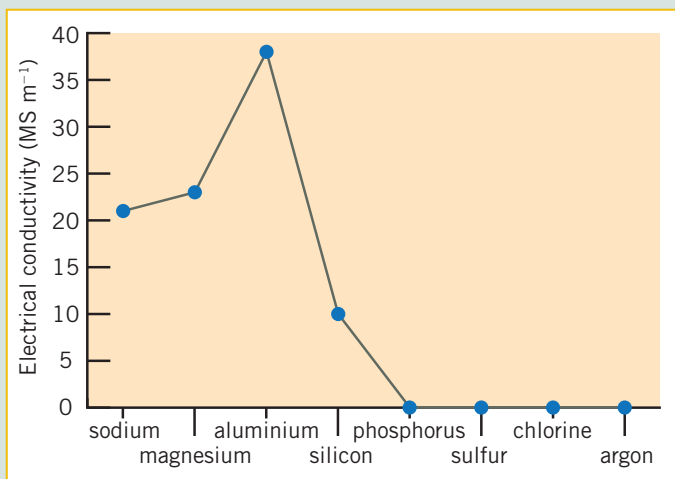
Suggest why metals only behave as superconductors at extremely low temperatures.

- 12 At times in bonding topics, reference is made to the ‘octet rule’. Essentially this ‘rule’ proposes that since there are eight electrons in the valence shell of the unreactive noble gases (except helium), chemical bonding in molecular substances will result in all atoms (except hydrogen) having a share of this stable number of eight electrons.

While this ‘rule’ is true for many covalent molecular compounds, in particular those involving period 2 elements as they are only able to accommodate eight electrons in their outermost shell, it does not apply to all possible molecular substances.

Each of the compounds listed below forms a non-octet structure. Draw an electron dot diagram for each.

- SCl<sub>6</sub>
- TeF<sub>4</sub>
- BCl<sub>3</sub>
- IF<sub>7</sub>
- PCl<sub>5</sub>



**Figure 2.27** The trend in electrical conductivities of the period 3 elements

- 13** The trend in electrical conductivity of the period 3 elements, in their solid state, is shown in the graph in Figure 2.27. Explain this trend in terms of the bonding and structure of the elements.
- 14** If energy is required to ionise metal atoms and to convert non-metal molecules to anions (negative ions), account for the fact that ionic compounds form so readily.
- 15** The ionisation energies for carbon and sodium are given in the table below.

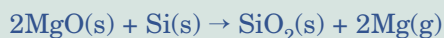
	Ionisation energy (kJ mol <sup>-1</sup> )					
	1st	2nd	3rd	4th	5th	6th
Carbon	1100	2372	4660	6271	38 093	47 580
Sodium	502	4569	6919	9550	13 356	16 616

- a** Give the electron configuration of carbon.
- b** Write equations to represent the first and the second ionisation of carbon.
- c** Explain why the second ionisation energy is larger than the first ionisation energy for carbon.
- d** Explain why there is a very large difference between the fourth and the fifth ionisation energies for carbon.
- e** Suggest a reason that might explain why the first ionisation energy of carbon is larger than the first ionisation energy of sodium.
- f** Using the ionisation energy data, discuss why metallic bonding holds the particles together in a piece of sodium, yet covalent bonding holds the atoms together in a diamond.
- 16** One of the reasons gold, silver and copper are used extensively in the jewellery industry is that they are reasonably soft metals, and are ductile and malleable. Gold, in particular, is so ductile and malleable that 1.0 g of it can be drawn into a wire 165 m long and 20  $\mu\text{m}$  thick or hammered into a 1.0 m<sup>2</sup> sheet only 0.050  $\mu\text{m}$  thick.
- a** What are the meanings of the words ‘ductile’ and ‘malleable’?
- b** Use a model of metallic bonding and structure to explain why metals are malleable and ductile.
- c** If 1.0 g of gold is shaped into a cube, what would the dimensions of this cube be? The density of gold is 19.3 g cm<sup>-3</sup>.
- d** How many atoms of gold would there be in this 1.0 g cube of gold?
- e** How many atoms thick is the sheet described above, that can be made from 1.0 g of gold?
- f** Suggest several other reasons, apart from softness, malleability and ductility, why gold, silver and copper are used to make jewellery.
- 17** One type of dry-chemical fire extinguisher suitable for use with electrical and flammable liquid fires contains powdered sodium hydrogencarbonate pressurised with nitrogen. When the sodium hydrogencarbonate is blown onto the fire, it decomposes at 60°C to form carbon dioxide and sodium carbonate. Initially the powdered sodium hydrogencarbonate and then the carbon dioxide and the newly formed solid sodium carbonate all smother the fire.
- a** Why is it not safe to use a water-based fire extinguisher on an electrical fire or a flammable liquid fire?
- b** Give the formulas of sodium hydrogencarbonate and sodium carbonate.
- c** Draw electron dot diagrams for sodium hydrogencarbonate, sodium carbonate and carbon dioxide.
- d** Write a balanced equation for the decomposition reaction sodium hydrogencarbonate undergoes when heated.
- e** Suggest an explanation for the way in which each of the three substances puts out a fire.
- f** Explain why, at the temperature of the fire, carbon dioxide is a gas, but sodium carbonate is a solid.

**18** Magnesium is a very versatile metal. It is a light-weight soft metal and even though it is quite reactive, it forms a tough impervious oxide layer that prevents further reaction with oxygen. It can be easily rolled, pounded, welded and riveted in virtually any shape, but more importantly, it forms low-density alloys that are strong. When alloyed with other metals such as aluminium and zinc, magnesium is used in objects such as aircraft bodies, car wheels, jet-engine parts, portable power tools, mobile phones, computer laptops and cameras.

Even though magnesium is not scarce (it is the eighth most abundant element in the Earth's crust), its extraction from the relevant minerals requires a significant amount of energy. This is because of magnesium's reactivity.

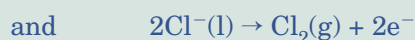
Commercially, two methods are used to produce magnesium—an electrolytic process and a thermal reduction process. In the thermal process, magnesium oxide, obtained from the mineral dolomite, is heated to about 1400°C with an alloy of silicon and iron, to form magnesium vapour:



The vapour is then condensed to form high-purity magnesium.

In the electrolytic method, the raw material used can either be seawater or a slurry of dolomite. In either case, the first step is the precipitation of magnesium ions from the liquid mixture in a reaction with calcium hydroxide. The magnesium hydroxide formed is then reacted with hydrochloric acid to produce a solution of magnesium chloride. This solution is evaporated and the solid obtained is heated strongly to form anhydrous magnesium chloride.

The magnesium chloride is mixed with calcium chloride and sodium chloride and the mixture is electrolysed in a cell using carbon anodes and steel cathodes. The electrode reactions that occur are:



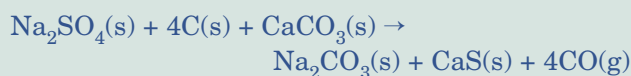
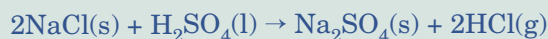
The molten magnesium floats to the top of the electrolytic mixture, from where it is collected and cast into ingots.

- a** The first four successive ionisation energies (in  $\text{MJ mol}^{-1}$ ) of magnesium are 0.744, 1.457, 7.739 and 10.547. Use this data to:
- explain why magnesium can be easily shaped
  - explain why magnesium forms an ionic compound when it reacts with non-metals
  - predict the formula of the ions formed by magnesium in these reactions. Explain your answer.
- b** Use electron dot diagrams to show what happens to the valence electrons during the reaction of magnesium with oxygen to form magnesium oxide.
- c** Suggest why magnesium is much less dense ( $1.7 \text{ g cm}^{-3}$ ) than some other commonly used metals such as iron ( $7.9 \text{ g cm}^{-3}$ ).
- d** Why is magnesium not found in its elemental form in the Earth's crust?
- e** Explain why magnesium becomes a stronger metal when it is alloyed with other metals.
- f** In the high-temperature conditions used in the thermal reduction production of magnesium, magnesium exists as a gas, but silicon dioxide is a solid. Discuss, in terms of bonding and structure concepts, why this is the case.
- g** Why can magnesium not be obtained by carrying out the electrolysis of seawater?
- h** Write equations for the two reactions that are used to produce magnesium chloride from magnesium ions in seawater.
- i** When a solution of magnesium chloride is evaporated, why does the water evaporate and not the magnesium chloride?
- j**
- Draw a labelled sketch of the electrolytic cell that might be used in the industrial production of magnesium from magnesium chloride described in the previous column.
  - Explain, in terms of their structure and bonding, why steel and carbon can be used as electrodes in this cell.
  - What product is formed at the anode and what product is formed at the cathode?
  - Estimate the approximate temperature at which the electrolytic cell operates. Explain your reasoning.
  - Why is it necessary to operate the cell at this temperature?
  - What is the purpose of mixing sodium and calcium chlorides with the magnesium chloride in the cell?

**k** To make the electrolytic production of magnesium more environmentally friendly and economical, suggest what might be done with the chlorine formed in the electrolysis cell.

**l** About 1 kg of magnesium can be recovered from 800 L of seawater; so the oceans are a virtually inexhaustible source of this metal. However, what is the major disadvantage with the production of magnesium by electrolysis?

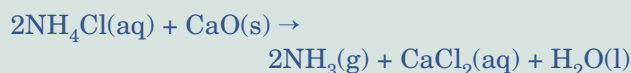
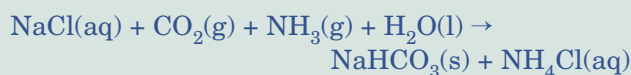
**19** Prior to the 1860s, the major industrial process for the manufacture of sodium carbonate, now used for making glass, water softeners, soaps and detergents, and as a cheap base, was the Leblanc process. The chemistry of this process is summarised in the equations below:



**a** The substances involved in these two equations exhibit ionic and covalent bonding. Classify each as either an ionic, covalent molecular or covalent network substance.

**b** From an environmental perspective, these two reactions are not regarded as 'friendly'. What are the issues that would ultimately see this process eliminated by the end of the 1860s?

Today, the Solvay process is used to manufacture sodium carbonate. The series of reactions involved in this process is summarised in the following equations:



**c** As with the Leblanc process, the compounds involved in these reactions exhibit both ionic and covalent bonding. Classify the reactants and products under the two headings (ionic or covalent molecular compounds) and draw electron dot diagrams for each.

**d** Why is it that the reactions summarised by these four equations are more environmentally friendly than the two reactions in the Leblanc process?





# 3

## Intermolecular bonding

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

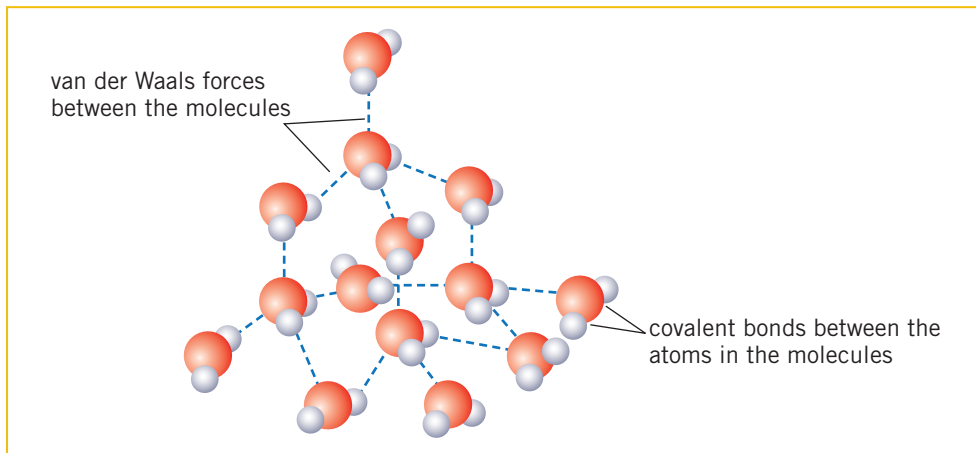
- distinguish between intramolecular bonding and intermolecular forces
- determine shapes of simple molecules
- use the concept of electronegativity to determine the polarity of molecules
- explain dispersion forces
- distinguish between dispersion forces and dipole–dipole forces
- identify hydrogen bonding as an extreme of dipole–dipole bonding
- describe the requirements for hydrogen bonding
- use the concept of van der Waals forces to explain some of the physical properties of covalent molecular substances.

Without covalent molecular substances life would not exist and the Earth would be a barren desert with the occasional volcano spewing lava onto the surface. The gases in the atmosphere, water in the oceans, ice in the polar caps and proteins, fats, nucleic acids and carbohydrates in living systems are all covalent molecular substances. Even though it is the covalent bonds that determine the chemical properties of these covalent molecular substances, it is the weak bonds between the molecules that determine their physical properties. Whether a substance is a solid, liquid or gas, whether one substance will dissolve in another, and the ability to bend and stretch or to adhere to another substance are just a few properties that depend on the weak intermolecular forces between molecules.



### 3.1 Van der Waals forces

In Unit 2A the kinetic molecular theory was introduced to explain the properties of gases. One of the postulates of this theory is that there are no attractive forces between particles in the gas phase. If this was true then a gas would never liquefy as there would be nothing causing the particles to remain close together after collision. However, even the lightest gas, hydrogen, will turn into a liquid if the temperature is lowered sufficiently ( $-253^{\circ}\text{C}$ ). In fact, even though the molecules are neutral, there are weak attractive forces between all molecules in substances. These weak intermolecular attractive forces are called van der Waals forces after Johannes van der Waals, a Dutch chemist who first proposed the existence of such forces. For example, in ice there are strong covalent bonds (intramolecular forces) between the H and O atoms in the  $\text{H}_2\text{O}$  molecules and weak van der Waals forces (intermolecular forces) between the  $\text{H}_2\text{O}$  molecules.



**Figure 3.1** There are both strong intramolecular (covalent bonds) and weak intermolecular (van der Waals) forces in ice. The open structure that results from the formation of the intermolecular bonds causes solid water (ice) to be less dense than liquid water.

While van der Waals forces may be weak, there is no doubt they are vital to life and important in chemical processes. Because of the existence of van der Waals forces, water is a liquid at room temperature, even though other molecules with comparable molecular masses are gases. Van der Waals forces hold animal and plant proteins in particular shapes so they can function in the required ways; they enable DNA (deoxyribonucleic acid) to carry out its role as the blueprint for life; they allow spiders and flies to stick to a ceiling; they are significant in determining which solutes will dissolve in which solvents and in allowing chemists to separate the components of air or crude petroleum.

Unlike ionic, covalent or metallic bonds, the intermolecular van der Waals forces are weak; they are less than 10% of the strength of the three strong bond types. These different types of strong and weak bonds or forces are compared on the next page.



**Figure 3.2** Coloured scanning electron micrograph of the underside of a gecko's foot. Geckos are able to climb vertically on smooth glass surfaces because of the weak forces between the glass and the large surface area of their feet, due to the presence of microscopic hairs.

**Strong bonds:**

- Attraction between positive and negative ions in a lattice—ionic bonding
- Attraction between positive metal ions and delocalised valence electrons—metallic bonding
- Attraction between two nuclei and one or more shared electron pairs—covalent bonding between atoms in molecules or in infinite lattices

**Weak intermolecular forces** (van der Waals forces):

- Attraction between all types of particles resulting from the particles being instantaneous dipoles—dispersion forces
- Attraction between polar molecules—dipole–dipole forces
- Attraction between polar molecules containing OH, NH or FH groups—hydrogen bonds
- Attraction between polar solvent water molecules and dissolved ions—ion–dipole attractions

The four types of weak intermolecular forces will be discussed in this chapter.

**\* Review exercise 3.1**

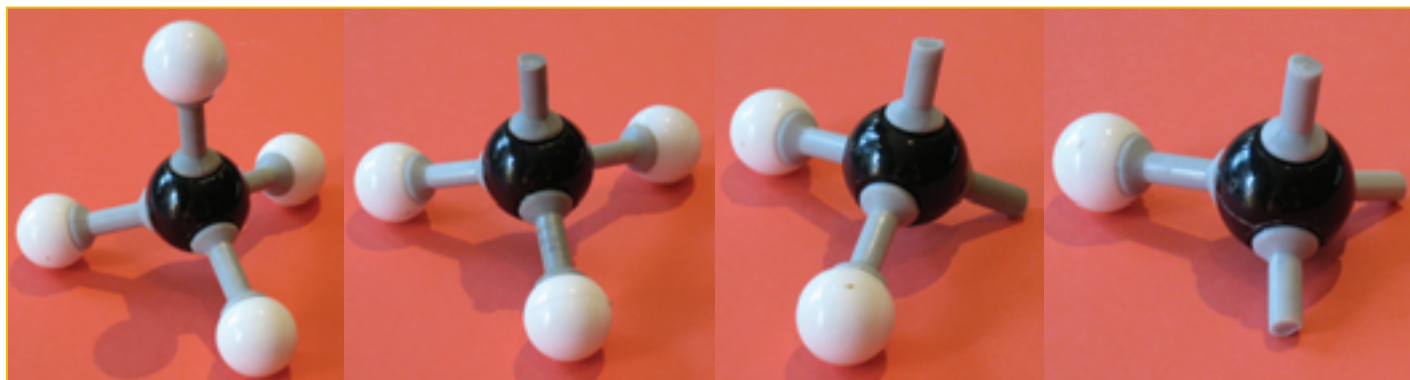
- 1 The boiling points of three liquids used as non-aqueous solvents are:  
ethanol 78°C    hexane 69°C    tetrachloroethene 121°C.
  - a Which of these substances would have the strongest intermolecular forces?
  - b Which of these liquids will therefore be the most volatile? Explain your reasoning.
- 2 Of the following changes, which involve the breaking of only intermolecular forces?
  - a Methane is burnt in air.
  - b A block of dry ice (solid carbon dioxide) sublimates.
  - c A piece of sodium metal is cut in half.
  - d Sodium chloride dissolves in water.
  - e Sugar dissolves in water.
  - f Cooking oil is boiled.
  - g A puddle of water evaporates.
  - h Electricity is passed through water to form oxygen and hydrogen.
  - i A sticky note is removed from a piece of paper.
- 3 Explain why, when crushing ice, the ice breaks up but the metal blades of the ice-crusher are not affected.

## 3.2 Shapes of molecules

The shape of a molecule is determined by the positions of the atoms that make up the molecule. The positions of the atoms in simple molecules depend on the arrangement of the electron pairs surrounding the central atom of the molecule.

The valence shell electron pair repulsion theory (VSEPR) can be used to predict the arrangement of the electron pairs around atoms. This theory states that the electron pairs in the valence shell (outer shell) of an atom repel each other, and as a result, these electron pairs are arranged as far apart as possible.

Figure 3.3 shows three-dimensional models of four different shapes of molecules.

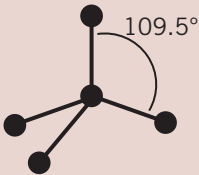
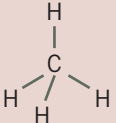
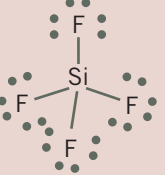
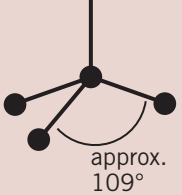
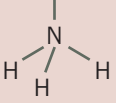
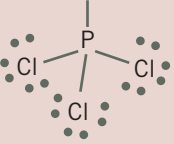
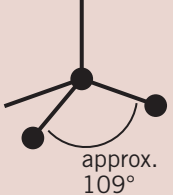
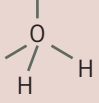

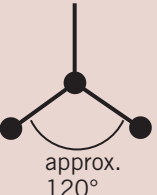
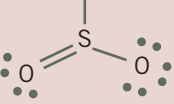


**Figure 3.3** Molecular models of the different molecular shapes based on the tetrahedral arrangement of four pairs of electrons around the central atom. From left to right: tetrahedral shape, pyramidal shape, V-shape, linear shape

Some of the common shapes of molecules are identified and explained in Table 3.1.

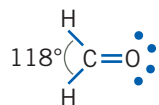
**TABLE 3.1** SOME COMMON SHAPES OF MOLECULES

Shape	Representation	Description	Examples
Linear		The shape of all diatomic molecules is linear, regardless of how many lone pairs are around each atom. In molecules that have only two areas of negative charge around the central atom, these areas of negative charge will be arranged $180^\circ$ apart, i.e. in a line. The angle between the bonds (called the bond angle) will be $180^\circ$ .	$\text{H}_2$ $\text{H} - \text{H}$ $\text{HCl}$ $\text{H} - \text{Cl}$ $\text{BeF}_2$ $\text{F} - \text{Be} - \text{F}$
Trigonal planar (triangular planar)		Three areas of negative charge around a central atom will be arranged $120^\circ$ apart. If these three areas of negative charge are pairs of bonding electrons, i.e. there are three atoms bonded to the central atom, then the molecule is said to have a trigonal planar shape. All four atoms are planar and the bond angles are $120^\circ$ .	$\text{BCl}_3$ $\text{Cl} - \text{B} - \text{Cl} - \text{Cl}$

Shape	Representation	Description	Examples
Tetrahedral		Four areas of negative charge around a central atom will be arranged $109.5^\circ$ apart. This arrangement of areas of negative charge is called a tetrahedral arrangement. The four atoms around the central atom will be positioned at the corners of a tetrahedron. The shape of the molecule is also called tetrahedral and the bond angles are $109.5^\circ$ .	$\text{CH}_4$  $\text{SiF}_4$ 
Pyramidal		In molecules of this shape, there are four areas of negative charge around the central atom, which will be arranged approximately $109^\circ$ apart, i.e. tetrahedrally. However, only three of these areas of negative charge are bonding pairs of electrons. One of the areas of negative charge is a lone pair. There will only be three atoms bonded to the central atom, but they will not be in the trigonal planar shape because the lone pair pushes the bonding pairs closer together, to give bond angles of less than $109^\circ$ . Lone pairs of electrons exert a slightly larger repulsive force than bonding pairs. This shape is called pyramidal.	$\text{NH}_3$  $\text{PCl}_3$ 
V-shaped (bent)		For this shape, there are four areas of negative charge arranged tetrahedrally around the central atom, but two of these areas are lone pairs, i.e. there are only two atoms bonded to the central atom. The bond angle will be less than $109^\circ$ because the lone pairs exert slightly greater repulsive forces than bonding pairs of electrons. The shape is called V-shaped, or bent.	$\text{H}_2\text{O}$  $\text{SBr}_2$ 
		In this molecule, there are only three areas of negative charge around the central atom. Two of these areas are bonding pairs of electrons and one is a lone pair. This shape is also called V-shaped, but the bond angle will be a little less than $120^\circ$ , again because of the greater repulsive force of the lone pair.	$\text{SO}_2$ 

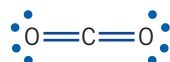
In molecules containing double or triple bonds, the same VSEPR principles apply. The double or triple bond is considered as if it is one region of negative charge exerting a repulsion on other bonding and non-bonding electron pairs around the central atom. In those situations where bond angles are being considered, a multiple bond will have greater repulsive influence than a single bond.

For example, for the methanal molecule,  $\text{H}_2\text{CO}$ :



there are three areas of negative charge around the central atom, so they will be arranged approximately  $120^\circ$  apart. Because each of these areas of negative charge are bonding pairs; that is, there are three atoms bonded to the central atom, the molecule will have a trigonal planar shape. The HCH bond angle will be less than  $120^\circ$  and the HCO bond angles will be a little larger than  $120^\circ$ .

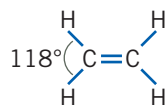
The carbon dioxide molecule,  $\text{CO}_2$ , is another example of a molecule involving double bonds.



This molecule has a linear shape because there are two regions of negative charge around the central atom, and these will be arranged  $180^\circ$  apart.

Several common molecules that do not fit the arrangement of atoms described previously are ethene and ethyne.

For the ethene molecule,  $\text{C}_2\text{H}_4$ :



there are three regions of negative charge around each of the carbon atoms. This will result in the bonds (the two single bonds and the double bond) around each carbon being arranged in the trigonal planar arrangement. For this arrangement to occur around each carbon atom, all the atoms in the molecule will be in the one plane and so the molecule is said to be planar in shape.

With the ethyne molecule,  $\text{C}_2\text{H}_2$ :



the two regions of negative charge around each carbon atom will be arranged  $180^\circ$  apart. The four atoms will therefore be in a line. This molecule is said to have a linear shape.

Figure 3.5 depicts several more examples of molecules and ions containing multiple bonds.

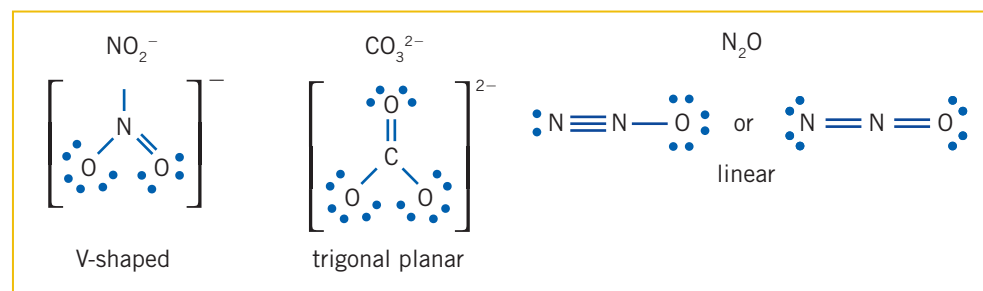


Figure 3.5 Molecular shapes of molecules and ions with multiple bonding

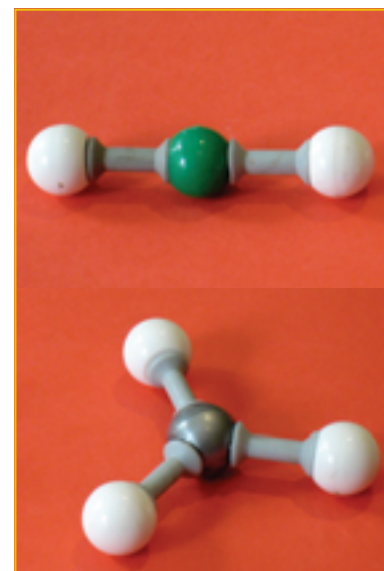


Figure 3.4 Models of molecules of  $\text{BeF}_2$  and  $\text{BF}_3$ , showing their linear and trigonal planar shapes respectively

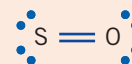
→ **Example 3.1**

Identify the shapes of the following molecules and ions.

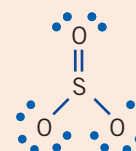
- a SO
- b SO<sub>3</sub>
- c SO<sub>3</sub><sup>2-</sup>
- d H<sub>2</sub>S
- e HCN

→ **Solution**

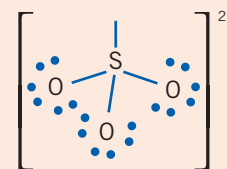
a Any diatomic molecule will be **linear**.



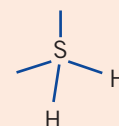
b In this molecule, there are three areas of negative charge around the central atom, so they will be arranged approximately 120° apart. There are three atoms bonded to the central S atom, so the structure is **trigonal planar**.



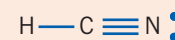
c There are four areas of negative charge around the central atom, so these three bonds and the lone pair will be organised in a tetrahedral arrangement, that is, approximately 109° apart. However, there are only three atoms bonded to the central S atom, so the ion is a **pyramidal shape**.



d There are four areas of negative charge around the central S atom and these will be arranged in a tetrahedral arrangement. There are only two atoms bonded to the central atom, so the molecule will be **V-shaped**.



e There are two areas of negative charge around the central C atom. These two areas will be arranged 180° apart to give a **linear** molecule.



## \* Review exercise 3.2

- 1 What is the basic electrostatic principle upon which the VSEPR hypothesis is based?
- 2 Draw line structures and state the shape of the molecules of the hydrides of the elements silicon to chlorine in period 3 of the periodic table.
- 3 **a** Draw an electron dot diagram of ethyne,  $C_2H_2$ , and hydrogen peroxide,  $H_2O_2$ .  
**b** Describe the differences in the intramolecular bonding in these two molecules.  
**c** Describe the difference in shape of these two molecules. Explain why there is a difference.
- 4 Line diagrams of various molecules are depicted in Figure 3.6 (these diagrams do not necessarily indicate the correct bond angles). For each of these molecules describe the correct shape and provide an estimate of the bond angle(s).

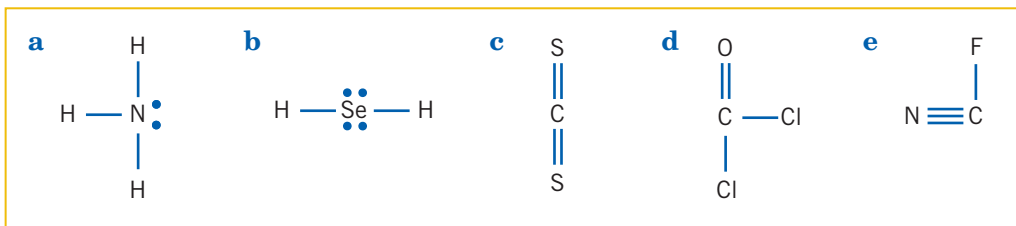


Figure 3.6

- 5 Draw line structures of the following molecules and ions, then identify their shape and give the approximate bond angles.
  - a  $CH_3F$
  - b  $HBr$
  - c  $OH^-$
  - d  $C_2F_2$
  - e  $OCl_2$
  - f  $SO_4^{2-}$
  - g  $PO_3^{3-}$

## 3.3 Electronegativity and bond polarity



Electronegativity was defined in Chapter 1 as the electron-attracting power of an atom when involved in a bond. As the atom gets larger, the electronegativity or electron-attracting power of the nucleus for the outermost electrons becomes smaller. In addition, the electronegativity or electron-attracting power increases as the nuclear core charge of the atom increases. (The nuclear core charge is a measure of the positive charge of the nucleus minus the shielding effect of inner shells of electrons.) As a consequence, the electronegativities of the elements decrease down any group and increase across a period from left to right (see section 1.4 for a more detailed discussion). These trends in electronegativity are shown in the periodic table in Figure 3.7.



Electronegativity increases →

Period	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1																		He
2	0.98 Li	1.57 Be											2.04 B	2.55 C	3.04 N	3.44 O	3.98 F	Ne
3	0.93 Na	1.31 Mg											1.61 Al	1.90 Si	2.19 P	2.58 S	3.16 Cl	Ar
4	0.82 K	1.00 Ca	1.36 Sc	1.54 Ti	1.63 V	1.66 Cr	1.55 Mn	1.83 Fe	1.88 Co	1.91 Ni	1.90 Cu	1.65 Zn	1.81 Ga	2.01 Ge	2.18 As	2.55 Se	2.96 Br	3.00 Kr
5	0.82 Rb	0.95 Sr	1.22 Y	1.33 Zr	1.6 Nb	2.16 Mo	1.9 Tc	2.2 Ru	2.28 Rh	2.20 Pd	1.93 Ag	1.69 Cd	1.78 In	1.96 Sn	2.05 Sb	2.1 Te	2.66 I	2.6 Xe
6	0.79 Cs	0.89 Ba	La*	1.3 Hf	1.5 Ta	2.36 W	1.9 Re	2.2 Os	2.20 Ir	2.28 Pt	2.54 Au	2.00 Hg	1.62 Tl	2.33 Pb	2.02 Bi	2.0 Po	2.2 At	Rn
7	0.7 Fr	0.9 Ra	Ac**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							
Lanthanides *			1.12 Ce	1.13 Pr	1.14 Nd	1.13 Pm	1.17 Sm	1.2 Eu	1.2 Gd	1.1 Tb	1.22 Dy	1.23 Ho	1.24 Er	1.25 Tm	1.1 Yb	1.27 Lu		
Actinides **			1.3 Th	1.5 Pa	1.38 U	1.36 Np	1.28 Pu	1.13 Am	1.28 Cm	1.3 Bk	1.3 Cf	1.3 Es	1.3 Fm	1.3 Md	1.3 No		Lr	

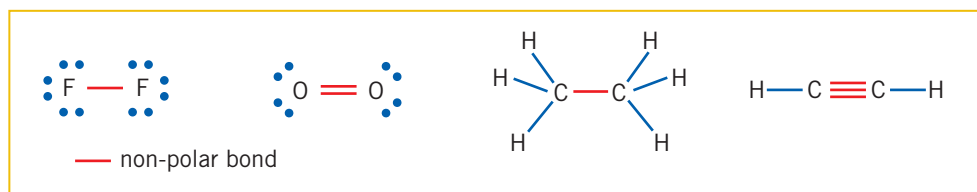
Electronegativity decreases ↓

2.20 — electronegativity  
 H — symbol

**Figure 3.7** Electronegativity increases across a period and decreases down a group.

### Non-polar bonds

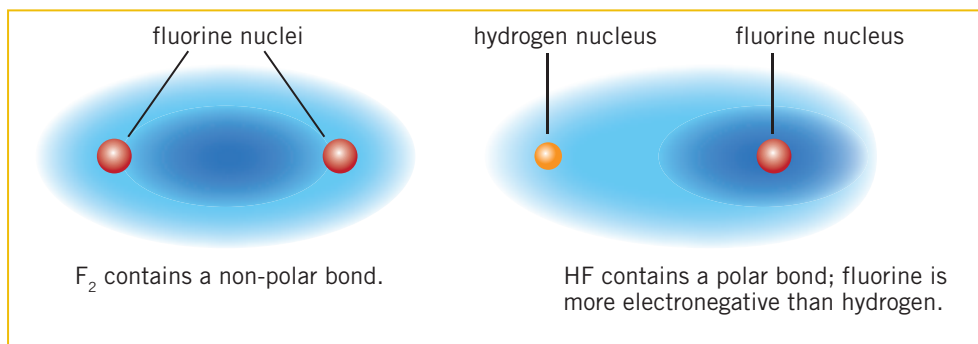
When a covalent bond forms between two identical atoms, for example, in  $\text{Cl}_2$ , the two electrons in the covalent bond are shared equally between the two atoms. This means these two electrons will 'spend equal time' moving around each atom. The type of bond where the electrons are equally shared is called a pure covalent bond, or a non-polar covalent bond. The covalent bonds shown in red in the molecules in Figure 3.8 are non-polar bonds.



**Figure 3.8** The bonds shown in red are non-polar bonds because the bonding electrons are equally shared between two identical atoms.

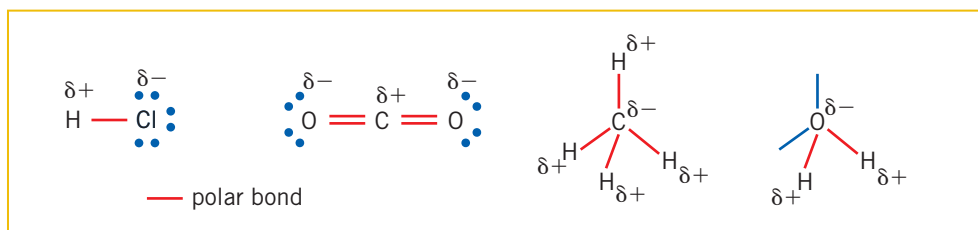
### Polar bonds

In a covalent bond formed between two different atoms, the electrons are normally not equally shared. The electrons will spend more time moving around the atom that has the higher electronegativity. This leads to an uneven charge distribution in the bond, with the region near the more electronegative atom having a partial (small) negative charge and the region near the other, less electronegative atom in the bond having a partial positive charge.



**Figure 3.9** For the non-polar bond in  $F_2$ , the electron cloud is positioned symmetrically around the two nuclei. For the polar bond in HF, the electron cloud is skewed towards the nucleus of the more electronegative atom.

When unequal sharing of electrons occurs, the amount of positive and negative charge on each of the two atoms bonded by the covalent bond is less than that on ions bonded by ionic bonds. The Greek letter delta,  $\delta$ , is used to represent the partial positive ( $\delta^+$ ) charge and partial negative ( $\delta^-$ ) charge on the two atoms. The bond is called a polar covalent bond when the electrons are unequally shared. Examples of molecules with polar covalent bonds are shown in Figure 3.10.



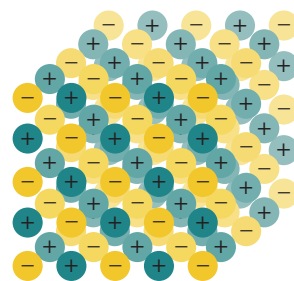
**Figure 3.10** Molecules containing polar covalent bonds (shown in red). In a polar covalent bond, the electrons are unequally shared because one atom attracts the shared electrons more than the other.

### Extreme polar bonds

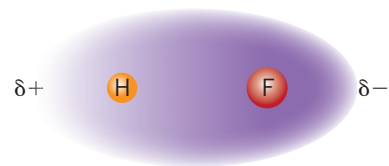
When two atoms with a large difference in electronegativities combine, such as sodium and fluorine, positive and negative ions are formed. The fluorine, with a large attraction for the valence electron of sodium, is assumed to take complete 'ownership' of the electron, leaving the sodium with a full +1 charge and giving the fluorine a full -1 charge. Usually, the bonds between positive and negative ions are regarded as being ionic, albeit this generalisation does not necessarily hold when the positive ion is formed from a metal that is in the middle of the periodic table. The effect of the electronegativity difference on the type of bond formed between fluorine and another element is shown in Figure 3.11.

Electronegativity difference between:

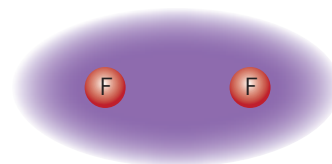
NaF Na and F is 3.0.  
Ionic bonds between ions.  
Valence electrons mostly move  
around the F<sup>-</sup> ion.



HF H and F is 1.8.  
Polar covalent bond.  
Shared electrons move  
around the F nucleus  
more than the H nucleus.



F<sub>2</sub> F and F is 0.  
Non-polar or pure covalent bond.  
Shared electrons spend equal  
time around each F nucleus.



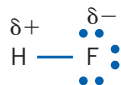
**Figure 3.11** Bond polarity ranges from non-polar (pure) covalent to ionic depending on the electronegativity difference between the bonded atoms.

### \* Review exercise 3.3

- 1 Draw line structures of the following molecules and identify the covalent bonds as either non-polar or polar.
  - a HBr
  - b SiCl<sub>4</sub>
  - c SO<sub>2</sub>
  - d N<sub>2</sub>H<sub>4</sub>
- 2 The following molecules have polar covalent bonds. Draw line structures of the molecules and indicate which end of each bond will have a partial positive charge and which end will have a partial negative charge.
  - a HI
  - b NBr<sub>3</sub>
  - c OCl<sub>2</sub>
- 3
  - a Describe how electronegativity changes across a period and down a group in the periodic table.
  - b Explain, using the concept of 'core charge', why fluorine is more electronegative than oxygen.
  - c Explain why chlorine is less electronegative than fluorine.

## 3.4 Polarity of molecules

Molecules in which there is an uneven charge distribution are called polar molecules. For example, in hydrogen fluoride, HF, the fluorine end of the molecule has a partial negative charge (because fluorine attracts electrons more than hydrogen does), and the hydrogen end of the molecule has a partial positive charge:



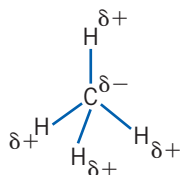
This molecule is therefore said to be polar.

The HF molecule can also be called an electric dipole or a dipole. An electric dipole comprises a negatively charged region separated by a distance from an equal but oppositely charged positive region. In any molecule that is a dipole, the centre of positive charge is separated from the centre of negative charge.

Other examples of diatomic polar molecules are HCl, HBr and CO. However, diatomic molecules such as  $\text{Cl}_2$  and  $\text{N}_2$ , where the electrons are equally shared in the covalent bond between the atoms, are not polar; they are non-polar molecules.

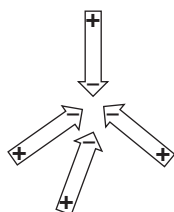
Diatomic molecules such as the hydrogen halides with a single polar covalent bond are obviously polar. However, when there is more than one polar covalent bond in the molecule, the overall polarity of the molecule depends not only on the presence of polar covalent bonds, but also on whether the molecule is symmetrical or asymmetrical. In this context, a symmetrical molecule is regarded as one in which the individual bond dipoles cancel one another or in which the centre of positive charge is at the same point as the centre of negative charge.

If a molecule is symmetrical, even if its bonds are polar, it will not be polar; in other words, it will be a non-polar molecule. For example, methane,  $\text{CH}_4$ , has slightly polar bonds, but because it has a symmetrical structure, it is a non-polar molecule:

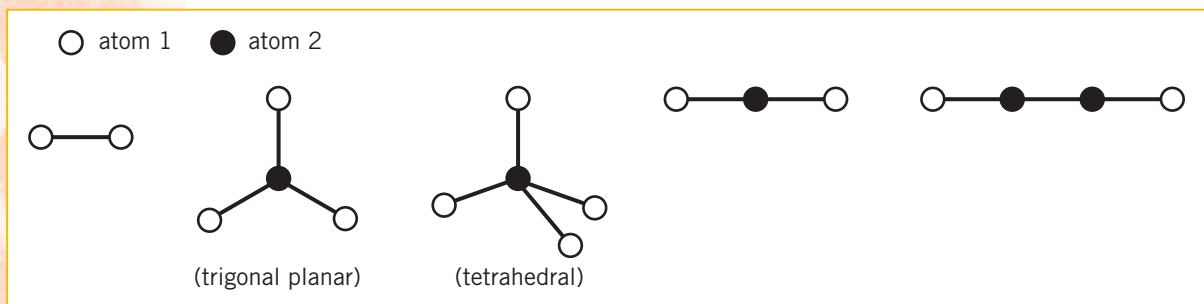


For this molecule, because of the symmetrical three-dimensional arrangement of the polar C–H bonds around the central carbon atom, the centre of partial positive charge will be in the same place as the partial negatively charged carbon atom. The molecule is therefore not a dipole; that is, it is a non-polar molecule.

Alternatively, the lack of polarity of this  $\text{CH}_4$  molecule can be explained using vectors. Each individual bond dipole can be represented by a vector with the arrowhead representing the negative end of the dipole. To then determine the overall polarity of the molecule, these vectors are added together, head to tail. In the case of the  $\text{CH}_4$  molecules, the sum of the three-dimensionally arranged vectors is zero:

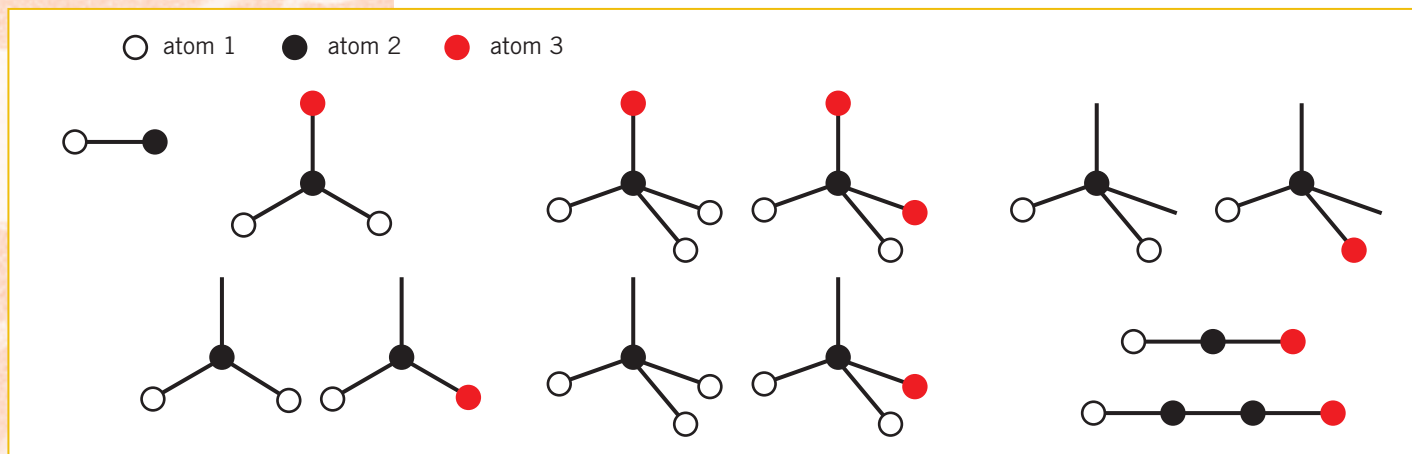


For any molecule that is symmetrical, the sum of the vectors representing the bond dipoles will be zero. This means the symmetrical molecule will not be a dipole; it will be a non-polar molecule. Examples of the arrangement of atoms in symmetrical, and therefore non-polar, molecules are represented in Figure 3.12.



**Figure 3.12** Symmetrical arrangements of atoms in molecules that are non-polar

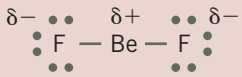
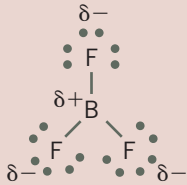
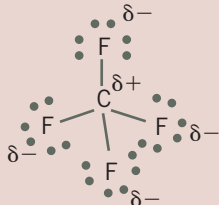

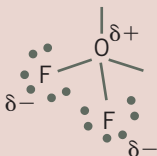

Figure 3.13 shows examples of asymmetrical (or non-symmetrical) arrangements of atoms in molecules. Molecules with these arrangements have net molecular polarity; in other words, they are polar.



**Figure 3.13** Examples of asymmetrical arrangements of atoms in molecules that are polar

The relationship between bond polarity, molecular symmetry and overall molecular polarity is explored further in Table 3.2 by examining the molecular fluorides of the elements of period 2.

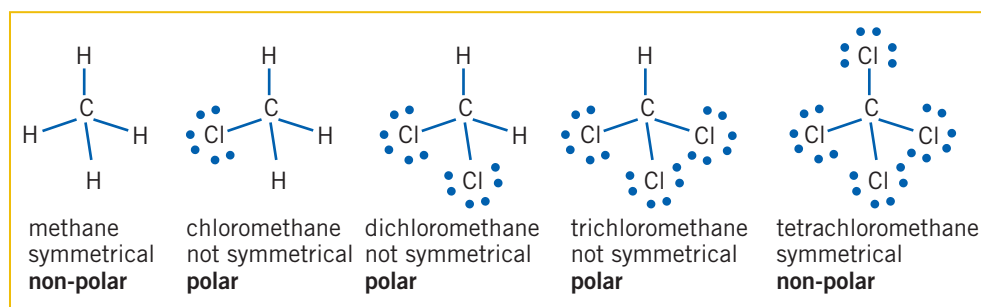
**TABLE 3.2 THE MOLECULAR FLUORIDES OF THE ELEMENTS OF PERIOD 2**

<p>Beryllium difluoride, <math>\text{BeF}_2</math>—a non-polar molecule (This fluoride exists in the gaseous phase as a covalent molecular compound.)</p>		<p>The difference in electronegativity between beryllium and fluorine is around 2.4, so the molecule contains polar covalent bonds. However, the molecular shape is linear as the two covalent bonds will orient themselves at <math>180^\circ</math> to maximise repulsions. As a consequence, the molecule is symmetrical and the vector sum of the two bond dipoles will be zero. (Or, the partial positive charge is on the beryllium atom, at the same point as the centre of partial negative charge.)</p>
<p>Boron trifluoride, <math>\text{BF}_3</math>—a non-polar molecule</p>		<p>The molecule has a trigonal planar shape. The difference in electronegativity between boron and fluorine is around 2, so the covalent bonds are polar. However, the partial positive charge and the centre of partial negative charge are both in the same position on the boron atom (or the vector sum of the bond dipoles would be zero); so although the molecule has polar covalent bonds, it is a non-polar molecule because of its symmetry.</p>
<p>Tetrafluoromethane, <math>\text{CF}_4</math>—a non-polar molecule</p>		<p>The pairs of electrons around the central atom are arranged tetrahedrally, and the molecule has a tetrahedral shape. Between carbon and fluorine the electronegativity difference is almost 1.5 so the bonds are polar covalent. However, once again the centres of partial positive and negative charges are located at the same place (on the central carbon atom) or the vector sum of the bond dipoles would be zero. The molecule is symmetrical and so overall has no polarity; it is a non-polar molecule.</p>
<p>Nitrogen trifluoride, <math>\text{NF}_3</math>—a polar molecule</p>		<p>The pairs of electrons around the central atom are arranged tetrahedrally, and the molecule has a pyramidal shape (because of the lone pair on the N atom). The nitrogen–fluorine bonds are polar, given that the electronegativity difference between nitrogen and fluorine is about 1. Moreover, the centres of partial positive and negative charges do not correspond. This molecule is not symmetrical and the individual bond dipoles do not cancel. Nitrogen trifluoride is a polar molecule.</p>
<p>Oxygen difluoride, <math>\text{OF}_2</math>—a polar molecule</p>		<p>This molecule is V-shaped. Once again the bonds between the central atom and the fluorine are polar. The electronegativity difference between oxygen and fluorine is about 0.5. As the molecule is not symmetrical, the centres of partial positive and negative charges do not overlap. The individual bond dipoles do not cancel and overall there is net molecular polarity; the molecule is polar.</p>
<p>Fluorine, <math>\text{F}_2</math>—a non-polar molecule</p>		<p>The F–F bond is not polar because the electrons are equally shared. The molecule must therefore be non-polar.</p>

In summary, a molecule will be polar if:

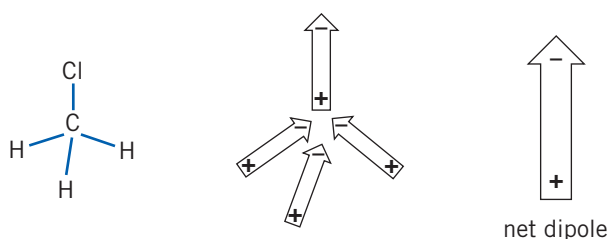
- it contains polar covalent bonds—bonds between atoms that do not have the same electronegativity, and
- it is asymmetrical—the centres of partial positive and negative charges do not correspond or the sum of the vectors representing the polarity of each bond is not zero.

The examples examined previously contained only two different types of atoms. Many molecules contain three or more different types of atoms. The same general ideas presented earlier can be used to determine whether these molecules are polar or non-polar. As indicated in the representations shown in Figure 3.13, often by introducing a third type of atom into a previously symmetrical molecule, the molecule becomes asymmetrical. For example, polarity of the series of chloro-substituted methane molecules is shown in Figure 3.14.



**Figure 3.14** This series of compounds shows the change in polarity of a molecule caused by introducing a different type of atom to the molecule.

In this series, even though all of these molecules have a tetrahedral shape, the polarity of the C–H bond is different in magnitude and direction from the polarity of the C–Cl bond (the order of electronegativity is  $\text{Cl} > \text{C} > \text{H}$ ). Therefore, in a molecule such as  $\text{CH}_3\text{Cl}$ , because the molecule is not symmetrical, the centre of partial positive charge will be in a different place to the centre of partial negative charge, or the vector sum of the bond dipoles (when the vectors are added head-to-tail) will no longer be zero:



For some molecules that are not as simple as the examples already covered, it is more difficult to determine whether or not they are symmetrical and therefore whether they are non-polar or polar. For example, hydrocarbons such as ethane,  $\text{CH}_3\text{--CH}_3$ , and propane,  $\text{CH}_3\text{--CH}_2\text{--CH}_3$ , are regarded as non-polar, even though it is difficult to determine this by examining their structural formulas.

Figure 3.15 shows some more examples of polar and non-polar molecules.

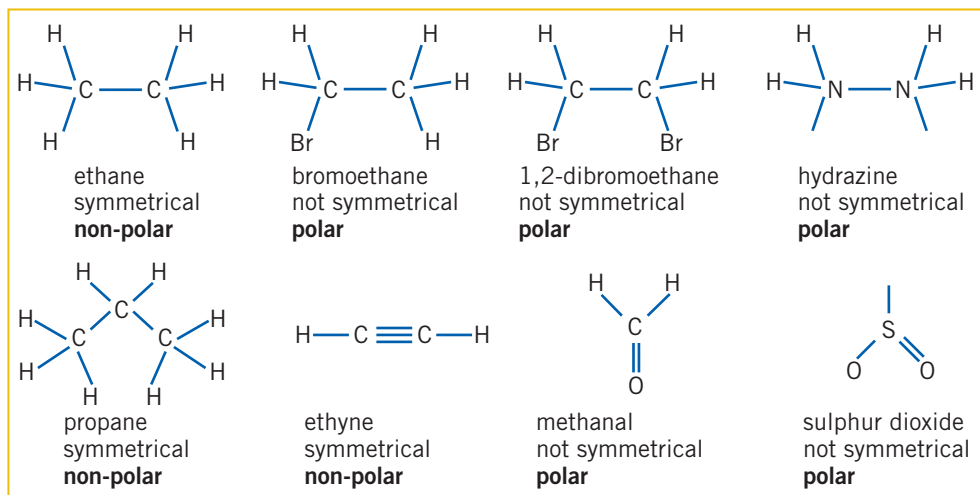


Figure 3.15 Some more examples of polar and non-polar molecules

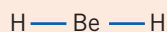
### → Example 3.2

Explain why:

- $\text{BeH}_2$  is not polar, but  $\text{H}_2\text{O}$  is polar
- $\text{SO}_3$  is not polar, but  $\text{NH}_3$  is polar.

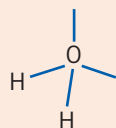
### → Solution

- a**  $\text{BeH}_2$ : this is an example of a non-octet molecule, with Be having a share of 4 valence electrons.



The two areas of negative charge will be arranged  $180^\circ$  apart around the Be atom to give a symmetrical molecule. This molecule is therefore not polar.

$\text{H}_2\text{O}$ : in this molecule the O atom has 8 valence electrons around it. The four pairs of electrons will be arranged tetrahedrally around the central O atom.



Only two of these pairs of electrons are bonding pairs, so the molecule is not symmetrical.  $\text{H}_2\text{O}$  is therefore a polar molecule. Alternatively, it could be reasoned that the lone pairs in the O atom repel the bonding pairs of electrons, pushing them closer together than occurs in  $\text{BeH}_2$ .

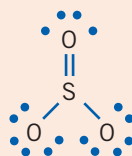
- b**  $\text{SO}_3$ : the total number of valence electrons in the molecule is:

$$3 \times 6 = 18 \text{ e}^- \text{ (from the 3 oxygen atoms)}$$

$$6 \text{ e}^- \text{ (from the sulfur atom)}$$

$$\text{total } 24 \text{ valence electrons}$$

These electrons are arranged to give the following structure:

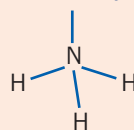


*continued*



Because there are three negative areas around the central atom, they will be arranged in a trigonal planar arrangement. Each of these negative areas are bonding pairs of electrons, and the three atoms bonded to the S atom are identical to one another. This is therefore a symmetrical molecule, meaning it is non-polar.

$\text{NH}_3$ : the total number of valence electrons in this molecule is 8 (5 from the N atom and 1 from each of the H atoms). The resulting four pairs of electrons will be arranged tetrahedrally around the N atom to give:



Because one of the pairs of electrons is a lone pair, this is not a symmetrical molecule and so it is polar. Alternatively, the lone pair that exists in this molecule, but was not present in the  $\text{SO}_3$  molecule, repels the bonding pairs of electrons, pushing them closer together, resulting in a non-symmetrical molecule.

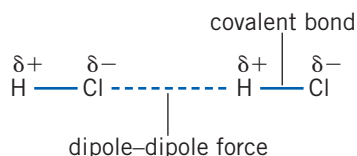
### \* Review exercise 3.4

- 1 What is the difference between the terms 'polar covalent bond' and 'polar molecule'?
- 2 a Which of the following molecules and ions would be regarded, in chemistry, as symmetrical?  
 $\text{CBr}_4$   $\text{H}_2\text{S}$   $\text{HI}$   $\text{CO}_2$   $\text{CHCl}_3$   $\text{SO}_4^{2-}$   $\text{NCl}_3$   $\text{HBr}$   $\text{NO}_2^-$   $\text{SO}_3^{2-}$   
 $\text{CH}_3\text{F}$   $\text{SCl}_2$   $\text{C}_2\text{H}_4$   
b Name the shapes of the molecules listed in part a.
- 3 Classify each of the following as an ionic, a polar covalent molecular or a non-polar covalent molecular substance.  
 $\text{SiCl}_4$   $\text{MgCl}_2$   $\text{CH}_3\text{Br}$   $\text{Cl}_2\text{O}$   $\text{PH}_3$   $\text{SrO}$   $\text{F}_2$   $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$   $\text{LiI}$
- 4 A positively charged Perspex rod is held near a thin stream of water from a tap. The stream is attracted towards the rod. Explain this observation and draw a diagram to show what is happening on the molecular scale to produce this phenomenon.

## 3.5 Dipole–dipole forces

Dipole–dipole forces are weak attractive forces that occur between polar molecules; that is, between molecular dipoles. These attractive forces occur because the part of the molecule that is slightly positively charged can be attracted to the slightly negative part of another molecule. Because the charges involved are only very small, the dipole–dipole forces are weak.

For example, the dipole–dipole force between two HCl molecules can be shown as:



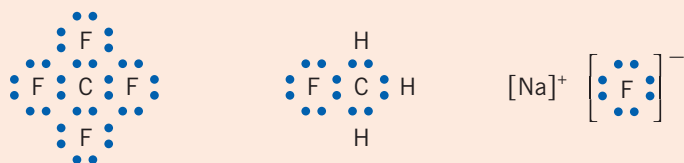
The more polar the molecules, the stronger the dipole–dipole forces will be. The strongest type of dipole–dipole force, called a hydrogen bond, will be discussed further in section 3.7.

### → Example 3.3

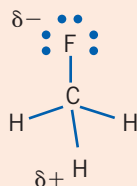
- Draw electron dot diagrams for  $\text{CF}_4$ ,  $\text{CH}_3\text{F}$  and  $\text{NaF}$ .
- The melting point of  $\text{CF}_4$  is  $-187^\circ\text{C}$  and the melting point for  $\text{CH}_3\text{F}$  is  $-140^\circ\text{C}$ . Propose an explanation for this difference.
- The melting point of  $\text{NaF}$  is  $993^\circ\text{C}$ . Explain why this is much higher than the melting point of  $\text{CH}_3\text{F}$ .

### → Solution

a



- $\text{CF}_4$  molecules are symmetrical and are therefore non-polar.  $\text{CH}_3\text{F}$  molecules are not symmetrical and so they are polar and will have dipole–dipole forces between them. There are weak attractive forces between the  $\text{CF}_4$  molecules (they are called dispersion forces) but they must be weaker than the dipole–dipole forces between the  $\text{CH}_3\text{F}$  molecules. The molecular substance with the stronger intermolecular forces will have the higher melting point.
- The  $\text{CH}_3\text{F}$  molecules are dipoles; they have a slightly positively charged end and a slightly negatively charged end due to the unequal sharing of the electrons.



There are weak dipole–dipole forces between the molecules because the slightly negatively charged end of one molecule will be attracted to the slightly positively charged end of another molecule.

$\text{NaF}$  is an ionic compound, composed of  $\text{Na}^+$  and  $\text{F}^-$  ions. These ions are held in the solid lattice by the attractive forces between the  $+1$  ions and the  $-1$  ions. Because these ions have a full positive and negative charge, the attractive forces will be larger than those between the molecules with only partial positive and negative charges. The ionic bonds are therefore much stronger than the dipole–dipole forces. As a result,  $\text{NaF}$  has a much higher melting point than  $\text{CH}_3\text{F}$ .

### \* Review exercise 3.5

- Which of the following substances will have dipole–dipole forces between their molecules?  
 $\text{Br}_2$     $\text{CH}_3\text{Br}$     $\text{CH}_2\text{Br}_2$     $\text{SBr}_2$     $\text{CBr}_4$     $\text{HBr}$     $\text{NBr}_3$     $\text{SiBr}_4$
- Explain the following observations.
  - Acetone,  $(\text{CH}_3)_2\text{CO}$ , is a liquid at room temperature, but butane,  $\text{C}_4\text{H}_{10}$ , is a gas.
  - Carbon monoxide has a higher melting point ( $-205^\circ\text{C}$ ) than oxygen ( $-219^\circ\text{C}$ ).
- Predict the substance with the higher boiling point, in each pair. Give a reason for your answer.
  - $\text{SiH}_4$  or  $\text{PH}_3$
  - $\text{PH}_3$  or  $\text{NH}_3$
  - $\text{Na}_3\text{P}$  or  $\text{PH}_3$

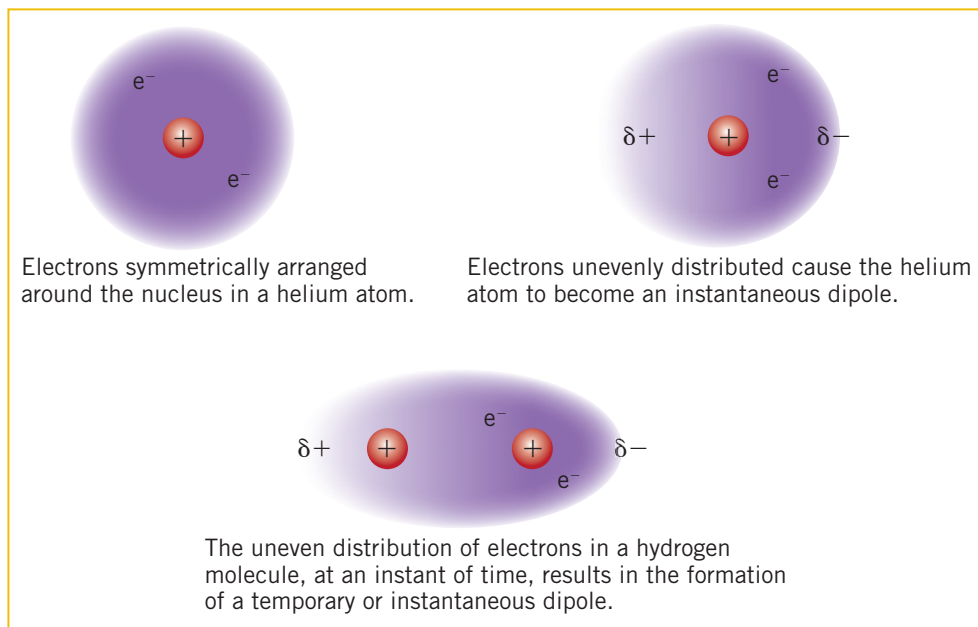


## 3.6 Dispersion forces

### What are dispersion forces?

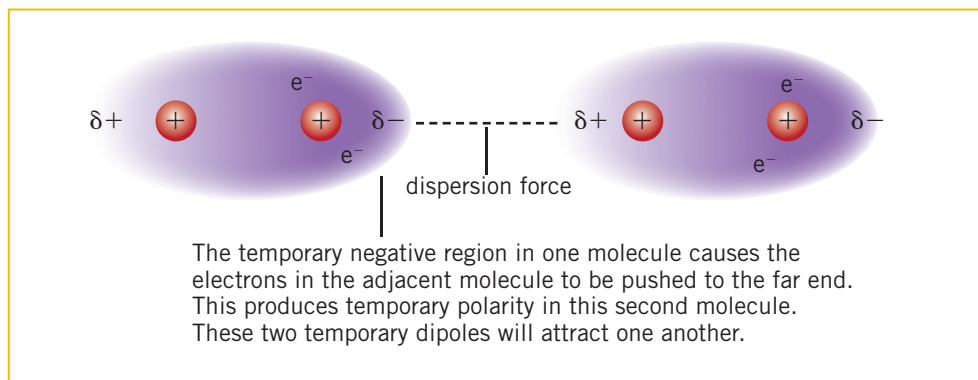
In molecular elements such as  $\text{H}_2$ ,  $\text{Cl}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{P}_4$  and  $\text{S}_8$ , the covalent bonds between the atoms are not polar because the atoms bonded together have the same electronegativity. Hence, the molecules are not polar. Similarly, molecules that contain polar covalent bonds but are symmetrical, for example,  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{SiCl}_4$ , are not molecular dipoles. As explained at the beginning of the chapter, all substances can be changed from the gaseous state to the liquid state. For this to happen, there must be attractive electrostatic forces between the particles. But how is it possible for there to be an electrostatic attraction between molecules or atoms that do not seem to be dipoles?

The absence of a permanent charge separation or dipole in a non-polar molecule does not preclude the possibility that at any instant the molecule might be a temporary dipole. This temporary polarity arises from the fact that the individual electrons in atoms and molecules are in constant motion and are not always symmetrically distributed across the atom or the molecule. It is this temporary, asymmetrical distribution of electron density that produces a temporary or instantaneous dipole, as shown in Figure 3.16.



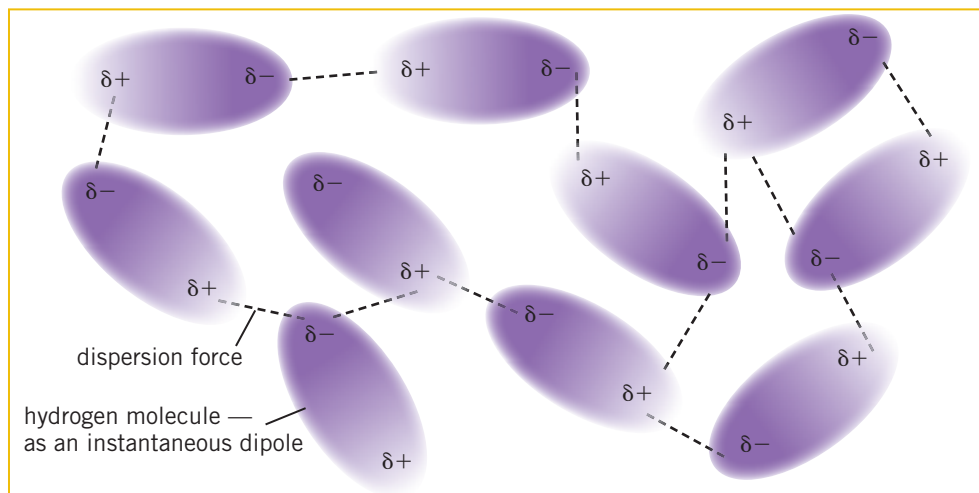
**Figure 3.16** The formation of an instantaneous dipole in a helium atom and a hydrogen molecule

If such an atom or molecule with its instantaneous polarity comes into close proximity to another atom or molecule, then the instantaneous dipole will induce polarity in the neighbouring atom or molecule, as shown for hydrogen molecules in Figure 3.17. These two temporary dipoles will then be attracted to one another. The attractive force that exists between two temporary dipoles is called a dispersion force.



**Figure 3.17** Dispersion force between two instantaneous dipoles

If the atoms or molecules are close enough to one another, this process of induction of polarity can happen throughout the sample, as represented in Figure 3.18 for a sample of liquid hydrogen. The dispersion forces that result will keep the atoms or molecules in the sample together.



**Figure 3.18** A representation of the dispersion forces between the molecules in liquid hydrogen. An instantaneous dipole in a hydrogen molecule can induce a dipole in its neighbouring molecule, which in turn can induce a dipole in another molecule and so on.

### Predicting strengths of dispersion forces

The best measure of the strength of the attractive forces between molecules can be obtained by examining the boiling points of the substances. Unlike melting, the process of boiling completely separates the molecules from one another (or the atoms in the case of the noble gases), breaking any attractive force that once existed between them.

The boiling points of the noble gases are provided in Table 3.3.

**TABLE 3.3 BOILING POINTS OF THE NOBLE GASES**

Noble gas	Boiling point (°C)
Helium	-269
Neon	-246
Argon	-186
Krypton	-152
Xenon	-108
Radon	-62

The only forces between the atoms of the noble gases are dispersion forces. It can therefore be inferred that because the boiling points of the noble gases increase down the group, the strength of the dispersion forces between the larger atoms must also increase. But why should the larger atoms have stronger dispersion forces between them?

The number of electrons in the noble gas atoms increases going down the group. In addition, the atomic radius increases, so the extra electrons also have a greater volume of space in which to move. As a consequence, for the larger atoms, with the larger number of electrons, there is a greater chance that these electrons will be arranged asymmetrically at any particular instant, compared to the smaller number of electrons in the smaller atoms. Atoms with more electrons are therefore likely to be temporary or instantaneous dipoles more often than atoms with a smaller number of electrons. Also, for the atoms with more electrons moving about, the partial charges on the temporary dipoles are likely to be larger. The increasing strength of the dispersion forces, the attractive forces

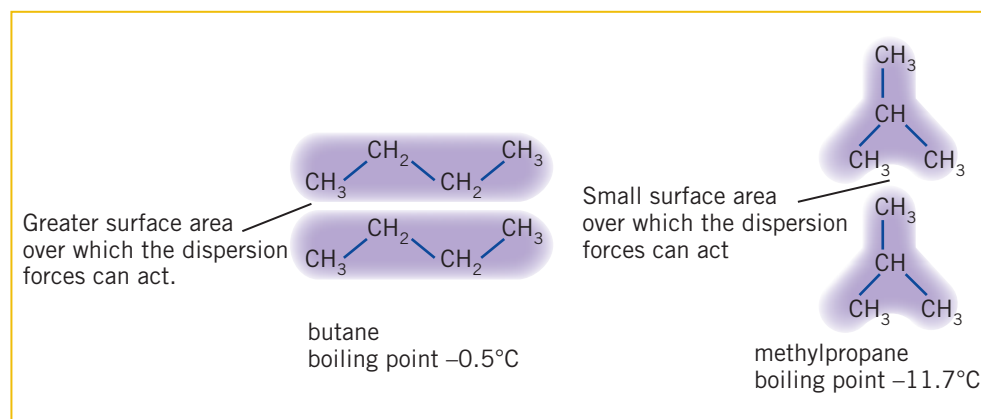
between instantaneous dipoles, going down the noble gas group can therefore be explained in terms of the increasing number of electrons in the larger atoms.

**TABLE 3.4 BOILING POINTS OF VARIOUS NON-POLAR MOLECULES**

Halogen molecules	Number of electrons	Boiling point (°C)	Symmetrical molecules with polar bonds	Number of electrons	Boiling point (°C)
F <sub>2</sub>	18 electrons	-188	Methane, CH <sub>4</sub>	10 electrons	-162
Cl <sub>2</sub>	34 electrons	-35	Silane, SiH <sub>4</sub>	18 electrons	-112
Br <sub>2</sub>	70 electrons	59	Tetrachloromethane, CCl <sub>4</sub>	74 electrons	77
I <sub>2</sub>	106 electrons	184	Tetrabromomethane, CBr <sub>4</sub>	146 electrons	190

The data in Table 3.4 also support the conclusion that dispersion forces increase with an increase in the number of electrons for a range of other molecules. Iodine with 106 electrons and 106 protons has a much higher boiling point than fluorine with just 18 electrons and 18 protons. Similarly, in molecules that contain polar covalent bonds but are symmetrical, the same trend of increasing boiling point with increasing number of electrons can be observed. For example, silane, SiH<sub>4</sub>, with 18 electrons has a higher boiling point than methane, CH<sub>4</sub>, with only 10 electrons.

Molecular shape also influences the strength of dispersion forces. The larger the surface area over which the electrons can develop an instantaneous dipole, and the closer the molecules can fit next to one another, the stronger the dispersion force will be between the molecules. Butane, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, and methylpropane, (CH<sub>3</sub>)<sub>3</sub>CH, are structural isomers. They are composed of the same number of carbon and hydrogen atoms and, as a result, have the same number of electrons. However, the boiling point of butane is 11°C higher than that of methylpropane. The greater surface area of the longer chain molecule, together with the fact that these chains can get into closer proximity to other butane molecules than can a group of methylpropane molecules, accounts for the stronger dispersion forces between the unbranched molecules (Figure 3.19).

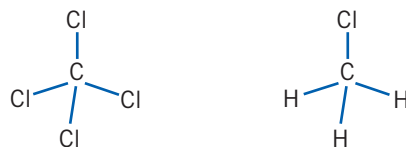


**Figure 3.19** Dispersion forces also depend on the shape of the molecules. Butane molecules have stronger dispersion forces between them than methylpropane molecules do.

Essentially, the electrons in all substances are in constant motion and so there will always be occasions when the electrons will not be evenly distributed around the atomic nuclei. It therefore follows that dispersion forces exist between the atoms, molecules and ions of all substances. However, when strong bonds are present between these particles, the influence of the dispersion forces becomes insignificant in determining the properties of a particular substance. For

example, sodium chloride has a high melting point mainly because of the strong electrostatic attractions between the positive and negative ions, not because of the dispersion forces that also exist between the positive and negative ions. In water molecules the oxygen and hydrogen atoms are held together because of the attractive forces between the shared electrons and the nuclei, not because of the very weak dispersion forces that exist between these atoms. However, for non-polar molecular substances and monatomic elements, dispersion forces are the only attractive force between the molecules and atoms respectively, so they are very significant in determining the physical properties of these substances.

For polar molecular substances that have dipole–dipole forces between their molecules, the dispersion forces can become more significant (stronger) than the dipole–dipole forces, depending on the number of electrons and the shape of the molecules. For example, tetrachloromethane,  $\text{CCl}_4$ , and chloromethane,  $\text{CH}_3\text{Cl}$ , have the following structures:



Tetrachloromethane is composed of symmetrical molecules and so will only have dispersion forces between its molecules. However, the molecules of chloromethane are not symmetrical and so there will be dipole–dipole forces as well as dispersion forces between these molecules. If dispersion forces are always weaker than dipole–dipole forces, chloromethane would be expected to have a higher boiling point than tetrachloromethane. This, however, is not the case. The boiling point of chloromethane is  $-24.2^\circ\text{C}$  and that for tetrachloromethane is  $76.5^\circ\text{C}$ . From this observation it can be concluded that the dispersion forces between the tetrachloromethane molecules are stronger than the dipole–dipole forces plus dispersion forces between the chloromethane molecules. The tetrachloromethane molecule has many more electrons (74) than the chloromethane molecule (26 electrons), so this conclusion is not surprising given that the strength of dispersion forces is dependent on the number of electrons and protons in the molecules.

Further evidence for the significance of the dispersion forces between polar molecules can be found in the boiling points of the hydrogen halides, HCl, HBr and HI (Table 3.5).

**TABLE 3.5 BOILING POINTS OF HYDROGEN HALIDES**

Hydrogen halide	Boiling point ( $^\circ\text{C}$ )	Number of electrons per molecule
HCl	-85	$1 + 17 = 18$
HBr	-67	$1 + 35 = 36$
HI	-35	$1 + 53 = 54$

On the basis of electronegativity differences, HCl is the most polar molecule, and HI the least polar, so HCl will have the strongest dipole–dipole forces. However, the boiling point of HCl is the lowest of the three. There is a significant difference in the number of electrons in these molecules, and as a result the dispersion forces between the two larger halides must be more significant (stronger) than the dipole–dipole forces.

While the relative strengths of the dispersion and dipole–dipole forces cannot always easily be determined, the existence of dispersion forces cannot be ignored.

However, the boiling points of polar molecules are likely to be higher than the boiling points of non-polar molecules with comparable number of electrons, because the polar molecules have both dispersion and dipole–dipole forces working to reinforce one another. The combination of the two weak intermolecular forces will be stronger than the dispersion forces alone.

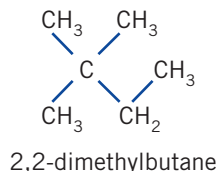
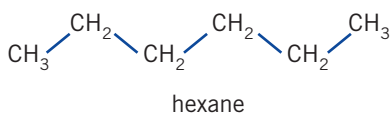
### \* Review exercise 3.6

- Which of the following substances have only dispersion forces between their molecules?  
 $O_2$     $HCl$     $H_2O$     $CO_2$     $SO_2$     $C_2H_2$     $CH_3-CH_3$     $PF_3$     $F_2$
- Why are covalent bonds stronger than dispersion forces?
- Use the data in Table 3.6 to explain the nature of the bonding present between the molecules and any trends in that bonding.

TABLE 3.6

Compound	Boiling point ( $^{\circ}C$ )
$CHF_3$	-84
$CF_4$	-128
$CHCl_3$	62
$CCl_4$	77

- Describe the similarities and differences between dispersion forces and dipole–dipole forces.
- Which of bromine,  $Br_2$ , or xenon,  $Xe$ , would be predicted to have the higher boiling point? Explain your answer.
  - Use the arguments developed in answering part a to make a prediction about the relative boiling points of fluorine,  $F_2$ , and argon,  $Ar$ .
- Predict which of hexane and 2,2-dimethylbutane, shown below, will have the higher boiling point. Explain your answer.





### 3.7 Hydrogen bonding

When polar molecules contain N–H, O–H or H–F groups, the dipole–dipole forces between the molecules become stronger than the normal dipole–dipole forces. This can be seen when comparing the graphs of the boiling points of the hydrides of groups 14 to 17, shown in Figure 3.20.

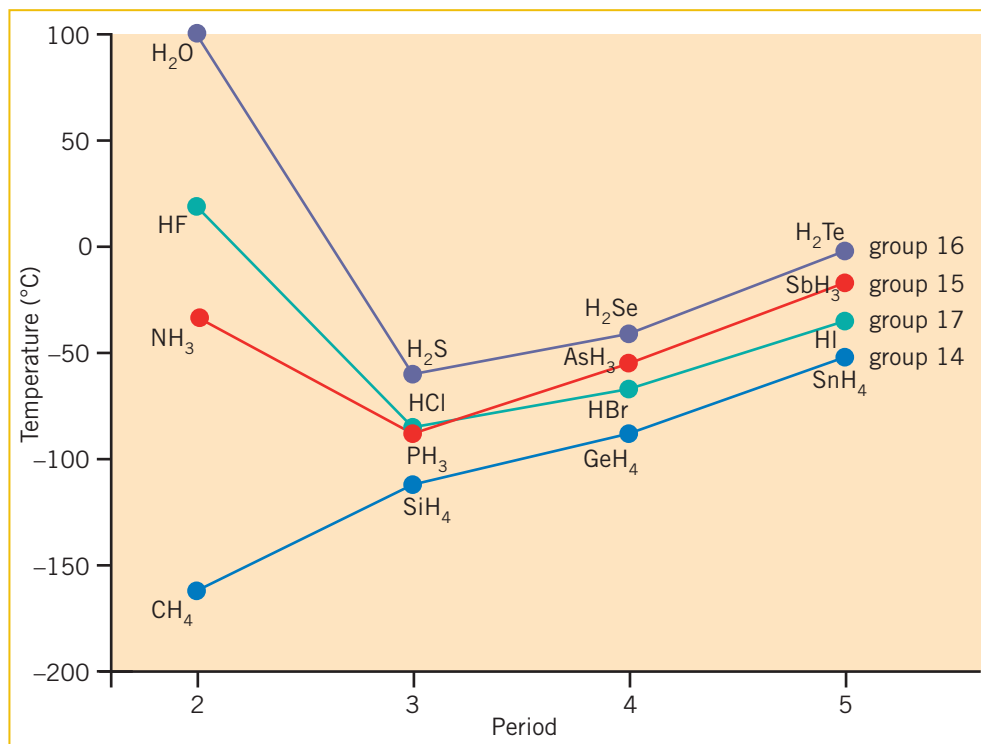


Figure 3.20 Boiling points of the hydrides of groups 14 to 17

The group 14 hydrides are all non-polar molecules and their boiling points increase predictably as a result of the increasing dispersion forces with increasing numbers of electrons.

The hydrides of groups 15, 16 and 17 are polar molecules and with the decreasing polarity of these molecules going down the group, the expectation is that their boiling points should also decrease. However, for three of the four hydrides in each series (the heaviest hydrides), the trend is an increase in boiling points. This trend must be due to an increase in the strength of the dispersion forces between the hydride molecules, as the number of electrons increases, going down the groups. However, the first member of each of the hydride series, NH<sub>3</sub> in group 15, H<sub>2</sub>O in group 16, and HF in group 17, has a much higher boiling point than the next hydride in each series. The significantly higher boiling point for the first member of each series indicates that a stronger intermolecular force must be present. Since the anomalous molecules have the least number of electrons in each series, this force cannot be just a dispersion force.

Nitrogen, oxygen and fluorine are the three most electronegative atoms in the periodic table. The covalent bond between these three atoms and a hydrogen atom will be very polar. In addition, the atomic radius of each of the atoms is small, so the partial positive and partial negative charges in each bond dipole will be confined to a small region of space. In other words, there will be a high charge density at each 'end' of each molecule, making them more polar than most other molecules. The intermolecular forces between these three molecules, NH<sub>3</sub>,

H<sub>2</sub>O and HF, will therefore be stronger than the normal dipole–dipole forces between many other polar molecules.

This phenomenon is not restricted to just NH<sub>3</sub>, H<sub>2</sub>O and HF. There are other examples in which the boiling point of a particular molecular substance seems to be higher than might be expected when comparing it to other molecules of similar molecular shape and number of electrons.

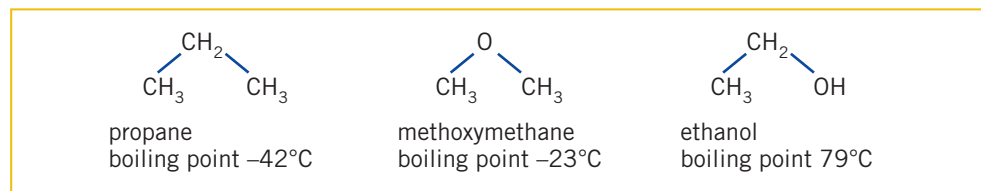


Figure 3.21 Boiling points of molecules with a similar number of electrons

As shown in Figure 3.21, the boiling point for propane, a typical non-polar alkane molecule, is  $-42^\circ\text{C}$ . Methoxymethane is an example of a class of organic compounds called ethers. It has a similar number of electrons to that of propane, so the dispersion forces between the molecules of each of the two substances should be of similar strength. However, methoxymethane is a polar molecule, so the higher boiling point is due to a combination of the dispersion and dipole–dipole forces between its molecules. Ethanol (an example of a group of important organic compounds called alcohols) is polar and has the same number of electrons as methoxymethane, yet its boiling point is over  $100^\circ\text{C}$  higher. How is it that the dispersion plus dipole–dipole forces in the alcohol are so much stronger than they are in the ether?

In many situations where a boiling point for a polar molecular compound is found to be significantly higher than that predicted, the common factor is the presence of at least one N–H, O–H or F–H bond in each of the molecules. The combination of the polarity of these covalent bonds, the high charge density on the small atoms involved in these bonds, and the fact that the hydrogen end of the bond is left as an almost bare proton, due to the attraction of the N, O or F for the shared electron pair in the covalent bond, results in the formation of a particularly ‘strong’ dipole–dipole force between molecules that contain such a covalent bond.

The name given to this strong form of the dipole–dipole force is hydrogen bond. While the term ‘bond’ is used in the name, the hydrogen bond is still a weak intermolecular attraction, ten times stronger than other dipole–dipole forces, but still only about one-tenth of the strength of an ionic or covalent bond.

The requirements for hydrogen bonding between two molecules can be summarised as:

- the presence in one molecule of at least one N–H, O–H or F–H covalent bond. This produces the strong bond dipole with the partial negative charge concentrated on the N, O or F, and the partial positive charge on the hydrogen atom, and
- the presence of another polar molecule containing at least one N, O or F atom with a non-bonding pair of electrons attached to this atom (Figure 3.23).

A hydrogen bond is therefore the attraction between the lone pair of electrons on the N, O or F atom of one polar molecule and the partial positively charged hydrogen, which is bonded to the N, O or F, on the second polar molecule.

Some examples of simple hydrogen bonding interactions are shown in Figure 3.23.

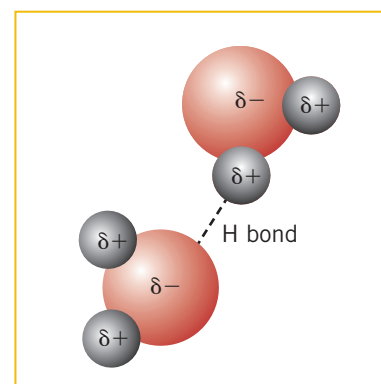


Figure 3.22 Hydrogen bonding interaction between water molecules

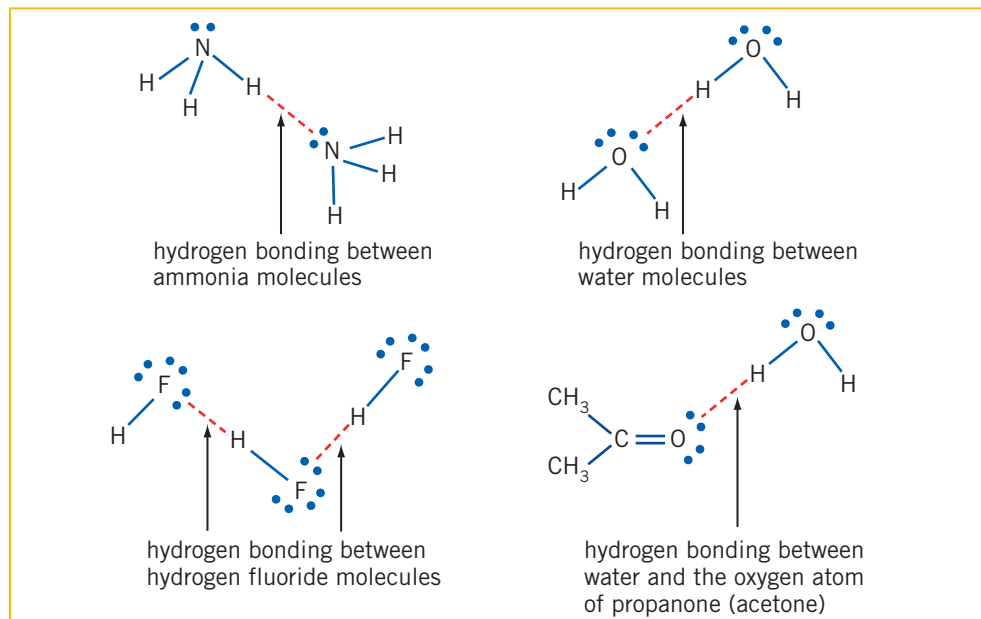


Figure 3.23 Examples of hydrogen bonding between molecules

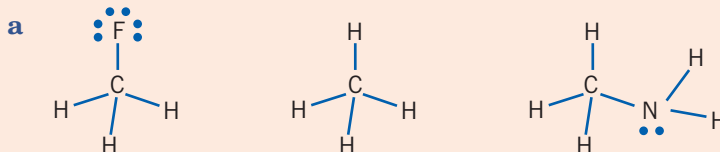
→ **Example 3.4**

a Draw the line structure of a molecule of each of the following substances.



- b Which of the substances in part a would have hydrogen bonding between its molecules?
- c Of these molecules, which would you expect to have the lowest boiling point and which the highest boiling point? Explain your answer.

→ **Solution**



b  $\text{CH}_3\text{NH}_2$  is the only substance that will have hydrogen bonding between its molecules. Even though  $\text{CH}_3\text{F}$  has F and H atoms in its molecules, the H atom needs to be covalently bonded to the F atom to give the hydrogen atom a sufficiently large partial positive charge to hydrogen bond to F in another molecule.

c  $\text{CH}_3\text{F}$  is a polar molecule and so there will be dipole–dipole forces as well as dispersion forces between these molecules.

$\text{CH}_4$  is a non-polar molecule, so there will only be dispersion forces between these molecules. Also because this molecule has fewer electrons than the  $\text{CH}_3\text{F}$  molecule, the dispersion forces between the  $\text{CH}_4$  molecules will be weaker than those between the  $\text{CH}_3\text{F}$  molecules.

$\text{CH}_3\text{NH}_2$  will have hydrogen bonding between its molecules (as well as dispersion forces).

$\text{CH}_4$  will have the lowest boiling point because it only has dispersion forces between its molecules (and these dispersion forces are weaker than the dispersion forces between the other molecules).  $\text{CH}_3\text{NH}_2$  will have the highest boiling point because it has hydrogen bonds between the molecules and these are stronger than other dipole–dipole forces (and the dispersion forces of the other two examples).

Hydrogen bonding between different molecules and parts of molecules plays a crucial role in biological processes. This type of bonding assists in determining the shape of biological molecules such as deoxyribonucleic acid (DNA) (Figure 3.25) and proteins (see Figure 13.9). DNA molecules are in the nuclei of all living cells. They act as a 'genetic blueprint' controlling the function and appearance of every living organism. These molecules contain the genetic information that is passed on from parents to their offspring. The hydrogen bonds are sufficiently strong to hold the double helix chains together during many cellular processes, yet they are weak enough for a few of them to break at a time during the vital processes of protein synthesis and cell reproduction.

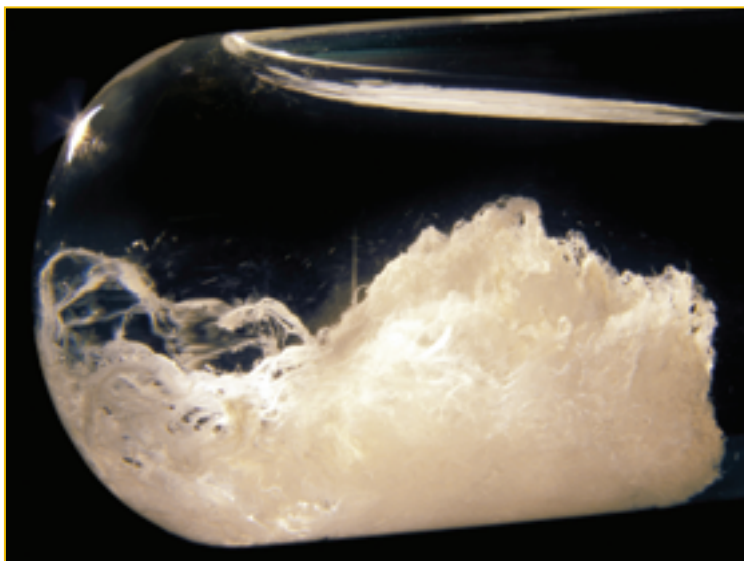


Figure 3.24 Extracted DNA from cells

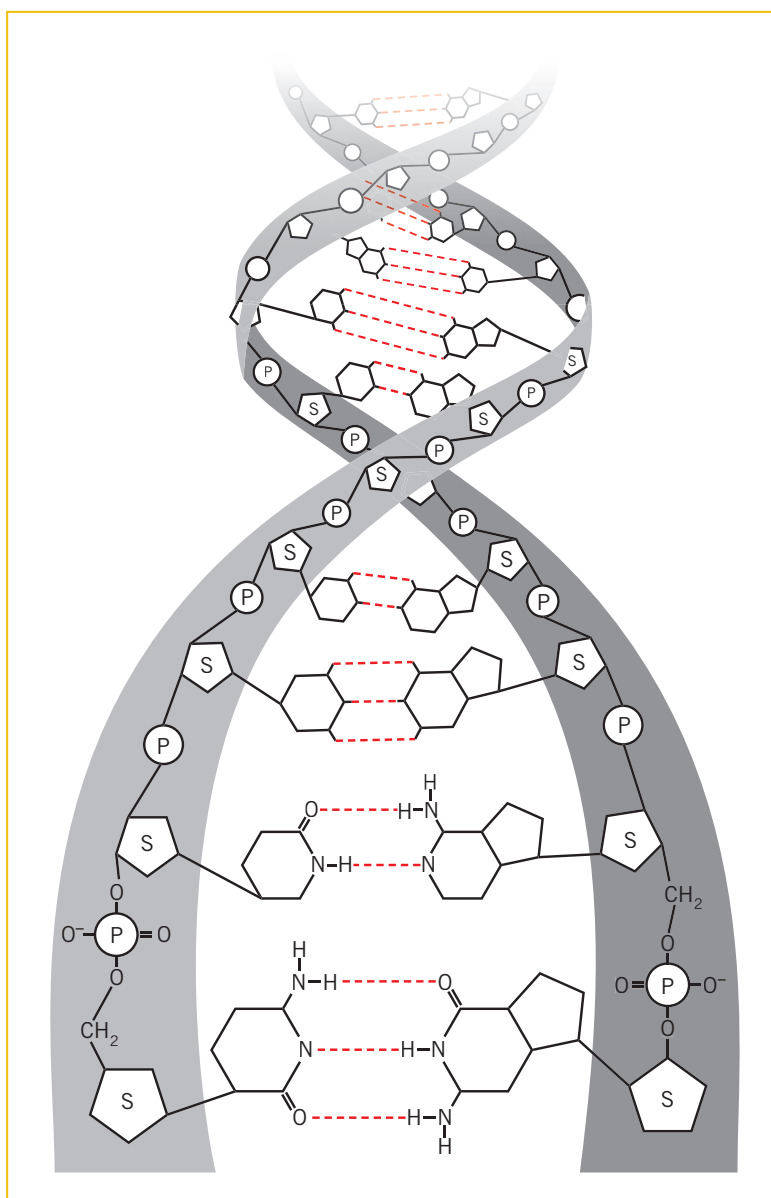


Figure 3.25 The DNA molecule consists of two chains of atoms held together by covalent bonds. But between these two chains are hydrogen bonds that give DNA its helical shape.

### \* Review exercise 3.7

- 1 Identify the type or types of intermolecular forces in the following substances.  
CHCl<sub>3</sub>    CH<sub>2</sub>F<sub>2</sub>    CBr<sub>4</sub>    CH<sub>3</sub>OH    CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>    HCN    S<sub>8</sub>    SO<sub>3</sub>    H<sub>2</sub>S
- 2 Explain the origin of each of the three types of van der Waals forces and explain why one is stronger than the other two.
- 3 The melting points of the group 17 hydrides are listed below.

Substance	HF	HCl	HBr	HI
Melting point (°C)	-85	-114	-87	-51

- Explain the following trends shown in these figures, in terms of the intermolecular forces in the substances.
- a Going down the group from HCl to HBr to HI, the melting points increase.  
b HF has a higher melting point than HCl.
- 4 For each of the following pairs of substances, predict the one with the higher melting point. Give a brief reason for your answer.
- a F<sub>2</sub> or HF  
b HF or H<sub>2</sub>O  
c NaCl or HCl  
d NH<sub>3</sub> or PH<sub>3</sub>  
e F<sub>2</sub> or Cl<sub>2</sub>  
f CH<sub>3</sub>CH<sub>2</sub>OH or CH<sub>3</sub>OH  
g CH<sub>4</sub> or C<sub>2</sub>H<sub>6</sub>
- 5 The formula of sulfuric acid can be written as (OH)<sub>2</sub>SO<sub>2</sub> to give a clearer idea of how the individual atoms are connected in the molecule. Sulfuric acid boils at 320°C. Fluorosulfuric acid, (HO)SO<sub>2</sub>F, has a boiling point of 170°C, while sulfuryl fluoride, SO<sub>2</sub>F<sub>2</sub>, has a boiling point of -55°C.
- a Draw line structures of the molecules of these three substances.  
b Account for the differences in the boiling points in terms of the intermolecular forces present.
- 6 Between which of the following pairs of substances will hydrogen bonding occur?
- a Water and ethanol (CH<sub>3</sub>CH<sub>2</sub>OH)  
b Ammonia and water  
c Phosphine, PH<sub>3</sub>, and water  
d CH<sub>3</sub>OCH<sub>3</sub> and HF  
e CH<sub>3</sub>COCH<sub>3</sub> and H<sub>2</sub>NNH<sub>2</sub>  
f CF<sub>4</sub> and water

## 3.8 Real bonding

All bonding is electrostatic in origin. Whether it is the attraction between positive metal ions and delocalised electrons, the attraction between oppositely charged ions, or the attraction between two nuclei for shared electrons, the source of the attractive force is the same. These three strong bond types are metallic, ionic and covalent bonds, respectively. However, except where the two atoms involved in the covalent bond are the same, or where the substance is a pure metal, all bonding involves some mix of these three types. One way of summarising these ideas is shown in Figure 3.26 where the three types of strong bonding are positioned at the vertices of a triangle. The nature of the bonding present in examples of compounds and elements is then shown in terms of the amounts of each of these three extremes that are present in the substances.

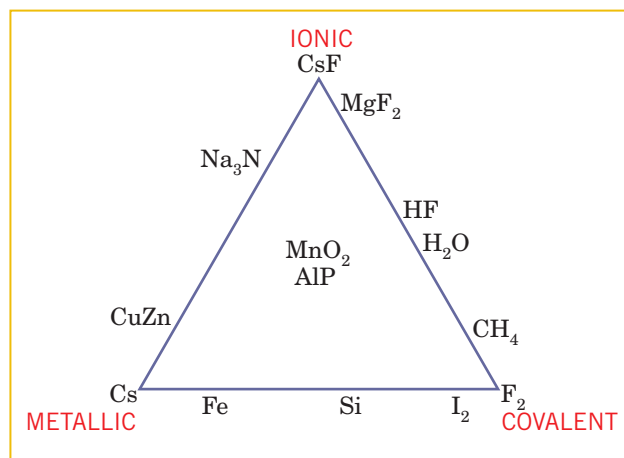


Figure 3.26 A bonding triangle showing that many substances exhibit bonding that is intermediate between ionic, covalent and metallic

### \* Review exercise 3.8

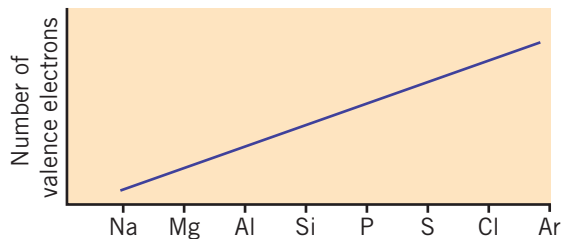
- Use electronegativity differences to explain the position of  $\text{CsF}$ ,  $\text{MgF}_2$ ,  $\text{HF}$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{F}_2$  on the continuum between ionic and covalent bonding in Figure 3.26.
  - Where would  $\text{F}_2\text{O}$  and  $\text{CaF}_2$  be placed?
- How does the concept of electronegativity help to explain the position of the elements listed along the continuum between metallic and covalent bonding?

### 3.9 More trends in properties across periods

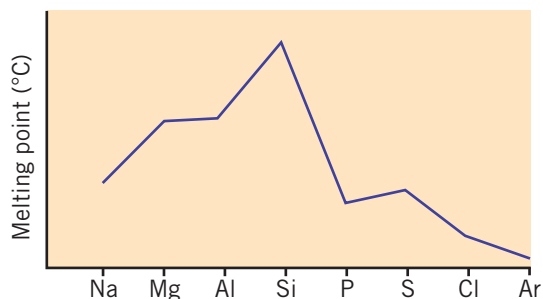


Earlier in Chapter 1, some trends shown by the elements across a period were discussed. Further trends are examined below. The third period (sodium to argon) has been used as a typical period.

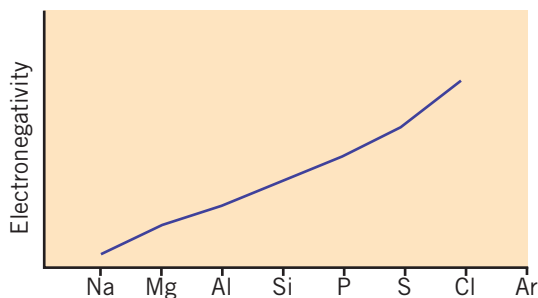
- Number of outer-shell or valence electrons increases across the period.



- Melting points and boiling points: The general trend for the melting points is shown in the graph below. These generally rise to group 14 elements, then decrease for groups 15–18. This trend can be explained in terms of the bonding of the elements. Groups 1, 2 and 13 elements are metals, with an increasing number of valence electrons, possibly increasing the strength of the metallic bonds. Group 14 elements are covalent network substances, with very high melting points. Groups 15–18 are molecular or monatomic, with only weak van der Waals forces between the particles.



- Types of substances across the period change from metals to amphoteric metals (semi-metals) to non-metals.
- Bonding in elements across the period changes from metallic to covalent bonding in a network lattice to covalent bonding in molecules.
- Electronegativity increases across the period.



- Types of compounds formed:
  - Groups 1, 2 and 13—ionic
  - Group 14—covalent molecular, covalent network, ionic
  - Groups 15–17—covalent molecular and ionic
  - Group 18—generally do not form compounds (the heavier noble gas elements form a few unstable covalent molecular compounds).
- Acid–base properties of oxides and hydroxides change from basic to amphoteric to acidic across the period.

### \* Review exercise 3.9

- 1 The trends in the melting points of oxides of the period 3 elements are shown in the graph in Figure 3.27.
- Draw electron dot or line representations of each compound.
  - Explain the melting point trends shown in this group of compounds.

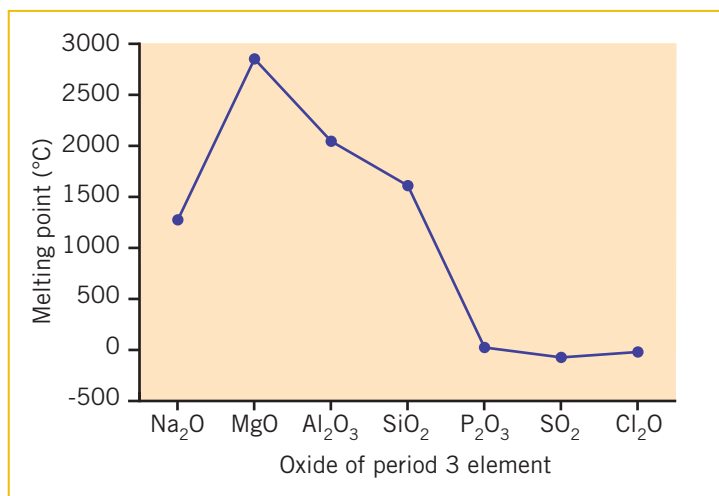


Figure 3.27





## MAJOR IDEAS

- The various types of intermolecular forces of attraction are collectively called van der Waals forces.
- Intermolecular forces include dispersion forces, dipole-dipole forces and hydrogen bonds.
- Molecular shape can be predicted using the valence shell electron pair repulsion hypothesis, which states that the valence electron pairs in an atom repel one another and are positioned as far apart as possible.
- Both bonding pairs and non-bonding pairs of electrons exert this repulsive force.
- Multiple bonds are regarded as a single area of negative charge when using the valence shell electron pair repulsion hypothesis.
- The shapes of simple molecules are listed in Table 3.7.

TABLE 3.7

Number of areas of negative charge around central atom	Number of lone pairs of electrons around central atom	Electron pair arrangement around central atom	Shape of molecule
1	0	Linear	Linear
2	0	Linear	Linear
3	0	Trigonal planar	Trigonal planar
4	0	Tetrahedral	Tetrahedral
4	1	Tetrahedral	Pyramidal
4	2	Tetrahedral	V-shaped or bent
4	3	Tetrahedral	Linear

- Non-bonding electron pairs and multiple bonds exert a slightly greater repulsive force than bonding electron pairs.
- A polar covalent bond is one in which there is a difference in the electronegativity of the atoms involved in the bond, causing the electrons to be attracted closer to the more electronegative atom.
- For a molecule to be polar, it must have at least one polar covalent bond and be asymmetrical. Such a molecule will be a dipole because the centres of positive and negative charges are at different points in the molecule.
- An alternative strategy for determining the polarity of a molecule with more than one polar bond is to undertake a vector addition of the individual bond dipoles.
- Dispersion forces exist between all molecules, atoms and ions and result from the attraction between instantaneous or induced dipoles.

- Dispersion forces are the only intermolecular forces between non-polar molecules and atoms of noble gases.
- Dispersion forces increase in strength with increasing number of electrons.
- Dispersion forces are also influenced by molecular shape—the greater the 'flat' surface area of the molecule, the stronger the dispersion force.
- Dipole-dipole forces are present between molecules that are polar.
- Hydrogen bonds are an extreme form of a dipole-dipole force.
- Hydrogen bonding takes place between polar molecules containing an N–H, O–H or F–H bond and other polar molecules containing N, O or F.
- Hydrogen bonds are about 10 times stronger than other van der Waals forces but about one-tenth of the strength of a covalent bond.

## QUESTIONS

- For each of the following pairs of substances predict which one of the pair will have the higher boiling point and explain your answer.
  - $C_3H_8$  or  $C_4H_{10}$
  - $SiH_4$  or  $CH_4$
  - HCl or HI
  - $H_2S$  or  $H_2O$
- Predict the shapes and bond angles of the following molecules or ions.
 

i	$SiCl_4$	ii	$NI_3$
iii	$SO_3$	iv	$SO_4^{2-}$
v	$H_2O$	vi	$CO_2$
vii	$SO_2$	viii	$NO_3^-$
ix	$AsH_3$		
  - For the neutral molecules in part a, which ones have polar bonds?
  - For the neutral molecules in part a, which ones are polar?
- Which of the following molecules or ions have a tetrahedral shape?  
 $SiH_4$   $PH_4^+$   $SO_4^{2-}$   $NH_3$   $CH_2Br_2$   $Cl_2$   $H_2S$
  - Which of the following molecules or ions have a linear shape?  
 $CH_4$   $HCl$   $PCl_3$   $SO_2$   $N_2$   $Br_2$   
 $H_2S$   $CO_2$   $NO_2^-$
  - Which of the following molecules have a V-shape?  
 $SO_2$   $PH_3$   $H_2S$   $OF_2$   $CO_2$   $CS_2$   $CCl_4$

d Which of the following molecules or ions have a pyramidal shape?



e Which of the following molecules or ions have a trigonal planar shape?



4 The order of boiling points of water, ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ , and ethoxyethane,  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ , is ethoxyethane < ethanol < water. However, for the sulfur analogues the order is  $\text{H}_2\text{S}$  <  $\text{CH}_3\text{CH}_2\text{SH}$  <  $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$ . Explain this difference.

5 Draw a line structure of a molecule that fulfils each of the following descriptions.

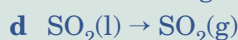
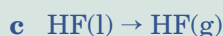
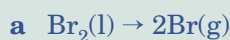
a A tetrahedral polar molecule formed between a period 2 element, iodine and hydrogen

b A V-shaped molecule formed between a period 3 element and chlorine

c A molecule, formed between a period 2 element and hydrogen, that contains four pairs of valence electrons but just one non-bonding pair of electrons

d A molecule, formed between a period 3 element and hydrogen, that has four valence pairs of electrons with three non-bonding pairs of electrons

6 Describe the attractive forces that have to be overcome in each of the following changes.



7 What is the name of the force or forces that opposes vapourisation of the following substances?

a hexane

b fluoroethane,  $\text{CH}_3\text{CH}_2\text{F}$

c hydrogen peroxide,  $\text{H}_2\text{O}_2$

8 Consider the following melting points.

Substance	$\text{CCl}_4$	$\text{CF}_4$	$\text{NaCl}$	$\text{O}_2$	$\text{NO}$
Melting point ( $^\circ\text{C}$ )	-23	-187	801	-219	-164

Discuss why:

a  $\text{CCl}_4$  has a higher melting point than  $\text{CF}_4$

b  $\text{NaCl}$  has a higher melting point than  $\text{CCl}_4$

c  $\text{O}_2$  has a lower melting point than  $\text{NO}$ .

9 Consider the following melting points.

Substance	$\text{H}_2$	$\text{F}_2$	$\text{HF}$	$\text{He}$	$\text{Ne}$	$\text{H}_2\text{O}$	$\text{CH}_4$
Melting point ( $^\circ\text{C}$ )	-259	-220	-83	-272	-249	0	-183

a Propose a reason for the difference in melting points of hydrogen and fluorine.

b Discuss why hydrogen fluoride has a higher melting point than either fluorine or hydrogen.

c Explain the difference in the melting points of fluorine and neon.

d Propose an explanation for the observation that  $\text{CH}_4$  has a lower melting point than  $\text{HF}$  and  $\text{H}_2\text{O}$  but a similar melting point to the four elements.

10 Dispersion forces are the only intermolecular forces present in paraffin wax yet it has reasonably high melting and boiling points for a covalent molecular compound. Suggest a possible explanation for this.

11 The boiling points of the hydrides of group 15 elements are shown below.

Hydride	$\text{NH}_3$	$\text{PH}_3$	$\text{AsH}_3$	$\text{SbH}_3$
Boiling point	$-33^\circ\text{C}$	$-90^\circ\text{C}$	$-59^\circ\text{C}$	$-21^\circ\text{C}$

a Why do the boiling points increase with increasing molecular mass for the hydrides  $\text{PH}_3$ ,  $\text{AsH}_3$  and  $\text{SbH}_3$ ?

b Why does ammonia have a much higher boiling point than expected from the trend shown by the other hydrides?

12 Explain why:

a bromine is a liquid at room temperature but chlorine is a gas

b ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , is a liquid at room temperature but carbon dioxide is a gas.

13 a What does the heat of vaporisation,  $\Delta H_{\text{vap}}$ , measure?

b The heats of vaporisation of three group 15 hydrides are shown below.

Hydride	$\Delta H_{\text{vap}}$ ( $\text{kJ mol}^{-1}$ )
$\text{NH}_3$	23.4
$\text{PH}_3$	14.6
$\text{AsH}_3$	17.5

Plot a graph of  $\Delta H_{\text{vap}}$  against number of electrons for each of these hydrides.

c Explain the observed values for the heats of vaporisation of the three hydrides.

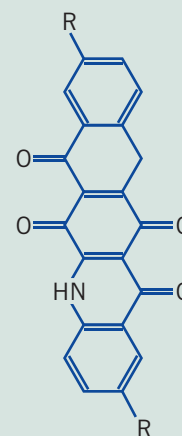
- d If ammonia did not behave anomalously what value of  $\Delta H_{\text{vap}}$  would you predict for  $\text{NH}_3$  if it continued the trend shown by the other two hydrides?
- e Determine the strength of the hydrogen bond in ammonia from this information.
- f The strength of the hydrogen bonding interaction in water has been determined to be around  $22 \text{ kJ mol}^{-1}$ . Explain the difference between the value for the strength of the hydrogen bonding interaction in ammonia and that in water.
- 14 In which of the following solutions would there be hydrogen bonding between the solute and solvent molecules?
- HCl dissolved in water
  - $\text{CH}_3\text{CH}_2\text{OH}$  dissolved in water
  - Acetic acid,  $\text{CH}_3\text{COOH}$ , dissolved in ethoxyethane,  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
  - $\text{NH}_4\text{Cl}$  dissolved in water
  - $\text{NH}_3$  dissolved in  $\text{CH}_3\text{OH}$
  - HF dissolved in  $\text{CH}_3\text{COCH}_3$
  - $\text{CCl}_4$  dissolved in  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- 15 Explain why it is possible to separate oxygen and nitrogen by fractional distillation of liquid air. Which of oxygen and nitrogen will have the higher boiling point? Justify your response.
- 16 In which of groups 1, 2, 14, 15 and 18 of the periodic table would you expect to find an element that satisfies the conditions stated below?
- An element having the highest possible first ionisation energy
  - An element having the lowest possible ionisation energy
  - An element that forms the molecular compounds  $\text{XO}_2$  and  $\text{XH}_4$
  - An element that forms the ionic compounds  $\text{ZCl}_2$  and  $\text{ZS}$
  - An element having an atomic number of 33
  - An element with one electron in its valence shell
  - An element that reacts with hydrogen to form a molecule that has a pyramidal shape
- 17 Explain why the melting points and boiling points of group 1 elements decrease down the group, but the melting points and boiling points of group 17 elements increase down the group.
- 18 Figure 3.28 shows some chlorides of elements from period 3 at room temperature. From left

to right these are sodium chloride, magnesium chloride, aluminium chloride, silicon tetrachloride, phosphorus trichloride and phosphorus pentachloride.

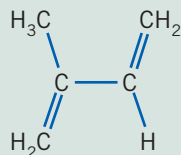


Figure 3.28

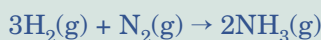
- Write the formulas of the six chlorides.
  - Describe the bonding in each of these six chlorides, including an electron dot diagram of each compound. (The last chloride is a non-octet compound.)
  - Explain why the first three chlorides are solids, but the next two chlorides are liquids.
  - Explain why one of the phosphorus chlorides is a liquid but the other is a solid at room temperature.
- 19 When you use a pencil to write on a piece of paper, layers of graphite from the pencil are left on the paper during the writing process.
- Graphite is regarded as non-polar. Why is this?
  - Paper is regarded as polar because it is essentially composed of cellulose, which is a polymer of glucose. (See Chapter 5, page 151, for the structural formula of glucose.) What type of bonding exists between graphite and paper?
  - Why can a pencil mark on paper be easily removed with an eraser?
- One of the dyes in a particular brand of ink has the structure shown on the right.
- What type of intermolecular bonding could this dye exhibit with paper? What feature in the dye molecule leads you to this conclusion?
  - Comment on whether it will be easier or harder to remove this dye from the paper than to remove the graphite.



Several years ago erasable pens were in fashion. These pens worked by leaving a layer of synthetic rubber (impregnated with a dye strongly attracted to the rubber) on the paper. The rubber in one of the patented pen varieties is made by joining together many molecules having the structure shown below.

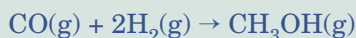


- f Explain how erasable pens work in terms of the intermolecular forces between the layer of black rubber and the paper.
- g What would you predict about the polarity of the black dye used to impregnate the rubber?
- 20 The industrial process for the production of ammonia involves the reaction between hydrogen and nitrogen in the presence of a suitable catalyst to form ammonia:



During the reaction, the products are cooled under pressure and the ammonia liquefies. The unreacted hydrogen and nitrogen are recycled.

- a Draw electron dot diagrams of the three molecules involved in this reaction.
- b Which will have the higher boiling point, hydrogen or nitrogen? Explain your answer.
- c How is it possible that the ammonia can be separated so easily from the other two gases?
- 21 In the laboratory production of hydrogen chloride, solid sodium chloride is heated with liquid sulfuric acid and immediately fumes of hydrogen chloride gas are evolved. In terms of the intermolecular bonding involved, explain why sulfuric acid is a liquid but hydrogen chloride is a gas under these conditions.
- 22 The production of methanol is achieved by the reaction of carbon monoxide with hydrogen in the presence of a suitable catalyst. The overall process can be represented simply as:



Using your knowledge of bonding, suggest how the methanol can be separated from any unreacted starting materials and explain your answer in terms of the bonding interactions involved.

- 23 Analysis of a recently discovered natural gas source shows the following composition:

Component	Percentage by volume
Methane	79.5
Ethane	7.2
Nitrogen	8.4
Carbon dioxide	0.5
Propane	2.8
Butane and other alkanes	1.6

In order to produce a commercially useful natural gas supply, some of these components have to be separated.

- a Knowing that carbon dioxide can be classified as an acidic oxide, suggest how it might be separated **chemically** from the other gases.
- b In devising a method for separating the methane from the other components, there is no need to remove the nitrogen. Why is this the case?
- c How would ethane and the other alkanes be separated from the methane? Explain your answer in terms of the intermolecular bonding between the molecules of the alkanes.
- 24 It has been argued that there is no such thing as an ionic bond. What are the reasons that are proposed to support this statement? Is it then possible for something to have a 'pure' covalent bond? Explain your answer.

A photograph of laboratory glassware on a metal tray. On the left is a beaker containing clear water. In the center is a test tube held by a clamp, containing a dark blue liquid. On the right is a beaker containing a light blue liquid. The background is a light-colored surface.

# 4

## Solutions

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

- define the words solute, solvent and solution, and give examples
- describe the bond-breaking and bond-formation processes that occur during dissolving
- explain the solubility of polar substances and lack of solubility of non-polar substances in water in terms of the bonding interactions that would need to occur during this process
- use the concept of ion-dipole bonds to explain the dissolving process of an ionic compound in water
- predict the relative solubilities of polar, non-polar and ionic compounds in polar and non-polar solvents
- perform mole calculations involving mass, molar mass and number of particles
- perform concentration calculations using units of  $\text{mol L}^{-1}$ ,  $\text{g L}^{-1}$ , ppm and percentage composition
- perform concentration calculations involving dilutions of solutions and the mixing of solutions.

We use solutions to clean our skin and our clothes. We drink solutions to maintain a healthy balance of dissolved substances in bodily fluids. We breathe a solution we call air and myriad industrial processes rely on the properties of solvents and solutions. In essence our quality of life is totally dependent on solutions and their properties.

What properties do different solvents have? What types of substances do they dissolve? How much dissolves? The answers to these and similar questions are critical for the development of an environmentally sensitive and sustainable chemical future.



## 4.1 Formation of solutions

When two substances are mixed together and a homogeneous mixture forms, it can be said that one substance has dissolved in the other to form a solution. In a homogeneous mixture, there is only one phase; there are no distinct boundaries separating the two substances mixed together. The dissolved substance has broken up into individual particles that are far too small to see. For example, when glucose ( $C_6H_{12}O_6$ ) dissolves in water, the glucose molecules that are organised in the solid lattice break away from the lattice to form individual molecules mixed with the water molecules (Figure 4.1). The glucose solution formed is therefore a homogeneous mixture of glucose molecules and water molecules.

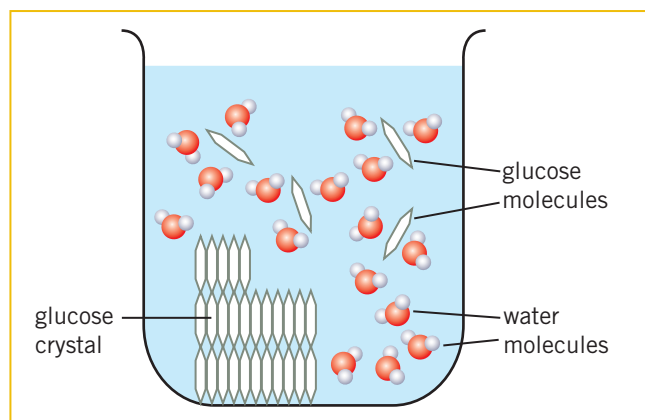


Figure 4.1 A model for glucose dissolving in water

If an insoluble substance such as oil or sand is added to water, a heterogeneous mixture is formed in which there are two phases. In the case of the oil mixture, one phase is water and the other is the oil, as shown in Figure 4.3, and with the sand mixture, one phase is again water but the other is the sand.

The words 'solute' and 'solvent' are often used when referring to the preparation of a solution. The substance that is present in the larger amount in the solution is usually referred to as the solvent. If 1 g of glucose is dissolved in 500 mL of water, the glucose is the solute and the water is the solvent. However, it is not always meaningful to identify the solute and the solvent in a solution. Air is a solution, but nitrogen, the gas present in the largest amount, is normally not referred to as the solvent and oxygen as a solute. Some examples of solutions are given in Table 4.1.



Figure 4.2 A solution (homogeneous mixture) of glucose and potassium chloride used for intravenous infusion



Figure 4.3 A heterogeneous mixture of oil and water

**TABLE 4.1** EXAMPLES OF SOLUTIONS

Type of solution	Examples
Solid in solid	'Silver' coins (nickel in copper), bronze (tin in copper), stainless steel (carbon, chromium in iron)
Solid in liquid	Cordial (sugar in water), seawater (sodium chloride and other salts 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 gas 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)

### The solution process

The formation of a solution from a solute and a solvent involves the rearrangement of bonds. For example, when a solid dissolves in a liquid:

- the bonds between the particles in the solid (solute) are broken as the particles move away to mix with the liquid (solvent)
- the bonds between the liquid particles are disrupted as the solute particles move in between them
- new bonds are formed between the solute particles and the liquid particles.

It is the relative strength of the bonds that need to be broken and the new ones formed that is a major factor in determining whether a solution forms when a possible solute is mixed with a solvent. Energy is required to break a bond; the stronger the bond, the more energy required. However, energy is released when a new bond is formed; the stronger the bond formed, the greater the amount of energy released. A logical conclusion derived from these statements would be that if the bonds being broken are of similar strength or weaker than the new bonds being formed, then the solute should dissolve in the solvent. This is found to be correct for the formation of many solutions, but it must be remembered that other factors, such as entropy (the tendency of a system to move towards a greater state of disorder), also influence the dissolving process.

### Mixing polar solutes and polar solvents

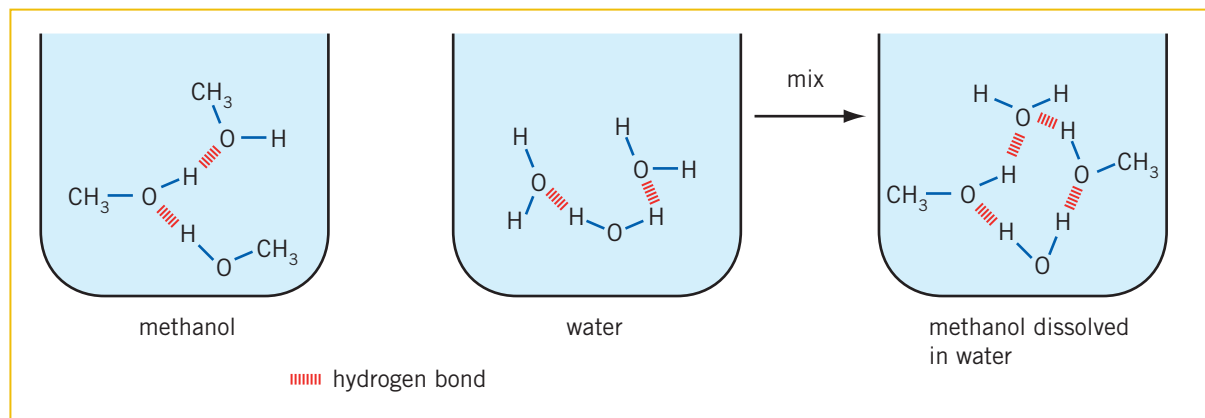
In Stage 2 of the chemistry course, a rule of thumb that 'like dissolves like' was introduced. From this rule, it could be concluded that a polar solute should dissolve in a polar solvent. In most cases, this is a reasonable conclusion; for instance, hydrogen chloride, HCl, ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ , and water are all polar substances and both hydrogen chloride and ethanol dissolve readily in water. However, can this rule be rationalised in terms of the bonds that are broken and formed during the dissolving process?

#### Methanol ( $\text{CH}_3\text{OH}$ ) dissolving in water

Methanol, a liquid at room temperature, is very soluble in water.

- The bonds that need to be broken in the dissolving process are the hydrogen bonds between the methanol molecules and the hydrogen bonds between the water molecules (Figure 4.4).
- The bonds that will be formed between the solute and the solvent, i.e. between the methanol and the water, are hydrogen bonds.

Similar types of bonds (hydrogen bonds) are being broken and formed, so it is likely that methanol will dissolve in water.



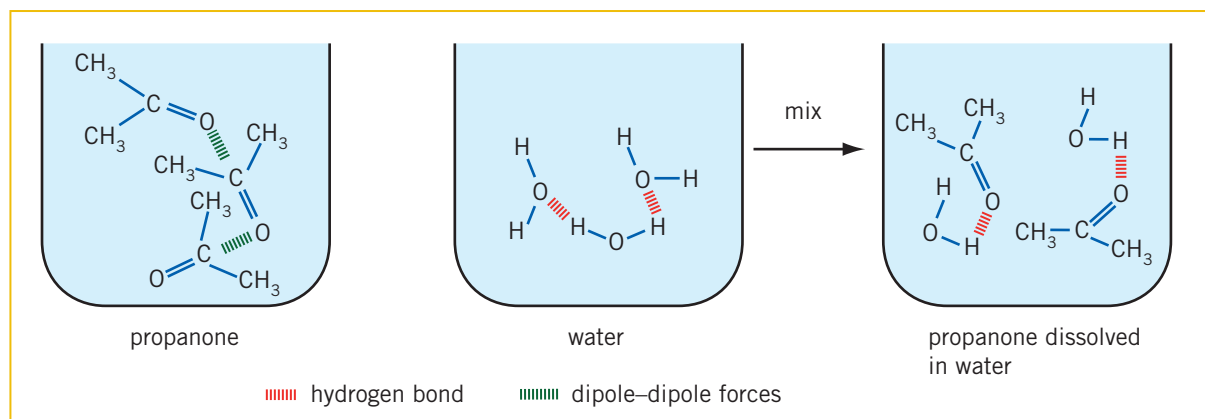
**Figure 4.4** When methanol dissolves in water, hydrogen bonds between both the solute and solvent molecules are broken, and hydrogen bonds are also formed between the solute and solvent molecules.

### Propanone (acetone) dissolving in water

Propanone is a polar liquid with dipole–dipole forces between its molecules. It is soluble in water.

- The bonds that need to be broken in the dissolving process are the dipole–dipole forces between the propanone molecules and the hydrogen bonds between the water molecules (Figure 4.5).
- The bonds that will be formed between the solute (propanone) and the solvent (water) molecules are hydrogen bonds.

Of the two types of bonds that need to be broken, one is a little weaker (dipole–dipole forces) and the other is of similar strength to the bonds that will be formed. It is therefore expected that propanone should dissolve in water.



**Figure 4.5** The dissolving of propanone in water

The above reasoning can also be used to explain the solubility of polar solutes in other polar solvents apart from water. For example, methanol and ethanol are both soluble in propanone because during the dissolving process, the two alcohols form hydrogen bonds with propanone, and hydrogen bonds and dipole–dipole forces are broken.



### Mixing a non-polar solute with a polar solvent

When tetrachloromethane ( $\text{CCl}_4$ ), a non-polar liquid, is mixed with water, it does not dissolve. A two-layered mixture is formed with the tetrachloromethane layer underneath the water layer (because tetrachloromethane is more dense than water).

This lack of solubility can be explained in terms of the bonds being broken and bonds that need to form for a solution to be produced.

Tetrachloromethane, being a non-polar substance, has only dispersion forces between its molecules.

- The bonds that will need to be broken during dissolving are the dispersion forces between the tetrachloromethane molecules and hydrogen bonds between the water molecules (Figure 4.6).
- The only bonds that can form between water and the tetrachloromethane molecules are dispersion forces.

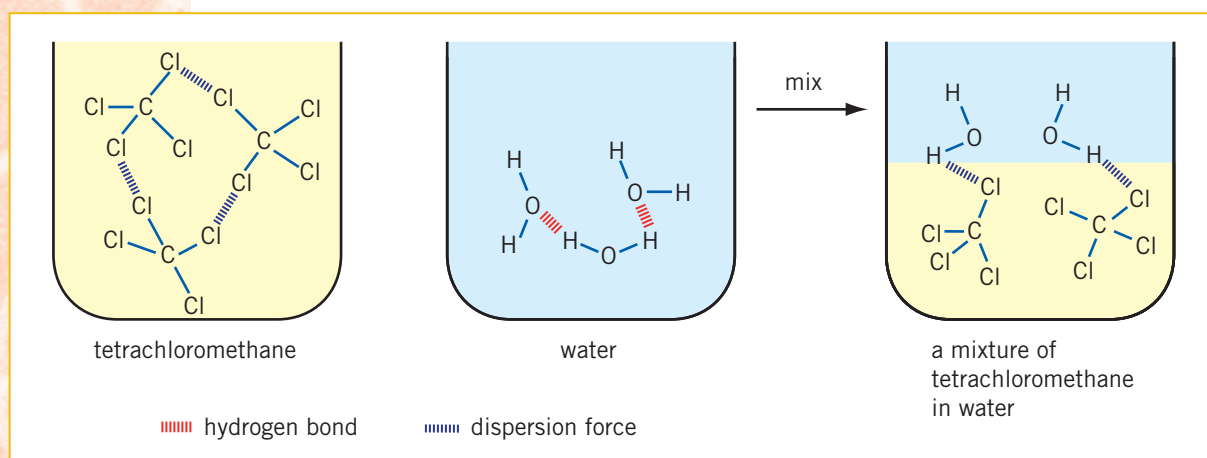


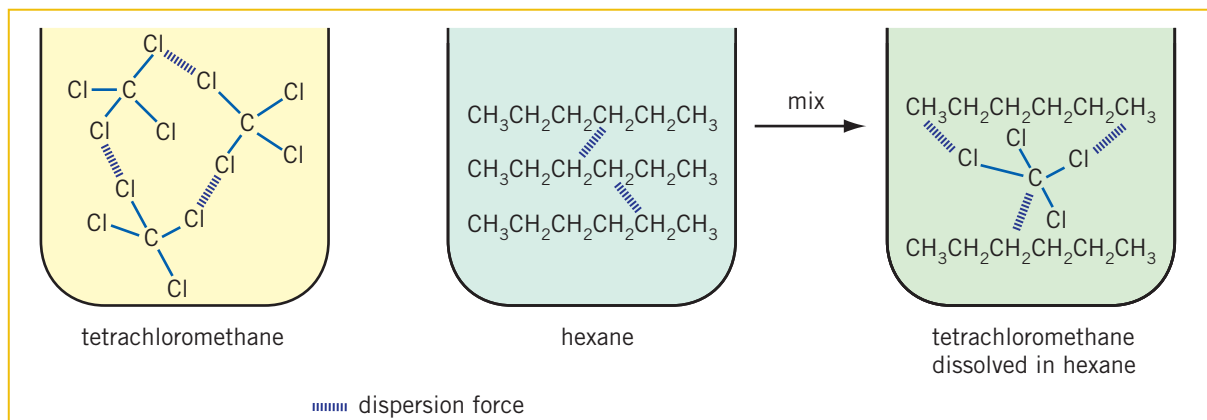
Figure 4.6 Tetrachloromethane does not dissolve in water.

Because the dispersion forces that could form between the solvent and solute molecules are weaker than the hydrogen bonds that need to break between the water molecules, it is unlikely that tetrachloromethane will dissolve in water.

### Mixing a non-polar solute with a non-polar solvent

If 'like dissolves like' is true, then a non-polar solute would be expected to dissolve in a non-polar solvent. For example, tetrachloromethane would be expected to dissolve in hexane,  $\text{C}_6\text{H}_{14}$ , which it does. This observation can be explained in terms of the model of bonds broken and bonds formed (Figure 4.7).

- The bonds that need to be broken are dispersion forces between the non-polar tetrachloromethane molecules and also dispersion forces between the non-polar hexane molecules.
- The bonds that will be formed during the dissolving process are dispersion forces between the tetrachloromethane molecules and the hexane molecules.



**Figure 4.7** The dissolving of tetrachloromethane in hexane

The bonds being broken and those forming are of a similar type (dispersion forces) and so it is highly likely that tetrachloromethane will dissolve in hexane.



### Do all polar substances dissolve in water, a highly polar solvent?

Some molecules contain a polar group, but the rest of the molecule is essentially non-polar. For example, the alcohol butan-1-ol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ , has an OH group that is polar. However, the chain of carbon and hydrogen atoms is non-polar and this can have an influence on the solubility of the alcohol in water.

The solubilities in water of the simple alcohols are shown in Table 4.2. As can be seen, the solubilities of these alcohols decrease as the length of the carbon chain increases.

**TABLE 4.2** SOLUBILITY OF SOME ALCOHOLS IN WATER AT 25°C

Name	Formula	Solubility (mol per 100 g water)
Methanol	$\text{CH}_3\text{OH}$	Completely miscible
Ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	Completely miscible
Propan-1-ol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	Completely miscible
Butan-1-ol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	0.11
Pentan-1-ol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	0.030
Hexan-1-ol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	0.0058
Heptan-1-ol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	0.00086
Octan-1-ol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	Completely immiscible

If an alcohol is to dissolve when added to water, hydrogen bonds between the alcohol molecules and between the water molecules must be broken. The new bonds formed will be the hydrogen bonds between the water and the alcohol molecules. From this reasoning, all the alcohols would be expected to be soluble in water. However, the hydrocarbon chain must have some effect. A possible reason for this is that even though the OH end of the alcohol molecule is able to form a hydrogen bond with water molecules, the hydrocarbon chain, being reasonably large compared to the water molecules, will have to push some water molecules apart to fit in between them. This would require some hydrogen bonds between the water molecules to be broken. Any new bonds that form between the water molecules and the hydrocarbon part of the alcohol molecule would be dispersion forces, which are weaker than the hydrogen bonds that need to be broken. Therefore, the alcohols with the longer hydrocarbon chains are expected to be less soluble in water than the alcohols with shorter chains.

So the answer to the initial question is that it is not only the polar portion of the molecule that determines whether a polar solute will dissolve in water; the rest of the molecule can also have some effect on the overall solubility properties of the compound.

Interestingly enough, the solubility of the alcohols in hexane, a non-polar solvent, increases as the length of the hydrocarbon chain increases. This is possibly because the alcohol molecule becomes less polar as the number of carbon and hydrogen atoms in the chain increases. Because the molecules with the longer hydrocarbon chain also contain more electrons, the dispersion forces between them and the hexane molecules will be larger than for the smaller molecules. If the alcohol molecules are large enough, there will be sufficient energy released, when forming the solvent–solute dispersion forces, to make up for the energy required to break the original hydrogen bonds between the alcohol molecules.

Ionic compounds can be considered to be very polar and so would be expected to dissolve in water. This will be discussed in section 4.2.

### Prediction of solubility of polar and non-polar substances

To enable the prediction of the solubility of substances, the relative polarities of the substances will need to be considered. Table 4.3 contains a list of typical polar and non-polar substances, ordered from most polar to least polar.

**TABLE 4.3 TYPICAL POLAR AND NON-POLAR SUBSTANCES**

Most polar	Type of substance	Examples and general comments	
↓	Ionic compounds	NaCl, K <sub>2</sub> CO <sub>3</sub>	
	Water	H <sub>2</sub> O	
	Carboxylic acids	CH <sub>3</sub> COOH (acetic acid) Contain the –COOH group. As the hydrocarbon chain increases in length, the carboxylic acids become less polar.	
	Alcohols	CH <sub>3</sub> CH <sub>2</sub> OH (ethanol/methylated spirits) Contain the –OH group. The more –OH groups present, the greater the polarity. As the hydrocarbon chain increases in length, the alcohols become less polar.	
	Ketones	CH <sub>3</sub> COCH <sub>3</sub> (propanone or acetone) Contain the –CO– group in the middle of a ‘carbon chain’. As the length of the hydrocarbon chains increase, the ketones become less polar.	
	Esters	CH <sub>3</sub> COOCH <sub>3</sub> (methyl ethanoate) Contain –COO–R, where R is a hydrocarbon chain. As the length of the hydrocarbon chains increase, the esters become less polar.	
	Polar haloalkanes	CHCl <sub>3</sub> Contain C, H and halogen atoms.	
	Least polar	Ethers	CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub> (ethoxyethane) Contain –O– where the oxygen is bonded to two carbon atoms. As the length of the hydrocarbon chains increase, the ethers become less polar.
		Non-polar	Hydrocarbons
	Non-polar haloalkanes		CCl <sub>4</sub> (tetrachloromethane)



**Figure 4.8** Cointreau is a solution of about 40 mL of ethanol in every 100 mL of solution and vinegar is a solution of about 6 g of acetic acid dissolved in every 100 mL of solution.

Predictions concerning degree of solubility can be made using the information in Table 4.3 and the general ideas that:

- polar (and ionic) solutes will dissolve in polar solvents
- non-polar solutes will dissolve in non-polar solvents
- the solubility of a polar solute, and an ionic compound, decreases as the polarity of the solvent decreases
- the solubility of a non-polar solute increases as the polarity of the solvent decreases.

For example:

- sodium chloride would be more soluble in water than in ethanol
- water would be more soluble in ethanol than in ethoxyethane
- butter (a non-polar substance) would be soluble in tetrachloromethane, slightly soluble in acetone, but insoluble in water.

#### → Example 4.1

Predict the solubility of the following substances in water and in petrol.

- ammonia,  $\text{NH}_3$
- methane,  $\text{CH}_4$
- calcium chloride

#### → Solution

Water is a highly polar solvent and petrol is composed of a mixture of hydrocarbons, so it is a non-polar solvent.

- Ammonia is composed of highly polar molecules, so it will dissolve in water but not in petrol.
- Methane is composed of non-polar molecules, so it will not dissolve in water but it will dissolve in petrol.
- Calcium chloride,  $\text{CaCl}_2$ , is an ionic compound that is soluble in water. It will not dissolve in petrol.

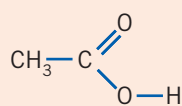
#### → Example 4.2

Predict the solubility of acetic acid,  $\text{CH}_3\text{COOH}$ , in water and in hexane. Explain your prediction in terms of the bonds broken and formed in the dissolving process.

*continued*

### → Solution

Acetic acid has the structure shown below:



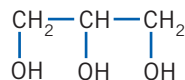
Because of the OH group, hydrogen bonds can form between the acetic acid molecules. Also because of the OH group and the double-bonded O atom, acetic acid can form hydrogen bonds with water.

If acetic acid is to dissolve in water, hydrogen bonds between the acetic acid molecules and between the water molecules need to be broken. However, hydrogen bonds can form between the water and acetic acid molecules in the solution. As a result, because bonds of similar strength will be broken and formed, acetic acid will dissolve in water.

If acetic acid were to dissolve in hexane, hydrogen bonds between the acetic acid molecules would need to be broken, as well as dispersion forces between the hexane molecules. However, only dispersion forces could form between acetic acid molecules and hexane molecules if a solution were to form. Because the bonds that could form, dispersion forces, are weaker than the hydrogen bonds that need to be broken, acetic acid will probably not dissolve in hexane.

### \* Review exercise 4.1

- 1 Which of the following substances would you expect to be soluble in water, and which in benzene ( $\text{C}_6\text{H}_6$ )?  
ethanol      ethane,  $\text{CH}_3\text{CH}_3$        $\text{CBr}_4$       HF      naphthalene ( $\text{C}_{10}\text{H}_8$ )      NaF
- 2 a Predict the order of solubility, from most to least soluble, of glycerol:

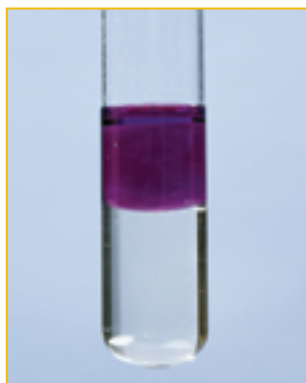


in the following solvents: water, benzene, acetone (propanone).

- b Repeat part a, but refer to the solubility of butane ( $\text{C}_4\text{H}_{10}$ ) in the solvents.
- 3 Some properties of three liquids are listed in the following table.

Name	Formula	Molecular mass	Melting point ( $^{\circ}\text{C}$ )	Boiling point ( $^{\circ}\text{C}$ )	Solubility in water at $20^{\circ}\text{C}$ (g in 100 mL)
Pentane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	74	-131.5	36.2	0.01
Ethoxyethane	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	72	-116	34.6	6.9
Butan-1-ol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	74	-89.2	117.7	7.4

- a Why is pentane the least soluble of the three liquids in water?
- b Explain, in terms of the bonds that need to be broken and the bonds that will form, why some butan-1-ol and ethoxyethane will dissolve in water.
- c Explain the differences in the melting points of the three substances.
- 4 Iodine,  $\text{I}_2$ , is a solid at room temperature. When iodine dissolves in water, it produces a yellow solution but it forms a purple solution when it dissolves in hexane. In an experiment, a small crystal of iodine was shaken with a mixture of 25 mL of water and 20 mL of hexane in a test tube. The mixture was then allowed to settle. The result obtained is shown in Figure 4.9.



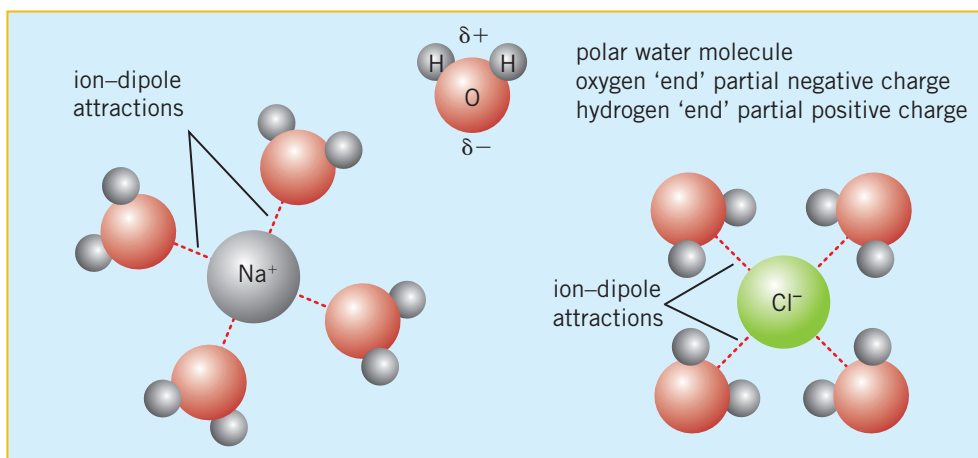
- a** Describe what the results show about the solubility of iodine in water and in hexane. (Hexane is less dense than water.)
- b** Explain your conclusions concerning the solubility of iodine in terms of the bonds being broken and formed during the dissolving process.

**Figure 4.9** Iodine shaken with some water and hexane

## 4.2 Dissolving ionic compounds in water

When an ionic compound dissolves in water, the same ideas expressed in the previous section also hold. Bonds will be broken and new bonds will form. When the ionic compound dissolves, the hydrogen bonds between the water molecules must be disturbed and the ionic bonds holding the ions in the lattice must also be broken. To provide the energy required for these bond-breaking processes, there must be new bonds formed between the separated ions and the water molecules in the solution.

Attractive forces do exist between ions and polar molecules such as water. This type of attractive force is called an ion–dipole force and it can be stronger than hydrogen bonds (but not as strong as the various forms of strong bonding). Positive ions attract the partial negatively charged ‘end’ of the water molecule, the lone pairs of the oxygen atoms. Negative ions attract the partial positively charged ‘end’ of the water molecule, the hydrogen atoms, as shown in Figure 4.10.



**Figure 4.10** Water molecules are attracted to the positive and negative ions in a solution by ion–dipole attractions.

Water molecules cluster around each ion in layers. For smaller monatomic ions like  $\text{Li}^+$ , four water molecules usually form the first layer, but for larger ions, typically six water molecules are in this layer. The first layer of water molecules is usually held quite tightly, with any further layers being held less tightly. For some ions, these water molecules remain bonded to the ion even when the solvent is evaporated to leave the solid ionic compound. For example, solid blue copper sulfate has five water molecules held by ion–dipole forces to the copper





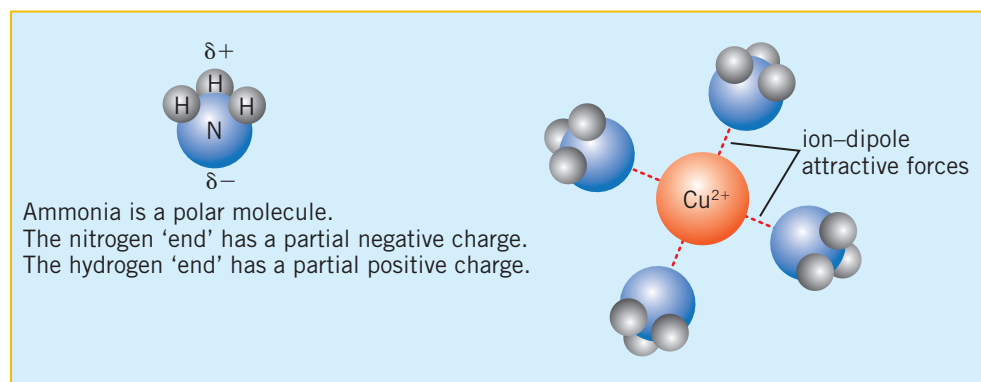
**Figure 4.11** The blue copper sulfate contains the complex ion  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ . Heating the hydrated copper sulfate breaks the ion–dipole forces between  $\text{Cu}^{2+}$  and  $\text{H}_2\text{O}$  and also between the remaining  $\text{H}_2\text{O}$  molecule and the sulfate ion. The water evaporates, leaving the white copper sulfate.

and sulfate ions. The copper ion has four water molecules attracted to it and the sulfate ion, one water molecule. When this solid is heated, the ion–dipole forces break and the water molecules vapourise to result in anhydrous copper sulfate, a white solid, forming.

The ions with the polar molecules around them are called complex ions, and their formula shows the number of ions in the first hydration layer. For example, in solution the copper ion has six water molecules in its first hydration layer and so its formula is  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ , but in blue copper sulfate crystals it has only four water molecules attracted to it so the formula of the complex ion is  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ . (Square brackets are put around the group of atoms/ions making up the complex ion.)

Ion–dipole forces also exist between other polar molecules and ions. For example, when an excess of ammonia solution is added to copper sulfate solution, a deep blue-coloured complex ion composed of a copper ion with four ammonia molecules bonded to it, with ion–dipole forces, forms. Its formula is  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ . This complex ion exists both in solution and in the solid form.

The first page of this chapter shows the formation of this dark blue copper tetraammine complex ion. When copper sulfate solution (right beaker) is mixed with ammonia solution (left beaker), a precipitate of  $\text{Cu}(\text{OH})_2$  forms first (bottom of test tube) followed by a dark blue solution of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ions (top layer in test tube).



**Figure 4.12** The  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion forms because the polar  $\text{NH}_3$  molecules are attracted to the positive  $\text{Cu}^{2+}$  ion by ion–dipole forces.

The polar molecules that are attracted to the positive and negative ions, during the formation of a complex ion, are often called ligands. A complex ion is therefore composed of a positive or negative ion and ligands, where the ligands are bonded to the ion by ion–dipole attractive forces.

Ionic compounds are not soluble in non-polar solvents. The only bonds that could form between the ions and the non-polar solvent molecules are dispersion forces, which presumably are not sufficiently strong to cause disruption of the ionic lattice.

Many ionic solids are also insoluble even in water. The reason for this insolubility is complex and beyond the scope of this course. A solubility table often used to predict the solubility of ionic compounds in water is given in Table 5.3 on page 128.

## \* Review exercise 4.2

- Which of the following substances would you predict to be soluble in water?  
sodium phosphate      propan-1-ol, C<sub>3</sub>H<sub>7</sub>OH      turpentine, C<sub>10</sub>H<sub>16</sub> (approximate)  
zinc carbonate      iron(III) sulfide      hydrogen bromide, HBr
- Draw the particles present in an aqueous solution of potassium cyanide, labelling the bonds between and within the particles. Identify which bonds are weak and which are strong.
- Explain what bonds are broken and formed during the dissolving of potassium bromide in water. Include diagrams to support your answer.
- Describe the bonding in the diamminesilver(I) complex ion, [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Draw a sketch of this complex ion, showing where these bonds are.

## 4.3 The mole concept (overview from Stage 2)

To measure the amount of solute dissolved in a solution or involved in a reaction, it is convenient to use the concept of the mole.

One mole (mol) is the amount of substance that contains  $6.022 \times 10^{23}$  particles of that substance.

For example:

- 1 mole of helium is composed of  $6.022 \times 10^{23}$  atoms of helium.
- 1 mole of water is composed of  $6.022 \times 10^{23}$  molecules of water.
- 1 mole of copper chloride is composed of  $6.022 \times 10^{23}$  formula units of CuCl<sub>2</sub>.

The number of particles in one mole, i.e.  $6.022 \times 10^{23}$ , is called the Avogadro constant.

One mole of any substance has a mass equal to its relative atomic, molecular or formula mass expressed in grams.

For example:

- 1 mole of helium has a mass of 4.003 g
- 1 mole of water, H<sub>2</sub>O, has a mass of  $(2 \times 1.008) + 16.00 = 18.016$  g
- 1 mole of copper chloride, CuCl<sub>2</sub>, has a mass of  $63.55 + (2 \times 35.45) = 134.45$  g

The relative atomic mass (or atomic weight) of an atom is the mass of that atom compared to the mass of a <sup>12</sup>C atom that is assigned a mass of 12 exactly. To determine the relative atomic mass of an element, the weighted average of the relative atomic masses of the isotopes present in the element is calculated. The relative atomic masses of the elements are shown in the periodic table on the inside front cover of this book.

Relative atomic mass does not have a unit. However, the molar mass of a substance, which is the mass of one mole of the substance, has a unit of g mol<sup>-1</sup>. Both the relative atomic mass and the molar mass of an element have the same numerical value.

Relative molecular mass and relative formula mass are determined by adding the relative atomic masses of the elements, including their relative proportions, shown in the chemical formulas.



Two useful equations relating the amount in mole of a substance, the number of particles present and the mass of the substance are:

$$\text{amount, in mole, of substance A} = \frac{\text{number of particles of A}}{6.022 \cdot 10^{23}} \text{ or } n = \frac{N}{6.022 \cdot 10^{23}}$$

$$\text{amount, in mole, of substance A} = \frac{\text{mass of A}}{\text{molar mass of A}} \text{ or } n = \frac{m}{M}$$

where  $n$  is amount in mol,  $N$  is number of particles,  $m$  is mass and  $M$  is molar mass.

#### → Example 4.3

- a** Calculate the relative formula mass of hydrated copper sulfate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .
- b** What is the molar mass of hydrated copper sulfate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ?

#### → Solution

- a** The relative formula mass is determined by adding the atomic masses of the atoms, taking into account the number of each type of atom, shown in the chemical formula.

$$\begin{aligned} \text{Relative formula mass of } \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \\ &= 63.55 + 32.06 + (4 \times 16.00) + 5 \times ((2 \times 1.008) + 16.00) \\ &= \mathbf{249.7} \end{aligned}$$

- b** Molar mass of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  = mass of 1 mole of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$   
=  $\mathbf{249.7 \text{ g mol}^{-1}}$

(Note: The relative formula mass has no unit, but molar mass has the unit of  $\text{g mol}^{-1}$ .)

#### → Example 4.4

How many molecules of water are in 225 mL of water, at 25°C (density of water at 25°C is  $1.000 \text{ g mL}^{-1}$ )?

#### → Solution

There are three steps in this calculation:

volume, density of water → mass of water → mole of water → number of molecules of water

**Step 1** Find the mass of  $\text{H}_2\text{O}$ .

Because the density of  $\text{H}_2\text{O}$  is  $1.000 \text{ g mL}^{-1}$ , 1 mL of  $\text{H}_2\text{O}$  has a mass of 1 g, so 225 mL of  $\text{H}_2\text{O}$  has a mass of 225 g

**Step 2** Find the amount in mole of  $\text{H}_2\text{O}$ .

$$\begin{aligned} \text{mole of } \text{H}_2\text{O} &= \frac{\text{mass of } \text{H}_2\text{O}}{\text{molar mass of } \text{H}_2\text{O}} \\ \text{molar mass of } \text{H}_2\text{O} &= (2 \times 1.008) + 16.00 = 18.016 \text{ g mol}^{-1} \\ \text{mole of } \text{H}_2\text{O} &= \frac{225}{18.016} = 12.49 \text{ mol} \end{aligned}$$

**Step 3** Find the number of molecules of  $\text{H}_2\text{O}$ .

$$\begin{aligned} \text{mole of } \text{H}_2\text{O} &= \frac{\text{number of molecules of } \text{H}_2\text{O}}{6.022 \cdot 10^{23}} \\ &= 12.49 \end{aligned}$$

$$\begin{aligned} \text{number of molecules of } \text{H}_2\text{O} &= 12.49 \times 6.022 \times 10^{23} \\ &= \mathbf{7.52 \times 10^{24} \text{ molecules}} \end{aligned}$$

(Note: In this problem, the final answer is quoted to 3 significant figures because the least accurate value given in the question (225 mL) is quoted to 3 significant figures. Throughout the question, the answer to any calculation is rounded off to 4 significant figures. The final answer to the problem is then rounded off to 3 significant figures. See Appendix 2 for more details concerning significant figures.)

#### → Example 4.5

Which has the larger mass, 0.200 mol of hexane,  $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$ , or  $2.11 \times 10^{23}$  molecules of ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ ?

#### → Solution

Hexane:

$$\text{mole of hexane} = \frac{\text{mass of hexane}}{\text{molar mass of hexane}}$$

$$\begin{aligned} \text{molar mass of hexane, } \text{CH}_3(\text{CH}_2)_4\text{CH}_3 \text{ or } \text{C}_6\text{H}_{14} &= (6 \times 12.01) + (14 \times 1.008) \\ &= 86.172 \text{ g mol}^{-1} \end{aligned}$$

$$0.200 = \frac{\text{mass of hexane}}{86.172}$$

$$\text{mass of hexane} = 0.200 \times 86.172 = 17.2 \text{ g}$$

Ethanol:

This involves two steps:

number of molecules of ethanol → mole of ethanol → mass of ethanol

**Step 1** Find the amount in mole of ethanol.

$$\begin{aligned} \text{mole of ethanol} &= \frac{\text{number of ethanol molecules}}{6.022 \cdot 10^{23}} \\ &= \frac{2.11 \cdot 10^{23}}{6.022 \cdot 10^{23}} = 0.3504 \text{ mol} \end{aligned}$$

**Step 2** Find the mass of ethanol.

$$\text{mole of ethanol} = \frac{\text{mass of ethanol}}{\text{molar mass of ethanol}}$$

$$\begin{aligned} \text{molar mass of ethanol, } \text{CH}_3\text{CH}_2\text{OH} \text{ or } \text{C}_2\text{H}_6\text{O} \\ &= (2 \times 12.01) + (6 \times 1.008) + 16.00 = 46.068 \text{ g mol}^{-1} \end{aligned}$$

$$0.3504 = \frac{\text{mass of ethanol}}{46.068}$$

$$\text{mass of ethanol} = 0.3504 \times 46.068 = 16.1 \text{ g}$$

The mass of hexane is 17.2 g and the mass of ethanol is 16.1 g, so **hexane has the larger mass.**

Sometimes chemists need to know the amount of part of a compound in a sample; for example, they may need to know the mass of nitrogen available to plants in a sample of the fertiliser ammonium nitrate. This information is obtained by considering the chemical formula of the compound.

The chemical formula shows the ratio in which the ions or atoms are present in the particular compound. For example, the formula of ammonium nitrate is  $\text{NH}_4\text{NO}_3$  and it shows that each formula unit of ammonium nitrate consists of:

1  $\text{NH}_4^+$  ion and 1  $\text{NO}_3^-$  ion

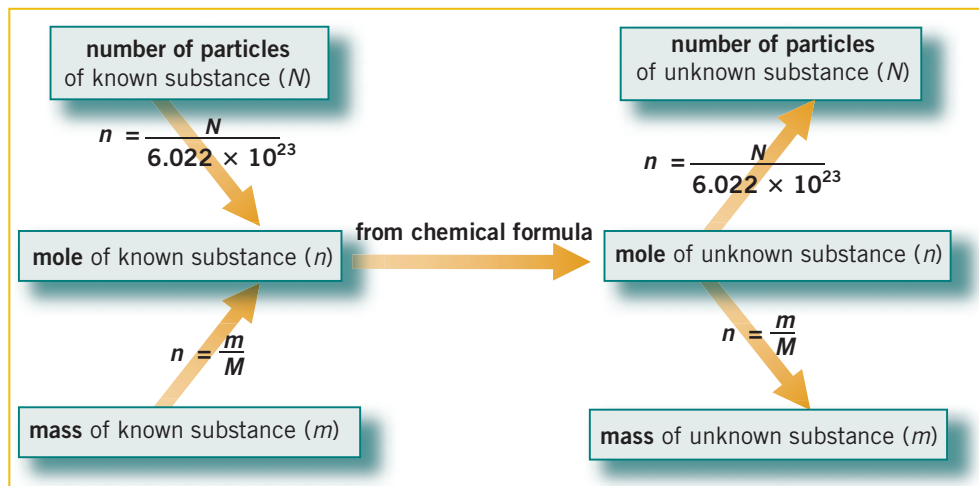
or 2 N atoms, 4 H atoms and 3 O atoms.

The chemical formula of a compound also shows the mole ratio of atoms or ions present in 1 mole of the compound. For example, in 1 mole of  $\text{NH}_4\text{NO}_3$  there are:

1 mole of  $\text{NH}_4^+$  ions and 1 mole of  $\text{NO}_3^-$  ions

or 2 mole of N atoms, 4 mole of H atoms and 3 mole of O atoms.

When carrying out calculations involving the relationships between amount in mole, mass and number of atoms, molecules or formula units of substances, a flow chart like the one shown in Figure 4.13 can help in deciding the steps that need to be undertaken.



**Figure 4.13** A flow chart that can be used to decide on the steps in a calculation involving the mass, mole and/or number of atoms, ions or molecules shown in a chemical formula

#### → Example 4.6

How many atoms of carbon are in a cube of sugar that has a mass of 4.82 g? Assume the sugar is pure sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ .

#### → Solution

There are three steps in this calculation:

mass of sugar → mole of sugar → mole of carbon → number of carbon atoms

**Step 1** Find the amount in mole of sugar.

$$\text{mole of sugar} = \frac{\text{mass of sugar}}{\text{molar mass of sugar}}$$

$$\text{molar mass of sugar, } \text{C}_{12}\text{H}_{22}\text{O}_{11}$$

$$= (12 \times 12.01) + (22 \times 1.008) + (11 \times 16.00) = 342.296 \text{ g mol}^{-1}$$

$$\text{mole of sugar} = \frac{4.82}{342.296} = 0.01408 \text{ mol}$$

**Step 2** Find the amount in mole of C.

1 mol of  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  contains 12 mol of C atoms

so 0.01408 mol of  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  contains  $12 \times 0.01408$

$$= 0.1690 \text{ mol of C atoms}$$

**Step 3** Find the number of C atoms.

$$\text{mole of C} = \frac{\text{number of C atoms}}{6.022 \cdot 10^{23}}$$

$$0.1690 = \frac{\text{number of C atoms}}{6.022 \cdot 10^{23}}$$

$$\text{number of C atoms} = 0.1690 \times 6.022 \times 10^{23} = \mathbf{1.02 \times 10^{23} \text{ C atoms}}$$

→ **Example 4.7**

One of the principle ores from which zinc is extracted is sphalerite. If a particular batch of sphalerite contains 95.6% by mass of zinc sulfide, what theoretical mass of zinc could be extracted from 1.00 tonne of this ore?

→ **Solution**

There are four steps in this calculation:

mass of ore → mass of zinc sulfide (ZnS) → mole of zinc sulfide → mole of zinc  
→ mass of zinc

**Step 1** Find the mass of zinc sulfide in the ore.

$$\text{mass of ore} = 1.00 \times 10^6 \text{ g}$$

$$\text{mass of pure ZnS} = 95.6\% \text{ of } 1.00 \times 10^6$$

$$= \frac{95.6}{100} \times 1.00 \times 10^6 = 9.56 \times 10^5 \text{ g}$$

**Step 2** Find the amount in mole of ZnS.

$$\text{mole of ZnS} = \frac{\text{mass of ZnS}}{\text{molar mass of ZnS}}$$

$$\text{molar mass of ZnS} = 65.38 + 32.06 = 97.44 \text{ g mol}^{-1}$$

$$\text{mole of ZnS} = \frac{9.56 \cdot 10^5}{97.44} = 9.811 \times 10^3 \text{ mol}$$

**Step 3** Find the amount in mole of Zn.

1 mole of ZnS contains 1 mole of Zn

so  $9.811 \times 10^3$  mole of ZnS contains  $9.811 \times 10^3$  mole of Zn

**Step 4** Find the mass of Zn.

$$\text{mole of Zn} = \frac{\text{mass of Zn}}{\text{molar mass of Zn}} \quad \text{molar mass of Zn} = 65.38 \text{ g mol}^{-1}$$

$$9.811 \times 10^3 = \frac{\text{mass of Zn}}{65.38}$$

$$\text{mass of Zn} = 9.811 \times 10^3 \times 65.38 = \mathbf{6.41 \times 10^5 \text{ g}} \text{ (or 0.641 tonne)}$$

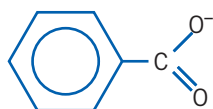
**\* Review exercise 4.3**

- What is the mass of  $5.03 \times 10^{22}$  molecules of carbon dioxide?
  - What is the amount, in mol, of sulfur in 18.5 g of aluminium sulfate?
  - What mass of oxygen would be in 0.624 g of calcium carbonate?
  - What is the relative atomic mass of a particular metal if  $4.86 \times 10^{-3}$  mol of the metal has a mass of 524 mg?

*continued*

### Review exercise 4.3 — continued

- 2 Constant exposure to mercury is known to produce long-term neurologic effects, especially in children. In Australia, the recommended safe level of mercury in drinking water has been set at  $0.0010 \text{ mg L}^{-1}$ . Calculate the number of atoms of mercury in  $1.0 \text{ L}$  of water with this concentration of mercury.
- 3 Because of its antibacterial and antifungal properties, calcium benzoate is used as a preservative in food and drinks such as fruit juices, jams, margarines and mayonnaise. The benzoate ion has a  $-1$  charge and its structure is shown below:



In the production of a  $112 \text{ kg}$  batch of strawberry jam, the supervisor was required to add  $0.425 \text{ mol}$  of calcium benzoate to the jam mixture. What mass of calcium benzoate would need to be weighed out to add to the jam?

- 4 Under typical summer conditions, a  $1.00 \text{ m}^3$  volume of dry air has a mass of  $1.17 \text{ kg}$ . Assuming air is composed  $75.5\%$  by mass of nitrogen,  $23.1\%$  by mass of oxygen and  $1.28\%$  by mass of argon, what volume of air would contain  $6.022 \times 10^{23}$  atoms in total? Assume the volumes are measured at the same temperature and pressure.
- 5 Around  $5000 \text{ BCE}$ , it was discovered that copper metal could be obtained by strongly heating malachite,  $\text{Cu}_2\text{CO}_3(\text{OH})_2$ , a green copper-containing mineral, in a fire. The copper produced was used to make items such as vessels, utensils, religious objects, spearheads and battle shields.
- a What mass of malachite would be required to make a battle shield that had a mass of  $3.2 \text{ kg}$ ?
- b Explain the advantage of using copper to make items such as those listed rather than using materials like stone or wood.



## 4.4 Solution concentrations

The concentration of a solution refers to the quantity of solute dissolved in a particular quantity of solution. The mass or volume of the solution includes the mass or volume of both the solute and the solvent.

Four methods commonly used to express solution concentration are:

- mole per litre,  $\text{mol L}^{-1}$
- gram per litre,  $\text{g L}^{-1}$
- parts per million, ppm
- percentage composition by mass.

### Concentration in mole per litre, $\text{mol L}^{-1}$ (molarity)

This method shows the amount in mole of solute dissolved in a litre of solution. For example, a  $2.00 \text{ mol L}^{-1}$  hydrochloric acid solution (or  $2.00 \text{ M HCl}$ ) contains  $2.00$  mole of  $\text{HCl}$  molecules dissolved in every  $1.00 \text{ L}$  of solution.

Concentration, in  $\text{mol L}^{-1}$ , can be calculated using the formula:

$$\text{concentration (mol L}^{-1}\text{)} = \frac{\text{mole of solute}}{\text{volume of solution in L}}$$

$$\text{or } c = \frac{n}{V} \text{ where } V \text{ is in litres.}$$

### → Example 4.8

What volume of  $0.0606 \text{ mol L}^{-1}$  sodium hydroxide solution contains  $1.50 \text{ g}$  of sodium hydroxide?

### → Solution

This calculation involves two steps:

mass of NaOH → mole of NaOH → volume of NaOH solution

**Step 1** Calculate the amount in mole of NaOH.

$$\text{mole of NaOH} = \frac{\text{mass of NaOH}}{\text{molar mass of NaOH}}$$

$$\text{molar mass of NaOH} = 22.99 + 16.00 + 1.008 = 39.998 \text{ g mol}^{-1}$$

$$\text{mole of NaOH} = \frac{1.50}{39.998} = 0.03750 \text{ mol}$$

**Step 2** Calculate the volume of NaOH solution.

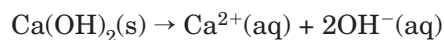
$$\text{concentration of NaOH solution} = \frac{\text{mole of NaOH}}{\text{volume of NaOH solution}}$$

$$0.0606 = \frac{0.03750}{\text{volume of NaOH solution}}$$

$$\text{volume of NaOH solution} = \frac{0.03750}{0.0606} = \mathbf{0.619 \text{ L}}$$

Some substances, when they dissolve in water, break up into smaller particles. When gaseous hydrogen chloride dissolves in water, the molecules of HCl ionise to form  $\text{H}^+$  and  $\text{Cl}^-$  ions. In the formation of a solution of sodium carbonate,  $\text{Na}_2\text{CO}_3$ , the ions break away from the solid lattice, so the solution is composed of  $\text{Na}^+$  and  $\text{CO}_3^{2-}$  ions (and water). The concentrations of these particles formed during the dissolving process can be determined from the concentration of the substance originally used to form the solution.

For example, if  $0.02$  mole of  $\text{Ca}(\text{OH})_2$  is dissolved in  $1 \text{ L}$  of solution, it is said that the concentration of the  $\text{Ca}(\text{OH})_2$  solution is  $0.02 \text{ mol L}^{-1}$ . This is sometimes written as  $0.02 \text{ mol L}^{-1} \text{ Ca}(\text{OH})_2$ . However, when this solid dissolves in the water, it breaks up into its individual ions according to the following equation:



As a result, there would be  $0.02$  mole of  $\text{Ca}^{2+}$  and  $2 \times 0.02 = 0.04$  mole of  $\text{OH}^-$  in the  $1 \text{ L}$  of solution. The concentration of these ions in the solution would therefore be  $0.02 \text{ mol L}^{-1}$  for the  $\text{Ca}^{2+}$  ions and  $0.04 \text{ mol L}^{-1}$  for the  $\text{OH}^-$  ions.

### → Example 4.9

$46.0 \text{ g}$  of potassium sulfate is dissolved in water to form  $570 \text{ mL}$  of solution. Calculate the concentration, in  $\text{mol L}^{-1}$ , of potassium ions in the solution.

### → Solution

There are three steps in this calculation:

mass of  $\text{K}_2\text{SO}_4$  → mole of  $\text{K}_2\text{SO}_4$  → mole of  $\text{K}^+$  ions → concentration of  $\text{K}^+$  ions

**Step 1** Calculate the amount in mole of  $\text{K}_2\text{SO}_4$ .

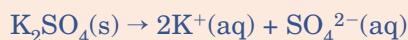
$$\text{mole of K}_2\text{SO}_4 = \frac{\text{mass of K}_2\text{SO}_4}{\text{molar mass of K}_2\text{SO}_4}$$

*continued*

$$\text{molar mass of K}_2\text{SO}_4 = (2 \times 39.10) + 32.06 + (4 \times 16.00) = 174.26 \text{ g mol}^{-1}$$

$$\text{mole of K}_2\text{SO}_4 = \frac{46.0}{174.26} = 0.2640 \text{ mol}$$

**Step 2** Calculate the amount in mole of  $\text{K}^+$ .



1 mol of  $\text{K}_2\text{SO}_4$  forms 2 mol of  $\text{K}^+$

so 0.2640 mol of  $\text{K}_2\text{SO}_4$  forms  $2 \times 0.2640 = 0.5280$  mol of  $\text{K}^+$

**Step 3** Calculate the concentration of  $\text{K}^+$ .

$$\begin{aligned} \text{concentration of K}^+ &= \frac{\text{mole of K}^+}{\text{volume of solution}} && \text{vol. of solution} = 0.570 \text{ L} \\ &= \frac{0.5280}{0.570} = \mathbf{0.926 \text{ mol L}^{-1}} \end{aligned}$$

### Concentration in gram per litre ( $\text{g L}^{-1}$ )

Concentration expressed in  $\text{g L}^{-1}$  indicates the mass of solute dissolved in a litre of solution. For example, if a solution of sodium chloride has a concentration of  $0.500 \text{ g L}^{-1}$ , then in 1.00 L of the solution there would be 0.500 g of NaCl.

The concentration, in  $\text{g L}^{-1}$ , can be calculated using the formula:

$$\text{concentration (g L}^{-1}\text{)} = \frac{\text{mass of solute in g}}{\text{volume of solution in L}}$$

#### → Example 4.10

The concentration of sodium chloride in a sample of seawater is  $11.2 \text{ g L}^{-1}$ . What amount, in mole, of chloride ions would be contained in 1.00 ML of seawater?

#### → Solution

There are three steps in this calculation:

concentration of NaCl in seawater → mass of NaCl → mole of NaCl → mole of  $\text{Cl}^-$

**Step 1** Find the mass of NaCl in 1.00 ML of seawater.

$$\text{concentration of NaCl solution in g L}^{-1} = \frac{\text{mass of NaCl}}{\text{volume of NaCl solution}}$$

$$\text{volume of solution} = 1.00 \times 10^6 \text{ L}$$

$$11.2 = \frac{\text{mass of NaCl}}{1.00 \cdot 10^6}$$

$$\text{mass of NaCl} = 11.2 \times 1.00 \times 10^6 = 1.12 \times 10^7 \text{ g}$$

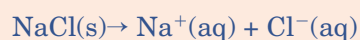
**Step 2** Find the amount in mole of NaCl.

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

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

$$\text{mole of NaCl} = \frac{1.12 \cdot 10^7}{58.44} = 1.916 \times 10^5 \text{ mol}$$

**Step 3** Find mole of  $\text{Cl}^-$ .



$$\text{mole of Cl}^- = \text{mole of NaCl} = \mathbf{1.92 \times 10^5 \text{ mol}}$$

## Concentration in parts per million (ppm)

When very small quantities of solute are dissolved to form a solution, the concentration is often measured in parts per million (ppm). For example, the concentration of sodium chloride in river water and the concentration of sulfur dioxide in air are frequently expressed in parts per million.

In simple terms, the concentration in parts per million can be thought of as the mass in grams of solute dissolved in 1 000 000 g of solution. However, usually the concentration in ppm is expressed as the mass in milligrams of solute dissolved in 1 kg of solution. For example, a solution of sodium chloride that has a concentration of 154 ppm contains 154 mg of sodium chloride dissolved in 1 kg of solution. A formula that can be used to calculate the concentration of a solution in ppm is:

$$\text{concentration in ppm} = \frac{\text{mass of solute in mg}}{\text{mass of solution in kg}}$$

Sometimes it is necessary to calculate the mass of a solution from its volume. The relationship between the mass of a solution and its volume is given by its density. This relationship is shown in the formula:

$$\text{density of solution} = \frac{\text{mass of solution}}{\text{volume of solution}}$$

where the mass and volume have the same units as those expressed in the density.

For example, if a solution has a density of  $1.2 \text{ g mL}^{-1}$ , it follows that 1 mL of the solution has a mass of 1.2 g.

### → Example 4.11

A saturated solution of calcium carbonate was found to contain 0.0198 g of calcium carbonate dissolved in 2000 g of solution. Calculate the concentration in ppm of calcium carbonate in the saturated solution.

### → Solution

mass of solute (calcium carbonate) in mg =  $0.0198 \times 1000 = 19.8 \text{ mg}$

mass of solution in kg =  $\frac{2000}{1000} = 2.000 \text{ kg}$

concentration of calcium carbonate in ppm =  $\frac{\text{mass of calcium carbonate in mg}}{\text{mass of solution in kg}}$   
 $= \frac{19.8}{2.000} = \mathbf{9.90 \text{ ppm}}$

### → Example 4.12

Drinking water is often treated with chlorine to kill bacteria. If the required concentration of chlorine in the drinking water was 0.800 ppm, what mass, in g, of chlorine would need to be added to 2500 kL of drinking water to attain this concentration? Assume the density of the drinking water is  $1 \text{ kg L}^{-1}$ .

### → Solution

volume of solution in L =  $2500 \times 1000 = 2.500 \times 10^6 \text{ L}$

From the density, 1 L of the drinking water will have a mass of 1 kg.

So mass of  $2.500 \times 10^6 \text{ L}$  of drinking water will be  $2.500 \times 10^6 \text{ kg}$ .

*continued*



$$\begin{aligned} \text{concentration of chlorine in ppm} &= \frac{\text{mass of chlorine in mg}}{\text{mass of solution in kg}} \\ 0.800 &= \frac{\text{mass of chlorine in mg}}{2.500 \cdot 10^6} \\ \text{mass of chlorine in mg} &= 0.800 \times 2.500 \times 10^6 = 2.000 \times 10^6 \text{ mg} \\ \text{mass of chlorine in g} &= \frac{2.000 \cdot 10^6}{1000} = \mathbf{2.00 \times 10^3 \text{ g}} \end{aligned}$$

### Concentration expressed as percentage composition

Concentration expressed as a percentage composition is referring to the percentage of solute in a particular solution. This may be on a mass (m) or volume (v) basis and leads to notations such as 10% (m/m), 5% (m/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. For example, a 1.5% (m/m) NaCl solution is one in which 1.5 g of sodium chloride is dissolved in 100 g of the solution; or in a wine with an alcohol content of 12% (v/v), there is 12 mL of alcohol (ethanol) dissolved in 100 mL of the wine.

To calculate the percentage composition of a solution in the different units, the following equations can be used:

$$\text{percentage composition by mass (\% m/m)} = \frac{\text{mass of solute in g}}{\text{mass of solution in g}} \times 100$$

$$\text{percentage composition by volume (\% v/v)} = \frac{\text{volume of solute in mL}}{\text{volume of solution in mL}} \times 100$$

$$\text{percentage composition by mass/volume (\% m/v)} = \frac{\text{mass of solute in g}}{\text{volume of solution in mL}} \times 100$$

#### → Example 4.13

Calculate the amount, in mole, of sodium ions present in 650 mL of a 2.00% (g/mL) sodium carbonate solution.

#### → Solution

This problem has three steps:

volume of solution → mass of Na<sub>2</sub>CO<sub>3</sub> → mole of Na<sub>2</sub>CO<sub>3</sub> → mole of Na<sup>+</sup>

$$\begin{aligned} \text{Step 1} \quad \text{mass of sodium carbonate in 650 mL of the 2\% solution} &= 2\% \text{ of } 650 \\ &= \frac{2.00}{100} \times 650 = 13.00 \text{ g} \end{aligned}$$

$$\text{Step 2} \quad \text{mole of Na}_2\text{CO}_3 = \frac{\text{mass of Na}_2\text{CO}_3}{\text{molar mass of Na}_2\text{CO}_3}$$

$$\text{molar mass of Na}_2\text{CO}_3 = (2 \times 22.99) + 12.01 + (3 \times 16.00) = 105.99 \text{ g mol}^{-1}$$

$$\text{mole of Na}_2\text{CO}_3 = \frac{13.00}{105.99} = 0.1227 \text{ mol}$$



1 mol of Na<sub>2</sub>CO<sub>3</sub> will form 2 mol of Na<sup>+</sup>

so 0.1227 mol of Na<sub>2</sub>CO<sub>3</sub> will form 2 × 0.1227 = **0.245 mol Na<sup>+</sup>**

## \* Review exercise 4.4

- 1 Calculate the concentration (in mol L<sup>-1</sup>) of chloride ions if 0.581 g of aluminium chloride is dissolved in sufficient water to make 250 mL of solution.
- 2 Sodium hydrogensulfite is added to wine as a preservative.
  - a If the recommended concentration is 0.010 mol L<sup>-1</sup> sodium hydrogensulfite, what mass of sodium hydrogensulfite would need to be added to a 450 L barrel of wine to achieve this concentration?
  - b What assumption did you make in this calculation?
- 3 A sample of tap water was found to contain 0.0472 g of NaCl per 250 g of solution. Calculate the concentration, in ppm, of NaCl in the tap water.
- 4 The label on a bottle of hospital-grade disinfectant states that the disinfectant contains 49.9 g L<sup>-1</sup> of sodium hypochlorite (NaClO) and 12.0 g L<sup>-1</sup> of sodium hydroxide. If these are the only two sources of sodium ions, calculate the concentration, in mol L<sup>-1</sup>, of sodium ions in this disinfectant.
- 5 The water supply of many cities is fluoridated, giving 1.00 ppm of F<sup>-</sup>. Express this concentration as mol of F<sup>-</sup> per L of solution, assuming 1.00 mL of solution has a mass of 1.00 g.
- 6 The concentration of calcium in milk is 0.114% (m/m) and the recommended daily amount of calcium consumed by a teenager is 1300 mg. How many glasses of milk would need to be consumed to achieve this recommended daily amount? Assume the volume of the glass is 250 mL and that 100 mL of milk has a mass of 103 g.

## 4.5 Diluting and mixing solutions

When more solvent is added to a solution, the concentration of the solution decreases. In this dilution process, the volume of the solution is increased, but the amount of solute remains constant. That is:

$$\text{mole of solute in concentrated solution} = \text{mole of solute in dilute solution}$$

A method sometimes used to calculate the new concentration of a diluted solution is based on the following reason.

$$\text{If } \begin{array}{l} \text{mole of solute in the initial concentrated solution} \\ = \text{mole of solute in the final diluted solution} \end{array}$$

and because

$$\text{mole of solute} = \text{concentration of solution} \times \text{volume of solution}$$

then it follows that:

$$\begin{array}{l} \text{concentration of initial solution} \times \text{initial volume} \\ = \text{concentration of final solution} \times \text{final volume} \end{array}$$

or

$$c_1V_1 = c_2V_2$$

where  $c_1$  and  $V_1$  refer to the concentrated solution before dilution and  $c_2$  and  $V_2$  refer to the diluted solution.

→ **Example 4.14**

325 mL of water is added to 655 mL of 0.213 mol L<sup>-1</sup> NaOH solution. Calculate the concentration, in mol L<sup>-1</sup>, of the dilute NaOH solution.

→ **Solution**

Several different ways in which this calculation can be done are explained below.

**Method 1**

This method has three steps:

concentration, volume of concentrated NaOH → mole of NaOH in concentrated solution → mole of NaOH in dilute solution → concentration of new dilute solution

**Step 1** Find the amount in mol of NaOH in the concentrated solution.

$$\text{concentration of original NaOH solution} = \frac{\text{mole of NaOH}}{\text{volume of original solution}}$$

$$\text{volume of original solution} = 655 \text{ mL} = 0.655 \text{ L}$$

$$0.213 = \frac{\text{mole of NaOH}}{0.655}$$

$$\text{mole of NaOH} = 0.213 \times 0.655 = 0.1395 \text{ mol}$$

**Step 2** Find the amount in mole of NaOH in the dilute solution.

$$\text{mole of NaOH in concentrated solution} = \text{mole of NaOH in dilute solution}$$

$$\text{so mole of NaOH in dilute solution} = 0.1395 \text{ mol}$$

**Step 3** Find the concentration of the dilute solution.

$$\text{concentration of dilute NaOH solution} = \frac{\text{mole of NaOH}}{\text{volume of dilute solution}}$$

$$\text{new volume of dilute solution} = 0.325 + 0.655 = 0.980 \text{ L}$$

$$\text{concentration of dilute NaOH solution} = \frac{0.1395}{0.980} = \mathbf{0.142 \text{ mol L}^{-1}}$$

**Method 2**

Because mole of NaOH in the concentrated solution

= mole of NaOH in the dilute solution

the relationship  $c_1V_1 = c_2V_2$  can be used.

$$c_1 = 0.213 \text{ mol L}^{-1}, V_1 = 655 \text{ mL}, V_2 = 655 + 325 = 980 \text{ mL}, c_2 = ?$$

$$0.213 \times 655 = 980 \times c_2$$

$$c_2 = \text{concentration of dilute NaOH solution} = \frac{0.213 \cdot 655}{980} = \mathbf{0.142 \text{ mol L}^{-1}}$$

When mixing two solutions, it is sometimes not possible to use  $c_1V_1 = c_2V_2$  in the calculation because the amount in mole of the solute changes. The method will therefore possibly involve calculating the new amount in mole of solute present in the mixture, and then the concentration or volume of the new mixture, whatever is asked in the question.

**→ Example 4.15**

1.20 L of 1.36 mol L<sup>-1</sup> MgCl<sub>2</sub> solution is added to 0.932 L of 1.27 mol L<sup>-1</sup> NaCl solution. Calculate the concentration, in mol L<sup>-1</sup>, of chloride ions in the resulting solution.

**→ Solution**

The steps in this calculation are:

concentration, volume of MgCl<sub>2</sub>(aq) → mole of MgCl<sub>2</sub> → mole of Cl<sup>-</sup> (A)

concentration, volume of NaCl(aq) → mole of NaCl → mole of Cl<sup>-</sup> (B)

then (A) + (B) = total mole of Cl<sup>-</sup> → concentration of Cl<sup>-</sup>

**Step 1** Find the amount in mole of MgCl<sub>2</sub>.

$$\text{concentration of MgCl}_2 \text{ solution} = \frac{\text{mole of MgCl}_2}{\text{volume of MgCl}_2 \text{ solution}}$$

$$1.36 = \frac{\text{mole of MgCl}_2}{1.20}$$

$$\text{mole of MgCl}_2 = 1.36 \times 1.20 = 1.632 \text{ mol}$$

**Step 2** Find the amount in mole of Cl<sup>-</sup> from MgCl<sub>2</sub>.



1 mol of MgCl<sub>2</sub> will form 2 mol of Cl<sup>-</sup>

so 1.632 mol of MgCl<sub>2</sub> will form 2 × 1.632 = 3.264 mol of Cl<sup>-</sup>

**Step 3** Find the amount in mole of NaCl.

$$\text{concentration of NaCl solution} = \frac{\text{mole of NaCl}}{\text{volume of NaCl solution}}$$

$$1.27 = \frac{\text{mole of NaCl}}{0.932}$$

$$\text{mole of NaCl} = 1.27 \times 0.932 = 1.184 \text{ mol}$$

**Step 4** Find the amount in mole of Cl<sup>-</sup> from NaCl.



1 mol of NaCl will form 1 mol of Cl<sup>-</sup>

so 1.184 mol of NaCl will form 1.184 mol of Cl<sup>-</sup>

**Step 5** Find the total mole of Cl<sup>-</sup>.

$$\text{total mole of Cl}^- = 3.264 + 1.184 = 4.448 \text{ mol}$$

**Step 6** Find the concentration of Cl<sup>-</sup> in new solution.

$$\text{new volume} = 1.20 + 0.932 = 2.132 \text{ L}$$

$$\begin{aligned} \text{concentration of Cl}^- \text{ in new solution} &= \frac{\text{mole of Cl}^-}{\text{volume of solution}} \\ &= \frac{4.448}{2.132} = \mathbf{2.09 \text{ mol L}^{-1}} \end{aligned}$$

### \* Review exercise 4.5

(Assume the volumes are additive in the following problems.)

- 1 116 mL of water is added to 22.0 mL of a  $3.72 \text{ g L}^{-1}$  sodium carbonate solution. Calculate the concentration, in  $\text{mol L}^{-1}$ , of the diluted sodium carbonate solution.
- 2 When fully charged, a car battery contains 33.5% (m/m)  $\text{H}_2\text{SO}_4$  solution. The concentration of concentrated sulfuric acid is 98.0% (m/m). To make up 250 g of the battery acid, what masses of water and concentrated acid need to be mixed together?
- 3 500 mL of distilled water was added to 320 mL of  $5.33 \text{ mol L}^{-1}$  sodium hydroxide solution. What amount, in mole, of hydroxide ions would be present in 20.0 mL of this diluted solution?
- 4 50.0 mL of  $0.126 \text{ mol L}^{-1}$  nitric acid is mixed with 70.0 mL of  $0.429 \text{ mol L}^{-1}$  nitric acid. Calculate the concentration of the resulting solution of nitric acid, in  $\text{g L}^{-1}$ .
- 5 Concentrated hydrochloric acid has a density of  $1.16 \text{ g mL}^{-1}$  and contains 32.0% by mass of hydrogen chloride. What volumes of this concentrated acid and of water would need to be mixed together to prepare 500 mL of a  $2.00 \text{ mol L}^{-1}$  HCl solution?



## MAJOR IDEAS

- A solution is a homogeneous mixture made from a solute dissolving in a solvent.
- When a solid dissolves, the particles that make up the solid break away from the solid lattice and mix with the solvent molecules.
- The formation of a solution involves the rearrangement of bonds:
  - The bonds between the particles in the solid (solute) are broken.
  - The bonds between the liquid particles are disrupted as the solute particles move in between them.
  - New bonds are formed between the solute particles and the liquid particles.
- The relative strengths of the bonds that need to be broken and the new ones formed is a major factor in determining whether a solution forms.
- If the bonds being broken are of similar strength or weaker than the new bonds being formed, then the solute should dissolve in the solvent.
- A rule of thumb used to predict solubilities is 'like dissolves like', e.g. a polar solvent should dissolve a polar solute.
- A solute with hydrogen bonds between the molecules should dissolve in water because the new bonds formed between the solute and water are also hydrogen bonds.
- A solute with only dispersion forces between its molecules (i.e. a non-polar solute) will not dissolve in water because hydrogen bonds need to be broken between the solvent (water) molecules, but only dispersion forces can form between the solute and solvent molecules.
- A non-polar solute will dissolve in a non-polar solvent because the bonds broken (between the solute and between the solvent molecules) are dispersion forces and the new bonds formed between the solute and solvent are also dispersion forces.
- For polar organic molecules such as alcohols:
  - the solubility in water decreases as the hydrocarbon chain increases in length
  - the solubility in a non-polar solvent decreases as the number of polar functional groups on the hydrocarbon chain increases.
- The solubility of a polar solute, and an ionic compound, decreases as the polarity of the solvent decreases.
- The solubility of a non-polar solute increases as the polarity of the solvent decreases.
- When ionic solids dissolve in water, the polar water molecules are attracted to the positive and negative ions. Ion-dipole forces hold the molecules to the ions.
- The ions with water molecules attracted to them are called complex ions.  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  is an example of a complex ion.
- One mole is the amount of substance that contains  $6.022 \times 10^{23}$  particles of that substance.
- One mole of any substance has a mass equal to its relative atomic, molecular or formula mass expressed in grams.
- The relative atomic mass (or atomic weight) of an atom is the mass of that atom compared to the mass of a  $^{12}\text{C}$  atom that is assigned a mass of 12 exactly.
- Amount, in mole, of substance A
$$= \frac{\text{number of particles of A}}{6.022 \cdot 10^{23}}$$
or  $n = \frac{N}{6.022 \cdot 10^{23}}$
- Amount, in mole, of substance A =  $\frac{\text{mass of A}}{\text{molar mass of A}}$ or  $n = \frac{m}{M}$
- The chemical formula of a compound shows the mole ratio of atoms or ions present in 1 mole of the compound.
- A flow chart showing the relationships between amount in mole, mass and number of atoms, molecules or formula units of substances is given in Figure 4.13.
- The concentration of a solution refers to the quantity of solute dissolved in a particular quantity of solution.
- Concentration can be measured in the units of  $\text{mol L}^{-1}$  or  $\text{g L}^{-1}$ .
  - concentration ( $\text{mol L}^{-1}$ ) =  $\frac{\text{mole of solute}}{\text{volume of solution in L}}$
  - concentration ( $\text{g L}^{-1}$ ) =  $\frac{\text{mass of solute in g}}{\text{volume of solution in L}}$
- Concentration can be expressed as parts per million, ppm, which indicates the mass in mg of solute dissolved in 1 kg of solution.
$$\text{concentration in ppm} = \frac{\text{mass of solute in mg}}{\text{mass of solution in kg}}$$
- Concentration can also be expressed as percentage composition, for example percentage composition by mass:
$$\text{percentage composition by mass (\% m/m)} = \frac{\text{mass of solute in g}}{\text{mass of solution in g}} \times 100$$
- When more solvent is added to a solution, the concentration of the solution decreases. Providing no solution is lost from the container:
  - mole of solute in concentrated solution = mole of solute in dilute solutionand
  - concentration of initial solution  $\times$  initial volume = concentration of final solution  $\times$  final volume  
or  $c_1 V_1 = c_2 V_2$

## QUESTIONS

- Which substance in each of the following pairs is likely to be more soluble in water? Explain your choices.
  - hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) or benzene ( $\text{C}_6\text{H}_6$ )
  - ethoxyethane ( $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ ) or hexane ( $\text{C}_6\text{H}_{14}$ )
  - chloroform ( $\text{CHCl}_3$ ) or magnesium chloride
  - iodine ( $\text{I}_2$ ) or hydrogen iodide ( $\text{HI}$ )
- Which would you expect to be more soluble in water: methanol ( $\text{CH}_3\text{OH}$ ) or hexan-1-ol ( $\text{C}_6\text{H}_{13}\text{OH}$ )?
  - Which would you expect to be more soluble in petrol: methanol ( $\text{CH}_3\text{OH}$ ) or hexan-1-ol ( $\text{C}_6\text{H}_{13}\text{OH}$ )?
- Two different mixtures have been formed by mixing ethanol with water and by mixing cooking oil with water.
  - Describe what these mixtures would look like.
  - Explain how you could separate the two liquids in each of the two mixtures.
- Figure 4.14 shows solutions of two cobalt(II) complex ions. The pink colour of the solution in the conical flask on the left is due to the presence of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  ions. The blue colour of the solution in the flask on the right is due to the presence of  $[\text{CoCl}_4]^{2-}$  ions.



Figure 4.14 Solutions of cobalt complex ions

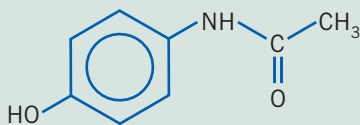
- Why are the charges of these two complex ions different?
  - For the two complex ions, draw simple line structures, showing and identifying the bonds that are present.
- Urea,  $\text{NH}_2\text{CONH}_2$  (relative formula mass = 60), melts at  $133^\circ\text{C}$ , whereas butane,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$  (relative formula mass = 58), has a melting point of  $-138^\circ\text{C}$ .
    - Draw line structures for the two molecules.
    - Which substance would you expect to be more soluble in water? Explain your reasoning in terms of the bond-breaking and bond-forming processes that occur during the formation of a solution.
    - Explain the different melting points of the two compounds.
  - If 10 drops of water have a volume of 5.00 mL, and the density of water is  $1.00\text{ g mL}^{-1}$ , how many molecules are in a single drop of water?
  - Uranium-238 atoms are the heaviest naturally occurring atoms. What is the mass, in grams, of a single uranium-238 atom if its relative atomic mass is 238.05?
  - Scientists have estimated that each square metre of the Earth's surface supports  $1.00 \times 10^7\text{ g}$  of gas above it. If this gas is 23.1% oxygen by mass, how many mole of oxygen,  $\text{O}_2$ , is there above each square metre of the Earth?
  - The principle source of bromine is seawater, which contains about 65 ppm of bromine in the form of bromide ions. Approximately 3.0 tonnes of bromine,  $\text{Br}_2$ , is extracted annually from seawater. If the average density of seawater is  $1.03\text{ g mL}^{-1}$ , how many litres of seawater would be required annually to produce this bromine?
    - Seawater also contains traces of gold. If a sample of seawater has a density of  $1.03\text{ g mL}^{-1}$  and an average gold content of  $6.00 \times 10^{-6}\text{ ppm}$ , how many atoms of gold are present in each millilitre of the seawater?
  - A sample of household cloudy ammonia is found to contain 5.00% ammonia, by mass. Its density is  $0.977\text{ g mL}^{-1}$ . What is the concentration, in  $\text{mol L}^{-1}$ , of this ammonia solution?
  - A student was required to make up a solution of sodium carbonate. She first weighed out the anhydrous solid, and then dissolved it in 250 mL of solution, in a volumetric flask. She obtained the following mass measurements:
 

mass of weighing bottle + anhydrous sodium carbonate = 26.193 g

mass of weighing bottle + traces of sodium carbonate remaining after pouring the solid into the volumetric flask = 23.712 g

Calculate the concentration of her sodium carbonate solution in  $\text{mol L}^{-1}$ .

- 12 The chemical name for paracetamol, a widely used analgesic, is *N*-(4-hydroxyphenyl)acetamide and it has the following structural formula:



- a Many covalent molecular substances are gases or liquids at room temperature, because of their low melting points. However, the melting point of paracetamol is  $169^{\circ}\text{C}$ , which is quite high for a covalent molecular substance. Why would you expect this substance to have a higher melting point than many other covalent molecular substances?
- b In the *British Pharmacopeia*, a book containing information about medicines dispensed by pharmacists, the solubility of paracetamol in several different solvents is recorded in the following way:
- Solubility:** 1 part of paracetamol is soluble in 70 parts of *water*, in 7 parts of *ethanol*, in 13 parts of *acetone*; also soluble in solutions of alkali hydroxides.
- In what mass of water and of ethanol would you expect 1 g of paracetamol to dissolve?
  - Explain why you would expect paracetamol to be soluble in water.
  - Is paracetamol more soluble in water or in ethanol?
  - Propose a reason for your answer to part iii.
  - Paracetamol is more soluble in a solution of sodium hydroxide than it is in pure water. Suggest a reason for this observation.
- 13 A mixture of 0.129 g of potassium chloride and 0.452 g of aluminium chloride is dissolved in a small amount of distilled water and then more water is added to make the volume of the solution up to 500 mL. Calculate the concentration, in  $\text{mol L}^{-1}$ , of chloride ions in the resulting solution.
- 14 What volume of  $6.14 \text{ mol L}^{-1}$  nitric acid would be required to prepared 500 mL of  $0.100 \text{ mol L}^{-1}$  nitric acid?
- 15 Fluoridation is the adjustment of fluoride ions in a water supply to an optimal concentration of approximately 1 ppm. Normal consumption of drinking water containing fluoride ions at a

concentration greater than 1 ppm is thought to lead to fluorosis, or mottling, of teeth in children.

Water supplies are often fluoridated by adding a 30% (m/m) solution of fluorosilicic acid,  $\text{H}_2\text{SiF}_6$ , supplied in 25 kg plastic drums. If the volume of the water in a holding tank is 0.10 GL, how many drums of the fluorosilicic acid solution need to be added to the water to produce a maximum 1 ppm concentration of fluoride ions?

Assume each molecule of  $\text{H}_2\text{SiF}_6$  can form six  $\text{F}^-$  ions and the density of the holding tank water is  $1 \text{ g mL}^{-1}$  ( $1 \text{ GL} = 10^9 \text{ L}$ ).

- 16 In one day a large coal-fired power station burns 2500 tonnes of coal. The coal contains 0.65% by mass of sulfur. When the coal burns, all of this sulfur forms sulfur dioxide.
- What mass of sulfur dioxide will be formed per day?
  - If all of this sulfur dioxide is trapped, by a thermal inversion, in a volume of air that is  $45 \text{ km} \times 65 \text{ km} \times 0.40 \text{ km}$ , will the level of sulfur dioxide in the air exceed the national air quality standard of  $80 \mu\text{g m}^{-3}$  of air (over a period of 24 hours)?
- 17 Copy and fill in the gaps in the table by naming the types of bonds that need to be broken and the type of bonds that could form when the solute/solvent pairs are mixed. Use this information to predict whether or not you would expect the solute to dissolve in the solvent.

	a	b	c
Solute	methanol, $\text{CH}_3\text{OH}$	$\text{CF}_4$	iodine, $\text{I}_2$
Solvent	water	water	kerosene, a hydrocarbon
Type(s) of bonds that need to be broken			
Type of bond that can form between solute and solvent			
Will the solute dissolve in the solvent?			



- 18** Over 90% of people whose blood assays show an ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) concentration of 0.0030 g per mL of blood demonstrate signs of obvious intoxication. The fatal concentration of ethanol is estimated at 0.0070 g per mL of blood. What is the volume of 80-proof Scotch whisky (40%  $\text{C}_2\text{H}_5\text{OH}$  by volume) that corresponds to the difference between an intoxicating dose and a fatal dose for a person whose blood volume is 6.5 L? (Assume all the ethanol goes directly into the blood and the density of ethanol is  $0.80 \text{ g mL}^{-1}$ .)
- 19** A solution of a powerful insecticide contains 10.3 g of the active agent per 100 mL of solution. A spray is prepared by diluting (with water) 5.0 mL of this solution to 2.5 L. After spraying, 45 mL of the spray remains adhering to the inside of the vessel. In order to clean the vessel, water is added to give a total volume of 5.00 L.

Assuming all volumes are additive, what is the mass of active agent in 100 mL of this final washing solution?

- 20** The glucose solution shown in Figure 4.2 contains 0.15% potassium chloride.
- From the other details on the label determine whether this is 0.15% m/m, m/v or v/v.
  - The container states that the solution contains 10 mmol potassium. Use the information from part a and other information on the label to show that there actually is 10 mmol of potassium ions present in the 500 mL solution. (1 mmol =  $10^{-3}$  mol).



# 5

## Reactions

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

- write and balance molecular and ionic equations for reactions
- predict the products and write ionic equations for precipitation reactions
- carry out calculations using the stoichiometric ratio shown in a balanced equation
- use the ideal gas equation,  $PV = nRT$ , in calculations
- calculate the percentage purity of a substance and the percentage yield of a reaction.



Figure 5.1 A blast furnace

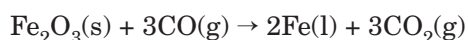


Figure 5.2 A precipitate of lead iodide forms when solutions of lead nitrate and sodium iodide are mixed.

## 5.1 Chemical reactions and equations

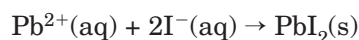
Chemical reactions are processes in which chemical changes occur and they are characterised by the formation of new substances. In a chemical reaction, the reactants undergo a chemical change to form the products. When iron(III) oxide reacts with carbon monoxide in a blast furnace, the new substances formed are iron and carbon dioxide. This is an example of a chemical reaction.

A chemical reaction can be represented by a chemical equation. The reactants and products involved in the chemical reaction are normally shown as formulas in this equation. During a chemical reaction, the number of atoms of each element and the total charge are conserved; that is, remain unchanged. To indicate this conservation of atoms during a reaction, a chemical equation is written as a 'balanced' equation. A chemical equation is said to be 'balanced' when the number of atoms of each element on each side of the equation are the same, and when the total charge on each side of the equation is the same. For example, the balanced equation for the reaction of iron with carbon monoxide in the blast furnace is:



The states of the substances involved in the reaction are often included in brackets after the formula of the relevant substance. The equation given above is called an overall or molecular equation, where all the chemicals present in the reaction mixture are shown.

Some reactions, particularly those involving ions in aqueous solution, are best represented by an ionic equation. In an ionic equation, only the actual species consumed and produced in the reaction are shown. These species can be ions, molecules or solids. The ions that are not changed during the reaction are called spectator ions and they are not included in the ionic equation. For example, when a solution of lead nitrate is mixed with a solution of sodium iodide, to form a precipitate of lead iodide, only the lead ions and iodide ions react. The ionic equation for this reaction is therefore written as:



The nitrate ions and sodium ions are not changed during the reaction; they remain dissolved in the solution, and so they are not included in the equation.

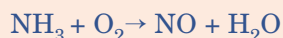
### → Example 5.1

Write balanced equations for the following reactions.

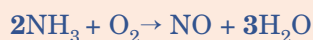
- One of the steps in the industrial production of nitric acid is the reaction of ammonia with oxygen, under high pressure, to form nitrogen monoxide and gaseous water.
- A precipitate of copper hydroxide forms when copper ions and hydroxide ions in solution react with one another.

### → Solution

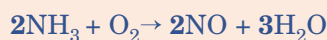
- a Step 1** Write the formulas of the reactants and products.



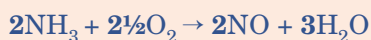
- Step 2** The N atoms are balanced, so balance the H atoms.



- Step 3** Rebalance the N atoms.



**Step 4** Balance the O atoms.



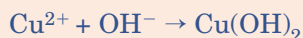
**Step 5** Only whole numbers are normally used in a balanced equation, so multiply by 2.



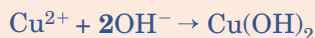
**Step 6** Include the states of each substance



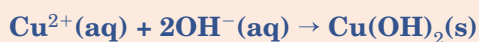
**b Step 1** Write the formulas of the reactants and products.



**Step 2** Balance the equation for atoms.



**Step 3** Check that the charges are balanced (which they are in this case) and include states.



## Writing ionic equations

When writing an ionic equation for a reaction, it is sometimes difficult to determine the spectator ions (the ions that are unchanged during the reaction) just by inspecting the formulas of the reactants. However, if for all the substances present in the reaction mixture, their formulas are written to show the form they are in, in the actual reaction mixture, then the spectator ions are easily recognised. Table 5.1 summarises the ways in which the formulas of reactants and products can be written when writing ionic equations.

**TABLE 5.1 WRITING FORMULAS IN IONIC EQUATIONS**

Type of substance	When writing ionic equations the substance is written as	Examples
Solutions of ionic compounds	'Separated' ions	Solution of sodium hydroxide: $\text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq})$ Solution of potassium chloride: $\text{K}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
Solid and insoluble ionic compounds, e.g. precipitates	Neutral formulas	Solid sodium carbonate: $\text{Na}_2\text{CO}_3(\text{s})$ Precipitate of silver chloride: $\text{AgCl}(\text{s})$
Strong acids	'Separated' ions	Hydrochloric acid: $\text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ Nitric acid: $\text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$ Sulfuric acid: $\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ (The $\text{H}^+$ ions will be balanced at the final step in writing the ionic equation.)
Other covalent molecular substances, including weak acids	Neutral formulas	Water: $\text{H}_2\text{O}(\text{l})$ Carbon dioxide: $\text{CO}_2(\text{g})$ Ammonia: $\text{NH}_3(\text{g})$ Hydrogen: $\text{H}_2(\text{g})$ Sulfur dioxide: $\text{SO}_2(\text{g})$ Acetic acid, $\text{CH}_3\text{COOH}(\text{aq})$
Metals	Neutral formulas	Magnesium: $\text{Mg}(\text{s})$ Aluminium: $\text{Al}(\text{s})$ Zinc: $\text{Zn}(\text{s})$

The following steps can be used to write an ionic equation:

- Step 1** Write the formulas of the reactants and products in the form shown in Table 5.1. (The balancing of atoms will be carried out in the last step.)
- Step 2** Determine which species have not changed during the reaction, and 'cancel out' these spectator ions.
- Step 3** Rewrite the formulas remaining and balance the equation in terms of both atoms and charge.

→ **Example 5.2**

Write ionic equations for the following reactions.

- a** When dilute nitric acid is added to solid calcium carbonate, the products formed are carbon dioxide, water and a solution of calcium nitrate.
- b** Hydrogen and a solution of magnesium acetate are formed in a relatively slow reaction that occurs when magnesium is mixed with acetic acid.

→ **Solution**

- a** Initially in the ionic equation, the substances will be written in the following ways:

Dilute nitric acid: Because it is a strong acid, it is completely ionised in solution, so it is written as separated ions,  $\text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$ .

Solid calcium carbonate: Because it is a solid ionic compound, the ions are bonded together in the ionic lattice, so the formula shows the ions 'joined' together,  $\text{CaCO}_3(\text{s})$ .

Carbon dioxide and water: Because they are composed of neutral molecules in the reaction mixture, their formulas will be shown as  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$ .

Solution of calcium nitrate: Because this ionic compound is dissolved in water, its ions are not bonded together in a lattice structure, so the formula will be written as 'separate' ions,  $\text{Ca}^{2+}(\text{aq}) + \text{NO}_3^-(\text{aq})$ .

- Step 1** Write the formulas of the reactants and products, as they exist in the reaction mixture.



- Step 2** 'Cancel out' the species that are not changed in the reaction, i.e. remove the formulas that are identical on both sides of the equation.

The  $\text{NO}_3^-(\text{aq})$  ion has remained unchanged during the reaction (it is the spectator ion), so the equation becomes:



- Step 3** Balance the atoms and charges in the equation.



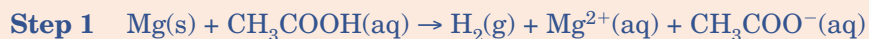
- b** The reactants and products will initially be written in the following ways:

Magnesium: Because it is a metal composed of neutral atoms, its formula is written as  $\text{Mg}(\text{s})$ .

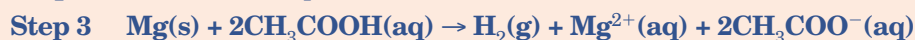
Acetic acid: This is a weak acid and when it dissolves in water, most of the molecules remain un-ionised, so its formula is written as  $\text{CH}_3\text{COOH}(\text{aq})$ .

Hydrogen: Because it is composed of neutral molecules, its formula is written as  $\text{H}_2(\text{g})$ .

Solution of magnesium acetate: This is a solution of an ionic compound with its ions dissociated in the solution, so it is shown as 'separated' ions  $\text{Mg}^{2+}(\text{aq}) + \text{CH}_3\text{COO}^{-}(\text{aq})$ .



**Step 2** There are no spectator ions.



Assessment questions sometimes ask for the observations to be predicted for a particular reaction. To answer these questions, the ionic equation is first written then any changes that occur during the reaction are determined. Some changes that are typically described in the observations are:

- the colour and odour of any gas produced
- the change in colour of the reaction solution
- whether or not a solid dissolves or is produced during the reaction
- the colour of an insoluble substance produced
- the disappearance or appearance of a smell during the reaction
- the change in appearance of the reactants
- an increase or decrease in temperature during the reaction.

The colours of ions and other substances are given in Table 5.2.

**TABLE 5.2 COLOUR OF SPECIES IN AQUEOUS SOLUTION**

Cation	Colour	Cation	Colour	Anion	Colour	Halogen	Colour
$\text{Al}^{3+}$	colourless	$\text{Pb}^{2+}$	colourless	$\text{Br}^{-}$	colourless	$\text{Cl}_2(\text{aq})$	pale yellow
$\text{NH}_4^{+}$	colourless	$\text{Mg}^{2+}$	colourless	$\text{Cl}^{-}$	colourless	$\text{Br}_2(\text{aq})$	orange
$\text{Ba}^{2+}$	colourless	$\text{Mn}^{2+}$	very pale pink	$\text{CrO}_4^{2-}$	yellow	$\text{I}_2(\text{aq})$	brown
$\text{Ca}^{2+}$	colourless	$\text{Ni}^{2+}$	green	$\text{Cr}_2\text{O}_7^{2-}$	orange		
$\text{Cr}^{3+}$	deep green	$\text{Ag}^{+}$	colourless	$\text{I}^{-}$	colourless	Halogen in organic solvent	
$\text{Co}^{2+}$	pink	$\text{Na}^{+}$	colourless	$\text{MnO}_4^{-}$	deep purple	Halogen	Colour
$\text{Cu}^{2+}$	blue	$\text{Sr}^{2+}$	colourless	$\text{PO}_4^{3-}$	colourless	$\text{Br}_2$	red
$\text{Fe}^{2+}$	pale green	$\text{Sn}^{2+}$	colourless	$\text{S}^{2-}$	colourless	$\text{I}_2$	purple
$\text{Fe}^{3+}$	brown	$\text{Zn}^{2+}$	colourless				
$\text{K}^{+}$	colourless						

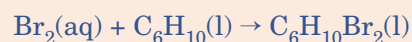
### → Example 5.3

Give the observations for the following reactions.

- a** The following reaction occurs when solid copper carbonate and hydrochloric acid are mixed:



- b** If a solution of bromine water is shaken with some cyclohexene, the following reaction occurs:



*continued*

→ **Solution**

- a** The blue-green solid dissolves to form a colourless odourless gas and a blue solution. (Note: The names of the reactants and products are not given in the observations.)
- b** The orange colour fades to produce two colourless layers of liquid.



**Figure 5.3** The reaction of copper carbonate with an acid

**\* Review exercise 5.1**

- 1** Write balanced chemical equations for the following reactions.
  - a** When heated at about 250°C, calcium nitrate decomposes to form calcium oxide, nitrogen dioxide and oxygen.
  - b** One of the most important minerals from which copper is extracted is chalcopyrites,  $\text{CuFeS}_2$ . In the first stage of the extraction process, chalcopyrites is roasted in air to produce copper(I) sulfide, iron(II) oxide and sulfur dioxide. During this roasting process, the copper mineral reacts with oxygen in the air.
  - c** Group 1 oxides can be prepared by reducing a nitrate with the metal; for example, potassium oxide can be formed when potassium is heated strongly with potassium nitrate. Nitrogen is also formed in the reaction.
  - d** Ammonia gas will not burn in air; however, it burns in pure oxygen, with a pale yellow-green flame. The products formed (at normal atmospheric conditions) are nitrogen and water vapour.
- 2** Give observations for the following reactions.
  - a** If chlorine is bubbled through a solution of sodium bromide, the following reaction occurs:
$$\text{Cl}_2(\text{g}) + 2\text{Br}^-(\text{aq}) \rightarrow \text{Br}_2(\text{aq}) + 2\text{Cl}^-(\text{aq})$$
  - b** When a strip of zinc is added to a dilute solution of copper sulfate, the copper ions are reduced according to the equation:
$$\text{Cu}^{2+}(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Zn}^{2+}(\text{aq})$$
- 3** Write ionic equations and give observations for the following reactions.
  - a** A solution of aluminium sulfate and water are formed when 2 mol  $\text{L}^{-1}$  sulfuric acid is added to solid aluminium oxide.
  - b** If hydrogen sulfide is bubbled into a chlorine solution, the products formed are sulfur and hydrochloric acid.
  - c** The products formed when solutions of acetic acid and potassium hydrogencarbonate are mixed are carbon dioxide, water and a solution of potassium acetate.
  - d** When 3 mol  $\text{L}^{-1}$  nitric acid is added to copper, a solution of copper nitrate, water and the colourless gas nitrogen monoxide form.

## 5.2 Precipitation reactions

Sometimes when two solutions of ionic substances are mixed, an insoluble substance, or a precipitate, will be produced. This precipitate is usually formed from the combination of the positive ion of one reactant and the negative ion of the other reactant. For example, when a solution of sodium bromide is added to a solution of silver nitrate, a precipitate of silver bromide will form, as shown in Figure 5.4.



Figure 5.4 A precipitate of silver bromide formed from mixing the two colourless solutions of silver nitrate and sodium bromide

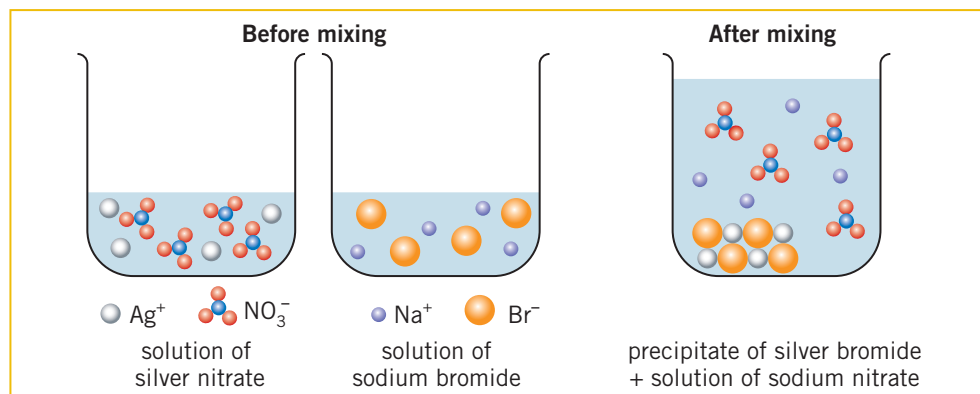
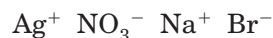
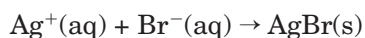


Figure 5.5 The reaction of solutions of sodium bromide and silver nitrate, represented at the particle level

As shown in Figure 5.5, before the two solutions of silver nitrate and sodium bromide are mixed, their ions are moving around independently in each solution. When the solutions are initially added together, before a reaction occurs, the mixture contains the following dissolved ions:



As the ions move around in the solution and collide with one another, the Ag<sup>+</sup> ions and the Br<sup>-</sup> ions react (join together) to form an insoluble ionic compound—silver bromide. The other pair of positive and negative ions, Na<sup>+</sup> and NO<sub>3</sub><sup>-</sup>, do not remain joined together when they collide because sodium nitrate is soluble in water. Therefore the only change that occurs when the two solutions are mixed is that the Ag<sup>+</sup> ions and the Br<sup>-</sup> ions join together to form AgBr(s). The Na<sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions remain unchanged in the solution during the reaction; they act as spectator ions. Because the ionic equation shows only the particles that have changed during the reaction, it becomes:



The precipitate formed in a precipitation reaction can be identified or predicted from the solubility rules shown in Table 5.3 on the next page.



**TABLE 5.3 SOLUBILITY RULES FOR IONIC SOLIDS IN WATER****Soluble in water**

Soluble	Exceptions	
	Insoluble	Slightly soluble
Most chlorides	AgCl	PbCl <sub>2</sub>
Most bromides	AgBr	PbBr <sub>2</sub>
Most iodides	AgI, PbI <sub>2</sub>	
All nitrates	No exceptions	
All acetates (ethanoates)		
Most sulfates	SrSO <sub>4</sub> , BaSO <sub>4</sub> , PbSO <sub>4</sub>	CaSO <sub>4</sub> , Ag <sub>2</sub> SO <sub>4</sub>

**Insoluble in water**

Insoluble	Exceptions	
	Soluble	Slightly soluble
Most hydroxides	NaOH, KOH, Ba(OH) <sub>2</sub> (NH <sub>4</sub> OH and AgOH do not exist)	Ca(OH) <sub>2</sub> , Sr(OH) <sub>2</sub>
Most carbonates	Na <sub>2</sub> CO <sub>3</sub> , K <sub>2</sub> CO <sub>3</sub> , (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	
Most phosphates	Na <sub>3</sub> PO <sub>4</sub> , K <sub>3</sub> PO <sub>4</sub> , (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	
Most sulfides	Na <sub>2</sub> S, K <sub>2</sub> S, (NH <sub>4</sub> ) <sub>2</sub> S	

Soluble = more than 0.1 mole dissolves per litre

Slightly soluble = between 0.01 and 0.1 mole dissolves per litre

Insoluble = less than 0.01 mole dissolves per litre

**→ Example 5.4**

Give the name and formula of any precipitate that forms in the following situations.

- A solution of sodium hydroxide is mixed with a solution of magnesium bromide.
- A solution of lead nitrate is mixed with a solution of potassium sulfate.
- A solution of calcium nitrate is mixed with a solution of sodium phosphate.
- A solution of copper chloride is mixed with a solution of zinc nitrate.

**→ Solution**

- a** The ions present in the reaction mixture are:



The two new compounds that could form are NaBr and Mg(OH)<sub>2</sub>.

NaBr is soluble in water, but Mg(OH)<sub>2</sub> is insoluble.

The precipitate will therefore be **magnesium hydroxide, Mg(OH)<sub>2</sub>**.

- b** The ions present in the reaction mixture are:



The two new compounds that could form are PbSO<sub>4</sub> and KNO<sub>3</sub>.

KNO<sub>3</sub> is soluble in water, but PbSO<sub>4</sub> is insoluble.

The precipitate will therefore be **lead sulfate, PbSO<sub>4</sub>**.

c The ions present in the reaction mixture are:



The two new compounds that could form are Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and NaNO<sub>3</sub>.

NaNO<sub>3</sub> is soluble in water, but Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is insoluble.

The precipitate will therefore be **calcium phosphate, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>**.

d The ions present in the reaction mixture are



The two new compounds that could form are Cu(NO<sub>3</sub>)<sub>2</sub> and ZnCl<sub>2</sub>.

Both Cu(NO<sub>3</sub>)<sub>2</sub> and ZnCl<sub>2</sub> are soluble in water, so there will be **no precipitate**.

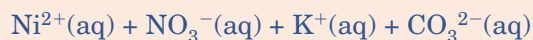
### → Example 5.5

Write ionic equations for the following precipitation reactions. Also, give the observations for each reaction.

- Solutions of nickel nitrate and potassium carbonate are mixed.
- A solution of 2 mol L<sup>-1</sup> sodium chloride and a solution of 2 mol L<sup>-1</sup> lead nitrate are mixed.
- Solutions of sodium hydroxide and iron(III) chloride are mixed.

### → Solution

a **Step 1** Write the formulas of the reactants, as they exist in the reaction mixture.

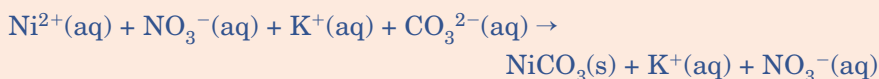


**Step 2** Determine the products in the reaction, that is, the precipitate.

Possible products: NiCO<sub>3</sub> insoluble, KNO<sub>3</sub> soluble.

Precipitate will be NiCO<sub>3</sub>.

**Step 3** In the equation, write the formulas of the products, as they exist in the reaction mixture.



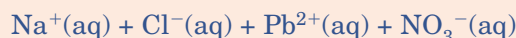
**Step 4** Cancel spectator ions and balance equation.

K<sup>+</sup> and NO<sub>3</sub><sup>-</sup> are spectator ions.

The ionic equation is **Ni<sup>2+</sup>(aq) + CO<sub>3</sub><sup>2-</sup>(aq) → NiCO<sub>3</sub>(s)**

**Observations:** The green solution and colourless solution combine to form a green precipitate.

b **Step 1** Write the formulas of the reactants, as they exist in the reaction mixture.



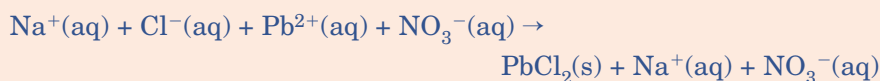
**Step 2** Determine the products in the reaction.

Possible products: PbCl<sub>2</sub> insoluble, NaNO<sub>3</sub> soluble.

Precipitate will be PbCl<sub>2</sub>.

**Step 3** In the equation, write the formulas of the products, as they exist in the reaction mixture.

*continued*



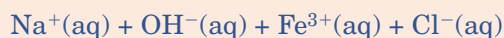
**Step 4** Cancel spectator ions and balance equation.

$\text{Na}^+$  and  $\text{NO}_3^-$  are spectator ions.

The ionic equation is  **$\text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{PbCl}_2(\text{s})$**

**Observations:** Two colourless solutions react to form a white precipitate.

- c Step 1** Write the formulas of the reactants, as they exist in the reaction mixture.

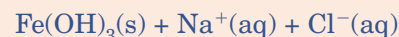
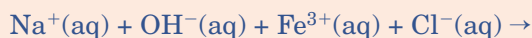


**Step 2** Determine the products in the reaction.

Possible products:  $\text{Fe}(\text{OH})_3$  insoluble,  $\text{NaCl}$  soluble.

Precipitate will be  $\text{Fe}(\text{OH})_3$ .

**Step 3** In the equation, write the formulas of the products, as they exist in the reaction mixture.



**Step 4** Cancel spectator ions and balance equation.

$\text{Na}^+$  and  $\text{Cl}^-$  are spectator ions.

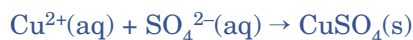
The ionic equation is  **$\text{Fe}^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq}) \rightarrow \text{Fe}(\text{OH})_3(\text{s})$**

**Observations:** An orange solution and a colourless solution react to form an orange precipitate.

## \* Review exercise 5.2

- Name and give the formula of the precipitate formed when the following solutions are mixed.
  - solution of silver nitrate + solution of potassium iodide
  - solution of potassium phosphate + solution of calcium nitrate
  - potassium hydroxide solution + barium nitrate solution
- Write an ionic equation for any reaction that may occur when the following solutions are mixed. Also give the observations.
  - solution of potassium chloride + solution of sodium hydroxide
  - sodium hydroxide solution + copper nitrate solution
  - solution of cobalt chloride + solution of sodium carbonate
  - lead nitrate solution + hydrochloric acid solution
- Identify and correct the mistake in each of the following.
  - The equation for the reaction that occurs when a solution of barium chloride is mixed with a solution of ammonium sulfate is:
 
$$\text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$$
  - The equation for the reaction that occurs when a solution of nickel(II) nitrate is mixed with a solution of sodium hydroxide is:
 
$$\text{Ni}^{2+}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{Ni}(\text{OH})_2(\text{s})$$

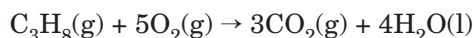
- c The equation for the reaction that occurs when a solution of copper chloride is mixed with a solution of sodium sulfate is:



- d When a solution of silver nitrate is mixed with hydrochloric acid solution, no reaction occurs because acids do not react with nitrates.

## 5.3 Stoichiometry

A balanced chemical equation shows the relationships between the number of particles of reactants and products in a chemical reaction. For example, the following balanced equation:



shows that 1 molecule of propane ( $\text{C}_3\text{H}_8$ ) will react with 5 molecules of oxygen to form 3 molecules of carbon dioxide and 4 molecules of water.

This stoichiometric ratio (the ratio shown in a balanced equation) between the reactants and the products they will form is also correct if the amount of each substance is expressed in mole. That is:

1 mol of  $\text{C}_3\text{H}_8$  reacts with 5 mol of  $\text{O}_2$  to form 3 mol of  $\text{CO}_2$  and 4 mol of  $\text{H}_2\text{O}$

or

2 mol of  $\text{C}_3\text{H}_8$  reacts with 10 mol of  $\text{O}_2$  to form 6 mol of  $\text{CO}_2$  and 8 mol of  $\text{H}_2\text{O}$

or

0.1 mol of  $\text{C}_3\text{H}_8$  reacts with 0.5 mol of  $\text{O}_2$  to form 0.3 mol of  $\text{CO}_2$  and 0.4 mol of  $\text{H}_2\text{O}$

### → Example 5.6

When ammonia reacts with oxygen, at high pressures, the products formed are nitrogen monoxide and water.

a What amount, in mol, of  $\text{H}_2\text{O}$  would form from the reaction of 0.6 mol of  $\text{NH}_3$ ?

b What amount, in mol, of  $\text{O}_2$  would be required to form 8.13 mol of NO?

### → Solution

A balanced equation for the reaction needs to be written to determine the stoichiometric ratio between the reactants and products.

The balanced equation is



a From the balanced equation:

4 mol of  $\text{NH}_3$  will form 6 mol of  $\text{H}_2\text{O}$

that is, 1 mol of  $\text{NH}_3$  will form  $\frac{6}{4}$  mol of  $\text{H}_2\text{O}$

so 0.6 mol of  $\text{NH}_3$  will form  $\frac{6}{4} \times 0.6 = \mathbf{0.9 \text{ mol of H}_2\text{O}}$

b From the balanced equation:

4 mol of NO will form from 5 mol of  $\text{O}_2$

that is, 1 mol of NO will form from  $\frac{5}{4}$  mol of  $\text{O}_2$

so 8.13 mol of NO will form from  $\frac{5}{4} \times 8.13 = \mathbf{10.2 \text{ mol of O}_2}$

If the amount of substance originally present or formed in the reaction mixture is given as a mass or concentration and volume of a solution, the mole ratio shown in the balanced equation is also used to determine the amount of a second substance involved in a reaction. The steps in this type of calculation are:

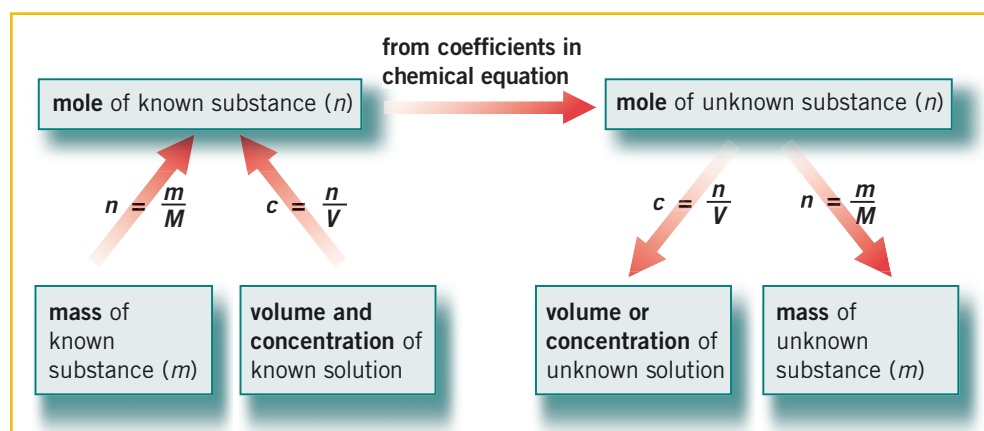
- 1 Determine the amount in mole of the given substance using an equation such as:

$$\text{mole} = \frac{\text{mass}}{\text{molar mass}} \quad \text{or} \quad n = \frac{m}{M}$$

$$\text{concentration} = \frac{\text{mole}}{\text{volume of solution}} \quad \text{or} \quad c = \frac{n}{V}$$

- 2 Use the stoichiometric ratio shown in the balanced equation to determine the amount in mole of the unknown substance.
- 3 Determine the mass, volume or concentration of the unknown substance.

These steps are represented in a flow chart shown in Figure 5.6.



**Figure 5.6** Flow chart showing the steps involved in stoichiometric calculations involving masses and volumes and concentrations of solutions

### → Example 5.7

The use of ethanol as an alternative fuel to petrol is now being considered seriously (and in some places used) by many countries. Ethanol is a renewable energy source because it can be produced from plant material such as sugar cane, corn and sorghum. The glucose in these plant materials is used by yeast as an energy source, and in this fermentation process ethanol is also formed:



If ethanol has a density of  $0.785 \text{ g mL}^{-1}$ , what volume of ethanol could be formed by the fermentation of  $1.00 \text{ kg}$  of glucose?

### → Solution

This calculation has four steps:

mass of glucose → mole of glucose → mole of ethanol → mass of ethanol → volume of ethanol

**Step 1**  $n(\text{glucose}) = \frac{m(\text{glucose})}{M(\text{glucose})}$

$$M(\text{C}_6\text{H}_{12}\text{O}_6) = (6 \times 12.01) + (12 \times 1.008) + (6 \times 16.00) = 180.156 \text{ g mol}^{-1}$$

$$n(\text{glucose}) = \frac{1.00 \cdot 10^3}{180.156} = 5.551 \text{ mol}$$

**Step 2** From the balanced equation:

1 mol of  $C_6H_{12}O_6$  will form 2 mol of  $C_2H_5OH$

or 5.551 mol of  $C_6H_{12}O_6$  will form  $2 \times 5.551 = 11.10$  mol of  $C_2H_5OH$

**Step 3**  $n(\text{ethanol}) = \frac{m(\text{ethanol})}{M(\text{ethanol})}$

$$M(C_2H_5OH) = (2 \times 12.01) + (6 \times 1.008) + 16.00 = 46.068 \text{ g mol}^{-1}$$

$$11.10 = \frac{m(\text{ethanol})}{46.068}$$

$$m(\text{ethanol}) = 11.10 \times 46.068 = 511.4 \text{ g}$$

**Step 4** density (ethanol) =  $\frac{\text{mass (ethanol)}}{\text{volume (ethanol)}}$

$$0.785 = \frac{511.4}{\text{volume (ethanol)}}$$

$$\text{volume of ethanol} = \frac{511.4}{0.785} = 651 \text{ mL}$$

### → Example 5.8

A careless student has spilt some sulfuric acid on the bench. To clean up the acid, sodium hydrogencarbonate can be sprinkled on it, causing neutralisation of the acid. The resultant solution can then be safely wiped up. The neutralisation reaction that occurs is:



What minimum mass of sodium hydrogencarbonate would be required to neutralise 34 mL of  $7.0 \text{ mol L}^{-1}$  sulfuric acid spilt on the bench?

### → Solution

This calculation has four steps:

concentration and volume of  $H_2SO_4$  → mole of  $H_2SO_4$  → mole of  $H^+$  →  
mole of  $NaHCO_3$  → mass of  $NaHCO_3$

**Step 1**  $c(H_2SO_4 \text{ solution}) = \frac{n(H_2SO_4)}{V(H_2SO_4 \text{ solution})}$

$$V(H_2SO_4 \text{ solution}) = 0.034 \text{ L}$$

$$7.0 = \frac{n(H_2SO_4)}{0.034}$$

$$n(H_2SO_4) = 7.0 \times 0.034 = 0.238 \text{ mol}$$

**Step 2**  $H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$

0.238 mol of  $H_2SO_4$  will form  $2 \times 0.238 = 0.476$  mol of  $H^+$

**Step 3** From the balanced equation:

1 mol of  $H^+$  will react with 1 mol of  $NaHCO_3$

so 0.476 mol of  $H^+$  will react with 0.476 mol of  $NaHCO_3$

**Step 4**  $n(NaHCO_3) = \frac{m(NaHCO_3)}{M(NaHCO_3)}$

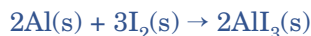
$$M(NaHCO_3) = 22.99 + 1.008 + 12.01 + (3 \times 16.00) = 84.008 \text{ g mol}^{-1}$$

$$0.476 = \frac{m(NaHCO_3)}{84.008}$$

$$m(NaHCO_3) = 0.476 \times 84.008 = 40 \text{ g}$$

### \* Review exercise 5.3

- 1 a When aluminium is heated strongly with iodine, the following reaction occurs:



What mass of iodine would be required to form 128 g of aluminium iodide?

- b Acid reacts with marble chips according to the equation:



What volume of 2.17 mol L<sup>-1</sup> hydrochloric acid would be required to react with 10.5 g of marble chips (calcium carbonate)?

- 2 Some students are to prepare hydrogen sulfide by reacting iron(II) sulfide with acid according to the equation:



Health authorities recommend that exposure to hydrogen sulfide be limited to concentrations less than 14.0 mg m<sup>-3</sup> of air.

What mass of iron(II) sulfide should the teacher make available to the class so that the average concentration in a 250 m<sup>3</sup> classroom will not exceed the recommended level?

- 3 Hydrogen peroxide, usually purchased as a 6% (by mass) solution, is used as a bleach for dyeing hair and as a disinfectant. The concentration of a hydrogen peroxide solution can be accurately determined by reacting the solution with potassium permanganate in the presence of acid:



10.00 g of the hydrogen peroxide solution was first diluted with water to a volume of 250.0 mL. It was then found that 25.00 mL of this diluted solution reacted with exactly 18.49 mL of 0.0128 mol L<sup>-1</sup> KMnO<sub>4</sub> solution. Calculate the percentage by mass of the original hydrogen peroxide solution.

- 4 Sulfuric acid can be manufactured by the following series of reactions:

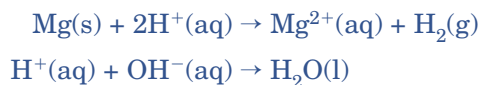


Calculate the mass of sulfuric acid that can be produced from 3.70 tonnes of iron pyrites (FeS<sub>2</sub>).

- 5 To determine the solubility of strontium hydroxide in water at 25°C, a saturated solution was prepared by adding an excess of powdered strontium hydroxide to 200 mL of water at 25°C. The mixture was filtered to remove the undissolved strontium hydroxide. 20.00 mL of the filtrate was then reacted with 0.103 mol L<sup>-1</sup> HNO<sub>3</sub> solution. The volume of the HNO<sub>3</sub> required to neutralise the dissolved strontium hydroxide was 14.21 mL.

- a Write equations for the dissolving of strontium hydroxide in water and for the reaction of the dissolved strontium hydroxide with nitric acid.
- b Calculate the solubility, in mole dissolved per litre of solution, of strontium hydroxide in water at 25°C.
- c How could you make sure the mixture obtained in the first step was a saturated solution?
- d Why was the mixture filtered before the reaction with nitric acid; i.e. why was the nitric acid not just added to the original mixture produced?

- 6 A 0.782 g strip of pure magnesium was added to 50.0 mL of a 1.54 mol L<sup>-1</sup> HCl solution. What volume of 0.285 mol L<sup>-1</sup> NaOH solution would be required to neutralise the hydrochloric acid left over from the reaction with magnesium?



## 5.4 Gases and stoichiometry

### Gas laws

During the 17th and 18th centuries, various relationships between the pressure, volume, temperature and amount in mole of gases were investigated. The following laws resulted from these investigations:

- *Boyle's law*: If the temperature of a gas is kept constant, the volume of a given mass of gas is inversely proportional to its pressure.

That is,  $V \propto \frac{1}{P}$  where the volumes and pressures are measured at a constant temperature and for a constant mass of gas.

- *Charles' law*: At constant pressure, the volume of a given mass of gas is directly proportional to its temperature on the kelvin scale.

This law can be represented as  $V \propto T$  for a constant mass of gas at a constant pressure, and where the temperature is in kelvin.  
(kelvin temperature = Celsius temperature + 273.1)

- *Avogadro's hypothesis*: Equal volumes of all gases, measured at the same temperature and pressure, contain equal numbers of particles (or amount in mole of particles).

That is,  $V \propto n$  where the volumes are measured at the same temperature and pressure.

The two laws and Avogadro's hypothesis can be summarised in the ideal gas equation. This equation gives the relationship between the volume, pressure, temperature and amount in mole of a sample of a gas.

$$PV = nRT$$

where  $P$  is the pressure,  $V$  is the volume,  $n$  is the amount in mole,  $R$  is a constant (the universal gas constant) and  $T$  is the temperature in kelvin.

The universal gas constant,  $R$ , has a value of 8.315 J mol<sup>-1</sup> K<sup>-1</sup>, when  $P$  is measured in kPa,  $V$  in L and  $T$  in K.

At times it is necessary to convert pressures to the units required in a particular equation. Several useful conversions are:

$$1 \text{ atmosphere} = 760 \text{ mmHg} = 101.3 \text{ kPa}$$



→ **Example 5.9**

What volume will 50.0 g of nitrogen gas occupy at 20.0°C and 200 kPa pressure?

→ **Solution**

$$\begin{aligned}n(\text{N}_2) &= \frac{m(\text{N}_2)}{M(\text{N}_2)} & M(\text{N}_2) &= 2 \times 14.01 = 28.02 \text{ g mol}^{-1} \\ &= \frac{50.0}{28.02} = 1.784 \text{ mol} \\ PV &= nRT & T \text{ in K} &= 20.0 + 273.1 = 293.1 \text{ K} \\ 200 \times V &= 1.784 \times 8.315 \times 293.1 \\ V &= \frac{1.784 \cdot 8.315 \cdot 293.1}{200} = \mathbf{21.7 \text{ L}}\end{aligned}$$

→ **Example 5.10**

Determine the possible identity of a gas if 0.0840 g of it occupies a volume of 430 mL at 0°C and 824 mmHg pressure.

→ **Solution**

The four steps in this calculation are:  
volume/pressure/temperature of gas → mole of gas → molar mass of gas →  
atomic mass of gas → identity of gas

**Step 1**  $PV = nRT$

$$V = 0.430 \text{ L}, T = 273.1 \text{ K}, P = \frac{824}{760} \times 101.3 = 109.8 \text{ kPa}$$

$$109.8 \times 0.430 = n \times 8.315 \times 273.1$$

$$n(\text{gas}) = \frac{109.8 \times 0.430}{8.315 \times 273.1} = 0.02079 \text{ mol}$$

**Step 2**

$$n(\text{gas}) = \frac{m(\text{gas})}{M(\text{gas})}$$

$$0.02080 = \frac{0.0840}{M(\text{gas})}$$

$$M(\text{gas}) = \frac{0.0840}{0.02079} = 4.04 \text{ g mol}^{-1}$$

**Steps 3 and 4**

If 1 mol of the gas has a mass of 4.04 g, then its atomic mass must be approximately 4.

The gas is therefore **helium**.

If the volume of a gas is known at STP, the amount of gas, in mole, can then be determined using the following formula:

$$\text{mole of gas} = \frac{\text{volume of gas (in L) at STP}}{22.41}$$

if the temperature is 0°C and pressure is 101.3 kPa (standard temperature and pressure conditions).

### Stoichiometric calculations involving gases

The volumes of any gaseous reactants and products in a reaction can be calculated using the stoichiometric mole ratio given in a balanced chemical equation. The flow chart shown in Figure 5.7 (an extension of Figure 5.6) shows the basic steps that could be carried out in such a calculation.

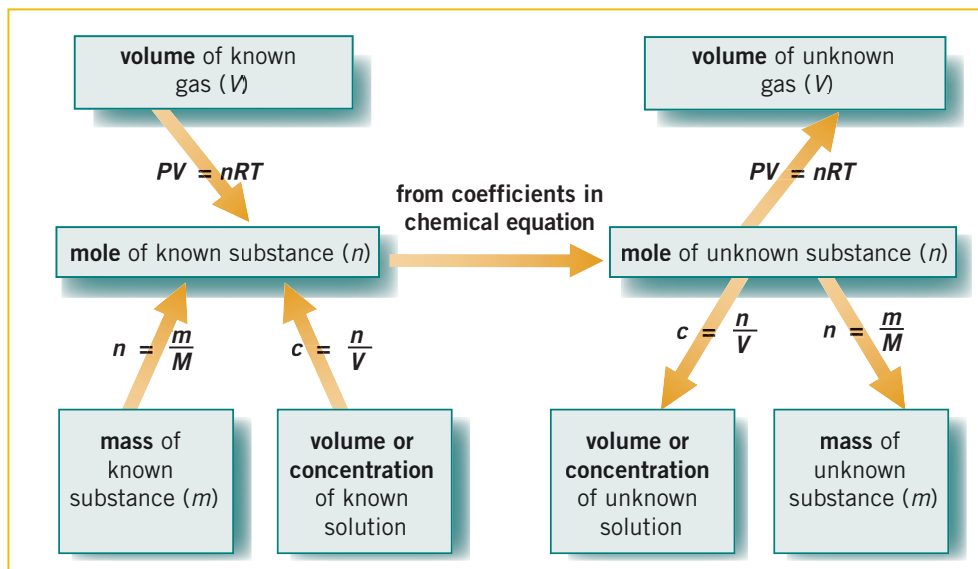
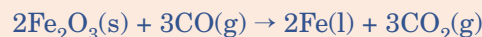


Figure 5.7 Stoichiometric mole flow chart involving mass, solution and gas calculations

### → Example 5.11

In the blast furnace, iron is produced when iron ore (iron(III) oxide) is reduced by carbon monoxide. Carbon dioxide is also produced in this reaction:



For every 1.00 tonne of iron formed, what volume of carbon dioxide at 15°C and 1.04 atm pressure would form?

### → Solution

There are three steps in this calculation:  
 mass of Fe → mole of Fe → mole of CO<sub>2</sub> → volume of CO<sub>2</sub>

**Step 1**  $n(\text{Fe}) = \frac{m(\text{Fe})}{M(\text{Fe})}$        $m(\text{Fe}) = 1.00 \times 10^6 \text{ g}$ ,  $M(\text{Fe}) = 55.85 \text{ g mol}^{-1}$

$$= \frac{1.00 \cdot 10^6}{55.85} = 1.791 \times 10^4 \text{ mol}$$

**Step 2** From the balanced equation:  
 2 mol of Fe formed with 3 mol of CO<sub>2</sub>  
 i.e. 1 mol of Fe formed with  $\frac{3}{2}$  mol of CO<sub>2</sub>  
 or  $1.791 \times 10^4$  mol of Fe formed with  $\frac{3}{2} \times 1.791 \times 10^4$   
 $= 2.686 \times 10^4 \text{ mol of CO}_2$

**Step 3**  $PV = nRT$

$$P = 1.04 \times 101.3 = 105.3 \text{ kPa}, T = 15 + 273.1 = 288.1 \text{ K}$$

$$105.3 \times V(\text{CO}_2) = 2.686 \times 10^4 \times 8.315 \times 288.1$$

$$V(\text{CO}_2) = \frac{2.686 \times 10^4 \times 8.315 \times 288.1}{105.3} = \mathbf{6.11 \times 10^5 \text{ L}}$$

## Gas volume/gas volume stoichiometric calculations

Using a balanced chemical equation, calculations involving the gas volumes of reactants and products can be carried out. These calculations are based on Gay-Lussac's law:

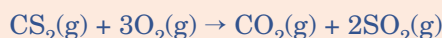
The volumes of different gases involved in a reaction, if measured at the same temperature and pressure, are in the same ratio as the coefficients in the balanced equation.

For example, for the reaction  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$ , assuming the volumes are measured at the same temperature and pressure for each reaction mixture:

- 2 L of  $\text{H}_2$  will react exactly with 1 L of  $\text{O}_2$  to form 2 L of gaseous  $\text{H}_2\text{O}$   
or 10 L of  $\text{H}_2$  will react exactly with 5 L of  $\text{O}_2$  to form 10 L of gaseous  $\text{H}_2\text{O}$   
or 0.4 mL of  $\text{H}_2$  will react exactly with 0.2 mL of  $\text{O}_2$  to form 0.4 mL of gaseous  $\text{H}_2\text{O}$

→ **Example 5.12**

If 5.28 L of oxygen reacts with carbon disulfide, what volume of carbon dioxide is produced? Assume the volumes are measured at the same temperature and pressure:



→ **Solution**

From balanced equation:

- 3 L of  $\text{O}_2$  will react to form 1 L of  $\text{CO}_2$   
or 1 L of  $\text{O}_2$  will react to form  $\frac{1}{3}$  L of  $\text{CO}_2$   
so 5.28 L of  $\text{O}_2$  will react to form  $\frac{1}{3} \times 5.28 = \mathbf{1.76 \text{ L}}$  of  $\text{CO}_2$

❖ **Review exercise 5.4**

- 1 If 4.63 g of methane,  $\text{CH}_4$ , is introduced into an evacuated 2.00 L container at a temperature of  $35.0^\circ\text{C}$ , what is the pressure in the container?
- 2 What mass of zinc will react with excess hydrochloric acid to produce 592 mL of hydrogen at  $20.0^\circ\text{C}$  and 834 mmHg pressure?

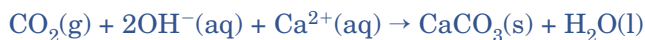


- 3 In a laboratory, 56.4 mL of dry sulfur dioxide gas at a temperature of  $T^\circ\text{C}$  and 98.0 kPa pressure was dissolved in a hydrogen peroxide solution to convert all the sulfur dioxide to sulfate ions:



Addition of excess barium chloride solution to the resultant solution gave 0.521 g of barium sulfate precipitate. What was the temperature,  $T$ , of the laboratory?

- 4 When 3.4 L of propane burns in an excess of air, what volume of carbon dioxide will be formed, assuming the volumes are measured at the same temperature and pressure?
- 5 To remove the carbon dioxide from the exhaust gases emerging from a factory, the exhaust gas is forced through a solution of calcium hydroxide. The reaction that occurs is:



If 15.0 kL, measured at  $29.5^\circ\text{C}$  and 108 kPa, of exhaust gas containing 3.10% carbon dioxide by volume was passed through a solution of  $0.486 \text{ mol L}^{-1}$  calcium hydroxide, what volume of this calcium hydroxide solution would be required to remove all the carbon dioxide?

- 6 Acrylonitrile is a colourless liquid that is used in the production of many acrylic fibres. It is produced by the ammoxidation of propene, in which a mixture of propene, ammonia and air is passed over a catalyst:

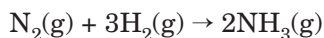


- a What minimum volume of ammonia and of air would be required to react with 236 L of propene, assuming air is 20.8% (by volume) oxygen and the volumes are measured at the same temperature and pressure?
- b Assuming the reaction is 100% complete, is it possible to calculate the amount of acrylonitrile produced in this reaction? If not, what additional information would be required for this calculation?

## 5.5 Limiting reagents

Sometimes two reactants are mixed in 'non-stoichiometric' amounts, resulting in one of these reactants not being completely consumed in the reaction. The reactant that is completely consumed is referred to as the limiting reagent and the reactant that remains after the reaction is the excess reagent. The amount of limiting reagent present in the reaction mixture determines the amount of products formed during the reaction.

For example when nitrogen reacts with hydrogen in the Haber process, the following reaction occurs:



This equation shows that hydrogen and nitrogen react with a 3:1 molar amount. The data given in Table 5.4 illustrates what happens when different mixtures of the reactants are reacted together (assuming the reaction is 100% complete).

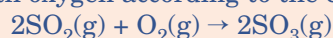
**TABLE 5.4** EXAMPLES OF LIMITING REAGENT MIXTURES FOR THE REACTION  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$

Initial amount of $\text{N}_2$	Initial amount of $\text{H}_2$	Limiting reagent	Excess reagent	Amount of $\text{NH}_3$ formed	Amount of excess reagent left after the reaction
1 mol	3 mol	neither	neither	$1 \times 2 = 2$ mol	0 mol
2 mol	3 mol	$\text{H}_2$	$\text{N}_2$	$\frac{2}{3} \times 3 = 2$ mol	$2 - 1 = 1$ mol of $\text{N}_2$
1 mol	4 mol	$\text{N}_2$	$\text{H}_2$	$1 \times 2 = 2$ mol	$4 - 3 = 1$ mol of $\text{H}_2$
2 mol	8 mol	$\text{N}_2$	$\text{H}_2$	$2 \times 2 = 4$ mol	$8 - 6 = 2$ mol of $\text{H}_2$
4 mol	6 mol	$\text{H}_2$	$\text{N}_2$	$\frac{2}{3} \times 6 = 4$ mol	$4 - 2 = 2$ mol of $\text{N}_2$
9 mol	9 mol	$\text{H}_2$	$\text{N}_2$	$\frac{2}{3} \times 9 = 6$ mol	$9 - 3 = 6$ mol of $\text{N}_2$

In stoichiometric calculations where the amounts of two reactants have been given, i.e. limiting reagent problems, the first step is to determine which reactant is the limiting reagent. It is then the amount of limiting reagent that is used to determine the amount of product produced.

### → Example 5.13

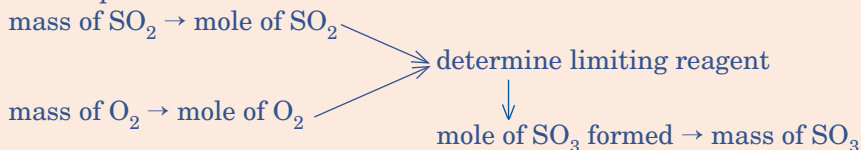
Sulfur dioxide reacts with oxygen according to the equation:



What mass of sulfur trioxide could be formed from the reaction of a mixture of 75.0 g of sulfur dioxide and 50.0 g of oxygen?

### → Solution

The steps involved in this calculation are:



Initial steps: For this question, the limiting reagent must first be identified.

$$\begin{aligned} n(\text{SO}_2) &= \frac{m(\text{SO}_2)}{M(\text{SO}_2)} & M(\text{SO}_2) &= 32.06 + (2 \times 16.00) = 64.06 \text{ g mol}^{-1} \\ &= \frac{75.0}{64.06} = 1.171 \text{ mol} \end{aligned}$$

$$\begin{aligned} n(\text{O}_2) &= \frac{m(\text{O}_2)}{M(\text{O}_2)} & M(\text{O}_2) &= 2 \times 16.00 = 32.00 \text{ g mol}^{-1} \\ &= \frac{50.0}{32.00} = 1.562 \text{ mol} \end{aligned}$$

From the balanced equation:

2 mol of  $\text{SO}_2$  will react with 1 mol of  $\text{O}_2$

or 1 mol of  $\text{SO}_2$  will react with  $\frac{1}{2}$  mol of  $\text{O}_2$

so 1.171 mol of  $\text{SO}_2$  will react with  $\frac{1}{2} \times 1.171 = 0.5855$  mol of  $\text{O}_2$

However, there is 1.562 mol of  $\text{O}_2$  present in the reaction mixture; in other words, there is too much  $\text{O}_2$  present to react with all the  $\text{SO}_2$ .

Therefore,  $\text{O}_2$  is in excess, so  $\text{SO}_2$  is the limiting reagent (it will react completely).

Next step: Calculate the amount in mole of  $\text{SO}_3$  that will form from the limiting reagent ( $\text{SO}_2$ ).

From the balanced equation: 1 mol of  $\text{SO}_2$  will form 1 mol of  $\text{SO}_3$

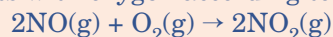
so 1.171 mol of  $\text{SO}_2$  will form 1.171 mol of  $\text{SO}_3$ .

Final step: Calculate the mass of  $\text{SO}_3$ .

$$\begin{aligned} n(\text{SO}_3) &= \frac{m(\text{SO}_3)}{M(\text{SO}_3)} & M(\text{SO}_3) &= 32.06 + (3 \times 16.00) = 80.06 \text{ g mol}^{-1} \\ 1.171 &= \frac{m(\text{SO}_3)}{80.06} \\ m(\text{SO}_3) &= 1.171 \times 80.06 = \mathbf{93.8 \text{ g}} \end{aligned}$$

### → Example 5.14

Nitrogen monoxide reacts with oxygen according to the equation:



What volume of nitrogen dioxide would be formed from a mixture of 100 mL of NO and 100 mL of oxygen gas? Assume all volumes are measured at the same temperature and pressure.

→ **Solution**

This is a limiting reagent problem.

**Step 1** Find the limiting reagent.

From the balanced equation: 2 mL of NO will react with 1 mL of O<sub>2</sub>  
so 100 mL of NO will react with 50 mL of O<sub>2</sub>.

But there is 100 mL of O<sub>2</sub> in the reaction mixture, i.e. too much O<sub>2</sub>  
so NO is the limiting reagent.

**Step 2** Find the volume of NO<sub>2</sub> formed.

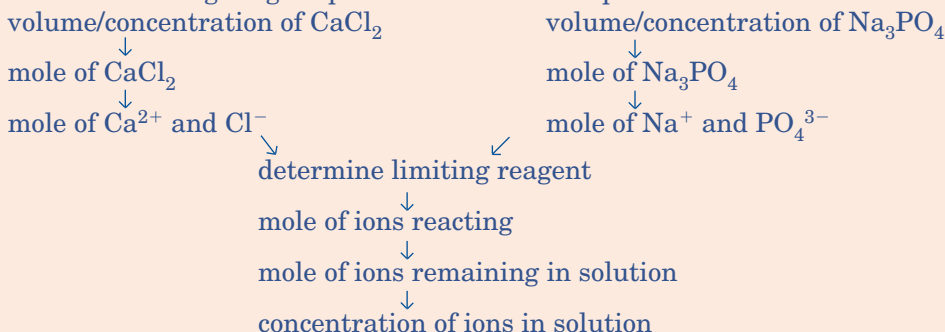
From the balanced equation: 2 mL of NO will form 2 mL of NO<sub>2</sub>  
so 100 mL of NO will form **100 mL** of NO<sub>2</sub>.

→ **Example 5.15**

45.2 mL of 0.189 mol L<sup>-1</sup> CaCl<sub>2</sub> solution was mixed with 34.8 mL of 0.127 mol L<sup>-1</sup> Na<sub>3</sub>PO<sub>4</sub> solution. Calculate the concentration of each of the remaining ions in solution after the precipitation reaction occurs between these two solutions.

→ **Solution**

This is a limiting reagent problem. The basic steps will be:



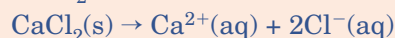
**Determining limiting reagent**

The equation for the reaction is:  $3\text{Ca}^{3+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{s})$

$$c(\text{CaCl}_2 \text{ solution}) = \frac{n(\text{CaCl}_2)}{V(\text{CaCl}_2 \text{ solution})}$$

$$0.189 = \frac{n(\text{CaCl}_2)}{0.0452}$$

$$n(\text{CaCl}_2) = 0.189 \times 0.0452 = 0.008543 \text{ mol}$$

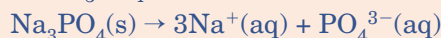


0.008543 mol of CaCl<sub>2</sub> will form 0.008543 mol of Ca<sup>2+</sup>  
and 2 × 0.008543 = 0.01709 mol of Cl<sup>-</sup>

$$c(\text{Na}_3\text{PO}_4 \text{ solution}) = \frac{n(\text{Na}_3\text{PO}_4)}{V(\text{Na}_3\text{PO}_4 \text{ solution})}$$

$$0.127 = \frac{n(\text{Na}_3\text{PO}_4)}{0.0348}$$

$$n(\text{Na}_3\text{PO}_4) = 0.127 \times 0.0348 = 0.004420 \text{ mol}$$



0.004420 mol of Na<sub>3</sub>PO<sub>4</sub> will form 3 × 0.004420 = 0.01326 mol of Na<sup>+</sup>  
and 0.004420 mol of PO<sub>4</sub><sup>3-</sup>.

*continued*

The solution before reaction therefore contains 0.008543 mol of  $\text{Ca}^{2+}$ , 0.01709 mol of  $\text{Cl}^-$ , 0.01326 mol of  $\text{Na}^+$  and 0.004420 mol of  $\text{PO}_4^{3-}$ .

From the balanced equation:

3 mol of  $\text{Ca}^{2+}$  will react with 2 mol of  $\text{PO}_4^{3-}$

or 1 mol of  $\text{Ca}^{2+}$  will react with  $\frac{2}{3}$  mol of  $\text{PO}_4^{3-}$

so 0.008543 mol of  $\text{Ca}^{2+}$  will react with  $\frac{2}{3} \times 0.008543$   
 $= 0.005695$  mol of  $\text{PO}_4^{3-}$

However, there is only 0.004420 mol of  $\text{PO}_4^{3-}$  in the mixture, so  $\text{PO}_4^{3-}$  is the limiting reagent. Because  $\text{PO}_4^{3-}$  will be completely consumed in the reaction, its concentration in the final solution will be 0 mol  $\text{L}^{-1}$ .

#### Calculating concentration of $\text{Ca}^{2+}$ remaining after reaction

From balanced equation:

2 mol of  $\text{PO}_4^{3-}$  will react with 3 mol of  $\text{Ca}^{2+}$

or 1 mol of  $\text{PO}_4^{3-}$  will react with  $\frac{3}{2}$  mol of  $\text{Ca}^{2+}$

so 0.004420 mol of  $\text{PO}_4^{3-}$  will react with  $\frac{3}{2} \times 0.004420$   
 $= 0.006630$  mol of  $\text{Ca}^{2+}$

mol of  $\text{Ca}^{2+}$  remaining in solution after reaction =  $0.008543 - 0.006630$   
 $= 0.001913$  mol

volume of new solution =  $0.0452 + 0.0348 = 0.0800$  L

$c(\text{Ca}^{2+} \text{ in final solution}) = \frac{n(\text{Ca}^{2+})}{V(\text{solution})} = \frac{0.001913}{0.0800} = 0.0239$  mol  $\text{L}^{-1}$

#### Calculating concentration of $\text{Cl}^-$ and $\text{Na}^+$ remaining after reaction

Neither  $\text{Cl}^-$  nor  $\text{Na}^+$  ions are involved in the reaction, the amount (in mol) of each remains unchanged; however, their concentrations will have changed because of the volume change:

$c(\text{Cl}^- \text{ in final solution}) = \frac{n(\text{Cl}^-)}{V(\text{solution})} = \frac{0.01709}{0.0800} = 0.214$  mol  $\text{L}^{-1}$

$c(\text{Na}^+ \text{ in final solution}) = \frac{n(\text{Na}^+)}{V(\text{solution})} = \frac{0.01326}{0.0800} = 0.166$  mol  $\text{L}^{-1}$

The final concentrations will be:

$c(\text{Ca}^{2+}) = 0.0239$  mol  $\text{L}^{-1}$ ,  $c(\text{Cl}^-) = 0.214$  mol  $\text{L}^{-1}$ ,  $c(\text{Na}^+) = 0.166$  mol  $\text{L}^{-1}$ ,  
 $c(\text{PO}_4^{3-}) = 0$  mol  $\text{L}^{-1}$

### \* Review exercise 5.5

- The Space Shuttle Orbiter uses methylhydrazine,  $\text{CH}_3\text{N}_2\text{H}_3$ , as a fuel. This substance is oxidised by dinitrogen tetroxide to provide energy for propulsion. These two liquid propellants ignite spontaneously on contact with one another to form carbon dioxide, nitrogen and gaseous water. During one mission, when the Orbiter was manoeuvred into orbit, a mixture of 1250 kg of methylhydrazine and 1350 kg of dinitrogen tetroxide was reacted to produce the required energy.
  - Write a balanced equation for the reaction of methylhydrazine with dinitrogen tetroxide.
  - Calculate the total amount, in mole, of gas produced in the reaction required to put the Orbiter into orbit.

- 2 0.120 g of aluminium is added to 6.38 mL of 2.03 mol L<sup>-1</sup> HCl and the evolved gas is collected at 24°C and 1.00 × 10<sup>5</sup> Pa. What volume of hydrogen will be produced?



- 3 In the production of nitric acid, one stage involves the catalytic oxidation of ammonia at 900°C:



- a What volume of the gas nitrogen monoxide (NO) will be produced by the complete oxidation of 4.00 L of ammonia?
- b Assuming 12.0 L of ammonia and 20.0 L of oxygen are mixed and reacted as completely as possible, what is the overall change (in L) in volume?  
(Assume all volumes are measured at the same temperature and pressure.)
- 4 A precipitation reaction occurs when 23.9 mL of 0.175 mol L<sup>-1</sup> CuCl<sub>2</sub> solution is added to 42.6 mL of 0.251 mol L<sup>-1</sup> Na<sub>3</sub>PO<sub>4</sub> solution. Calculate:
- a the mass of precipitate formed
- b the concentration of each of the ions remaining in the solution after the reaction.
- 5 0.700 g of potassium hydroxide was dissolved in 50.0 mL of 0.800 mol L<sup>-1</sup> sulfuric acid. Calculate the concentration of sulfuric acid in the mixture after the reaction. (Assume no volume change occurred.)

## 5.6 Stoichiometry and percentages

Often problems either give information concerning the percentage purity of a particular substance or the percentage yield of a reaction, or they ask for percentages such as these to be calculated.

The percentage purity, by mass, of a substance can be calculated using the formula:

$$\text{percentage purity of the material} = \frac{\text{mass of pure substance}}{\text{mass of impure substance}} \times 100$$

The percentage yield of a reaction is a measure of how much product was actually produced compared to the theoretical amount expected to be produced. This theoretical amount can be calculated using the stoichiometric ratio given in the balanced chemical equation. One equation that can be used to determine the percentage yield of a reaction is:

$$\text{percentage yield of a reaction} = \frac{\text{mass of product actually obtained}}{\text{theoretical mass of product expected}} \times 100$$

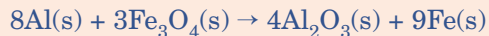
The amount in mole of the product formed, compared to the theoretical amount in mole, can also be used to determine the percentage yield, as can the actual and theoretical volumes (measured at the same temperature and pressure) of a gaseous product.



→ **Example 5.16**

**Calculation of the percentage purity of a substance**

Aluminium reacts with iron oxide according to the equation:



When 24.0 g of an impure sample of aluminium was reacted with iron oxide, 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 Fe → mole of Fe → mole of Al → mass of Al → % purity of Al sample

**Step 1**  $n(\text{Fe}) = \frac{m(\text{Fe})}{M(\text{Fe})}$   $M(\text{Fe}) = 55.85 \text{ g mol}^{-1}$

$$= \frac{45.7}{55.85} = 0.8183 \text{ mol}$$

**Step 2** From the balanced equation:

9 mol of Fe are formed from 8 mol of Al

or 1 mol of Fe is formed from  $\frac{8}{9}$  mole of Al

so 0.8183 mol of Fe are formed from  $\frac{8}{9} \times 0.8183 = 0.7274$  mol of Al

**Step 3**  $n(\text{Al}) = \frac{m(\text{Al})}{M(\text{Al})}$   $M(\text{Al}) = 26.98 \text{ g mol}^{-1}$

$$0.7274 = \frac{m(\text{Al})}{26.98}$$
$$m(\text{Al}) = 0.7274 \times 26.98 = 19.63 \text{ g}$$

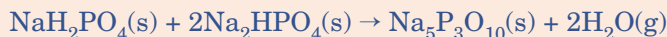
**Step 4** Percentage purity of the Al sample =  $\frac{\text{mass of pure Al}}{\text{mass of impure sample}} \times 100$

$$= \frac{19.63}{24.0} \times 100 = 81.8\%$$

→ **Example 5.17**

**Calculation of a percentage yield of a reaction**

Sodium tripolyphosphate (NaTPP) is used as a builder in detergents. Its function is to react with calcium ions that may be present in any 'hard' water. It does, however, contribute in a major way to the overgrowth of algae in rivers and lakes. NaTPP is produced by heating a mixture of the  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  salts:



If 2.50 tonnes of  $\text{Na}_2\text{HPO}_4$  is heated with a stoichiometric amount of  $\text{NaH}_2\text{PO}_4$ , 3.08 tonnes of NaTPP is produced. What is the percentage yield of the process?

→ **Solution**

The steps are:

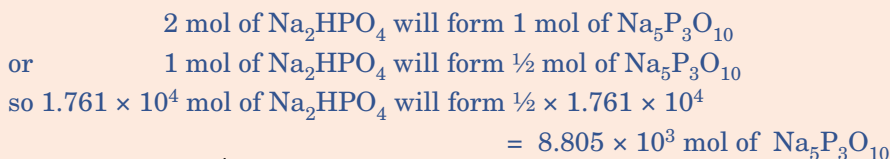
mass of  $\text{Na}_2\text{HPO}_4$  → mole of  $\text{Na}_2\text{HPO}_4$  → mole of  $\text{Na}_5\text{P}_3\text{O}_{10}$  → mass of  $\text{Na}_5\text{P}_3\text{O}_{10}$

calculation of theoretical mass of  $\text{Na}_5\text{P}_3\text{O}_{10}$  → percentage yield

**Step 1**  $n(\text{Na}_2\text{HPO}_4) = \frac{m(\text{Na}_2\text{HPO}_4)}{M(\text{Na}_2\text{HPO}_4)}$

$$M(\text{Na}_2\text{HPO}_4) = (2 \times 22.99) + 1.008 + 30.97 + (4 \times 16.00) = 141.958 \text{ g mol}^{-1}$$
$$n(\text{Na}_2\text{HPO}_4) = \frac{2.50 \cdot 10^6}{141.958} = 1.761 \times 10^4 \text{ mol}$$

**Step 2** From balanced equation:



$$\text{Step 3 } n(\text{Na}_5\text{P}_3\text{O}_{10}) = \frac{m(\text{Na}_5\text{P}_3\text{O}_{10})}{M(\text{Na}_5\text{P}_3\text{O}_{10})}$$

$$M(\text{Na}_5\text{P}_3\text{O}_{10}) = (5 \times 22.99) + (3 \times 30.97) + (10 \times 16.00) = 367.86 \text{ g mol}^{-1}$$

$$8.805 \times 10^3 = \frac{m(\text{Na}_5\text{P}_3\text{O}_{10})}{367.86}$$

$$m(\text{Na}_5\text{P}_3\text{O}_{10}) = 8.805 \times 10^3 \times 367.86 = 3.239 \times 10^6 \text{ g} = 3.239 \text{ tonnes}$$

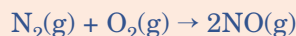
**Step 4** From 2.50 tonnes of  $\text{Na}_2\text{HPO}_4$  you would expect to form 3.239 tonnes of  $\text{Na}_5\text{P}_3\text{O}_{10}$ , but only 3.08 tonnes actually formed.

$$\begin{aligned} \text{percentage yield} &= \frac{\text{mass of Na}_5\text{P}_3\text{O}_{10} \text{ actually formed}}{\text{theoretical mass of Na}_5\text{P}_3\text{O}_{10}} \times 100 \\ &= \frac{3.08}{3.239} \times 100 = \mathbf{95.1\%} \end{aligned}$$

### → Example 5.18

#### Calculation of a percentage yield of a reaction

One of the first methods used to produce nitrogen monoxide, a substance from which nitric acid is produced, involved heating a mixture of nitrogen and oxygen to about  $3000^\circ\text{C}$  using the electric discharge of a carbon arc:



This reaction was not very efficient, as shown in the figures below and was replaced by the more economical oxidation of ammonia.

In a trial experiment of the direct oxidation of nitrogen process, 2.00 L of nitrogen was reacted with a slight excess of oxygen and 0.0675 L of nitrogen monoxide was produced. Assuming the volumes were measured at the same temperature and pressure, calculate the percentage yield of this reaction.

### → Solution

The steps are volume of  $\text{N}_2 \rightarrow$  volume of NO

$\underbrace{\hspace{10em}}_{\text{calculation of theoretical volume of NO}} \rightarrow \text{percentage yield of reaction}$

**Step 1** From balanced equation: 1 L of  $\text{N}_2$  would form 2 L of NO

so 2.00 L of  $\text{N}_2$  would form 4.00 L of NO.

**Step 2** The theoretical (or predicted) volume of NO formed is 4.00 L; however, only 0.0675 L was formed.

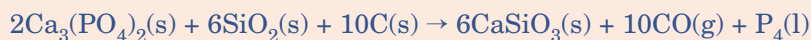
$$\begin{aligned} \text{percentage yield} &= \frac{\text{volume of product actually obtained}}{\text{theoretical volume of product}} \times 100 \\ &= \frac{0.0675}{4.00} \times 100 = \mathbf{1.69\%} \end{aligned}$$

*continued*

→ **Example 5.19**

**Calculation involving the determination of the amount of product, using the percentage yield of the reaction**

White phosphorus is prepared commercially according to the overall reaction:



What mass of silicon dioxide is needed to produce 1.0 kg of phosphorus if the process is only 90% efficient?

→ **Solution**

The steps are

mass of  $\text{P}_4$  → mole of  $\text{P}_4$  → mole of  $\text{SiO}_2$  (for 100% yield) → mass of  $\text{SiO}_2$  (for 100% yield) → actual mass of  $\text{SiO}_2$  required

**Step 1**  $n(\text{P}_4) = \frac{m(\text{P}_4)}{M(\text{P}_4)}$   $M(\text{P}_4) = 4 \times 30.97 = 123.88 \text{ g mol}^{-1}$   
 $= \frac{1.0 \cdot 10^3}{123.88} = 8.07 \text{ mol}$

**Step 2** From the balanced equation:

1 mol of  $\text{P}_4$  would form from 6 mol of  $\text{SiO}_2$

so 8.07 mol of  $\text{P}_4$  would form from  $6 \times 8.07 = 48.4 \text{ mol}$  of  $\text{SiO}_2$

**Step 3**  $n(\text{SiO}_2) = \frac{m(\text{SiO}_2)}{M(\text{SiO}_2)}$   
 $M(\text{SiO}_2) = 28.09 + (2 \times 16.00) = 60.09 \text{ g mol}^{-1}$   
 $48.4 = \frac{m(\text{SiO}_2)}{60.09}$   
 $m(\text{SiO}_2) = 48.4 \times 60.09 = 2910 \text{ g}$

**Step 4** 2910 g of  $\text{SiO}_2$  is required to form 1.00 kg of phosphorus if the reaction yield is 100%. However, during the reaction only 90% of the available mass of  $\text{SiO}_2$  actually produces  $\text{P}_4$ . As a result, more than 2910 g of  $\text{SiO}_2$  needs to be used in the reaction.

90% of the available mass of  $\text{SiO}_2 = 2910 \text{ g}$

$$\frac{90}{100} \times \text{available mass of SiO}_2 = 2910$$

$$\text{available mass of SiO}_2 = 2910 \times \frac{100}{90} = 3230 \text{ g}$$

That is, **3200 g or 3.2 kg** of  $\text{SiO}_2$  is required to produce 1.0 kg of  $\text{P}_4$



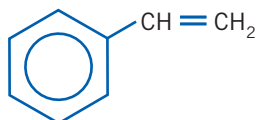
**\* Review exercise 5.6**

- 1 A sample of potassium chlorate to be used as a weed killer has been contaminated with sand ( $\text{SiO}_2$ ). When heated, the chlorate decomposes according to the equation:



The sand resists decomposition. If 20.0 g of the sample yields 387 mL of oxygen at 77°C and 714 mmHg pressure, what is the percentage purity of the potassium chlorate sample?

- 2 When coal is burnt, any sulfur present will also burn to form sulfur dioxide, which is a major contributor to acid rain. To remove the sulfur dioxide from the exhaust gases produced in a coal-powered power plant, it can be reacted with calcium oxide. Calcium sulfite is formed in this reaction.
- Write equations for the combustion of sulfur and the reaction of sulfur dioxide with calcium oxide.
  - A particular power station burns 2500 tonnes of coal per day. If the coal contains 2.4%, by mass, of sulfur, what mass of calcium sulfite would be produced daily in the purification process?
- 3 Styrene,  $C_6H_5CH=CH_2$ , is used extensively in the production of synthetic rubber and plastics such as polystyrene foam. Its structural formula is shown below:



- Industrially, styrene is produced by the catalytic dehydrogenation of ethylbenzene:
 
$$C_6H_5-CH_2CH_3(g) \rightarrow C_6H_5-CH=CH_2(g) + H_2(g)$$
 Pure ethylbenzene is heated to around  $630^\circ C$  and passed over a metal oxide catalyst to form styrene. If 34.8 kg of ethylbenzene flows into the catalyst chamber, and 12.9 kg of styrene is produced, what is the percentage yield of this reaction?
  - The mixture that emerges from the catalyst chamber is separated to produce pure styrene, unreacted ethylbenzene and hydrogen. What do you think is done with the unreacted ethylbenzene?
- 4 Zinc is a widely used metal in society; for instance, it is used to galvanise iron to prevent corrosion of the iron. Zinc is extracted from its sulfide ore in a multistep procedure that initially involves concentration of the ore by froth flotation followed by roasting. Zinc sulfide is converted into zinc oxide in the roasting process. At this stage, the zinc oxide mixture still contains impurities. Sulfuric acid is used to leach (dissolve) the zinc from the oxide mixture, forming a solution of zinc sulfate:



Electrolysis of the zinc sulfate solution is then undertaken to produce zinc that is 99.995% pure:



Calculate the mass of zinc obtained, after the leaching and electrolysis processes of a particular batch of zinc oxide mixture, given the data below:

mass of zinc oxide mixture used	$4.1 \times 10^6$ g
percentage by mass of zinc oxide in this mixture	51%
percentage yield of the leaching reaction	76%
percentage yield of the electrolysis reaction	92%

- 5 1.94 g of marble (impure calcium carbonate) was dissolved in 50.0 mL of  $1.29 \text{ mol L}^{-1}$  HCl:



The unreacted acid was exactly neutralised by 27.5 mL of  $1.05 \text{ mol L}^{-1}$  NaOH:



Calculate the percentage, by mass, of calcium carbonate in the marble.

## MAJOR IDEAS

- Chemical reactions are processes in which chemical changes occur and they are characterised by the formation of new substances.
- A chemical reaction can be represented by a balanced chemical equation.
- A chemical equation is said to be 'balanced' when the number of atoms of each element on each side of the equation are the same, and when the total charge on each side of the equation is the same.
- In an ionic equation, only the actual species consumed and produced in the reaction are shown.
- Table 5.1 details how different types of substances can be written in an ionic equation.
- A precipitation reaction is one in which two solutions are mixed and an insoluble substance (the precipitate) forms.
- The solubilities of substances can be predicted using a solubility table like Table 5.3.
- When the solutions of two ionic compounds are mixed, a precipitate will form if two of the ions combine to form an insoluble substance.
- A balanced chemical equation shows the relationships between the number of particles of reactants and products in a chemical reaction. It also shows the mole ratio (the stoichiometric ratio) in which the reactants will react and the products will form.
- The steps involved in stoichiometric calculations involving masses and volumes and concentrations of solutions can be shown on a flow chart (see Figure 5.6).
- Kelvin temperature = Celsius temperature + 273.1
- The relationships between the volumes ( $V$ ), pressures ( $P$ ), temperatures ( $T$ ) and amounts ( $n$ ), in mol, of gases are shown in a variety of equations:
  - Boyle's law:  $V \propto \frac{1}{P}$  where  $V$  and  $P$  are measured at a constant temperature and for a constant mass of gas
  - Charles' law:  $V \propto T(\text{K})$  where  $V$  and  $T$  are measured at a constant pressure and for a constant amount of gas. The temperature is expressed in kelvin.
  - Avogadro's hypothesis:  $V \propto n$  where  $V$  is measured at constant temperature and pressure.
  - Ideal gas equation:  $PV = nRT$  where  $P$  is the pressure,  $V$  is the volume,  $n$  is the amount in mole,  $R$  is a constant (the Universal gas constant) and  $T$  is the kelvin temperature.
- The universal gas constant,  $R$ , has a value of  $8.315 \text{ J mol}^{-1} \text{ K}^{-1}$ , when  $P$  is measured in kPa,  $V$  in L and  $T$  in K.
- Pressure conversions:  
1 atmosphere = 760 mmHg = 101.3 kPa

- Stoichiometry calculations can also involve gases, as shown in the flow chart in Figure 5.7.
- According to Gay-Lussac's law, the volume ratio of gases involved in a reaction is the same as the mole ratio given in the balanced equation.
- When two reactants are mixed in 'non-stoichiometric' amounts, resulting in one of these reactants not being completely consumed in the reaction, the excess reagent is the reactant left over after the reaction and the limiting reagent is the reactant completely consumed.
- The amount of limiting reagent is used to calculate the amount of product formed.
- Percentage purity of the material = 
$$\frac{\text{mass of pure substance}}{\text{mass of impure substance}} \times 100$$
- Percentage yield of a reaction = 
$$\frac{\text{mass of product actually obtained}}{\text{theoretical mass of product expected}} \times 100$$

## QUESTIONS

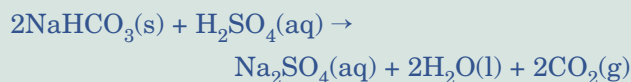
- 1 Figure 5.8 shows the result of adding a solution of sodium chromate to a solution of silver nitrate.



Figure 5.8

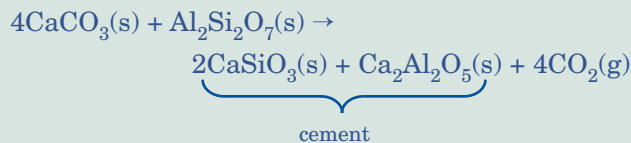
- a Describe and explain what happened when the two solutions were mixed.
  - b Write an ionic equation for the reaction that occurred in the test tube.
- 2 Write ionic equations for the following reactions, and give the observations.
    - a A solution of aluminium chloride is mixed with a solution of sodium sulfide.
    - b Hydrochloric acid is mixed with a solution of lead nitrate.

- c Sulfur dioxide, water and a solution of potassium chloride are formed when hydrochloric acid is added to solid potassium sulfite.
  - d Solutions of sulfuric acid and lithium hydroxide are mixed.
  - e A solution of nickel nitrate is added to a solution of sodium hydroxide.
  - f Copper oxide is added to a solution of 2 mol L<sup>-1</sup> acetic acid and the mixture is heated. A solution of copper acetate and water is formed.
- 3 One type of fire extinguisher depends on the reaction of sodium hydrogencarbonate with sulfuric acid to produce carbon dioxide. The equation for the reaction is:

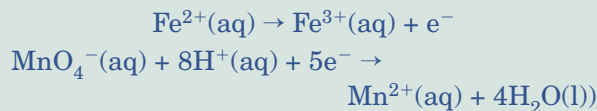


If a fire extinguisher is designed to hold  $5.00 \times 10^2$  g of sodium hydrogencarbonate, calculate:

- a the volume of 12.0 mol L<sup>-1</sup> sulfuric acid that would be required to react completely with the sodium hydrogencarbonate
  - b the volume of carbon dioxide produced at a temperature of 23°C and 99.4 kPa pressure.
- 4 The cathode ray tube of a television set has a volume of about 5.00 L. The pressure inside it is typically 0.100 Pa at 25.0°C. Estimate the number of molecules it contains.
- 5 Cement is a mixture of calcium and aluminium silicates, formed by heating limestone, CaCO<sub>3</sub>, with clay at a temperature of around 1400°C. An equation that can be used to represent this complex reaction is:

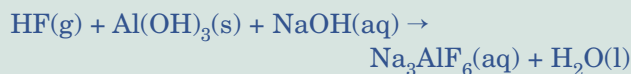


- a Calculate the mass of limestone required to make a 25 kg bag of cement.
  - b After water, concrete is the second-most used resource globally. Cement is the key ingredient of concrete. However, there are concerns that the cement-production process cannot be regarded as being 'environmentally friendly'. Suggest some of the reasons for these concerns.
- 6 Chlorine gas can be produced in the laboratory by reacting hydrochloric acid with manganese dioxide. If 23.6 g of MnO<sub>2</sub> is added to 50.0 mL of 4.11 mol L<sup>-1</sup> HCl, what volume of Cl<sub>2</sub> at 102 kPa and 28°C will be formed? (MnCl<sub>2</sub> and H<sub>2</sub>O are also formed in the reaction.)
- 7 During city travel, a Holden Commodore consumes on average 1.0 L of petrol every 11 km travelled. In one year the car travels 12 000 km.
- a Assuming petrol is 100% octane (density of 0.70 g mL<sup>-1</sup>) and that its combustion in the car engine yields only carbon dioxide and water, calculate the volume of carbon dioxide, at 25°C and 100 kPa pressure, produced by the car in one year.
  - b In Perth there are approximately 1.1 million cars. Estimate the approximate volume of carbon dioxide produced by the cars in Perth in one year if they all have characteristics similar to a Holden Commodore.
- 8 A 5.87 g sample of iron tablets, whose active ingredient is hydrated iron(II) sulfate, was ground to a powder and dissolved in a dilute solution of sulfuric acid. It was found that 19.86 mL of 0.01040 mol L<sup>-1</sup> KMnO<sub>4</sub> solution was required to react with all of the iron(II) ions in the sample.
- a What was the percentage, by mass, of iron in the tablets, assuming it was present as iron(II) ions?  
(The two half-equations for the redox reaction are:



- b In this redox reaction, which reactant has acted as the reductant and which as the oxidant?
  - c What observations would you expect for the reaction of Fe<sup>2+</sup> with MnO<sub>4</sub><sup>-</sup>?
  - d The label on the bottle containing the iron tablets stated that a 0.50 g tablet contains 5.0 mg of iron. Does your figure, obtained in part a, agree with the amount? If not, propose a reason for why the values may be different.
- 9 Gravimetric analysis can be used to determine the concentration of calcium ions in milk. 150 mL of milk was mixed with excess potassium carbonate solution. The white precipitate obtained was filtered off, washed with water and dried. It had a mass of 0.368 g. Calculate the concentration in g L<sup>-1</sup> of calcium ions in the milk.

- 10** During the production of aluminium, aluminium oxide is dissolved in molten cryolite,  $\text{Na}_3\text{AlF}_6$ . Electricity is then passed through this mixture to produce aluminium at the cathode. Cryolite is a naturally occurring mineral, but it can also be manufactured in a process where the following is the key reaction, shown as an unbalanced equation:



If a 95.4% yield is obtained in this process, what mass of cryolite would be obtained when a mixture of the following composition reacts?

0.340 ML of gaseous HF, measured at 318 kPa and 92°C

471 kg of  $\text{Al}(\text{OH})_3$

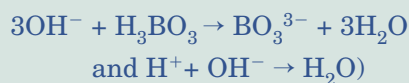
1.15 m<sup>3</sup> of 52.3% by mass NaOH solution with a density of 1.54 g mL<sup>-1</sup>

- 11** Boron trichloride hydrolyses readily according to the equation:



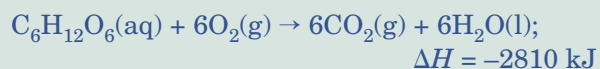
If the boric acid produced in the reaction is triprotic, what volume of 6.82 mol L<sup>-1</sup> potassium hydroxide is required to neutralise the acid solution resulting from the hydrolysis of 6.77 g of boron trichloride?

(Hint: The neutralising reactions are:



- 12** 2.40 g of a metallic oxide of type MO was dissolved in 100 mL of 1.00 mol L<sup>-1</sup> hydrochloric acid. The resulting liquid was made up to 500 mL with distilled water. 50.0 mL of the diluted solution then required 20.2 mL of 0.204 mol L<sup>-1</sup> sodium hydroxide for neutralisation. Calculate the atomic mass of the element M.
- 13** An average adult female breathes in about 12 kg of air a day. Inhaled air contains about 21% by volume of oxygen and exhaled air about 16% by volume of oxygen.
- Assuming the density of air is 1.2 g L<sup>-1</sup>, calculate the volume of oxygen used by an average adult female in a day.
  - If the volume of the oxygen is measured at 20°C and 100 kPa, how many molecules of oxygen are used each day?
  - Why does the oxygen content of the air decrease after it has been inhaled into the body?

- d** The reaction between oxygen and glucose can be represented by the following equation:

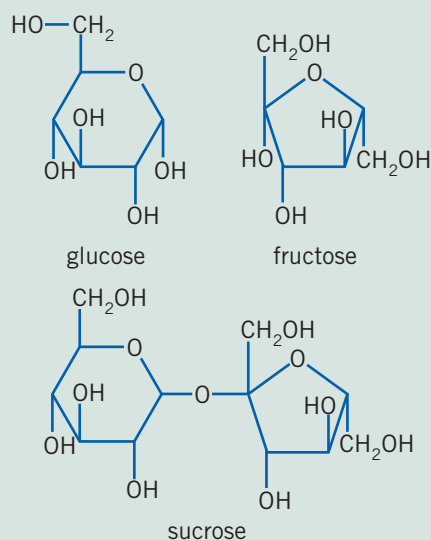


- What volume of carbon dioxide, at 20°C and 100 kPa, would be formed from the oxygen used by the female adult in a day?
  - How much heat would be generated daily by the reaction of the oxygen with glucose in the respiration process?
- 14** In some countries a flocculating agent is used to help remove very fine suspended solids from domestic water supplies. Aluminium hydroxide, a gelatinous precipitate, is often used as the flocculating agent. As the precipitate settles to the bottom of the sedimentation tank, it carries most of the suspended matter with it. The aluminium hydroxide is formed within the tank by adding aluminium sulfate and calcium hydroxide to the cloudy drinking water. In this process, it is vital that these two substances are mixed in the correct proportions to prevent any health issues that may arise if too much aluminium (in the form of ions) remains dissolved in the drinking water. If too much calcium hydroxide is added, the excess hydroxide ions can react with the amphoteric aluminium hydroxide to form the water soluble complex ion  $[\text{Al}(\text{OH})_4]^-$ .
- Write an ionic equation for the production of aluminium hydroxide in the sedimentation tanks.
  - Write an ionic equation for the formation of  $[\text{Al}(\text{OH})_4]^-$  that occurs if excess hydroxide ions are present in the tank.
  - Without knowing any better, a worker added 22.4 tonnes each of aluminium sulfate and calcium hydroxide to a 2.57 ML sedimentation tank.
    - Which of the two reactants is in excess?
    - What mass of aluminium hydroxide will form in the precipitation reaction?
    - If the calcium hydroxide is in excess, calculate the amount in mole of the complex ion that will form, assuming its formation reaction is 100% complete.
    - Calculate the concentration of sulfate ions and calcium ions dissolved in the water.
    - Your solubility table shows calcium sulfate as being a slightly soluble substance. If the solubility of calcium sulfate is 0.21 g per 100 mL of water, would you expect any calcium sulfate to precipitate in the tank?

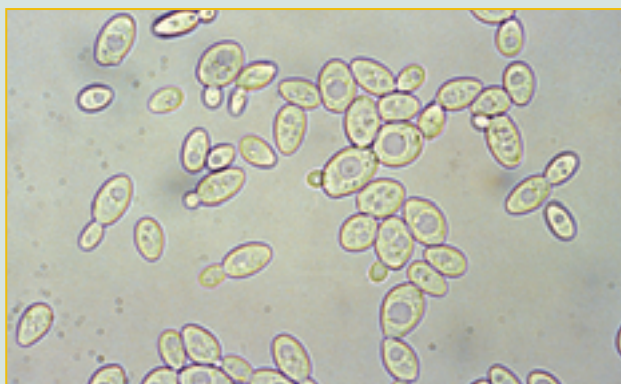
**d i** Describe the types of bonds present in the complex ion,  $[\text{Al}(\text{OH})_4]^-$ .

**ii** Draw a line structure of this complex ion.

- 15** Ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ , is proving to be a worthwhile renewable fuel for vehicles that may one day replace the presently used non-renewable hydrocarbon-based fuels. One method used for the production of ethanol is the fermentation of monosaccharides, such as glucose and fructose, by yeast. In the fermentation reaction, the monosaccharides form ethanol and carbon dioxide. The structural formulas of glucose, fructose and sucrose are given below:



(For simplicity, the carbon and hydrogen atoms in the rings have not been shown in these diagrams.)



**Figure 5.9** Brewer's yeast cells, some of which are shown reproducing by budding

Often the starting materials used for the production of ethanol by fermentation are disaccharides, such as sucrose, or polysaccharides, such as starch, rather than monosaccharides. A by-product of the

sugar-refining industry, molasses, is commonly used as the raw material for these saccharides.

Molasses, a thick dark-coloured liquid, is composed approximately 40%, by mass, of sucrose and 20% each, by mass, of glucose and fructose. Water is added to dilute the molasses to  $150\text{--}200\text{ g L}^{-1}$  total sugar (glucose + fructose + sucrose). The pH is adjusted to 4–5 and yeast is mixed in. After about 36 hours at  $30^\circ\text{C}$ , the mixture contains  $60\text{--}90\text{ g L}^{-1}$  of ethanol.

- a** What reaction must occur before the sucrose present in the molasses can be used by the yeast in the fermentation process?
- b** Write an equation for the fermentation process.
- c** How could the pH be adjusted, assuming the molasses mixture has a pH of about 7?
- d** Calculate the approximate theoretical yield of ethanol that can be obtained from a diluted molasses solution containing  $150\text{ g L}^{-1}$  total sugar. Explain any assumptions you made.
- e** Compare the theoretical yield of ethanol (your answer to part d) with the actual yield obtained after 36 hours.
- f** After 36 hours, the yield of ethanol does not increase significantly. Propose an explanation for this observation.
- g** Which would you expect to have the higher boiling point, glucose or ethanol? Explain your reasoning.
- h** Use your answer to part g to describe a method that could be utilised to obtain the ethanol from the molasses mixture. What assumptions have you made?
- i** **RESEARCH** Design an investigation to study one factor that might affect the rate of the fermentation process of a molasses solution.

- 16** Oxygen is one of the most commercially important gases obtained from the atmosphere. At least half of the pure oxygen produced is utilised in the steel industry. The oxygen is blown through the molten impure iron to react with some of the impurities present, such as carbon and sulfur, to produce an alloy of iron (steel) possessing the required properties. Oxygen is very important in the health industry where it is used to assist patients with breathing difficulties such as premature babies and pneumonia patients. The reaction of oxygen



with acetylene, producing a temperature of around  $3450^{\circ}\text{C}$ , is also used by metal workers and plumbers to cut and weld steel.

Air is composed of 78% by volume nitrogen, 21% oxygen, 0.03% argon, 0.03% carbon dioxide and traces of other gases. Oxygen is isolated from air by a process called cryogenic (cold temperature) distillation, which depends on the gases having different boiling points. The boiling points of the three most abundant gases in the atmosphere are  $-196^{\circ}\text{C}$  (nitrogen),  $-183^{\circ}\text{C}$  (oxygen) and  $-186^{\circ}\text{C}$  (argon). Modern separation plants can isolate samples of these gases that are 99.9999% pure using the method described as follows.

In this industrial process, the air is first purified, to remove unwanted components such as dust, water vapour and carbon dioxide, and then compressed and cooled. A portion of the purified compressed air is decompressed in a device called a centrifugal expander. As the air expands, its temperature drops until it begins to liquefy at about  $-190^{\circ}\text{C}$ . The liquid air is fed into the top of a fractional distillation column containing perforated trays. At the same time, the remaining compressed portion of the air is fed into the bottom of the column. The gaseous air rises up the tower, bubbling through the liquid air which is trickling down through the holes in the trays. Because the gas is warmer than the liquid, the liquid is heated a little and begins to boil. The gas also cools down and a temperature gradient is set up in the tower with the temperature at the bottom being warmer than the temperature at the top. The gas with the lowest boiling point will therefore boil off from the liquid air higher up the column. Oxygen has the highest boiling point of the three gases and so it remains a liquid at the bottom of the column. It is collected from here either as a liquid or compressed into gas cylinders at a pressure of around  $1.55 \times 10^4$  kPa.

- a Draw electron dot diagrams for  $\text{O}_2$ ,  $\text{N}_2$  and Ar.
- b Discuss why oxygen and nitrogen exist as diatomic molecules, but argon does not.
- c Explain why:
  - i oxygen, nitrogen and argon have very low boiling points
  - ii oxygen has a higher boiling point than nitrogen.
- d Discuss why argon has a lower boiling point than oxygen.
- e A particular cryogenic distillation plant produces liquid oxygen at a rate of  $310 \text{ m}^3$  per hour.
  - i Assuming all of the processes are 100% efficient, and the density of liquid oxygen is  $1.15 \text{ g cm}^{-3}$ , what volume of air, at a pressure of 101.3 kPa and  $20^{\circ}\text{C}$ , would be required by the plant in a 24-hour period?
  - ii The oxygen produced in these plants is often stored under a pressure of  $1.55 \times 10^4$  kPa, at  $20^{\circ}\text{C}$ , in gas cylinders to be used for oxygen therapy and resuscitation. If each of these cylinders has a volume of 680 L, how many cylinders could be filled with oxygen in 1 hour?
- f During the distillation process which of the three elements present will vaporise first as the liquid air moves down the column? Explain your answer.
- g Explain why air liquefies at a temperature of about  $-190^{\circ}\text{C}$  and not at  $-196^{\circ}\text{C}$  (the boiling point of the gas present in the largest amount).
- h
  - i What is an alloy? How does the structure of an alloy differ from that of the pure metal element?
  - ii Why is iron from the blast furnace converted into steel rather than being used as formed in the blast furnace?
  - iii Write an equation for two of the reactions that occur when the oxygen is blown through the hot iron during the steel-making process.
- i Why is pure oxygen used, rather than air, to react with the acetylene during oxy-acetylene welding?
- j
  - i Write an equation for the combustion of acetylene (ethyne).
  - ii If the heat of combustion of acetylene is  $1301 \text{ kJ mol}^{-1}$ , how much heat would be produced from the reaction of 15.0 L of acetylene with 15.0 L of oxygen, if the volumes are measured at  $25^{\circ}\text{C}$  and 101.3 kPa pressure?

A circular illustration of an industrial chemical plant. On the left, a yellow cylindrical tank sits on a grey base with a burner underneath, emitting orange flames. Yellow lumps are piled on a tray above the burner. A yellow pipe with an arrow pointing right enters the top of the tank, and another yellow pipe with an arrow pointing down exits from the side. In the center, a taller yellow cylindrical tank with a conical bottom is surrounded by a network of red pipes. A yellow pipe with an arrow pointing right enters the top, and another yellow pipe with an arrow pointing down exits from the side. On the right, a green cylindrical tank with a conical bottom is connected to a network of blue and green pipes. A green pipe with an arrow pointing down enters the top, and another green pipe with an arrow pointing right exits from the side. The background is a dark blue sky with grey industrial structures.

# 6

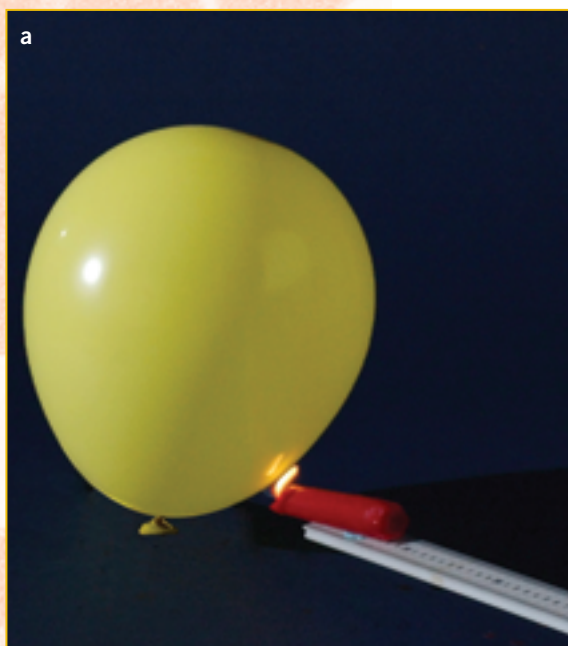
## Rates and equilibrium

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

- draw and explain the shape of energy profile diagrams for exothermic and endothermic reactions
- use the collision theory to explain the effects of catalysts, temperature, concentration and state of subdivision on reaction rates
- describe and explain the characteristics of a system in dynamic equilibrium
- write equilibrium law expressions
- explain the relative proportions of reactants and products in an equilibrium system by considering the equilibrium constant
- using Le Châtelier's principle, predict and explain how changes in temperature, concentration, volume and presence of a catalyst affect an equilibrium system
- use rates and equilibrium concepts to explain conditions used in industrial processes.

Our consumer society is built around a vast chemical industry. At the heart of this industry is the development, optimisation and monitoring of the chemical concepts and processes explored in this course. Fundamental to the transformation of raw materials into a range of consumer products are two questions: 'How quickly can we get the products?' and 'How much product can we get from our raw materials?' Answers to these questions are found in the chemical principles of reaction rates and equilibrium.

## 6.1 Rates of reactions



**Figure 6.1 (a)** Before ignition. A mixture of hydrogen and oxygen in a balloon. If any reaction is occurring between these two gases in the balloon, it must be extremely slow.



**(b)** After ignition. The result of igniting the hydrogen/oxygen mixture in the balloon. The explosive reaction between these two gases, once ignited, is very rapid.

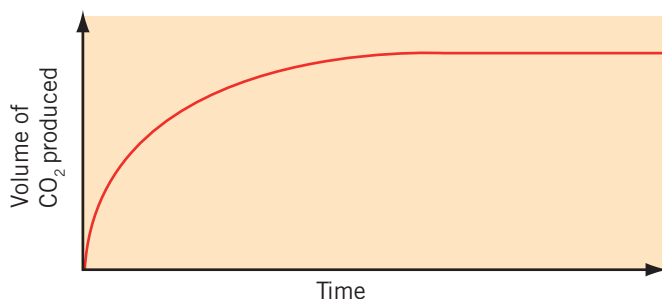
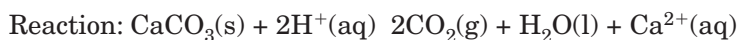
### The concept of reaction rate

The rate of a reaction can be determined by measuring the change in the amount of one of the reactants or one of the products of the reaction, in a given time interval. Often the change in the mass, concentration or volume of a substance is used in such a determination.

The reaction rate during a particular time interval can be calculated using a formula such as:

$$\text{reaction rate} = \frac{\text{change in quantity of reactant (or product) in the time interval}}{\text{time interval}}$$

A graph of the amount of substance present versus time can be plotted to show how the reaction rate changes during a reaction. A typical reaction rate graph is given on the next page for the reaction of calcium carbonate with excess acid to produce carbon dioxide:



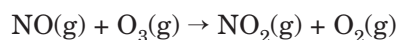
The slope of the graph at any particular time gives the reaction rate for this reaction at that time. The graph shows that the reaction begins very quickly (steepest slope) and the rate then decreases until it becomes zero and no more  $\text{CO}_2$  is formed. At this stage, the reaction is complete because the calcium carbonate has been completely consumed.

### Collision theory and activation energy

To assist in understanding and predicting the rates of reactions, the collision theory has been proposed. According to this theory, for a reaction to occur:

- the reactant particles must collide
- the reacting particles must collide with sufficient energy to react; there must be sufficient energy in the collision to disrupt the bonds in the reactant particles
- on collision, the particles must have the correct orientation (for the breaking of bonds and the forming of new bonds).

When two molecules react, for example, the  $\text{NO}$  and  $\text{O}_3$  molecules in the reaction:



bonds must be broken and new bonds formed. In this example, an  $\text{O}-\text{O}$  bond in  $\text{O}_3$  must be broken, and a new  $\text{N}-\text{O}$  bond must be formed. Energy is required to break bonds, and this energy comes from the kinetic energy possessed by the colliding molecules.

When the reactant particles collide, the kinetic energy of the colliding particles is transformed into potential energy as bonds begin to break in the reacting particles. As a result, the potential energy of the system increases. If there is sufficient energy in the reacting system, bonds in the colliding particles will break and new bonds will begin to form to produce the products. As the new bonds form, the potential energy of the system decreases. In each reaction, there is therefore a maximum potential energy stage reached. The species or intermediate that exists at this stage is called the transition state or the activated complex of the reaction (see Figures 6.2 and 6.3).

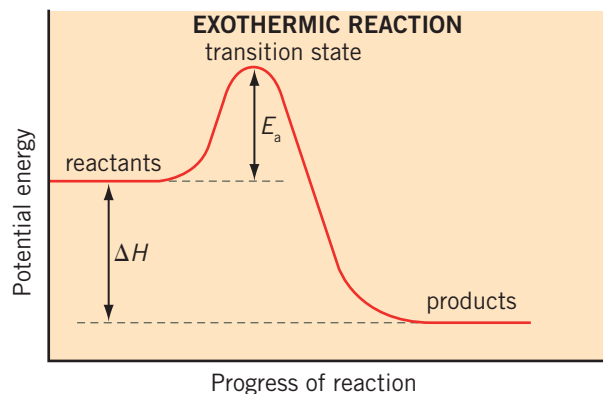
The transition state, or activated complex, in a reaction:

- is the highest potential energy state for the reacting system
- corresponds to some stage in the reaction at which bond breaking and bond formation is taking place
- is unstable, having no more than a temporary existence.

If a reaction is to occur, the colliding reactant particles must have sufficient kinetic energy to result in the formation of the transition state. This minimum amount of energy required for a reaction to take place is called the activation energy for the reaction.



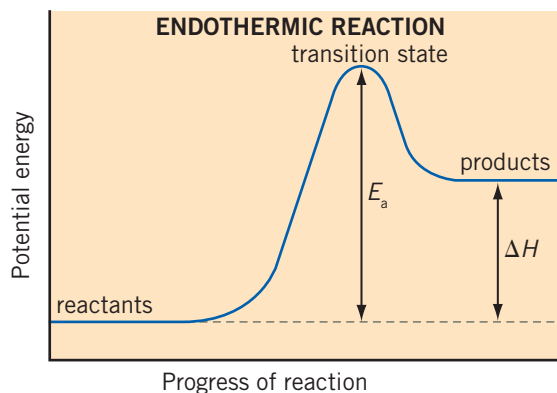
The changes in potential energy of a reacting system can be shown on a potential energy diagram. Typical potential energy graphs (or energy profile diagrams) for an exothermic and an endothermic reaction are shown in Figures 6.2 and 6.3, together with a summary of important points about these reactions.



For an exothermic reaction:

- the products have less potential energy than the reactants
- heat energy is released during the reaction and an increase in the temperature of the surroundings occurs
- the heat of reaction ( $\Delta H$ ) is the difference between the energy of the products and the energy of the reactants. For an exothermic reaction,  $\Delta H$  has a negative value (energy of products – energy of reactants)
- the activation energy ( $E_a$ ) for the forward reaction is the difference between the energy of the transition state and the energy of the reactants.

Figure 6.2 The potential energy changes that occur during an exothermic reaction



For an endothermic reaction:

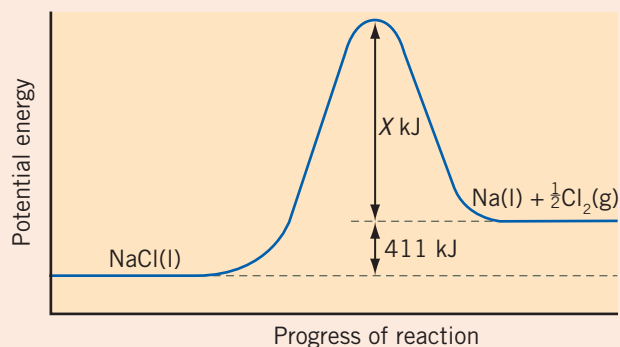
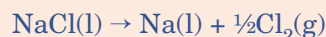
- the products have more potential energy than the reactants
- $\Delta H$  is positive (energy of products – energy of reactants)
- heat energy is absorbed from the surroundings during the reaction and as a result a decrease in the temperature of the surroundings occurs
- the activation energy for the forward reaction is the difference between the energy of the transition state and the energy of the reactants.

Figure 6.3 The potential energy changes that occur during an endothermic reaction

The size of the activation energy can have an effect on the reaction rate. In general, if a reaction has a very large activation energy, it will probably be a very slow reaction, particularly at room temperature, but if it has a very small activation energy, it will most likely be a fast reaction at room temperature. For example, at room temperature a mixture of methane (natural gas) and oxygen does not react because the reaction has a large activation energy. To make a reaction occur, the mixture needs to be heated (to increase the number of particles with the required activation energy to react). However, once the reaction has started, because it is exothermic, it can then produce the heat required for the reaction to continue at the increased rate.

### → Example 6.1

The energy profile diagram below is for the electrolysis of sodium chloride:



- Is the reaction exothermic or endothermic?
- What is the activation energy of the forward reaction?
- What is the activation energy for the reverse reaction?
- What is the  $\Delta H$  for the reaction  $\text{Na(l)} + \frac{1}{2}\text{Cl}_2\text{(g)} \rightarrow \text{NaCl(l)}$ ?

### → Solution

- Endothermic (the products have a larger potential energy than the reactants).
- $(411 + X)$  kJ (the energy difference between the transition state and the reactants)
- $X$  kJ
- $-411$  kJ

## Factors that affect reaction rates

Various factors are known to affect the rate of a reaction. These factors can be explained in terms of the collision theory and by using potential energy diagrams.

### The nature of the reactants

Reactions that involve the breaking of strong bonds, such as covalent bonds, are sometimes slow. However, the reactions of ions in solution often involve just the collision of ions, and so tend to occur rapidly. For example, reactions involving molecules, such as methane with oxygen (combustion), are often slow at room temperature, but precipitation reactions occur rapidly.



In general, if other factors affecting reaction rates are equal, reactions with high activation energies will be slower than reactions with low activation energies. Activation energy is related to the ease with which bonds are broken. Thus, reactions in which strong bonds have to be broken, for instance, covalent bonds, tend to have high activation energies, and so often they are slow, particularly at room temperature.

### The concentration of the reactants

Increasing the concentration of a solution (that is, increasing the amount of reactant in a particular volume of solution) can result in an increase in reaction rate. Increasing the concentration or partial pressure of a gas in a mixture of gases or increasing the total pressure by decreasing the volume of the mixture of gases can also result in an increase in reaction rate. Similarly, a decrease in the concentration of a reactant can decrease the reaction rate.

For particles to react, they must collide. Therefore, if the concentration of one of the reactants is increased (or the partial pressure of a gas in a gas mixture is increased), there will be a greater chance of the reactant particles colliding and so reacting.

### The state of subdivision of the reactants

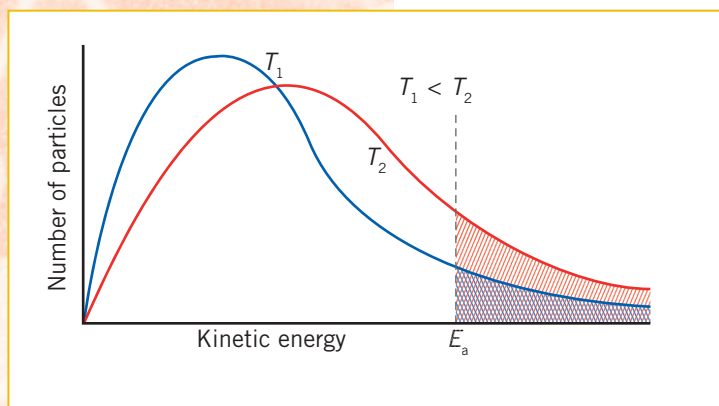
In heterogeneous systems, the greater the surface area of one reactant (or the greater the extent of subdivision of the reactant) that is exposed to the second reactant, the greater the reaction rate. Correspondingly, a decrease in the state of subdivision will result in a decrease in the reaction rate. This means that a reactant in its powdered form will react quicker than if it was all in one piece.

If the surface area of a reactant is increased, then more of it is exposed to collision with the particles of other reactants, thus increasing the reaction rate.

### Temperature

The rates of all chemical reactions (both exothermic and endothermic reactions) increase with increasing temperature. Likewise, a decrease in temperature will cause a decrease in the reaction rate.

An increase in temperature will result in an increase in the average kinetic energy of the particles. As a consequence, a greater proportion of reactant particles will have sufficient energy to supply the activation energy needed for reaction, and so the reaction rate will increase.



**Figure 6.4** When the temperature of a substance is increased, the average kinetic energy of its particles increases and now more particles will have the required activation energy,  $E_a$ , to react.

This can be seen by examining graphs showing the distribution of kinetic energies of particles at differing temperatures (Figure 6.4). At a temperature of  $T_1$ , the range of kinetic energies possessed by the particles in a particular gas sample can be represented as in the graph on the left. If the temperature of the gas is increased to  $T_2$ , then the average kinetic energy of the gas particles increases and the distribution of the energies changes.

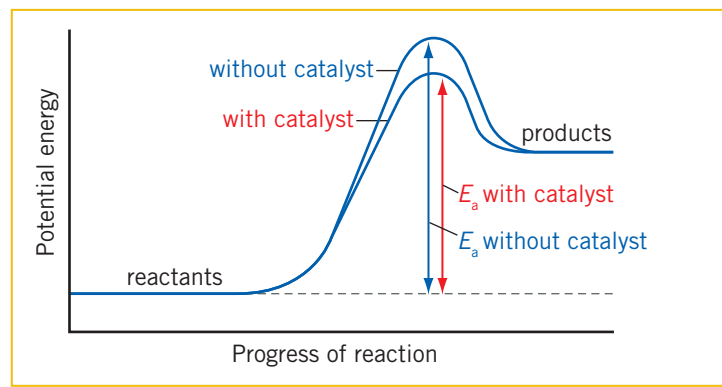
If a particular reaction has an activation energy of  $E_a$ , then from the graph it can be seen that at the higher temperature,  $T_2$ , more particles (represented by the area under the graph) will have enough energy to overcome the activation energy 'barrier', than at the lower temperature,  $T_1$ .

A less significant reason for the increase in reaction rate when the temperature is increased is that with an increase in temperature, the particles will move faster and so collide more often.

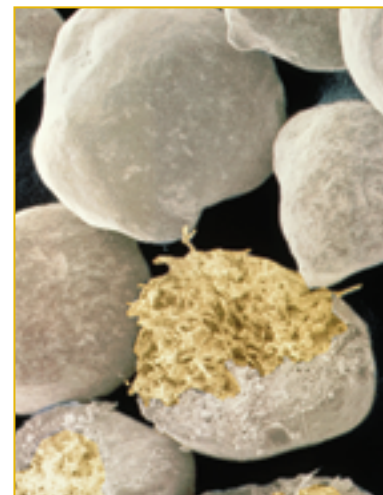
### Catalysts

A catalyst can be used to increase the rate of reaction. A catalyst is a substance that increases the rate of a reaction without being permanently consumed in the reaction.

Catalysts act by providing an alternative reaction pathway that has a smaller activation energy than the activation energy for the uncatalysed reaction. As a result, at a particular temperature, in the presence of a catalyst, more collisions will result in a reaction because more particles will have sufficient energy to react. The effect of a catalyst on a reaction can be shown in a potential energy diagram where the catalysed reaction has a lower activation energy than the uncatalysed reaction (Figure 6.6).



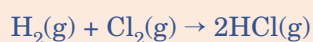
**Figure 6.6** A catalysed reaction will have a lower activation energy than the uncatalysed reaction.



**Figure 6.5** A scanning electron micrograph of granules of a washing powder that contains enzymes. Enzymes are biological catalysts. Some of the granules are partially open, showing the enzymes which assist in the cleansing action of the washing powder.

### → Example 6.2

The major use of hydrogen chloride is in the manufacture of hydrochloric acid. Even though hydrogen chloride is recovered as a by-product of some industrial processes, it can also be produced industrially from the reaction of hydrogen and chlorine gases:



At room temperature this is a very slow reaction. Suggest ways in which the rate of this reaction could be increased to make it a viable industrial process. Explain your choice of conditions in terms of the collision theory.

### → Solution

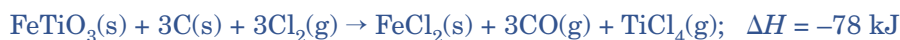
Using the following conditions would increase the reaction rate:

- Increase the temperature—when the temperature of a substance is increased, the average kinetic energy of its particles increases. As a result, when they collide, more particles will now have the required activation energy necessary for a reaction to occur.
- Increase the partial pressures of the two gases (i.e. ‘squash’ more of the gases into the reaction chamber)—this will result in a larger concentration of the reacting particles. As a result, there will be a greater chance of collisions between these particles and therefore a greater chance of a reaction.
- Use a catalyst—a catalyst provides an alternative pathway that has a lower activation energy than the original pathway. As a consequence, more colliding particles will now have the activation energy necessary for a reaction to occur.



## \* Review exercise 6.1

- 1 In an experiment, 1 g of powdered zinc is dissolved in 100 mL of 4 mol L<sup>-1</sup> hydrochloric acid with the production of considerable quantities of heat. Which of the following actions will decrease the *initial rate* of production of hydrogen?
  - a Heating the reaction mixture
  - b Using 100 mL of 2 mol L<sup>-1</sup> hydrochloric acid rather than 100 mL of 4 mol L<sup>-1</sup> hydrochloric acid
  - c Stirring the reaction mixture
  - d Adding a small volume of copper sulfate solution (acts as a catalyst)
  - e Using the same mass of zinc, but using granulated (chunks) zinc
  - f Using 5 g of the original powdered zinc instead of 1 g
  - g Adding 100 mL of water to the original mixture
- 2 Titanium is extracted from its ore, ilmenite, a shiny black mineral present in granite. Ilmenite has the formula FeTiO<sub>3</sub>. In the extraction process, the ore is mixed with coke (a source of carbon) and heated in an atmosphere of chlorine:



The reaction yields the volatile TiCl<sub>4</sub>, which can be isolated and reacted further to form titanium.

Which of the following will increase the rate of the reaction given above?

- a Decreasing the temperature
  - b Increasing the pressure of chlorine
  - c Using large chunks of ilmenite and coke
  - d Grinding the FeTiO<sub>3</sub> and C and mixing them thoroughly
- 3 The thermite reaction has been used to weld lengths of rail tracks to one another. In this process, a finely ground mixture of aluminium powder and iron(III) oxide react to produce aluminium oxide and white-hot molten iron. Burning magnesium is used to ignite the reaction mixture.
    - a Write a balanced equation for the reaction of aluminium with iron(III) oxide.
    - b
      - i Is the reaction of aluminium with iron oxide exothermic or endothermic? How do you know?
      - ii Would you expect the value of  $\Delta H$  to be large or small?
    - c Does this reaction have a high or low activation energy? Explain your reasoning.
    - d Draw a potential energy diagram for the reaction between aluminium and iron(III) oxide.



Figure 6.7 The thermite reaction. Sparks of molten iron and a cloud of aluminium oxide can be seen.

4 Use the collision theory to explain the following observations of reactions:

a Urea is used as a fertiliser because of its high nitrogen content. Industrially it is prepared in the following reaction:

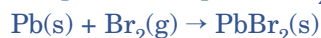


In the first step in this process, the ammonia and carbon dioxide are reacted at a pressure of approximately 10 000 kPa (approximately 100 times atmospheric pressure).

b Meat is stored in the refrigerator to keep it 'fresh' longer.

c In many metal extraction processes, one of the first steps is to crush the ore to fine particles.

d Two reactions that produce lead bromide are:



The first reaction occurs spontaneously at room temperature, but the reactants need to be quite strongly heated for the second reaction to occur.

e Buta-1,3-diene,  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ , is used in the manufacture of vehicle tyres. It is produced in a dehydrogenation reaction of butane:



Even when butane is heated to over 600°C, this reaction will only readily occur if the hot alkane is passed over a bed of a metal oxide, such as iron(III) oxide.

f When a splint that is glowing in air is placed in a flask of pure oxygen, it bursts into flames.

5 Consider the following observations made during a particular experiment involving the oxidation of sugar with potassium chlorate:

Observation I. Some sugar was mixed thoroughly with potassium chlorate and heated, but no reaction was observed.

Observation II. When a drop of concentrated phosphoric acid was added to the sugar mixture, a violent reaction occurred, releasing a large amount of heat and light energy.

Observation III. The amount of concentrated phosphoric acid remaining after the experiment was found to be the same as at the beginning.

a What does observation I suggest about the activation energy for the reaction between sugar and potassium chlorate?

b Explain how the concentrated phosphoric acid causes the violent reaction.

c Is the reaction exothermic or endothermic?

d Give two ways in which you could possibly increase the rate of the reaction between sugar and potassium chlorate without using the phosphoric acid.

6 Industrial diamonds can be made by heating artificial graphite or carbon-containing substances such as coal to temperatures of about 2000°C, at a pressure near 13 000 kPa:



a Make sketches of the structures of graphite and diamond showing the type or types of bonding that exists in these two allotropes.

b Suggest why such rigorous conditions are required to convert graphite into diamond.

c Would you expect this reaction to have a high or low activation energy? Explain your answer.

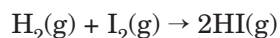
d Sketch an energy profile diagram for the conversion reaction of graphite to diamond.

e Predict the conditions necessary to reverse the reaction, i.e. to convert diamond back to graphite.

## 6.2 Reversible processes

Not all reactions go to completion. Even after a long reaction time, some reaction systems remain a mixture of reactants and products. This observation can be explained using the idea that reactions are reversible; that is, the products in a reaction are able to react to reform the reactants.

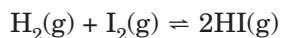
The reaction of hydrogen with iodine to form hydrogen iodide is an example of a reaction that does not go to completion:



If some hydrogen and iodine are mixed and allowed to react, the forward reaction rate is initially fast, but as the concentrations of the reactants decrease, the forward reaction rate also decreases.

However, as hydrogen iodide forms, it can react via the reverse reaction, to reform hydrogen and iodine. The rate of this reverse reaction is initially zero, but it increases as the amount of hydrogen iodide formed increases (Figure 6.8).

A stage is finally reached where the rate of the forward reaction is equal to the rate of the reverse reaction, which means hydrogen iodide is being formed as quickly as it is decomposing to re-form the reactants. When this stage is reached, the system is said to be at equilibrium. To indicate that a reaction is at equilibrium, a double arrow is used rather than a single arrow:



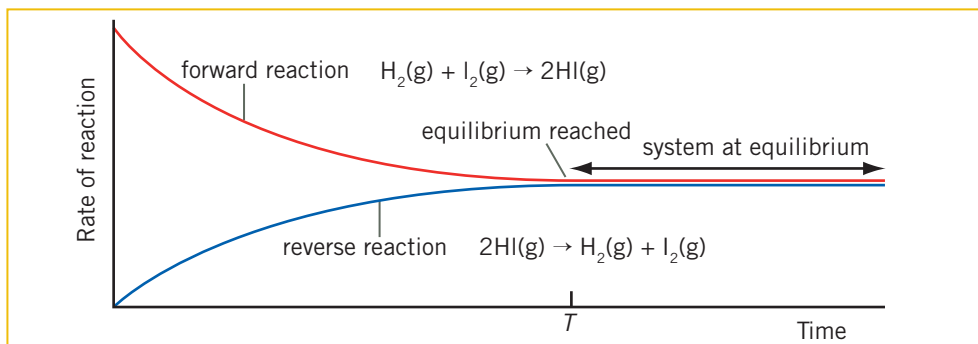
When a chemical reaction system is at equilibrium:

- the amounts, or concentrations, of the reactants and products present remain constant with time and as a result the macroscopic properties, such as colour, of the system remain unchanged with time
- the rates of the forward and reverse reactions are equal. This means chemical equilibrium is dynamic because the reactions have not stopped. At equilibrium, the reverse and forward reactions are still occurring, but at the same rate.

The changes in the rates of the forward and reverse reactions, during the formation of an equilibrium system, can be graphically represented. So also can the changes in the amounts of the reactants and products.

For example, if 0.10 mol of hydrogen and 0.10 mol of iodine are placed in a 1 L vessel and allowed to react at 490°C, it is found that when the reaction has reached equilibrium, 0.023 mol of hydrogen and 0.023 mol of iodine remain (i.e. 0.077 mol of each has reacted), and 0.154 mol of hydrogen iodide has formed. When this reaction system has reached equilibrium, its purple colour, due to the presence of iodine vapour, remains constant with time. This is because the concentration of iodine at equilibrium does not change as it is reacting and being formed at the same rate.

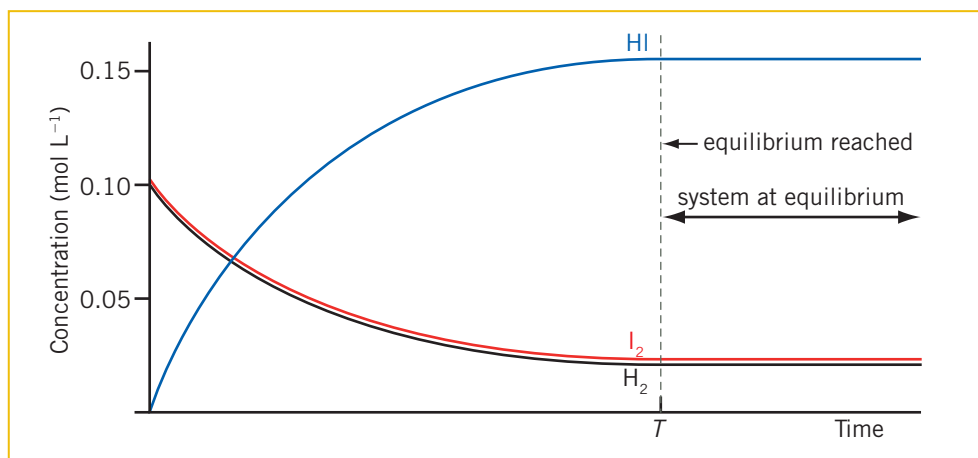
The graph of rate versus time for this equilibrium reaction,  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ , is shown in Figure 6.8.



**Figure 6.8** The graph of rate versus time for the formation of the equilibrium reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) = 2\text{HI}(\text{g})$ , beginning with the reactants  $\text{H}_2$  and  $\text{I}_2$ .

Initially the concentrations of  $\text{H}_2$  and  $\text{I}_2$  in the flask are relatively large, so the rate of the forward reaction at the beginning is large. It slows down, though, as the reactants are consumed. At the beginning of the experiment, there is no HI in the flask so the rate of the reverse reaction is zero. However, as HI is formed in the forward reaction, the rate of the reverse reaction increases. Finally, as shown in the graph at time  $T$ , both rates become equal and the system is at equilibrium. As long as the rates remain equal, the system will be at equilibrium and the amounts of  $\text{H}_2$ ,  $\text{I}_2$  and HI will remain constant over time.

The graph showing the changes in the concentrations of the three substances involved in the experiment described previously is given in Figure 6.9.



**Figure 6.9** The graph shows how the concentrations change when hydrogen and iodine are allowed to react to form the equilibrium mixture  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) = 2\text{HI}(\text{g})$ .

The reaction mixture at the beginning of the experiment is composed of only  $\text{H}_2$  and  $\text{I}_2$  with concentrations of  $0.10 \text{ mol L}^{-1}$ . No HI is present. As the reaction begins, the concentrations of  $\text{H}_2$  and  $\text{I}_2$  decrease as they react with one another. They decrease at the same rate because these two reactants react in a 1:1 mole ratio. Over time, the concentration of HI increases as more is produced in the forward reaction. Because the stoichiometric ratio between each of the reactants and HI is 1:2, the concentration of HI will increase more than the reactant concentrations decrease. Finally, at time  $T$ , when the forward and reverse reaction rates become equal, there is no net change in the concentrations; that is, they remain constant over time. This is when the system is at equilibrium. The system will remain at equilibrium until a change is made to it.

## Equilibrium in physical systems

Dynamic equilibrium can also be established in physical systems, for example, the evaporation of a liquid in a closed container or the dissolving of a solid in a liquid.

### Equilibrium vapour pressure

When a liquid is placed in a closed container, some of the liquid evaporates to produce a vapour above the liquid. Some of this vapour also condenses to re-form the liquid. If left long enough, equilibrium will be established between the liquid and the vapour. At this stage, the rate at which the liquid is evaporating will equal the rate at which the vapour is condensing, so molecules will be escaping from the liquid at the same rate as they are re-entering the liquid phase. The amount of liquid and vapour present will remain constant with time and the pressure exerted by the vapour (the equilibrium vapour pressure) will be a constant, at a particular temperature.

### Solution equilibria

When a solid is placed in a liquid, some of the solid begins to dissolve as the particles of the solid break away from the lattice and mix with the solvent's particles. These dissolved particles can also crystallise out of solution to re-form the solid. If sufficient solid is present, equilibrium will be established between the solid and the dissolved particles when the particles are dissolving at the same rate at which they are crystallising. As this stage, the amount of solid present will remain constant, and the amount of dissolved substance will also be constant. This equilibrium mixture is called a saturated solution.

## \* Review exercise 6.2

- Which of the following represent systems at equilibrium?
  - An open bottle of perfume
  - A lump of sugar slowly dissolving in water
  - A solution that has been formed from the reaction of copper ions and ammonia ( $\text{Cu}^{2+} + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4]^{2+}$ ). The blue colour of the solution remains constant
  - A mixture that has been formed by adding silver nitrate solution to sodium chloride solution. The mass of precipitate on the bottom of the closed beaker, and the appearance of the solution, remain constant with time
  - An open bottle of fizzy drink
- Ethanol is a volatile liquid and if it is left in a bottle with the lid on, the following equilibrium is established quite quickly:



If, however, the lid is left off the bottle, this equilibrium system cannot be set up. Explain why equilibrium can be set up in the closed bottle but not in the open bottle.

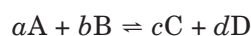
- The solubility of sodium chloride in water at 25°C is 36 g per 100 mL water. 40 g of sodium chloride is added to 100 mL of water (at 25°C) and after being stirred for a while, a lid is put on the beaker and the mixture is left to reach equilibrium.

- a Will there be any solid remaining on the bottom of the beaker in the equilibrium mixture? Explain your reasoning.
- b What 'reactions' will still be occurring in this equilibrium mixture?
- c i Sketch a graph to show how the rates of these reactions changed from the time the salt was first added to the beaker up until equilibrium was established.  
ii Similarly, sketch a graph showing how the concentration of sodium ions and chloride ions in the water changed over time.
- d An experiment that can be carried out to show that dynamic equilibrium has been established in the beaker is to add a tiny crystal of sodium chloride containing radioactive sodium ions to the solid at the bottom of the equilibrium mixture. Explain how this would show that the equilibrium system is 'dynamic'.
- e Why could an equilibrium mixture have not been formed if the 40 g of salt was added to 200 mL of water at 25°C?

## 6.3 The equilibrium law



It has been found experimentally that for any reaction at equilibrium, for example, for the general reaction:



the fraction

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

has a constant value, called the equilibrium constant ( $K$ ), at a particular temperature.

(In this fraction expression, which is sometimes called the equilibrium law expression, [A], [B], [C] and [D] represent the concentrations of A–D in mol L<sup>-1</sup>, and the lower-case letters  $a$ ,  $b$ ,  $c$  and  $d$  are the same value as the balancing numbers in the chemical equation.)

This relationship between the equilibrium concentrations of the reactants and products and the equilibrium constant,  $K$ , is referred to as the equilibrium law. The equilibrium law can be expressed as:

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

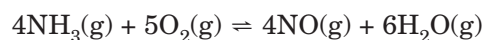
where the concentrations of the four substances are their concentrations in the equilibrium mixture at a particular temperature.

It can be concluded from the equilibrium law that no matter how a particular equilibrium mixture at a specific temperature is formed, the value of the equilibrium law expression for the relevant reaction has a constant value (the equilibrium constant). This conclusion can be supported by experimental data. Table 6.1 contains data for the reaction  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ , showing that no matter what the initial concentrations of the reactants or products are, when the concentrations at equilibrium are included in the equilibrium law expression, the value of this expression is the same, providing the temperature remains constant. Only a change in temperature can change the value of the equilibrium constant for a particular reaction.

**TABLE 6.1 DATA CONFIRMING THAT THE EQUILIBRIUM CONSTANT FOR THE REACTION  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  HAS A CONSTANT VALUE FOR DIFFERENT REACTION MIXTURES**

Temp. (°C)	Initial concentrations (mol L <sup>-1</sup> )			Final concentrations in the equilibrium mixture (mol L <sup>-1</sup> )			Equilibrium constant $\frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$
	H <sub>2</sub>	I <sub>2</sub>	HI	H <sub>2</sub>	I <sub>2</sub>	HI	
490	1.0	1.0	0	0.228	0.228	1.544	45.9
490	0	0	1.0	0.114	0.114	0.772	45.9
490	1.0	2.0	3.0	0.316	1.316	4.368	45.9

Equilibrium law expressions can be written for all reactions. For example, the equilibrium law expression for the reaction:



would be

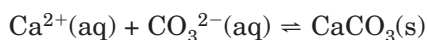
$$K = \frac{[\text{NO}]^4 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^5}$$

When writing these equilibrium law expressions:

- the concentrations of the products are written on the top line of the fraction, and the concentrations of the reactants are written on the bottom line
- if there are two or more reactants or products, their concentrations are multiplied together
- the power to which the concentration of a particular substance is raised is the same as the balancing number, for that same substance, in the chemical equation.

The equilibrium law expression does not include substances that are solids or pure liquids, because their concentrations do not vary from one reaction to the next.

For example, the equilibrium law expression for the reaction:



would be

$$K = \frac{1}{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}$$

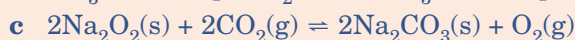
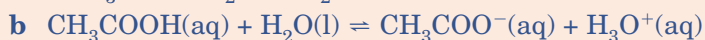
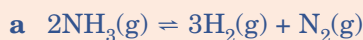
Further examples of equilibrium law expressions for different reactions are given in Table 6.2.

**TABLE 6.2 EXAMPLES OF EQUILIBRIUM LAW EXPRESSIONS FOR DIFFERENT REACTIONS, AND VALUES OF EQUILIBRIUM CONSTANTS AT PARTICULAR TEMPERATURES**

Equation for reaction	Equilibrium law expression	Equilibrium constant
$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$	$\frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$	280 at 725°C
$\text{Cu}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$	$[\text{Cu}^{2+}] [\text{OH}^-]^2$	$5 \times 10^{-20}$ at 25°C
$2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$	$\frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$	4.8 at 100°C
$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	$[\text{CO}_2]$	$2.5 \times 10^{-3}$ at 800°C
$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$	$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$	$4.8 \times 10^{-5}$ at 25°C

→ **Example 6.3**

Write the equilibrium law expression for the following reactions:



→ **Solution**

a 
$$K = \frac{[\text{H}_2]^3[\text{N}_2]}{[\text{NH}_3]^2}$$

b 
$$K = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

Because  $\text{H}_2\text{O}$  is in the liquid state, it is not included in the fraction.

c 
$$K = \frac{[\text{O}_2]}{[\text{CO}_2]^2}$$

$\text{Na}_2\text{O}_2$  and  $\text{Na}_2\text{CO}_3$  are present as solids and so they are not included in the fraction.

An equilibrium constant has the following characteristics:

- It is a constant value for a particular equation representing a reaction at a given temperature.
- If the temperature of a reaction is changed, then the value of the equilibrium constant also changes.
- It indicates the relative proportions of reactants and products in an equilibrium mixture. If the equilibrium constant has a very large value, it means large concentrations of products and very small concentrations of reactants are present; in other words, the reaction is almost 100% complete. If the equilibrium constant is very small, then the concentrations of reactants must be very large and the concentrations of products very small, which means the reaction would be almost insignificant. The size of the equilibrium constant gives an indication of the extent of the reaction.
- It provides no indication of the rate of the reaction, i.e. it does not indicate how quickly a particular reaction reaches equilibrium.



### \* Review exercise 6.3

- Write the equilibrium law expression for each of the following reactions.
  - $\text{P}_4(\text{g}) + 6\text{H}_2(\text{g}) \rightleftharpoons 4\text{PH}_3(\text{g})$
  - $\text{Al}^{3+}(\text{aq}) + 3\text{OH}^{-}(\text{aq}) \rightleftharpoons \text{Al}(\text{OH})_3(\text{s})$
  - $2\text{C}_2\text{H}_6(\text{g}) + 7\text{O}_2(\text{g}) \rightleftharpoons 4\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$
  - $\text{PbCl}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$
  - $\text{H}_2\text{SO}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons 2\text{H}_3\text{O}^{+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$
- Comment on the relative concentrations, at the quoted temperatures, of reactants and products in the equilibrium mixtures of the following reactions.
    - $\text{C}(\text{s}) + \text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}); \quad K = 1 \times 10^{15}$  at  $200^\circ\text{C}$
    - $\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq}); \quad K = 3 \times 10^{-10}$  at  $25^\circ\text{C}$
    - $\text{H}_3\text{PO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{PO}_4^{-}(\text{aq}) + \text{H}_3\text{O}^{+}(\text{aq}); \quad K = 2 \times 10^{-3}$  at  $25^\circ\text{C}$
  - Comment on the rate of the above reactions in reaching equilibrium, using only the data given.



## 6.4 Predicting the effect of changes to equilibrium systems

Changes can be made to a system at equilibrium, for example, by changing the temperature or volume, or by adding more reactant. Because these changes may have an immediate effect on the concentration of one or more of the reactants or products and change the rate of either or both of the forward or reverse reactions, the system may no longer be in equilibrium. When this occurs, the system will re-establish equilibrium by forming more of the products or reactants until the forward and reverse reaction rates are again equal, and the value of the equilibrium law expression is again equal to the equilibrium constant at the relevant temperature.

The effect of various changes on a chemical equilibrium system can be predicted using Le Châtelier's principle:

'If a system at equilibrium is subjected to a change in conditions, the system will adjust to re-establish equilibrium in such a way as to partially counteract (oppose) the imposed change.'

In the late 19th century, Henri Le Châtelier established this principle by observing what happens to many chemical equilibrium systems when changes are made to them.

### Change in concentration

#### Increasing the concentration of one of the reactants or products

(Note: In the following explanations, the use of the words 'reactant' and 'product' are in the context of the given equation. The substances on the left-hand side of the equilibrium arrow are referred to as the 'reactants' whether the forward or reverse reaction is occurring. Similarly, the substances on the right-hand side of the arrow are referred to as the 'products', regardless of the direction of the reaction.)

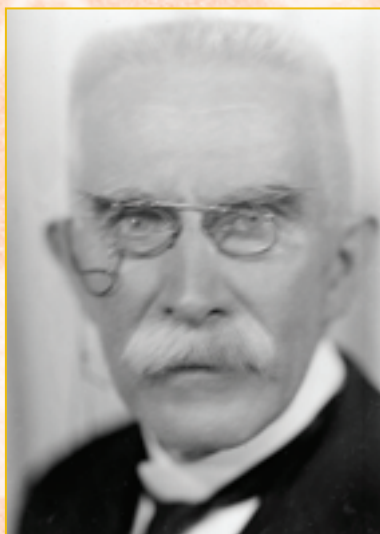
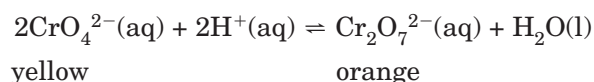


Figure 6.10 Henri Le Châtelier

If the concentration of one of the reactants in an equilibrium mixture is increased, for example, by adding more of the substance, the mixture will no longer be at equilibrium. This can be inferred because the equilibrium law expression will no longer equal the value of the equilibrium constant. According to Le Châtelier's principle, the system will, however, re-establish equilibrium in a way that will result in a decrease in the concentration of the added substance. In other words, in reaching equilibrium again, some of the added substance will be consumed.

A better understanding of what happens to an equilibrium system when more of one of the reactants is added can be gained by looking at the effect on the forward and reverse reaction rates by this addition, and by examining the changes in concentrations of each of the substances involved in the reaction.

An equilibrium system in which changes, caused by the addition or removal of a reactant or product, can be easily observed is the one that exists between yellow chromate ions and orange dichromate ions in an acidic solution:

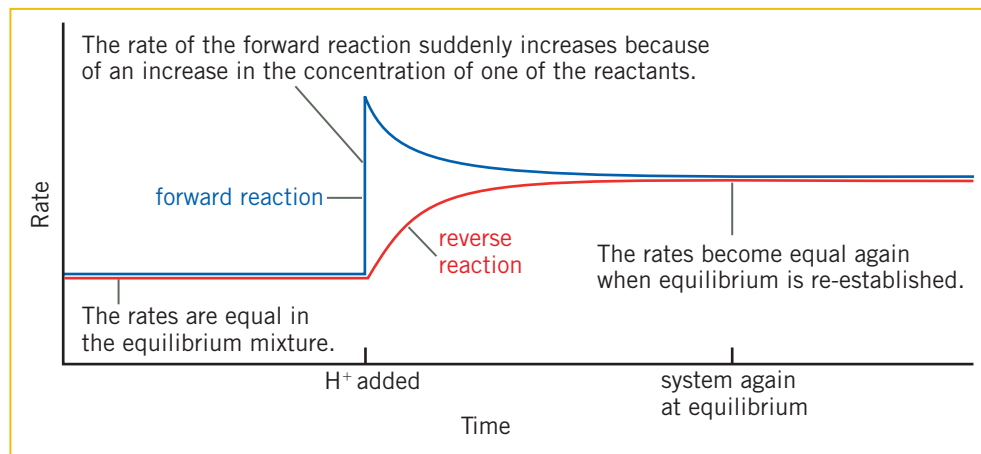


In Figure 6.11, a particular equilibrium mixture of this reaction is shown in the beaker on the left. When a few drops of concentrated hydrochloric acid are added to this equilibrium mixture, the mixture turns a deeper orange colour, as shown in the beaker on the right.

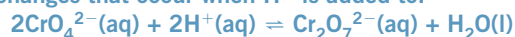
In the original equilibrium mixture, the rate of the forward reaction is the same as the rate of the reverse reaction, and the concentrations of each of the substances are not changing. However, as soon as the acid is added, the concentration of  $\text{H}^+$  ions increases, causing an immediate increase in the rate of the forward reaction, as shown in the rate versus time graph in Figure 6.12. This means that the system is no longer at equilibrium.



**Figure 6.11** When acid is added to the chromate/dichromate equilibrium system (on the left), it changes to a darker orange (on the right).



**Figure 6.12** The rate changes that occur when  $\text{H}^+$  is added to:



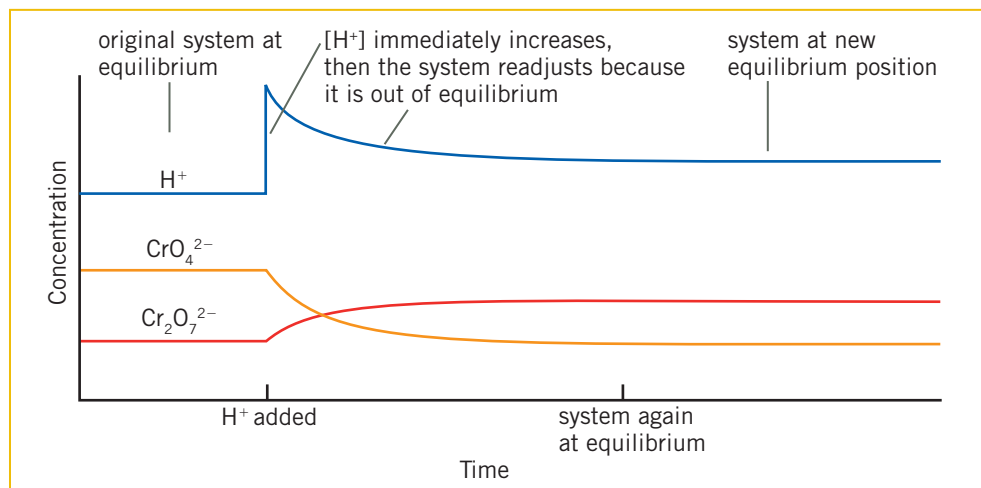
As the forward reaction is now proceeding at a greater rate than the reverse reaction, the concentrations of the  $\text{CrO}_4^{2-}$  and  $\text{H}^+$  ions will begin to decrease. This will result in a decrease in the rate of the forward reaction. That is to say, after the initial increase in the forward reaction rate, the rate will then begin to decrease. At the same time, because the forward reaction proceeds at a greater rate, more product is formed, leading to an increase in the rate of the reverse reaction, as shown in Figure 6.12.

Finally the forward reaction rate and the reverse reaction rate will again become equal and equilibrium will be re-established. The forward and reverse reaction rates in the new equilibrium mixture will be greater than the rates in the initial equilibrium mixture, because there is a greater concentration of most of the substances present.

Because, during the re-establishment of the new equilibrium position, the rate of the forward reaction was faster than the rate of the reverse reaction for some time, more of the product, the orange  $\text{Cr}_2\text{O}_7^{2-}$  ions, will be present in the final mixture than in the initial mixture. This will result in the final mixture being more orange in colour than the initial mixture.

The changes that occur in the concentration of each of the substances in the equilibrium mixture can also be shown graphically (Figure 6.13). In this graph, the initial concentrations and the amount of acid added have been arbitrarily chosen to enable the changes that take place to be illustrated. The actual concentration of each substance depends on the equilibrium constant, the amount of each substance originally mixed together and the temperature. Also, the change in concentration of the water has not been considered because, being the solvent, it is present in a large amount compared to the other substances and so the small amount produced in the reaction will not significantly alter its concentration.

In the initial equilibrium mixture, the concentration of each of the substances remains constant with time. However, when the acid is added, the concentration of the  $\text{H}^+$  ions immediately increases. Then to get back to equilibrium, because the rate of the forward reaction is faster than the rate of the reverse reaction, an overall net reaction towards the right occurs (or it is said that the position of equilibrium moves or shifts towards the products, or that the products are favoured.). This results in a decrease in the amount (and concentration) of  $\text{H}^+$  and  $\text{CrO}_4^{2-}$ , and an increase in the amount and concentration of  $\text{Cr}_2\text{O}_7^{2-}$ . Once equilibrium is again achieved, when the rates are equal once more, the concentrations remain constant with time.



**Figure 6.13** The concentration changes that occur when acid is added to an equilibrium mixture of  $2\text{CrO}_4^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) = \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

According to the stoichiometric ratios shown in the balanced equation, the reactants will react in a 1:1 mole ratio. As a consequence, in getting back to equilibrium, the amount in mole of  $\text{H}^+$  and  $\text{CrO}_4^{2-}$  that react must be equal and so their concentrations will decrease by the same amount. The stoichiometric ratio between  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  is 2:1, so the amount in mole of  $\text{Cr}_2\text{O}_7^{2-}$

formed in the reaction will increase by only half compared to the decrease in each of the reactants. The increase in the concentration of  $\text{Cr}_2\text{O}_7^{2-}$  is therefore half the decrease in the concentration of  $\text{CrO}_4^{2-}$ .

The equilibrium constant for a particular reaction is always the same unless the temperature is changed. This means that at the new equilibrium position the value of the equilibrium law expression:

$$\frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{CrO}_4^{2-}]^2 [\text{H}^+]^2}$$

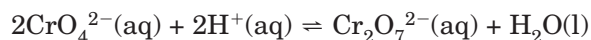
must be the same as it was for the original equilibrium mixture. For this to happen, and to account for the net forward reaction that occurs, at the new equilibrium position, the concentrations (and masses) of  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{H}^+$  will be greater, and the concentration (and mass) of  $\text{CrO}_4^{2-}$  will be smaller than before the addition of the acid, as shown in the graph in Figure 6.13. Note that the concentration of  $\text{H}^+$  at the new equilibrium position remains larger than before the addition of the acid ( $\text{H}^+$ ). The change made to the concentration of  $\text{H}^+$  is never completely overcome in the shift to re-establish equilibrium.

An alternative way of explaining why the equilibrium position shifts towards the products when one of the reactants is added is in terms of the equilibrium law expression. In the initial equilibrium mixture, the value of this fraction equals the equilibrium constant,  $K$ , for this reaction at the specific temperature.

$$\frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{CrO}_4^{2-}]^2 [\text{H}^+]^2} = K$$

When acid is added to the mixture, the concentration of  $\text{H}^+$  is increased, which means that the value of the fraction is now smaller than that of the equilibrium constant,  $K$ . For the fraction to again become equal to  $K$ , the top line needs to be increased and/or the bottom line decreased. This can be achieved if the net reaction proceeds towards the right, to form more products and reduce the amount of reactants.

To recap the main points concerning the prediction or explanation of what happens when acid ( $\text{H}^+$ ) is added to the following equilibrium system:

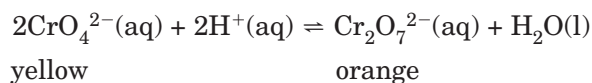


- According to Le Châtelier's principle, to oppose the change, some of the added  $\text{H}^+$  will need to be 'removed'. For this to happen, the equilibrium position will shift towards the products, or a net reaction will occur towards the right.
- This will occur because the rate of the forward reaction is larger than the rate of the reverse reaction until equilibrium is re-established.
- In the net reaction that occurs to get back to equilibrium, some of the  $\text{CrO}_4^{2-}$  and  $\text{H}^+$  will react to produce more  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{H}_2\text{O}$ .
- As a result, at the new equilibrium position, the concentration of  $\text{CrO}_4^{2-}$  will be smaller, and the concentration of the  $\text{Cr}_2\text{O}_7^{2-}$  will be larger than before the change was made.
- The concentration of the  $\text{H}^+$  at the new equilibrium position will be larger than it was before the acid was added to the original mixture because even though some of it reacted in getting back to equilibrium, the total amount added is not completely consumed; in other words, the change made to the system is not completely opposed.
- The addition of one of the reactants has resulted in more of the products being present in the new equilibrium mixture.
- The value of the equilibrium constant is the same for both the initial equilibrium mixture and the final equilibrium mixture, even though the concentrations of the reactants and products will have changed.

### Decreasing the concentration of one of the reactants or products

If the concentration of one of the reactants or products is decreased, the system will re-establish equilibrium in a way that will lead to an increase in the concentration of the removed substance. The concentrations of the other substances in the reaction will also change in reaching the new equilibrium position.

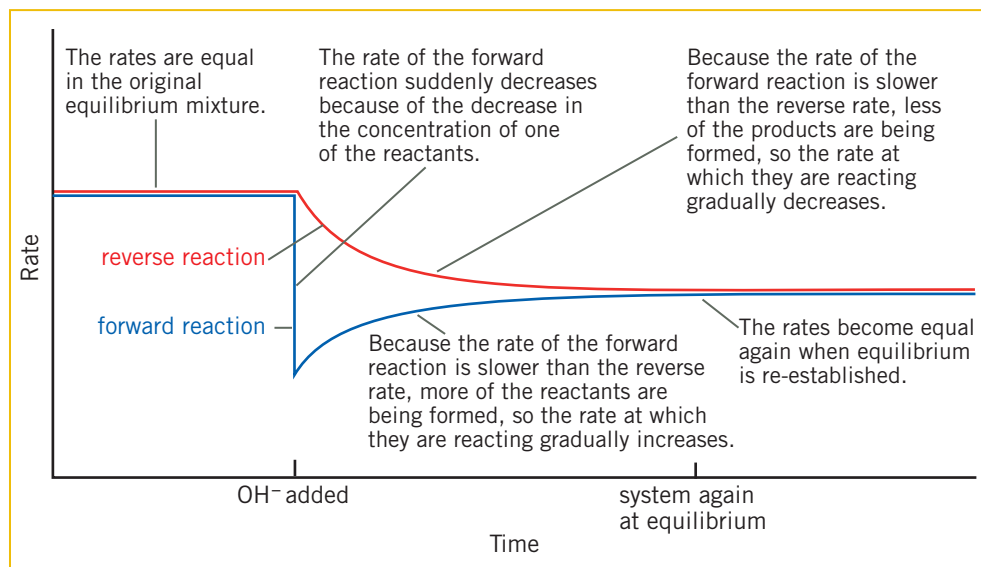
For example, if a few drops of a concentrated solution of sodium hydroxide are added to an orange-coloured equilibrium mixture of the following reaction:



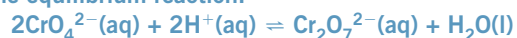
the mixture goes yellow.

The  $\text{OH}^-$  ions that have been added to the equilibrium mixture will react with the  $\text{H}^+$  ions and remove some of them from the equilibrium mixture. The change being made in this example is therefore a decrease in the amount of one of the reactants,  $\text{H}^+$ . According to Le Châtelier's principle, if there is a decrease in the concentration of  $\text{H}^+$ , a net reaction to produce more  $\text{H}^+$  (or a shift towards the reactants) will occur to re-establish equilibrium.

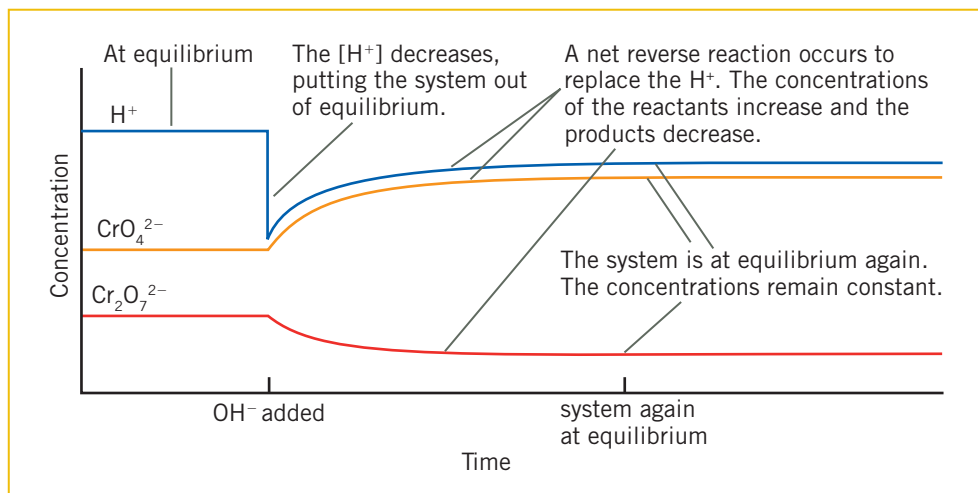
This equilibrium shift towards making more reactants occurs because when the concentration of  $\text{H}^+$  is decreased, the rate of the forward reaction becomes slower than the rate of the reverse reaction. This is another way of saying that there will be an overall net reaction in the reverse direction. The changes in rates that occur in this example are given and explained in the graph in Figure 6.14.



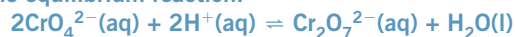
**Figure 6.14** The rate versus time graph showing the changes in rates that occur when some  $\text{H}^+$  is removed from the equilibrium reaction:



The concentration versus time graph for this reaction in which  $\text{H}^+$  has been removed from the mixture, by adding  $\text{OH}^-$ , is shown in Figure 6.15.



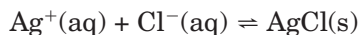
**Figure 6.15** A graph showing how the concentrations of the substances change when some  $\text{H}^+$  is removed from the equilibrium reaction:



At the new equilibrium position:

- the concentration of  $\text{CrO}_4^{2-}$  will be larger and the concentration of  $\text{Cr}_2\text{O}_7^{2-}$  will be smaller than in the original mixture (this is why the mixture became less orange and more yellow in colour)
- the concentration of  $\text{H}^+$  will be smaller than what it was in the original mixture (it was decreased because of the addition of  $\text{OH}^-$  and even though it increases in getting back to equilibrium, it will remain smaller than its original concentration—the ‘change’ is never completely opposed)
- the rates of the forward reaction and reverse reaction are equal but less than they were in the original mixture
- the equilibrium constant for the new equilibrium mixture will be the same as that for the original mixture.

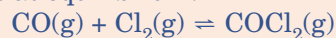
If an equilibrium system involves a solid or a pure liquid, then a change in the mass of this solid or pure liquid will not put the system out of equilibrium (unless the liquid causes the volume to change). For example, if the following reaction is at equilibrium:



and more solid  $\text{AgCl}$  is added to the mixture, the system will not be put out of equilibrium, and so no change in the concentrations of  $\text{Ag}^+$  and  $\text{Cl}^-$  will occur.

#### → Example 6.4

The following reaction is at equilibrium:



If this reaction is put out of equilibrium by the changes described below, compare the concentrations of each substance at the new equilibrium position with those in the original mixture.

- The partial pressure of  $\text{COCl}_2$  is increased by introducing more of it into the reaction vessel without changing the volume.
- A small amount of a chemical that absorbs carbon monoxide is added to the reaction vessel without changing the volume.

*continued*

### → Solution

- a** Increasing the partial pressure of  $\text{COCl}_2$ , by adding more  $\text{COCl}_2$  to the equilibrium mixture, will cause a shift in the equilibrium position so as to 'remove' some of the  $\text{COCl}_2$ . That is, the shift will be towards the left or the reactants (because when the  $\text{COCl}_2$  is added, the rate of the reverse reaction becomes greater than the rate of the forward reaction). This will result in an increase in the concentrations of  $\text{CO}$  and  $\text{Cl}_2$ . The concentration of  $\text{COCl}_2$  is initially increased and then in getting back to equilibrium, some of it is consumed, but the concentration never 'gets back' to its original value. That is, the concentration of  $\text{COCl}_2$  will remain higher than its original value.

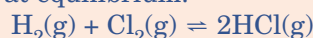
In summary, at the new equilibrium position, **all of the concentrations will be larger** than in the original mixture.

- b** The change made to the system is that the concentration (or partial pressure) of  $\text{CO}$  has been reduced. The system will readjust to partially replace this  $\text{CO}$  by a net reaction towards the reactants occurring (the rate of the forward reaction becomes slower than the rate of the reverse reaction). The concentration of  $\text{COCl}_2$  will become smaller and the concentration of the  $\text{Cl}_2$  will become larger. In re-establishing equilibrium, more  $\text{CO}$  is formed; however, the initial change is never 'overcome' so the concentration of  $\text{CO}$  will be smaller than in the original mixture.

In summary, the concentrations of  **$\text{COCl}_2$  and  $\text{CO}$  will be smaller**, and the concentration of  **$\text{Cl}_2$  will be larger**.

### → Example 6.5

The following reaction is at equilibrium:



When a small amount of ammonia gas is introduced into the reaction flask, it reacts with some of the  $\text{HCl}$  to form a very small amount of solid. Assuming the volume of the vessel does not change, compare the following in the new equilibrium mixture to that in the original mixture:

- the concentrations of the reactants and product
- the rates of the forward and reverse reactions
- the equilibrium constant for the reaction.

### → Solution

The change made to the equilibrium mixture is that the concentration (or partial pressure) of  $\text{HCl}$  has been decreased. This will cause a net reaction in the direction of the products, to form more  $\text{HCl}$ .

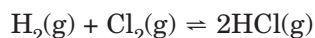
- The concentrations of  **$\text{H}_2$  and  $\text{Cl}_2$  will be less** in the new equilibrium mixture. The concentration of  **$\text{HCl}$  will also be less** (even though some  $\text{HCl}$  was produced as the system reacted to get back to equilibrium, the original change is not completely opposed).
- In the new equilibrium mixture, the rates of the forward and reverse reactions will again be equal but they will be **slower** than those in the original equilibrium mixture (less material is now present in the mixture).
- Assuming the temperature has not changed, the equilibrium constant for the new mixture will be **the same** as the equilibrium constant for the original mixture.

## Change in volume (or pressure) of a gaseous system

If the volume of a gaseous equilibrium system is changed, then the concentrations of the substances making up that system will also be changed. An increase in volume will cause a decrease in the concentrations, and a decrease in volume will cause an increase in the concentrations. Whether these changes in concentrations put the system out of equilibrium depends on the relative number of reactant and product particles (not including solids or pure liquids) involved in the reaction, as shown in the balanced chemical equation.

When the reaction contains equal numbers of particles on both sides of the equation, for example,  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$  where two molecules (particles) react to form two molecules, then the system will not be put out of equilibrium by a change in volume. If, however, the reaction has different numbers of particles on each side of the equation, for example,  $\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{NOCl}_2(\text{g})$  where two molecules react to form one molecule, then the system will be put out of equilibrium by a change in volume.

These conclusions can be explained by examining the changes to the equilibrium law expression as a result of the change in volume, and consequent changes in concentrations. For the equilibrium system:



the equilibrium law expression is:

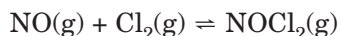
$$\frac{[\text{HCl}]^2}{[\text{H}_2][\text{Cl}_2]}$$

and at equilibrium this fraction has a constant value for this reaction system at a particular temperature. If the volume of the reaction vessel containing the equilibrium mixture is halved, for example, then the concentrations of the three different substances in the vessel will all double. The equilibrium law expression will therefore become:

$$\frac{2[\text{HCl}] \times 2[\text{HCl}]}{2[\text{H}_2] \times 2[\text{Cl}_2]}$$

Because the top line of the fraction has increased by the same factor as the bottom line, the value of the fraction is unchanged by the concentration changes. That is, the system is not put out of equilibrium by a change in volume of the reaction vessel.

For the second example:



the equilibrium law expression is:

$$\frac{[\text{NOCl}_2]}{[\text{NO}][\text{Cl}_2]}$$

If the volume of the vessel containing this equilibrium mixture is halved, doubling each concentration, the equilibrium law expression then becomes:

$$\frac{2[\text{NOCl}_2]}{2[\text{NO}] \times 2[\text{Cl}_2]}$$

The bottom line of the fraction is now twice that of the top line; that is, the value of the fraction has changed and will no longer be equal to the equilibrium constant. The system will therefore be out of equilibrium.

These equilibrium law expressions can also be used to determine the direction the equilibrium position will shift to get back to equilibrium. For the second example above, to re-establish equilibrium, after the decrease in volume, the fraction will need to be increased in value because it is now smaller than the equilibrium constant. In other words, the concentration of the product will need

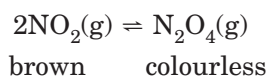


to increase and the concentrations of the reactants decrease. The net reaction that occurs will be in the forward direction to increase the amount of product present and decrease the amount of reactants.

The effect of a change in volume on an equilibrium mixture can also be predicted using Le Châtelier's principle. However, this is best done if the change in volume made to a system is interpreted in terms of the resulting change in pressure. If the volume of the reaction vessel is increased, then the total pressure of gases in the vessel will decrease. Alternatively, if the volume of the reaction vessel is decreased, the total pressure of the gases will increase.

When the total pressure of a gaseous equilibrium system is increased, by decreasing its volume, the system re-establishes equilibrium by reducing the total pressure. This is done by decreasing the overall number of particles in the gaseous system. For this to happen, the equilibrium position shifts towards the side of the reaction with the least number of particles. Correspondingly, if the total pressure of an equilibrium system is decreased, by increasing the volume, then the equilibrium position will move towards the side of the reaction with the greater number of particles. This would cause an increase in the pressure inside the reaction vessel.

A reaction that is often used to demonstrate the effect of a change in volume on an equilibrium system involves the brown nitrogen dioxide gas and the colourless dinitrogen tetraoxide gas:

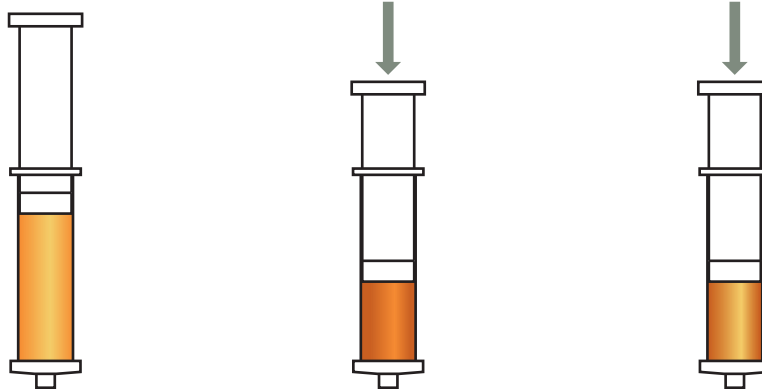


This is an equilibrium system in which there are an unequal number of reactant and product particles shown in the equation (two molecules of  $\text{NO}_2$  will form one molecule of  $\text{N}_2\text{O}_4$ ). As a result, this system will be put out of equilibrium by a change in volume and the consequent total pressure change. For example, if the plunger of a syringe containing the  $\text{NO}_2/\text{N}_2\text{O}_4$  equilibrium mixture is pushed in, to reduce the volume of the mixture, the brown mixture first darkens, then within a matter of seconds, the colour goes a lighter brown, as shown in Figure 6.16. However, the final colour of the mixture at the reduced volume is darker than the colour of the original equilibrium mixture.

Gas syringe containing the equilibrium mixture of  $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ . It is brown because of the presence of the  $\text{NO}_2$ .

The plunger is pushed in, compressing the gas, making it a darker brown. The decrease in volume has put the system out of equilibrium.

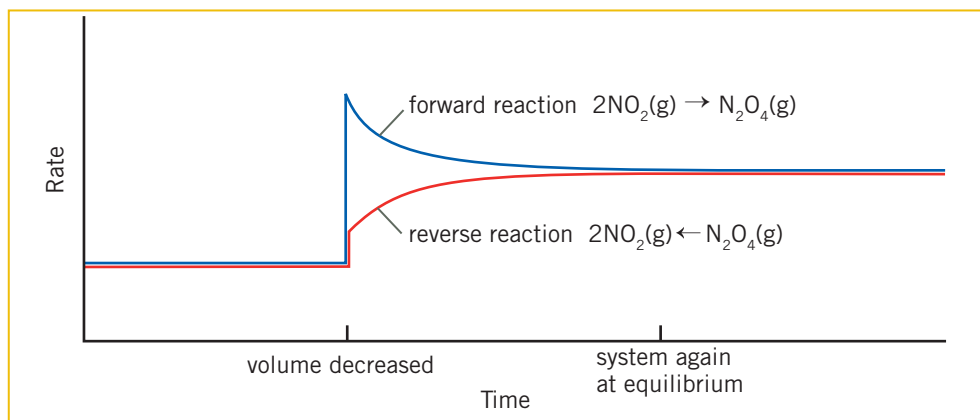
To get back to equilibrium, a net forward reaction occurs, consuming some of the brown  $\text{NO}_2$ , so the colour becomes lighter resulting in the new equilibrium mixture.



**Figure 6.16** The syringe contains the equilibrium mixture  $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ . When the volume of the mixture is decreased, the colour of the mixture first darkens, then goes a lighter brown as equilibrium is re-established.

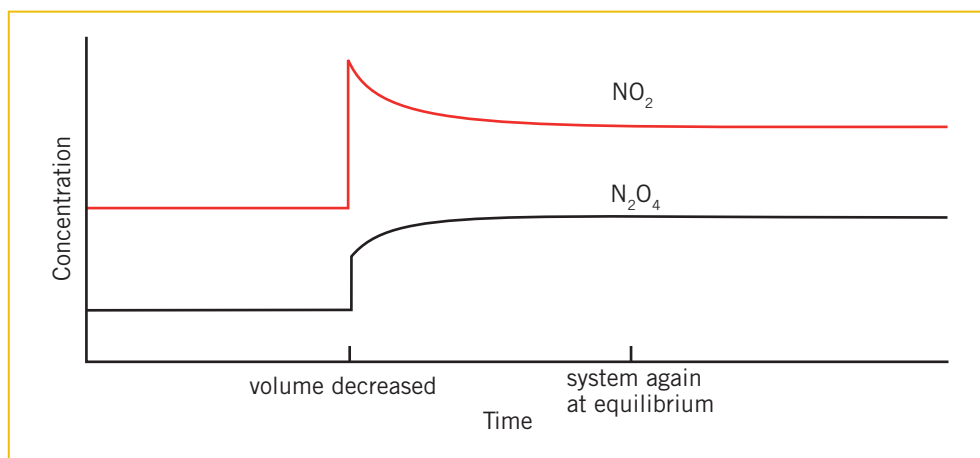
When the plunger is first pushed in, the  $\text{NO}_2$  molecules are pushed closer together making the mixture go a darker brown colour. This decrease in volume has also increased the total pressure of the mixture, putting the reaction system out of equilibrium. To oppose this change, i.e. to decrease the pressure, a net forward reaction occurs to reduce the number of particles present in the mixture. This will reduce the number of  $\text{NO}_2$  particles in the mixture and so the dark brown colour becomes lighter. However, the change made to the system is never completely overcome, so the brown colour does not return to its original colour (the concentration of  $\text{NO}_2$  does not return to its original value).

Graphs showing the changes in rates and concentrations can also be drawn for this example. The rate versus time graph shown in Figure 6.17 indicates that as soon as the volume is decreased, both the forward and reverse reaction rates increase. This occurs because both the  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  particles are pushed closer together and so they will collide more often. The forward reaction rate increases more than the reverse reaction rate, putting the system out of equilibrium. When equilibrium is re-established the rates again are equal, but faster than in the original mixture.



**Figure 6.17** This graph shows how the forward and reverse rates change when the volume of the  $2\text{NO}_2(\text{g}) = \text{N}_2\text{O}_4(\text{g})$  equilibrium system is reduced.

The concentration versus time graph in Figure 6.18 shows that when the volume is decreased the concentrations of both  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  increase immediately.

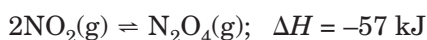


**Figure 6.18** The graph shows the concentration changes that occur when the volume of the  $2\text{NO}_2(\text{g}) = \text{N}_2\text{O}_4(\text{g})$  equilibrium system is reduced.

To get back to equilibrium, a net forward reaction occurs to produce more  $\text{N}_2\text{O}_4$  and consume some of the  $\text{NO}_2$ . This leads to the concentration of  $\text{NO}_2$  decreasing and the concentration of  $\text{N}_2\text{O}_4$  increasing, until equilibrium is again reached. The concentrations then remain constant over time because the reaction rates are now again equal.

### Change in temperature

To predict the effect of changing the temperature on an equilibrium system, knowledge of the heat of reaction of the system is required. For example, the heat of reaction for the reaction of  $\text{NO}_2$  to form  $\text{N}_2\text{O}_4$  can be expressed in the following equation:



An alternative way of expressing this information is:



Both equations show that the forward reaction is exothermic, which means when  $\text{NO}_2$  reacts to form  $\text{N}_2\text{O}_4$ , heat will be released to the surroundings. It also follows that the reverse reaction is endothermic; that is, when  $\text{N}_2\text{O}_4$  decomposes to form  $\text{NO}_2$  heat is absorbed from the surroundings.

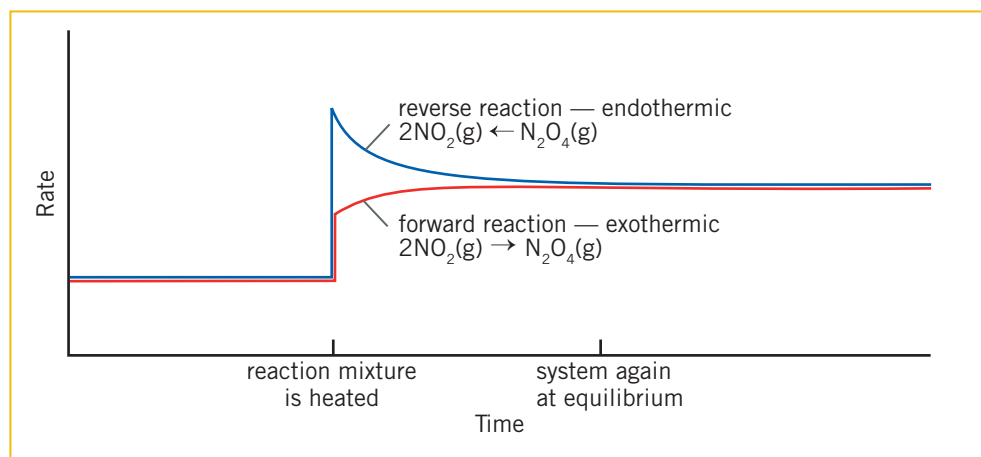
According to Le Châtelier's principle it can be predicted that if an equilibrium system is heated, the system will adjust by removing or absorbing heat. This means the endothermic reaction will be favoured, or in other words, the equilibrium position will shift in the endothermic direction. For instance, with



**Figure 6.19** The centre sealed tube contains an equilibrium mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ . The tube on the left has been heated and the one on the right has been cooled, causing shifts in the equilibrium positions.

the  $\text{NO}_2/\text{N}_2\text{O}_4$  reaction shown on the previous page, if the equilibrium mixture is heated, the reverse reaction, the endothermic reaction, would be favoured in an attempt to remove the added heat. The mixture should therefore become more brown as more  $\text{NO}_2$  is formed. This experiment is shown in Figure 6.19. The tube in the middle contains the unheated  $\text{NO}_2/\text{N}_2\text{O}_4$  equilibrium mixture and the tube on the left has been heated and it contains the darker coloured mixture at the new equilibrium position.

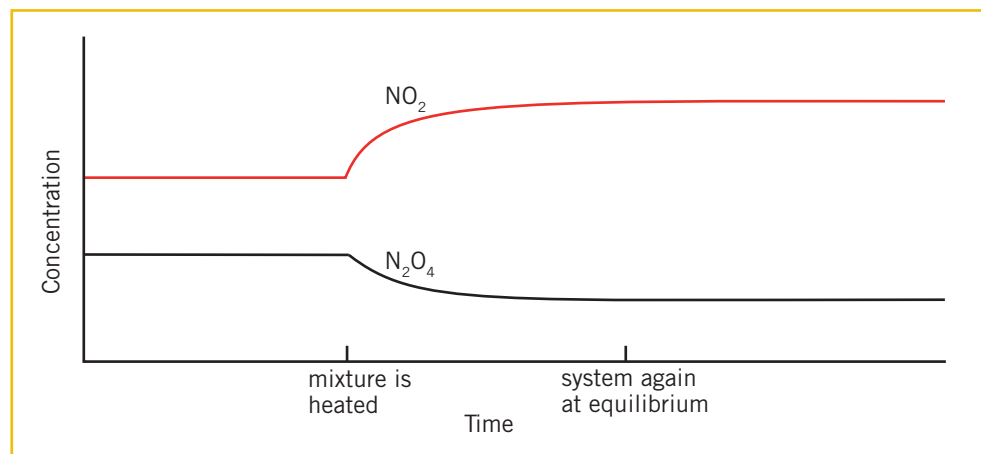
Graphs showing the changes in the rates and concentrations for the heating of the  $2\text{NO}_2(\text{g}) = \text{N}_2\text{O}_4(\text{g}) + 57 \text{ kJ}$  equilibrium system are given in Figures 6.20 and 6.21.



**Figure 6.20** The rate versus time graph shows the changes that occur when the  $2\text{NO}_2(\text{g}) = \text{N}_2\text{O}_4(\text{g}) + 57 \text{ kJ}$  equilibrium system is heated.

The graph in Figure 6.20 shows that when the system is heated, both the forward and reverse rates increase, but the endothermic reaction increases more than the exothermic reaction. The endothermic reaction is always affected more by a temperature change than the exothermic reaction. This is true even when the system is cooled; the endothermic reaction rate decreases more than the exothermic reaction rate.

As shown in the graph (Figure 6.20), because the rates are no longer equal when the mixture is heated, the system is no longer in equilibrium. When equilibrium is re-established, the rates are equal but they are both faster than in the equilibrium mixture at the lower temperature.

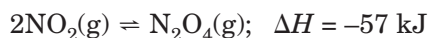


**Figure 6.21** The graph shows how the concentrations of the  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  change when the  $2\text{NO}_2(\text{g}) = \text{N}_2\text{O}_4(\text{g}) + 57 \text{ kJ}$  equilibrium mixture is heated.



The graph in Figure 6.21 shows that when the  $\text{NO}_2/\text{N}_2\text{O}_4$  equilibrium mixture is heated, there is no sudden change in the concentrations; they only change during the re-establishing of equilibrium. Because this process favours the reverse direction, the concentration of  $\text{NO}_2$  increases and the concentration of  $\text{N}_2\text{O}_4$  decreases until the new equilibrium position is reached. Then the concentrations remain constant with time.

Similar reasoning to that given previously can be applied to an equilibrium system when it is cooled, i.e. has its temperature decreased. For example, if the following equilibrium reaction is cooled:



the system will adjust by 'trying' to produce heat, which means the exothermic reaction is favoured. For this system, a net reaction in the forward direction would occur. Figure 6.19 shows what happens when a sealed tube of this equilibrium mixture is placed in ice (the tube on the right). The colour of the mixture has become paler because some of the  $\text{NO}_2$  is consumed quicker than it is produced as the equilibrium position shifts towards the products to re-establish equilibrium.

When the temperature of an equilibrium system is changed, the value of the equilibrium constant is changed. If the forward reaction is an exothermic reaction ( $\Delta H$  is negative) then an increase in temperature will result in a decrease in the value of  $K$ , and a decrease in temperature will result in an increase in the value of  $K$ . If the forward reaction is an endothermic reaction ( $\Delta H$  is positive) then an increase in temperature will result in an increase in the value of  $K$ , and a decrease in temperature will result in a decrease in the value of  $K$ .

For example, for the equilibrium system:



because the forward reaction is exothermic ( $\Delta H$  is negative), if the temperature is increased, the value of  $K$  will decrease. If the temperature is decreased, the value of  $K$  will increase.



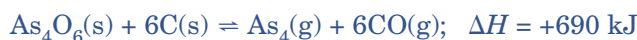
### Addition of a catalyst

When a catalyst is added to a reversible reaction, it lowers the activation energy for both the forward and reverse reactions. This results in an increase in the rate of both the forward and reverse reactions by the same amount. As a result, a catalyst does not affect the extent of the reaction, i.e. the relative proportions of reactants or products obtained in the equilibrium mixture, but it does allow the equilibrium position to be reached more quickly.

If a catalyst is added to a system already at equilibrium, this system will not be put out of equilibrium. The presence of the catalyst will have no effect on the amounts or concentrations of the reactants and products present at equilibrium. However, the rates of both the forward and reverse reactions will be increased equally.

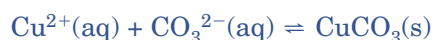
## \* Review exercise 6.4

- 1 Arsenic can be extracted from its ore by first reacting the ore with oxygen (called roasting) to form solid  $\text{As}_4\text{O}_6$ , which is then reduced using carbon:



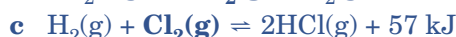
Predict the direction of the shift in the equilibrium position, and whether or not the products are favoured in this shift, in response to each of the following changes in conditions.

- Increase in the partial pressure of CO
  - Addition of carbon
  - Removal of gaseous arsenic
  - Increase in temperature
- 2 When a solution containing copper ions is mixed with a solution containing carbonate ions, a precipitate of copper carbonate forms, and the following equilibrium exists:



What effect would the following changes have on the amount of precipitate present?

- A few drops of a concentrated solution of copper sulfate are added.
  - A few drops of concentrated acid are added.
- 3 For each of the following reactions, state the effect on the concentration of the bold substance if the equilibrium system is heated:



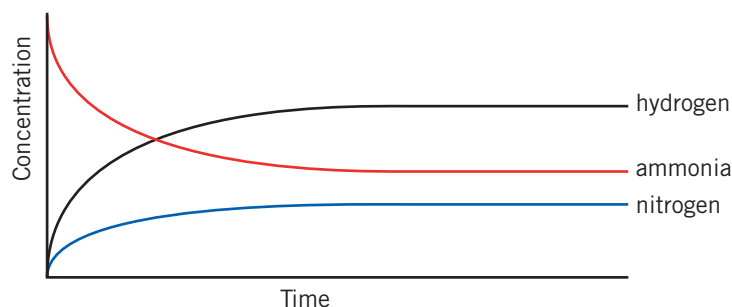
- 4 For each of the following reactions, determine:
- the direction of the shift in the equilibrium position
  - whether  $K$  will increase or decrease,
- when the temperature of the equilibrium system is decreased.



- 5 1 mol of ammonia was placed in a vessel at a very high temperature, and the system was allowed to reach equilibrium according to the reaction:



Below is a graph showing how the concentrations of the substances varied as the equilibrium position was being reached.



*continued*

### Review exercise 6.4 — continued

Redraw the graph, then answer the following questions.

- Indicate on your graph the time at which equilibrium is reached.
  - The same experiment is repeated, but this time a catalyst is added to the ammonia prior to any reaction. On your graph, sketch the graphs you would expect for this catalysed reaction.
- 6 Consider the following equilibrium reaction, carried out at 40°C:



Which of the following conditions will result in a larger yield of  $\text{PCl}_5$ ?

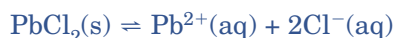
- Decreasing the volume of the reaction vessel
  - Decreasing the reaction temperature
  - Adding a catalyst
  - Increasing the partial pressure of  $\text{Cl}_2(\text{g})$  in the reaction mixture
  - Adding more  $\text{P}_4(\text{s})$  to the reaction mixture
  - Grinding the phosphorus before the reaction
- 7 Silver ions react with iron(II) ions in the following equilibrium:



An equilibrium system is created by mixing equal volumes of 0.100 mol L<sup>-1</sup> silver nitrate solution and 0.100 mol L<sup>-1</sup> iron(II) sulfate solution at a temperature of 25°C.

Give the effect of each of the changes in conditions described below, on the amount of iron(III) ions at the new equilibrium position, compared to the original equilibrium mixture. Write 'increase', 'decrease' or 'no difference'.

- The temperature is increased to 50°C.
  - A catalyst is added while the original temperature and volume are maintained.
  - A few drops of a concentrated solution of iron(II) nitrate solution are added at 25°C.
  - Some small pieces of silver foil are added at 25°C.
  - Some sodium chloride is added with stirring at 25°C.
- 8 A saturated solution of lead chloride is prepared in a beaker. There is still some solid remaining at the bottom of the beaker. Because the solution is saturated, the following equilibrium system exists:



Why does adding more solid  $\text{PbCl}_2$  to the beaker not put the system out of equilibrium? Explain your answer in terms of:

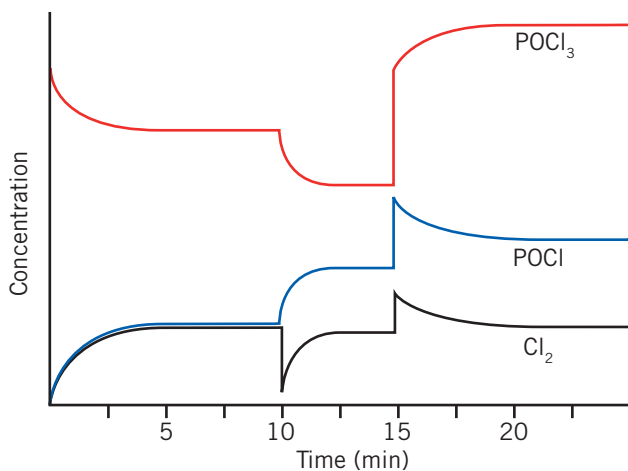
- reactions rates
  - the equilibrium law expression.
- 9 For which of the following equilibrium systems would an increase in volume (which results in a decrease in pressure of the system) cause the formation of more product?
- $2\text{CH}_4(\text{g}) \rightleftharpoons \text{C}_2\text{H}_2(\text{g}) + 3\text{H}_2(\text{g})$
  - $\text{H}_2(\text{g}) + \text{F}_2(\text{g}) \rightleftharpoons 2\text{HF}(\text{g})$
  - $2\text{CH}_3\text{OH}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CH}_2\text{O}(\text{g}) + 2\text{H}_2\text{O}(\text{g})$

10 The concentrations of the three substances in the reaction system:



are shown in the graph.

- What substance, or substances, were initially introduced to the reaction flask at the beginning of the experiment?
- Account for the horizontal section of the graphs between the 5- and 10-minute marks.
- Suggest what might have been done to the system at the 10-minute mark.
- At approximately what time did the system again reach equilibrium after this first change in conditions?
- Suggest what might have been done to the system at the 15-minute mark.
- What was the immediate effect on the concentrations of the substances in the system when the change occurred at the 15-minute mark?
- In which direction did the equilibrium position move to again reach equilibrium after the change at 15 minutes?
- If a catalyst was added to the reaction system at the 23-minute mark, in what way would you expect the graphs to change? Explain your answer.



## 6.5 Industrial processes

### Production of ammonia

At the beginning of the 20th century our food supply depended on rare deposits of nitrate salts, generally only found in desert regions because of the solubility of nitrates, and on a few species of bacteria.

Plants need a continuous supply of nitrogen to make amino acids and proteins as well as other biologically important molecules such as DNA. While 78% of the atmosphere is molecular nitrogen,  $\text{N}_2$ , the gas is not readily converted into a form that is soluble and can be taken in through the roots of plants.

Some microorganisms, including the *Rhizobium* species (Figure 6.22), are able to use a biological catalyst (the enzyme nitrogenase) to convert atmospheric nitrogen to ammonia ( $\text{NH}_3$ ) or ammonium ions ( $\text{NH}_4^+$ ). These bacteria form nodules on the roots of leguminous plants such as clover, peas and beans and provide their host plant with the nitrogen compounds it needs in return for the carbohydrate, protein and oxygen the bacteria needs. This process of converting atmospheric nitrogen into a soluble form used by plants is called nitrogen fixation.

Farmers can provide the nitrogen for the growth of non-leguminous plants by planting legume crops and digging them into the soil prior to sowing another crop. In addition, animal manure can provide the required nitrogen in a soluble



Figure 6.22 A scanning electron micrograph of *Rhizobium* sp. (red) that are present in the nodules on the roots of a pea plant

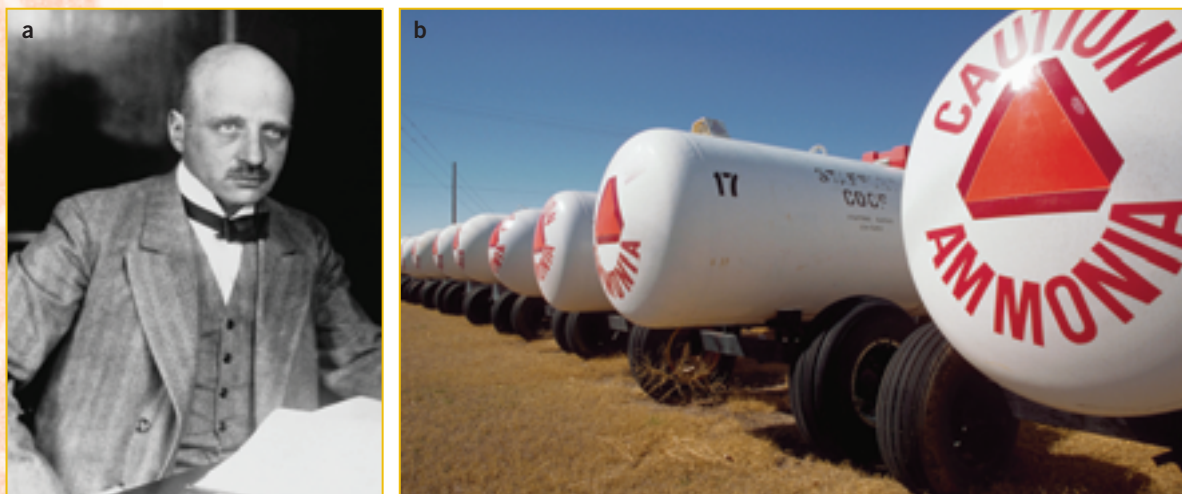


form. Prior to about 1910, the other main supply of nitrogenous fertiliser for agriculture came from sodium or potassium nitrate deposits in the Earth's crust. The Atacama Desert in Chile was a major source of these nitrates up until the first few decades of the 20th century.

In 1913, as a result of the combined efforts of Fritz Haber and Carl Bosch, the first commercial production of ammonia from atmospheric nitrogen and hydrogen (obtained from natural gas) was achieved. This method of synthesis of ammonia, known as the Haber process, can be represented simply as:

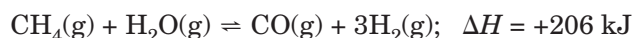


It was now possible for countries to manufacture their own fertiliser, in the form of liquid ammonia, ammonium salts and nitrates, without having to import nitrates from Chile.

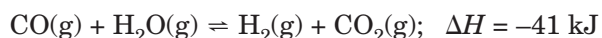


**Figure 6.23** (a) Fritz Haber (1868–1934), Nobel Prize winner, 1918. (b) Liquid ammonia is used by farmers to directly inject into the soil. The high solubility of ammonia in water ensures that it is locked in the moist soil ready for use.

In Western Australia, two companies that produce ammonia by the Haber process are Wesfarmers CSBP at Kwinana and Burrup Fertilisers (BFPL) near Karratha. These companies use natural gas (methane) as the source of hydrogen for the process. The natural gas is combined with steam in the presence of a nickel catalyst in a process called steam reforming:



Both carbon monoxide and carbon dioxide are 'poisons' for the catalyst used in the Haber process, so in a second reaction, the carbon monoxide is converted to carbon dioxide and more hydrogen in the presence of steam. This process is referred to as the 'shift' reaction:



At Kwinana a partnership between CSBP and Alcoa has resulted in the unwanted carbon dioxide waste product from CSBP being used to treat the alkaline waste product from the refining of bauxite into alumina. As a result, CSBP no longer pumps up to 70 000 tonnes of carbon dioxide annually into the atmosphere, and Alcoa can safely use the 'red mud' waste from its bauxite refining as a road base, building material and soil additive.

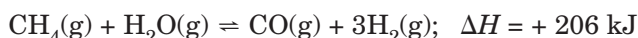
Steam reforming, the 'shift' reaction and the Haber process are all examples of equilibrium reactions. Le Châtelier's principle can be used in each case to predict the conditions of temperature and pressure that should optimise the production

of the desired material. However, the application of Le Châtelier's principle to synthesis on an industrial scale does not consider important issues of reaction rates or production costs.



Figure 6.24 Ammonia-producing plant near Karratha on the Burrup peninsula in Western Australia

### Steam reforming



This reaction is endothermic and results in the formation of four molecules in the gas phase from two molecules of reactant. According to Le Châtelier's principle the following conclusions can be reached:

- Low pressure causes a system to shift the position of equilibrium to the side of the equation having the larger number of molecules. In this reaction, since two molecules of reactant are consumed in the formation of four molecules of product, it can be predicted that the formation of the desired product ( $\text{H}_2$ ) is favoured at low pressure.
- High temperature favours the endothermic reaction. The steam reforming process is highly endothermic so the optimum conditions for the formation of hydrogen involve high temperatures. The equilibrium constant for the reaction will be larger at a higher temperature, meaning the reaction will occur to a greater extent.

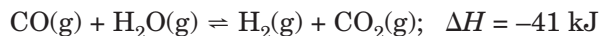
Considering the rate of this reaction, the following conclusions can be made:

- High pressure of the reacting gases basically means high concentrations and so a greater chance for effective collisions. The best reaction rate will be achieved at high pressure.
- High temperature will favour the maximum reaction rate as more collisions will have enough energy to overcome the activation energy barrier.
- A catalyst will increase the reaction rate by providing an alternative reaction pathway with a lower activation energy.

The reactions conditions for commercial production of hydrogen involve high temperatures (700–1000°C) as predicted by both Le Châtelier's principle and optimum rate considerations. Pressures around 1–2 MPa (about

10–20 atmospheres) are used despite the prediction, according to Le Châtelier's principle, of optimum yield at low pressure. This pressure is not regarded as particularly high for an industrial process; however, it is still high enough to ensure a sufficiently fast reaction rate. A nickel catalyst is used in the reaction to increase the rate at which equilibrium is reached.

### 'Shift' reaction



This reaction is exothermic and there is no change in the number of molecules when reactants are converted into products (two molecules of reactants become two molecules of products). According to Le Châtelier's principle, the following conclusions can be reached:

- Since pressure changes only shift the position of equilibrium when there is a difference between the number of molecules of reactants and products in the equation, there is no advantage in equilibrium yield to be gained by changing the pressure.
- Low temperature favours the exothermic process. The 'shift' reaction is exothermic so the optimum conditions for the best yield of carbon dioxide and hydrogen is to use a low temperature. As the temperature is decreased, the equilibrium constant for the forward reaction will increase.

Considering the rate of this reaction the following can be concluded:

- High pressure of the reacting gases effectively means high concentrations and so a greater chance for successful collisions. The best reaction rate will be achieved at high pressure.
- High temperature will favour the maximum reaction rate as more particles, on collision, will have sufficient energy to provide the required activation energy.
- A catalyst will increase the reaction rate because the new pathway it provides will have a lower activation energy.

In the commercial production, the gases involved in the 'shift' reaction are already at a moderately high pressure (from the steam reforming process) and so there is no provision made to change these conditions. The temperatures used in this next stage of production are marginally lower than those of the steam reforming process, depending on the catalyst used. However, for most industrial productions, intermediate temperatures between 200°C and 500°C are used in order to achieve the maximum rate at which equilibrium is achieved. Various catalysts are used for the 'shift' reaction, and as is the case for many industrial reactions, they are composed of compounds of the transition metals such as  $\text{Fe}_3\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CuO}$  and  $\text{ZnO}$ .

### The Haber process



In this exothermic reaction four molecules of reactant are changed into two molecules of product. According to Le Châtelier's principle, the following conclusions can be reached:

- Increasing the pressure exerted on an equilibrium system results in a shift of the position of equilibrium to favour the production of fewer molecules. This results in a decrease of the increased pressure change 'imposed' on the mixture. Since the number of molecules of ammonia on the product side of the equation is less than the number of molecules of reactants, an increase in pressure will favour the production of a higher yield of ammonia.

- Low temperature favours the exothermic process. The Haber process is exothermic so the optimum conditions for best yield are when the temperature is low. As the temperature is decreased the equilibrium constant for the production of ammonia (an exothermic reaction) will increase, resulting in more product being present in the equilibrium mixture.

Considering the rate of this reaction, the following conclusions can be made:

- High pressure of the reacting gases effectively means high concentrations and so a greater chance for effective collisions. The best reaction rate will be achieved at high pressure.
- High temperature will favour the maximum reaction rate as the kinetic energy of the particles is larger, so more collisions will have enough energy to overcome the activation energy barrier.
- A catalyst will increase the reaction rate by providing a new reaction pathway with a lower activation energy.

Once again, there is a conflict with the conditions for best yield and those predicted for the best rate. Figure 6.25 shows how the yield of ammonia changes with pressure for various temperature conditions.

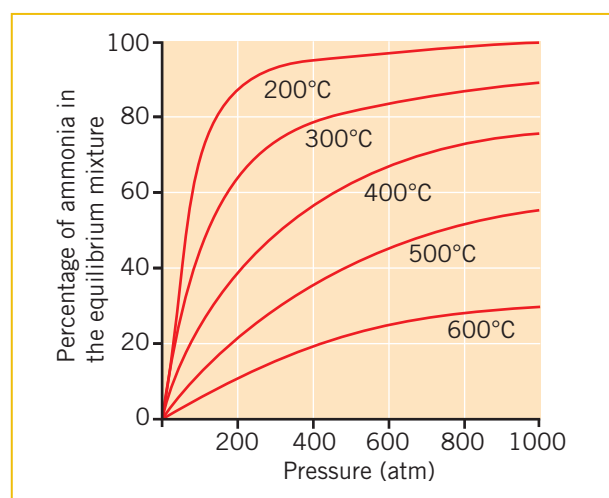


Figure 6.25 Percentage of ammonia present in an equilibrium mixture at varying pressure and temperature

The compromise conditions for the majority of industrial plants using the Haber process include the following:

- introducing the nitrogen and hydrogen into the converter in the 1:3 stoichiometric ratio
- pressures between 100 and 250 atmospheres (10–25 MPa). If the pressure is too high economic and safety issues become significant. To build a plant that will operate at higher pressures adds to production costs. Having to compress gases to even higher pressures than those used raises production costs and also adds risks to workers at the plant
- temperatures ranging from 350°C to 550°C. While this lowers the yield and the rate, enough ammonia is still produced fast enough
- using a porous catalyst based on iron oxide ( $\text{Fe}_3\text{O}_4$ ). The large surface area of the porous catalyst maximises the contact with the reactants, and therefore the rate at which equilibrium is reached.

Using these conditions, around 20–30% of the hydrogen and nitrogen mixture is converted to ammonia. As the hot gases exit the converter they are cooled, and at the pressure used for the reaction, the ammonia liquefies. The mixture of unreacted nitrogen and hydrogen is then returned to the converter where it is



Figure 6.27 Hazard label for stored bulk ammonia

mixed with fresh nitrogen and hydrogen. Ultimately the conversion of nitrogen and hydrogen is around 98%.

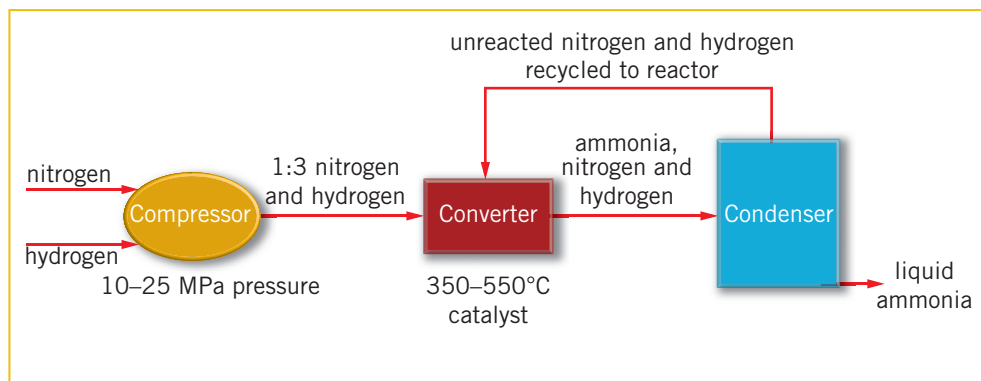


Figure 6.26 Flow chart of the Haber process

The reaction between nitrogen and hydrogen is exothermic and so the temperature of the gases increases during the reaction. Since this increase in temperature during the reaction will lower the yield, this 'waste' heat is used to heat the incoming mixture of nitrogen and hydrogen.

CSBP stores the liquid ammonia and uses it for the manufacture of other chemicals. BFPL pumps the liquid ammonia to the port at Dampier where it is exported, primarily to Indonesia, India and Japan.

### Safety and environmental concerns

Ammonia has a boiling point of  $-33^{\circ}\text{C}$  at atmospheric pressure and is a toxic gas at room temperature. Its vapour can damage eyes and the respiratory system, so safety issues are paramount in any commercial production. The ammonia production plant must be well ventilated and safety equipment such as breathing apparatus and rubber gloves and boots are readily available. The fact that ammonia is a gas at room temperature and is lighter than air means that any accidental spillage is likely to disperse quickly. A modern ammonia manufacturing plant will ensure that safe operating conditions are maintained and that the workforce is kept up to date with all issues associated with the safe operation and maintenance of the plant.

Issues associated with the management of waste in the production of ammonia have been considered above. The Haber process has been used to make ammonia for well over 80 years and many efficiencies have been introduced. Ammonia is arguably one of the most important commercially produced chemicals. Its use in the manufacture of fertilisers has resulted in a significant increase in global population growth since 1930. More than 40% of the world's population depend on fertilisers from ammonia in the production of their food. In September 2008 Jan Erisman and others in an article published in *Nature Geoscience* suggested that 'the lives of around half of humanity are made possible by Haber-Bosch nitrogen.'

In the future, it is speculated that issues of sustainability and environmental concerns will prompt changes in the production and use of ammonia. These changes include:

- reduced demand for growth in ammonia production caused by the decrease in global fertility rates that may see population growth level out
- research on optimum amounts of nitrogen that are needed for plant growth

- modification of crops to utilise nitrogen more efficiently from other sources. Perhaps the large-scale use of biological catalysis for nitrogen fixation
- changes in the way in which ammonia is used to manufacture other chemicals. Less reliance on ammonia resulting from a 'greener' approach to chemical synthesis.

## Production of nitric acid

Adjacent to the ammonia production plant in Kwinana, CSBP has a facility to convert ammonia into nitric acid via the Ostwald process. The bulk of the nitric acid produced is mixed with ammonia in the production of ammonium nitrate, which is used as a fertiliser and as an explosive in the mining industry. Nitric acid can also be used to make other nitrogenous fertilisers.

The Ostwald process involves three stages:

- the oxidation of ammonia to nitrogen monoxide, NO
- further oxidation of nitrogen monoxide to nitrogen dioxide
- reaction between nitrogen dioxide and water to produce a solution of nitric acid.

A flow chart for the conversion of ammonia into nitric acid is shown in Figure 6.29.

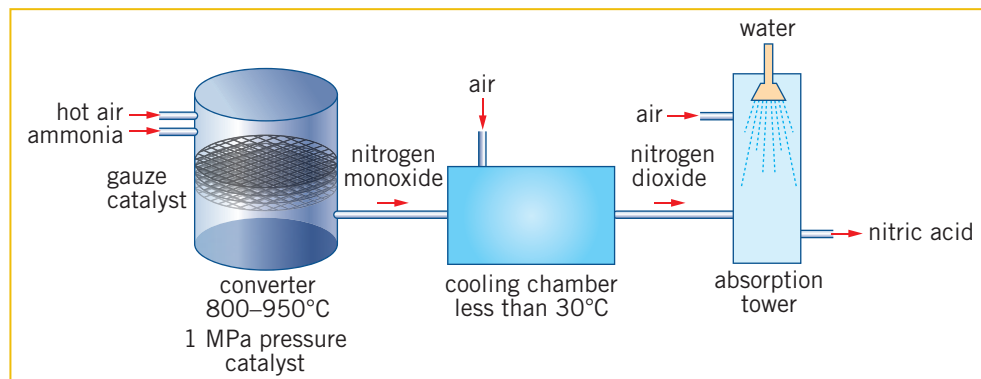
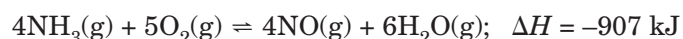


Figure 6.29 Flow chart for the three stages in the conversion of ammonia into nitric acid

The first stage of the process involves the conversion of ammonia into nitrogen monoxide:



Application of Le Châtelier's principle to this reaction would lead to the following conclusions about maximising the yield of NO:

- Low pressure promotes a shift in the position of equilibrium favouring the production of a larger number of molecules. Since nine molecules of reactants are converted to ten molecules of products, it can be predicted that the highest yield of NO will be obtained at the lowest pressure.
- Low temperature favours the exothermic reaction. Since this reaction is highly exothermic, it is expected that the highest yield of NO will be obtained the lowest temperature.

The conditions for optimum rate are the same as those predicted for the production of ammonia:

- High pressure of the reacting gases effectively means high concentrations and so a greater chance for effective collisions. The best reaction rate will be achieved at high pressure.



Figure 6.28 Wilhelm Ostwald (1853–1932). He received the Nobel Prize in Chemistry in 1909 for contributions to the understanding of rates and equilibrium.



- High temperature will favour the maximum reaction rate as more collisions will have enough energy to supply the required activation energy.
- A catalyst lowers the activation energy for the reaction, so more particles will have the required activation energy for a reaction to occur. This results in an increase in the reaction rate.

However, this reaction is made more complex by the fact that ammonia can also be oxidised in air to produce nitrogen or dinitrogen monoxide,  $N_2O$ . As a result of these competing reactions, the simple application of rate and yield predictions does not directly predict the ideal conditions for the production of the required product, nitrogen monoxide,  $NO$ .

Commercially the reaction takes place at temperatures between  $800^\circ\text{C}$  and  $950^\circ\text{C}$ , and moderate pressures of the order of 10–12 atmospheres (1 MPa). Several layers of gauze made from a platinum/rhodium alloy (the catalyst) provide a large surface area for the reaction. Finally, the contact time of the gases on the hot catalyst is kept to thousandths of a second to minimise the other possible reactions of ammonia.

By careful selection of the catalyst and the use of conditions that represent a compromise between the highest rate and the highest yield, the oxidation of ammonia to nitrogen monoxide,  $NO$ , achieves around 95% conversion.

The nitrogen monoxide from this first reaction is mixed with more air and is converted to nitrogen dioxide according to the equation:



Of the three reactions in the Ostwald process, this is the slowest and both yield and rate are highly dependent on pressure and temperature.

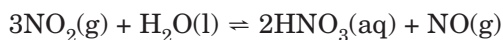
If Le Châtelier's principle is applied to this reaction, the following predictions can be made:

- High pressure promotes a shift in the position of equilibrium, favouring the production of the least number of molecules. Since three molecules of reactants are converted to two molecules of product, the yield from this reaction will be increased at high pressure.
- Low temperature favours the exothermic reaction. Because in this case the reaction is exothermic, the highest yield will be achieved at the lowest temperature.

In previous examples, the rate of reaction has increased as the temperature has increased. This particular reaction is different from those normally encountered because the rate of the forward reaction increases as the temperature decreases.

The gases emerging from the first stage of the Ostwald process are rapidly cooled to below  $30^\circ\text{C}$ , more air is added and, if necessary, the pressure is increased slightly. Under these conditions, virtually all the nitrogen monoxide is converted to nitrogen dioxide.

In the final stage, the nitrogen dioxide is passed, usually at a pressure higher than atmospheric, to the bottom of the absorption tower where the rising gas meets a counter flow of water. The tower is packed with an inert material to increase the surface area and to maximise contact between the nitrogen dioxide and the water. The overall reaction in the tower can be summarised as:



Unreacted nitrogen monoxide is returned to the second reaction stage for further oxidation with air.

Distillation of the nitric acid solution obtained in the final reaction can lead to a solution that is around 68% by mass  $\text{HNO}_3$ .

At the CSBP Kwinana plant, the nitric acid solution is mixed with ammonia. An exothermic reaction takes place to produce a hot, concentrated solution of ammonium nitrate. This hot solution is sprayed from the top of a tower and during its descent the droplets lose water by evaporation and are converted to solid granules of ammonium nitrate.

### Production of sulfuric acid: the contact process



Western Mining Corporation owns the Kalgoorlie Nickel Smelter, in Western Australia, that produces a large amount of sulfur dioxide as a waste product of nickel refining. A sulfuric acid plant has been constructed adjacent to the nickel smelter to convert the sulfur dioxide into a valuable industrial chemical.

The stages in the contact process can be summarised as:



The use of a waste product from one industrial process as a starting material for the synthesis of another valuable product makes this reaction an attractive environmental proposition.

The key to the contact process is the oxidation of sulfur dioxide to sulfur trioxide, summarised in the equation:



The reaction is carried out in a four-stage converter as shown in the flow diagram in Figure 6.30.

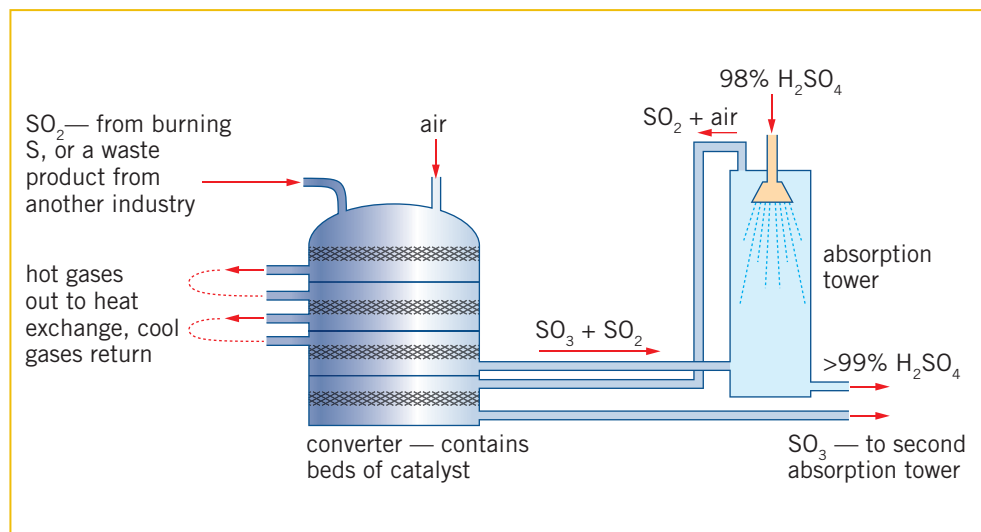


Figure 6.30 The conversion of sulfur dioxide to sulfuric acid in the contact process

Applying Le Châtelier's principle to this reaction, the conditions for the best yield of sulfur trioxide can be predicted:

- High pressures favour a shift in the position of equilibrium to the side having the least number of molecules. Since in this reaction, three molecules (two of sulfur dioxide and one of oxygen) become two molecules (two of sulfur dioxide), high pressure should favour the yield of sulfur trioxide.
- The reaction is exothermic so any decrease in temperature would favour the products. The maximum yield of sulfur trioxide will therefore be achieved at the lowest possible temperature.



The best reaction rate will be obtained at high temperature, high pressure and in the presence of a catalyst.

As has been often the case in the industrial reactions examined in this text, there is a conflict between the conditions for best rate and best yield when considering the temperature conditions for the reaction. For the contact process, both equilibrium and rate considerations support the use of high pressure. The commercial reality is that to operate at an elevated pressure introduces cost and safety issues. The conditions chosen for the industrial process are a compromise based on these considerations.

In practice, the mixture of sulfur dioxide and excess air is heated to around 400–500°C at a pressure just marginally higher than atmospheric pressure. As the mixture passes over the first porous bed of catalyst (vanadium pentoxide), some of the sulfur dioxide is oxidised to sulfur trioxide in the exothermic reaction. The temperature of the gases may rise beyond 600°C, which will reduce the yield, so this gas from the first bed is cooled by passing it out of the converter and using its excess heat energy to warm the incoming air and sulfur dioxide. Once cooled back to the optimum reaction conditions, the mixture of sulfur trioxide, sulfur dioxide and air is passed back over the second catalyst bed. Again, the exit gases are cooled in a heat exchange process before being passed over the third catalyst bed.

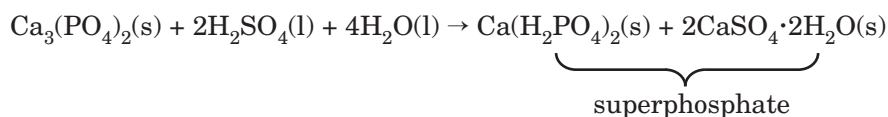
After passing over this third catalyst bed, the gas mixture, which contains a high percentage of sulfur trioxide, is fed into the absorption tower where the gases moving up the tower meet a spray of 98% sulfuric acid. The sulfur dioxide does not dissolve in the acid, but sulfur trioxide combines with the small amount of water in the sulfuric acid, increasing the concentration of the sulfuric acid to 100%. This acid is carefully diluted back to 98% and some of it is recycled back to the absorption towers.

The alternative procedure of simply allowing sulfur trioxide to dissolve in a stream of water (as was used in the final step of the Ostwald process for nitric acid), is not employed as the reaction between sulfur trioxide and water is highly exothermic and a mist of sulfuric acid droplets forms. Because this mist takes a long time to condense, it would hold up the overall process.

The mixture of unreacted sulfur dioxide and air emerging from the first absorption tower is warmed to 400°C or beyond and passed across the fourth catalyst bed before it is carried to the second absorption tower.

Overall, the conversion of sulfur dioxide to sulfuric acid is in excess of 99% under these conditions so there is no reason for looking to improve the process any further by altering the reaction conditions.

Over 70% of the sulfuric acid manufactured in Australia is used to make fertilisers, particularly superphosphate. Much of Australia's soil is deficient in phosphorus, an essential nutrient for plants. In the manufacture of superphosphate, insoluble calcium phosphate is converted to a more soluble form as a combined salt of calcium dihydrogenphosphate and calcium sulfate.



## \* Review exercise 6.5

- 1 Construct a flow chart of the synthesis of ammonia from methane and air.
- 2 A farmer is looking to add a nitrogenous fertiliser to one of his fields. He has a choice of purchasing a 50 kg bag of ammonium nitrate or urea,  $\text{CO}(\text{NH}_2)_2$ .
  - a Which fertiliser will give the most nitrogen to the soil per 50 kg bag?
  - b What other factors would the farmer need to consider prior to making a final decision?
- 3 In a particular industrial process in the gas phase it is discovered that when either the temperature is increased or the volume of the reaction vessel is decreased the yield of product increases. What conclusions can you make about the particular reaction involved?
- 4 A selection of the twelve principles of green chemistry is listed below:
  - It is better to prevent waste than to clean up waste that has been produced.
  - The reaction should be designed to maximise the involvement of all of the reacting materials into the final product.
  - Where possible, the reaction should use and generate material that has little or no toxicity.
  - Energy requirements for a process should have minimal environmental and economic impact.
  - Materials consumed in the process should be renewable.
  - Products of reactions should be designed to break down harmlessly after they have served their specific function.
  - Substances and reaction conditions chosen should minimise the potential for accidents.

For each of the Haber, Ostwald and contact processes, conduct a separate audit of the reactions and processes involved against each of these principles.

- 5 In each of the three industrial processes considered in this section, the starting materials need to be purified prior to entering the reaction chamber. Why is this necessary?
- 6 Write the equilibrium law expressions for all of the equilibrium reactions in the Haber, Ostwald and contact processes.
- 7 In each of the three industrial processes identified in question 6, the temperature of the reaction mixture increases in the converter.
  - a What causes the temperature to increase?
  - b What are the consequences of allowing this to happen, and what is done to address these consequences?
- 8 This question refers to the Haber process.
  - a At 200 atm pressure the yield of ammonia doubles if the temperature is dropped from  $500^\circ\text{C}$  to  $400^\circ\text{C}$ . Why do the manufacturers continue to use the higher temperature?
  - b Alternatively, if the temperature is kept the same and the pressure inside the reaction chamber is tripled, the yield doubles. Why do the manufactures continue to use the lower pressure?
- 9 The reaction for the absorption of nitrogen dioxide in water in the final stage of the Ostwald process can be written in an alternative way as:

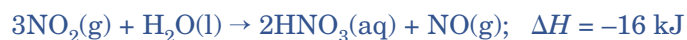


This equation accounts for the recycling of the NO that occurs in commercial production.

*continued*

### Review exercise 6.5 — continued

- a** Using this equation and the other two reactions starting with ammonia and oxygen, derive the overall equation for the reaction between ammonia and oxygen to produce nitric acid as a one-step equation.
- b** Prior to the Ostwald process, nitric acid was produced by heating a nitrate with concentrated sulfuric acid and distilling off the more volatile nitric acid. Write the equation for the reaction between sodium nitrate and sulfuric acid to produce nitric acid.
- c** The second principle of green chemistry proposes that synthetic methods should seek to incorporate as many of the atoms in the reactants as possible into the desired product. The percentage atom economy for a reaction expresses the mass of atoms in the desired product compared to the total mass of atoms in all the reactants as a percentage.
- Calculate the percentage atom economy for the overall reactions in parts a and b above.
  - Which process is 'greener'?
  - Are there any other 'green chemistry' issues to be considered other than atom economy, in comparing these two methods of production of nitric acid for environmental sensitivity and sustainability?
- 10** What are the individual oxidation number changes in nitrogen taking place in the conversion of atmospheric nitrogen into nitric acid during the Haber process followed by the Ostwald processes?
- 11** The final step of the Ostwald process and the contact process involve the reaction of an oxide with water to produce a solution of the appropriate acid:



- a** Compare the change in the oxidation number of nitrogen and the oxidation number of sulfur in these two processes.
- b** Compare these two processes in terms of the industrial conditions that are used in each reaction and account for the differences between the two.
- 12 a** Why would using a powdered catalyst rather than large lumps of a catalyst in a reaction produce a faster chemical reaction?
- b** In both the Haber process and the contact process the catalyst used is in the form of pellets or hollow cylinders. Why are powdered catalysts not used in these industrial reactions?
- 13** The synthesis gas that is formed in the first stages of the Haber process is a mixture of carbon monoxide, carbon dioxide and hydrogen. This mixture can be used industrially to produce methanol according to the following equations:

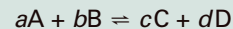


- a** What conditions would you choose for the best yield from these two reactions? Explain your choice of conditions.
- b** What conditions would you choose for the fastest rate of reaction? Explain your choice of conditions.
- c** The industrial production of methanol from synthesis gas involves a catalysed reaction at relatively low pressure and a temperature between 200°C and 300°C. Explain the reasons why these conditions are chosen.
- d** Suggest what type of element might be involved in the catalyst that is used and draw and label an energy profile diagram to show how a catalyst affects the reaction.

## MAJOR IDEAS

- The rate of a reaction can be determined by measuring the change in the amount of one of the reactants or one of the products of the reaction, in a given time interval.
- Reaction rate = 
$$\frac{\text{change in quantity of reactant (or product) in the time interval}}{\text{time interval}}$$
- The slope of a graph of quantity of reactant or product versus time at any particular time gives the reaction rate at that time.
- According to the collision theory, for a reaction to occur:
  - the reactant particles must collide
  - the reacting particles must collide with sufficient energy to react, i.e. with the required activation energy
  - on collision, the particles must have the correct orientation.
- Activation energy is the minimum energy required by colliding particles for a reaction to occur.
- The transition state, or activated complex, in a reaction:
  - is the highest potential energy state for the reacting system
  - corresponds to some stage in the reaction at which bond breaking and bond formation are taking place
  - is unstable, having no more than a temporary existence.
- The potential energy of a reacting system changes during the reaction, as shown in Figures 6.2 and 6.3.
- The activation energy of the forward reaction is the energy difference between the transition state and the reactants.
- The change in enthalpy,  $\Delta H$ , of a reaction is the difference in enthalpy (potential energy) between the products and the reactants.
- For an exothermic reaction:
  - the products have less potential energy than the reactants
  - $\Delta H$  is negative (energy of products – energy of reactants)
  - the temperature of the surroundings increases.
- For an endothermic reaction:
  - the products have more potential energy than the reactants
  - $\Delta H$  is positive
  - the temperature of the surroundings decreases.
- Spontaneous reactions at room temperature tend to have small activation energies.
- Factors that affect reaction rates are:
  - nature of the reactants—breaking covalent bonds requires more energy, therefore resulting in a slower rate than reactions just involving collision

- concentration of the reactants
- changing the concentration of a solution or partial pressure of a gas—alters the rate of collision of reacting particles
- state of subdivision of the reactants—changing the surface area of the reactants alters the rate of collision of reacting particles
- changing the temperature—alters the average kinetic energy of the particles, therefore changing the number of particles with the required activation energy to react
- using a catalyst—catalysts are not permanently consumed in the reaction. They provide an alternative reaction pathway with a smaller activation energy than the activation energy for the uncatalysed reaction.
- Not all reactions go to completion, because reactions are reversible.
- When a chemical reaction system is at equilibrium:
  - the concentrations of the reactants and products present remain constant with time
  - the rates of the forward and reverse reactions are equal.
- Dynamic equilibrium can also be established in physical systems, for example, equilibrium vapour pressure and saturated solutions.
- The equilibrium law: for any reaction at equilibrium, for example, for the general reaction:



the fraction  $\frac{[C]^c [D]^d}{[A]^a [B]^b}$  has a constant value, the equilibrium constant ( $K$ ), at a particular temperature.

The equilibrium law expression does not include substances that are solids or pure liquids.

- An equilibrium constant:
  - is a constant value for a particular equation representing a reaction at a given temperature
  - changes in value if the temperature of a reaction is changed
  - indicates the extent of the reaction
  - provides no indication of the rate at which the equilibrium position is reached.
- Le Châtelier's principle states:

'If a system at equilibrium is subjected to a change in conditions, the system will adjust to re-establish equilibrium in such a way as to partially counteract (oppose) the imposed change.'
- Equilibrium systems are put out of equilibrium when changes are made that increase or decrease the value of the equilibrium constant expression and alter the forward and/or reverse reaction rates by different degrees.
- Equilibrium systems can be put out of equilibrium by various changes as shown on the next page.

## Change

## Direction favoured to re-establish equilibrium

Increase in concentration or partial pressure of a reactant or product

To decrease the concentration of that reactant or product

Decrease in concentration or partial pressure of a reactant or product

To increase the concentration of that reactant or product

Increase the volume of a gaseous system

To increase the number of gaseous particles

Decrease the volume of a gaseous system

To decrease the number of gaseous particles

Increase the temperature

To decrease the temperature by moving in the endothermic direction

Decrease the temperature

To increase the temperature by moving in the exothermic direction

Add a catalyst

No effect

- When a change is made to an equilibrium system that puts it out of equilibrium, this imposed change is only partially counteracted in the re-establishment of equilibrium.
- Catalysts do not change the position of equilibrium but they allow the system to reach equilibrium quicker.
- When a change has been made, the effect on the rates at the new equilibrium position compared to the rates at the original equilibrium position are summarised below:

## Change made to the system at equilibrium

## Forward and reverse reaction rates at new equilibrium position compared to rates at original position

Reactant or product added

Rates equal but increased

Reactant or product removed

Rates equal but decreased

Volume increased

Rates equal but decreased

Volume decreased

Rates equal but increased

Temperature increased

Rates equal but increased

Temperature decreased

Rates equal but decreased

Catalyst added

Rates equal but increased

- In industrial chemical processes, the maximum yield of product for the minimum cost is sought. Factors affecting reaction rates, equilibrium and economics have to be considered in planning industrial processes and chemical plants. Because factors affecting reaction rates and equilibrium are sometimes in conflict, a compromise set of conditions may be needed in which a reasonable yield is obtained at a satisfactory rate and cost.

## QUESTIONS

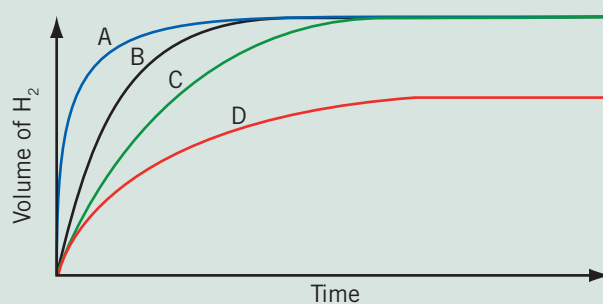
- 1 Under conditions when it is not possible to light a fire, one of the ways to provide hot food is by the reaction of magnesium and water:



$$\Delta H = -352.6 \text{ kJ}$$

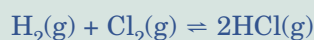
The food is stored in a bag made of aluminium and plastic. This food bag is then placed in a second bag that contains magnesium powder. A small amount of water is added to begin the heating process.

- Would it be safe to seal the outer bag to 'keep the heat in'? Explain your answer.
  - Why did the bag contain powdered magnesium and not just a strip of magnesium?
  - If the bag contains 23 g of magnesium and 20 mL of water was added, how much heat would be produced?
  - Draw an energy level diagram for the reaction.
- 2 Figure 6.1 (at the beginning of the chapter) shows a mixture of hydrogen and oxygen in a balloon both before and after ignition. Explain, in terms of the collision theory, why:
- the mixture of the two gases is reasonably stable at room temperature
  - lighting the mixture with a burning match results in a reaction between the two gases
  - the burning reaction continues, without any additional heating, until one of the reactants is completely consumed.
- 3 The four different experiments, involving the reaction of zinc with some hydrochloric acid, described on the next page, were carried out and the volume of hydrogen produced was measured over time. The results obtained are shown in the graphs below.



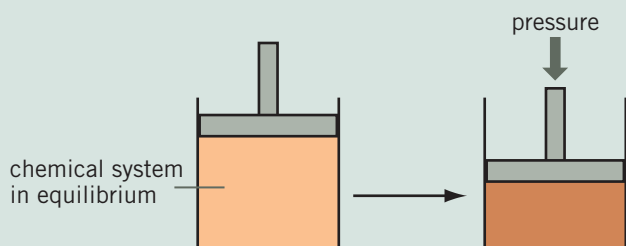
Experiment	Mass and type of zinc used	Volume and concentration of HCl(aq)	Temperature	Presence of catalyst
1	7 g granulated zinc (lumps)	200 mL of 1 mol L <sup>-1</sup> HCl	25°C	No
2	7 g powdered zinc	200 mL of 1 mol L <sup>-1</sup> HCl	25°C	No
3	7 g powdered zinc	200 mL of 1 mol L <sup>-1</sup> HCl	85°C	No
4	7 g granulated zinc	150 mL of 1 mol L <sup>-1</sup> HCl	25°C	No

- a Decide which graph was obtained for each experiment.
- b Explain in terms of the collision theory why the shapes are different for these experiments.
- 4 What will happen to the amount in mole of chlorine, in equilibrium with hydrogen and hydrogen chloride in the reaction:



when the following changes are made to equilibrium mixtures (assuming the volume and temperature remain constant)?

- a Hydrogen gas is added.
- b A small amount of water is added (assume HCl is much more soluble in water than Cl<sub>2</sub>).
- c Hydrogen gas is removed.
- d Some gaseous ethene is added. Ethene undergoes an addition reaction with chlorine.
- e Argon gas (a noble gas) is added.
- 5 For each of the following reactions, state the effect on the concentration of the bold substance if the equilibrium system is subjected to an increase in temperature.
- a **N<sub>2</sub>(g)** + 3H<sub>2</sub>(g) ⇌ 2NH<sub>3</sub>(g); ΔH = -92 kJ
- b 2H<sub>2</sub>O(g) ⇌ 2H<sub>2</sub>(g) + **O<sub>2</sub>(g)**; ΔH = +110 kJ
- c H<sub>2</sub>(g) + Cl<sub>2</sub>(g) ⇌ **2HCl(g)**; ΔH = -57 kJ
- 6 Various syringes were fitted with freely moving pistons. Each syringe contained a chemical system that had been allowed to come to equilibrium at room temperature. A greater pressure was then exerted on each syringe.



In which of the following equilibrium systems would this increase in pressure cause less products to be formed?

- a CaCO<sub>3</sub>(s) ⇌ CaO(s) + CO<sub>2</sub>(g)
- b CO(g) + H<sub>2</sub>O(g) ⇌ CO<sub>2</sub>(g) + H<sub>2</sub>(g)
- c 4NH<sub>3</sub>(g) + 5O<sub>2</sub>(g) ⇌ 4NO(g) + 6H<sub>2</sub>O(g)
- d 2NO<sub>2</sub>(g) ⇌ N<sub>2</sub>O<sub>4</sub>(g)
- 7 The dissociation of carbonyl bromide is given by the following equation:



Predict in each case whether the amount of carbonyl bromide is increased, decreased or unaffected in the equilibrium mixture if:

- a carbon monoxide is added to the reaction vessel at constant volume and temperature
- b the temperature is increased, at constant volume
- c a catalyst is added
- d ethene is introduced to the flask at constant volume and temperature. Ethene reacts with bromine
- e the equilibrium gas mixture in the reaction flask is allowed to expand by opening a tap leading to an evacuated second vessel of the same volume. The temperature is allowed to return to the original temperature.
- 8 Iodine monochloride, ICl, is a brown liquid. It reacts with chlorine gas to form a yellow, crystalline compound, iodine trichloride, ICl<sub>3</sub>. All three species exist in an equilibrium mixture in a container:



- a If the lid of the container is left off, explain why the yellow crystals start to disappear.
- b If more chlorine gas is pumped into the container will the amount of brown liquid present increase, decrease or remain unchanged, as equilibrium is re-established?

- c If the volume of the container is suddenly decreased, will the amount of brown liquid increase, decrease or remain the same, as equilibrium is re-established?
- d If the volume of the container is increased, will the concentration of  $\text{Cl}_2$  be larger, smaller or unchanged (compared to before the volume change) when the system reaches equilibrium again?
- e Explain why, if a little more yellow solid is added to the container, the amount of brown liquid present does not change.

9 Write the equilibrium law expressions for the following reactions.

- a  $2\text{Hg}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{HgO}(\text{s})$
- b  $\text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HSO}_3^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- c  $2\text{H}_2\text{S}(\text{g}) + 3\text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g}) + 2\text{SO}_2(\text{g})$

10 At elevated temperatures HI decomposes to form hydrogen gas and iodine vapour:



Iodine vapour is violet, whereas HI is colourless.

- a How will a student recognise that the system has reached equilibrium?
- b Would a measurement of gas pressure at constant volume and temperature be a suitable technique for determining whether equilibrium has been established? Briefly explain your answer.
- c At  $500^\circ\text{C}$ , 2.0 mol of HI was injected into an empty 1 L container. Equilibrium was established in 1 hour and 1.20 mol of HI was found to be present in the equilibrium mixture. The equilibrium mixture was left undisturbed in the container for the next 30 minutes.  
Sketch a graph of concentration against time for this system, showing how the concentrations of HI,  $\text{H}_2$  and  $\text{I}_2$  changed during the  $1\frac{1}{2}$  hour interval.
- d The enthalpy change ( $\Delta H$ ) for the reaction is +10 kJ. How will the value of the equilibrium constant ( $K$ ) change (increase, decrease or remain the same) if the temperature is increased?
- e If a catalyst is included with the HI at the beginning of the reaction, how will the value of the equilibrium constant ( $K$ ) be affected (increase, decrease or remain the same)?

11 Is the following statement true or false?

'Reactions with large equilibrium constants are very fast.'

Explain your answer.

12 The equilibrium  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$  is established in a closed vessel of fixed volume at  $25^\circ\text{C}$ , and the concentration of  $\text{N}_2\text{O}_4$  is  $0.001 \text{ mol L}^{-1}$  at equilibrium.

The temperature is raised to  $65^\circ\text{C}$ , and when equilibrium is re-established the concentration of  $\text{N}_2\text{O}_4$  is  $0.0001 \text{ mol L}^{-1}$ .

Which of the following statements may be deduced from the data given?

- a The equilibrium constant at  $25^\circ\text{C}$  is  $1 \times 10^3$ .
- b The forward reaction is exothermic.
- c The reverse reaction is exothermic.
- d The rate of attainment of equilibrium in this system is very low.
- 13 A catalyst cannot affect the position of equilibrium. Why was the discovery of an appropriate catalyst vital for use in the Haber process for ammonia production?
- $$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$
- 14 In section 6.5 environmental and safety issues associated with the production of ammonia were detailed. Undertake a similar analysis of the environmental and safety issues associated with the production of nitric acid in the Ostwald process and sulfuric acid in the contact process.
- 15 Two important industrial reactions are the dehydrogenation of ethane,  $\text{C}_2\text{H}_6$ , and the reaction of carbon monoxide with hydrogen to produce methanol,  $\text{CH}_3\text{OH}$ . The first is an endothermic reaction that produces ethene,  $\text{C}_2\text{H}_4$ , while the second reaction liberates heat energy.
- a Write balanced equations for these two reactions.
- b Write the equilibrium law expression for each reaction.
- c Use collision theory and Le Châtelier's principle to predict the conditions necessary for the fastest reaction and the maximum yield.

- 16** The Fischer–Tropsch synthesis of petroleum-based liquids has been known since the 1920s. More recently it has been proposed as an option in the conversion of coal into petroleum. In its original form the synthesis involved the reaction of carbon monoxide with hydrogen in the presence of a catalyst based on iron oxide. A recent speculative hypothesis suggests that petroleum might be naturally synthesised from carbon monoxide and carbon dioxide in the presence of hydrogen during tectonic plate activity when these gases are subjected to high temperatures and pressures in the presence of iron-based minerals in the molten magma.
- Assuming that the starting materials in the Fischer–Tropsch synthesis are carbon monoxide and hydrogen, write an equation for the equilibrium between these two gases producing octane,  $C_8H_{18}$ . What is the likely other product of the reaction?
  - Write the equilibrium law expression for this reaction.
  - What pressure conditions would favour the formation of octane in this reaction? Are these conditions present in tectonic plates?
  - According to the chemical literature the use of high temperatures favours a faster reaction and a higher conversion to products for this reaction. What further information does this reveal about the equation that you generated in part a?
  - In practice the reaction is carried out at  $200^\circ\text{C}$  over an iron–cobalt catalyst and then the mixture is rapidly cooled to room temperature. Considering the nature of the reactants and products discuss why this rapid cooling might be employed in a commercial synthesis.



## Unit 3A Review Questions

## \*PART A: MULTIPLE-CHOICE QUESTIONS

1 How many protons and electrons are in a sulfite ion?

- A 24 protons, 26 electrons  
 B 24 protons, 22 electrons  
 C 40 protons, 42 electrons  
 D 48 protons, 50 electrons

2 Consider the elements in the table.

Element	Q	R	X	T	Z
Group in periodic table	1	2	14	16	17

The compound which is most likely to be a non-conductor of electricity in the molten state is:

- A  $XZ_4$   
 B RT  
 C  $RZ_2$   
 D QZ

3 Which of the following is a list of substances in the solid state that have a crystalline structure made up of discrete molecules?

- A phosphorus pentoxide, sulfur dioxide, silicon dioxide  
 B iodine, magnesium, oxygen  
 C carbon dioxide, zinc oxide, hydrogen chloride  
 D silicon tetrachloride, chlorine, sulfur dichloride

4 The angle between N-F bonds in a molecule of  $NF_3$  would be closest to:

- A  $90\frac{1}{4}$   
 B  $109.5\frac{1}{4}$   
 C  $120\frac{1}{4}$   
 D  $180\frac{1}{4}$

5 Consider the following compounds:

methanol	$CH_3OH$
ethane	$C_2H_6$
fluoromethane	$CH_3F$
methanamine	$CH_3NH_2$

The order of increasing boiling points for these compounds is:

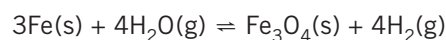
- A ethane < methanamine < methanol < fluoromethane  
 B fluoromethane < methanol < methanamine < ethane  
 C ethane < methanol < methanamine < fluoromethane  
 D ethane < fluoromethane < methanamine < methanol

6 The rates of all chemical reactions increase with a rise in temperature. Which of the following comments about this statement is correct?

This statement is:

- A true, since the activation energies of all reactions increase with a rise in temperature  
 B false, since the rate of an endothermic reaction decreases with a rise in temperature  
 C true, since a greater proportion of molecular collisions will result in a reaction  
 D false, since the equilibrium constant for a reaction is independent of the temperature.

7 Which is the correct equilibrium constant expression for the following equation?



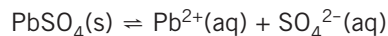
- A  $\frac{[Fe_3O_4][H_2]}{[Fe][H_2O]}$   
 B  $\frac{[Fe_3O_4][H_2]^4}{[Fe]^3[H_2O]}$   
 C  $\frac{[Fe_3O_4] + 4[H_2]}{3[Fe] + 4[H_2O]}$   
 D  $\frac{[H_2]^4}{[H_2O]^4}$

8 Which of the following is/are affected by the addition of a catalyst to a reaction?

- i the activation energy  
 ii the enthalpy change  
 iii the reaction mechanism  
 iv the equilibrium constant

- A i only  
 B i and iii only  
 C i, ii and iii only  
 D i, ii, iii and iv

9 A solution of lead sulfate was prepared using a slight excess of lead sulfate so that some remained undissolved. The following equilibrium was established in the flask:



A small amount of  $10 \text{ mol L}^{-1}$  sulfuric acid was then added to the flask. Which statement best describes what happens after this addition?

- A No change is observed.
- B More lead sulfate is precipitated.
- C Some lead sulfate dissolves.
- D The concentration of lead ions increases.

10 Hydrogen bromide has a low melting point because it consists of:

- A oppositely charged ions bonded by weak electrostatic attractive forces
- B positive ions electrostatically attracted to delocalised electrons
- C non-metal atoms covalently linked in a lattice
- D molecules linked by weak intermolecular attractive forces.

11 The formation of methanol from hydrogen and carbon monoxide can be represented by:



Decreasing the temperature of this equilibrium system will:

- A decrease the rate of the forward reaction and increase the rate of the reverse reaction
- B decrease the rate of the forward reaction to a greater extent than it will decrease the rate of the reverse reaction
- C decrease the rate of the reverse reaction to a greater extent than it will decrease the rate of the forward reaction
- D decrease the rate of only the forward reaction.

12 Which of the following statements about the trends down group 17 in the periodic table is false?

- A The boiling points of the hydrides decrease.
- B The electronegativities decrease.
- C The first ionisation energies decrease.
- D The strengths of the dispersion forces between the molecules of the elements increase.

13 A substance contains polar molecules, has intramolecular covalent bonding and exhibits intermolecular hydrogen bonding. Of the following it could only be:

- A  $\text{CHF}_3\text{(g)}$
- B  $\text{H}_2\text{(g)}$
- C  $\text{NH}_3\text{(l)}$
- D  $\text{KOH(s)}$

14 One mole of sulfur dioxide and one mole of carbon dioxide have an equal:

- i mass
- ii number of molecules
- iii number of atoms
- iv number of electrons.

Which of these alternatives are correct?

- A ii, iii and iv
- B i and iii
- C i, ii and iii
- D ii and iii

15 The atomic weight of thallium is given in a chemical data book as 204.37. This means that:

- A the weighted average mass of thallium atoms, relative to carbon-12, is 204.37
- B each atom of thallium has a mass of 204.37 g
- C all the isotopes of thallium have a mass of 204
- D the mass of one mole of the most common isotope of thallium is 204.37 g.

16 Two colourless liquids were mixed and a white precipitate formed. The two colourless liquids may have been:

- A a solution of sodium hydroxide and a solution of iron(III) chloride
- B water and hexane
- C a solution of calcium chloride and a solution of sodium carbonate
- D a solution of magnesium nitrate and a solution of potassium sulfate.

17 What volume would 0.400 g of sulfur dioxide occupy at  $26\frac{1}{4}^\circ\text{C}$  if its pressure was 150 kPa?

- A 0.00900 L
- B 0.104 L
- C 6.63 L
- D 2330 L

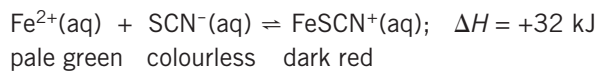
18 Which of the following does *not* have the electron configuration of 2, 8, 8?

- A Ar
- B  $\text{Ca}^{2+}$
- C Cl
- D  $\text{P}^{3-}$

19 If 150 mL of water was added to 200 mL of  $0.239 \text{ mol L}^{-1} \text{ AlCl}_3$  solution, the concentration of chloride ions in the final solution would be:

- A 0.137 mol L<sup>-1</sup>  
 B 0.358 mol L<sup>-1</sup>  
 C 0.410 mol L<sup>-1</sup>  
 D 0.717 mol L<sup>-1</sup>

20 Consider the following system at equilibrium:



Which of the following changes made to this equilibrium system will cause the mixture to be darker red in colour at the new equilibrium position compared to the colour at the original equilibrium position?

- A The volume of the solution is doubled by adding water.  
 B The temperature is decreased.  
 C A few drops of a concentrated solution of NaSCN are added.  
 D A few drops of a concentrated solution of NaOH are added.

## PART B: SHORT-ANSWER QUESTIONS

1 Choose an example of a molecule or an ion from the list provided that matches each of the descriptions given below. While there may be more than one molecule or ion that matches the description, only one example for each description is required.



- a A non-polar tetrahedral species  
 b A polar linear species  
 c A V-shaped, or bent, polar species  
 d A species that contains both polar and non-polar covalent bonds  
 e A non-polar trigonal planar species  
 f A species that can form hydrogen bonds between its molecules
- 2 The successive ionisation energies of three elements, with fictitious symbols, are given in the table below.

Element	Successive ionisation energies (MJ mol <sup>-1</sup> )							
	I	II	III	IV	V	VI	VII	VIII
A	1.018	1.909	2.918	4.963	6.280	21.275	25.404	26.861
D	0.744	1.457	7.7739	10.547	13.636	18.001	21.710	25.663
E	0.793	1.583	3.238	4.362	16.098	19.791	23.793	29.259

- a Explain why, for each of these elements, their second ionisation energy is greater than their first ionisation energy.  
 b To which group in the periodic table would you expect element E to belong?  
 c If element D reacts with chlorine to form a compound, what formula would you expect this compound have?  
 d How many valence electrons would you expect element A to have?

3 What type or types of weak bonding exist between the molecules in the following substances?

- a nitrogen, N<sub>2</sub>  
 b SF<sub>2</sub>  
 c CH<sub>3</sub>F  
 d SiH<sub>4</sub>  
 e CH<sub>3</sub>NH<sub>2</sub>  
 f SO<sub>2</sub>

4 Mercury, at high levels, may damage the brain, kidneys, and developing foetus. In drinking water, the safety limit set by most countries is  $2 \cdot 10^{-3}$  parts of mercury per million parts of drinking water ( $2 \cdot 10^{-3}$  ppm). How many atoms of mercury would there be in 1 L of water with this safe concentration? (Assume the density of the water is 1 g mL<sup>-1</sup>.)

5 Propose explanations for the following observations.

- a Iodine monochloride, ICl, has a lower melting point (27¼C) than iodine monobromide, IBr (42¼C).  
 b Hydrogen fluoride, HF, is a liquid at 10¼C but fluorine, F<sub>2</sub>, is a gas.  
 c Lithium chloride, LiCl, has a melting point of 610¼C, but tetrachloromethane, CCl<sub>4</sub>, has a melting point of -23¼C.  
 d The boiling point (118¼C) of acetic acid, CH<sub>3</sub>COOH, is higher than that of butane, C<sub>4</sub>H<sub>10</sub> (-1¼C), yet lower than that of trichloroacetic acid, CCl<sub>3</sub>COOH (198¼C).  
 e Ethane, C<sub>2</sub>H<sub>6</sub>, and hexane, C<sub>6</sub>H<sub>14</sub>, are both hydrocarbons yet ethane is a gas at room temperature but hexane is a liquid.

6 Draw up the following table in your book.

	Solute	Solvent	Type(s) of bonds that need to be broken	Type of bond that can form between solute and solvent	Will the solute dissolve in the solvent?
a	Methanol, CH <sub>3</sub> OH	Water			
b	CF <sub>4</sub>	Water			
c	Iodine, I <sub>2</sub>	Kerosene, a hydrocarbon			

Fill in the gaps, naming the types of bonds that need to be broken and the type of bonds that could form when the solute/solvent pairs are mixed. Use this information to then predict whether or not you would expect the solute to dissolve in the solvent.

7 Explain, in terms of the collision theory, why even though paper is made from wood, paper burns much more readily than a piece of wood.

8 Hydrogen peroxide decomposes slowly to form oxygen gas and water. However, in the presence of small pieces of sheep liver, it bubbles rapidly because of the catalytic effect of certain liver enzymes.

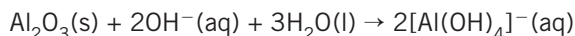
- Explain, in terms of the collision theory, how a catalyst can increase the rate of a reaction.
- Why do living things only require small amounts of each of the different types of enzymes necessary to carry out life-sustaining chemical reactions?

9 Aluminium occurs naturally on Earth as its oxide in deposits of the mineral bauxite, and it is from this ore that the metal is extracted. The bauxite mined at Weipa, Western Australia, contains 71.0%, by mass, aluminium oxide.

Aluminium production involves two main steps:

**Step 1** Purification of the ore

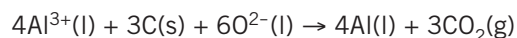
The bauxite is added to hot sodium hydroxide solution and the resultant mixture is allowed to settle. The solution from this mixture is then cooled and seeded to form crystals. The crystals are isolated and heated strongly to form pure aluminium oxide. The reactions involved in these processes are:



This purification process is 89.0% efficient.

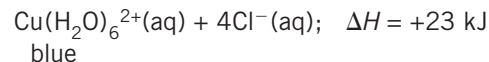
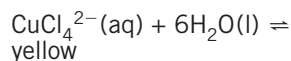
**Step 2** Electrolytic reduction of Al<sub>2</sub>O<sub>3</sub>

The pure aluminium oxide is dissolved in molten cryolite and, using carbon electrodes, an electric current is passed through the hot solution to form aluminium:



This reduction process is 96.0% efficient.

- Calculate the mass of aluminium expected to form from 4.00 tonnes of bauxite mined at Weipa.
  - Would you expect aluminium oxide to have a high or low melting point? Explain your answer in terms of the bonding in this compound.
  - Explain why aluminium oxide needs to be in the liquid state before an electric current can be passed through it.
  - The tetrahydroxyluminate complex ion, [Al(OH)<sub>4</sub>]<sup>-</sup>, exhibits two types of bonding (apart from dispersion forces). Describe these two types of bonding and draw a structural formula of the complex ion showing where the two types of bonding are in the species.
- 10 A solution of copper ions in hydrochloric acid usually has a green colour owing to the existence of the complex [CuCl<sub>4</sub>]<sup>2-</sup>(aq), which is yellow, in equilibrium with [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>(aq), which is blue:



If the following changes are made to the green equilibrium mixture, state what will happen to the colour of the solution.

- A few drops of concentrated HCl are added.
- Water is added so that the volume is doubled.
- The mixture is gently heated.

Experiment	Temperature (°C)	[COCl <sub>2</sub> ] at equilibrium (mol L <sup>-1</sup> )	[CO] at equilibrium (mol L <sup>-1</sup> )	[Cl <sub>2</sub> ] at equilibrium (mol L <sup>-1</sup> )	Equilibrium constant
1	400	1.770	0.061	0.061	0.021
2	600	1.426	0.217	0.217	0.033
3	900	0.559	0.214	0.214	0.082

- 11** The gas phosgene, COCl<sub>2</sub>, decomposes into the gases carbon monoxide and chlorine, establishing the equilibrium:



In a series of experiments, data shown in the table above were obtained at a pressure of 2 atmospheres.

- a** The pressure of the Experiment 3 equilibrium mixture is increased to 4 atmospheres by decreasing the volume, and the reaction is allowed to reach equilibrium again.  
At the new equilibrium position, will the equilibrium constant and the masses of each of the three substances have increased, decreased or remained unchanged?
- b** Suppose a new sample of the gas mixture is taken. What is the value of the equilibrium constant at 600°C if the equilibrium concentration of CO is 0.420 mol L<sup>-1</sup>?
- c** Is the forward reaction of COCl<sub>2</sub>(g) ⇌ CO(g) + Cl<sub>2</sub>(g) exothermic or endothermic?
- 12** The following table contains information about the melting points and solubilities in water of some compounds.

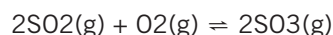
Compound	Melting point (°C)	Solubility in water
Ethanol	-114	Soluble
Butan-1-ol	-89	Slightly soluble
Butane	-138	Insoluble
Iodine	114	Insoluble
Sodium iodide	660	Soluble

Discuss the intermolecular and interionic forces involved in each of the substances, and so account for the melting points and solubilities.

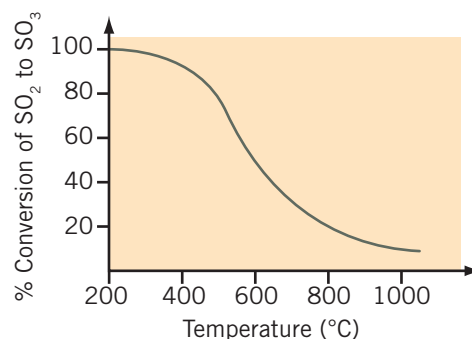
- 13** In a reaction between lead nitrate solution and sodium iodide solution, lead iodide is precipitated as a yellow solid. 108 mL of 0.823 mol L<sup>-1</sup> lead nitrate solution is mixed with 145 mL of 0.722 mol L<sup>-1</sup> sodium iodide solution.
- a** Write an ionic equation for the precipitation reaction.
- b** What mass of lead iodide is precipitated?

- c** What is the concentration of each of the four ions (lead, nitrate, sodium and iodide ions) in the final reaction mixture?

- 14** A 1.000 g sample which contained 65.00% by mass of Na<sub>2</sub>SO<sub>4</sub> and 35.00% by mass of another metal sulfate, MSO<sub>4</sub>, is dissolved in water and the sulfate ions are precipitated as BaSO<sub>4</sub>. If the precipitate weighs 1.6090 g, what is the relative atomic mass of M?
- 15** The conversion of sulfur dioxide to sulfur trioxide is a vital reaction in the production of sulfuric acid:



The graph shown below describes the % conversion/temperature relationship for this reaction, the pressure being maintained at 1 atmosphere. Considering this data, discuss the optimal operating conditions (temperature, pressure and use of catalyst) for the industrial production of sulfur trioxide from sulfur dioxide.





# 7

## Acids and bases in aqueous solution

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

- explain the self-ionisation of water by applying an understanding of electrolytes
- explain and apply the Arrhenius and Brønsted–Lowry models to describe acid and bases
- explain the differences between weak and strong acids and bases in solution
- explain what polyprotic acids are
- calculate pH values of solutions and mixtures of solutions
- describe the effect temperature change has on pH
- predict and explain the acidic or basic nature of salts
- describe and explain the conjugate nature of buffer solutions
- use Le Châtelier's principle to explain how a buffer resists pH changes
- explain how the buffering capacity of a buffer can be changed.

What do citrus fruits, car batteries, carbonated soft drinks, dental decay, indigestion, yoghurt and *trans* fats have in common? All contain or are associated with substances called acids.

Bases such as sodium hydroxide and ammonia are used for cleaning, calcium hydroxide is used in water and sewage treatment, the weakly basic sodium hydrogencarbonate,  $\text{NaHCO}_3$ , is used in cooking and to relieve indigestion, while sodium carbonate is used, among other things, to remove hardness from water.

The survival of animal and plant life in an aquatic environment, the ability to get oxygen to cells in the body for respiration, and the rate at which metals are corroded are all influenced by the presence of acids or bases in solution.



Figure 7.1 (a) Acids and (b) bases associated with a modern lifestyle

## 7.1 What are acids and bases?

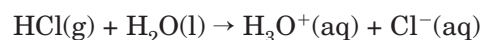
### Electrolytes

One characteristic acids and bases share is that when they form aqueous solutions, these solutions conduct electricity. Any substance that conducts electricity when dissolved in water is called an electrolyte. For example, sodium chloride dissociates (breaks apart) in water to form a conducting solution:



Consequently, sodium chloride is an electrolyte. Molten electrolytes are also possible, but in this chapter the focus will be on aqueous solutions of electrolytes.

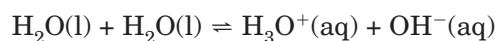
All ionic compounds are electrolytes, but not all electrolytes are ionic compounds. Hydrogen chloride is a covalent molecular gas at room temperature, but when dissolved in water, it forms a solution that conducts electricity. This conductivity is due to the presence of ions that are formed when hydrogen chloride reacts with water:



Hydrogen chloride is an example of a strong electrolyte because it completely ionises in solution. Ionic compounds are also strong electrolytes.

A weak electrolyte is a substance that produces very few ions in solution. Most of the substance remains as neutral molecules dissolved in the water. Acetic acid,  $\text{CH}_3\text{COOH}$ , and ammonia,  $\text{NH}_3$ , are examples of weak electrolytes. Some substances such as glucose, ethanol and sucrose do not form any ions when they dissolve in water. These are referred to as non-electrolytes.

For acid–base chemistry in aqueous solution, the fact that covalent molecular water itself is a very weak electrolyte is important. The self-ionisation of water is represented as:



The value of the equilibrium constant for this reaction is very small ( $1 \times 10^{-14}$ ) at  $25^\circ\text{C}$ . As a result the concentration of ions in pure water is very small.

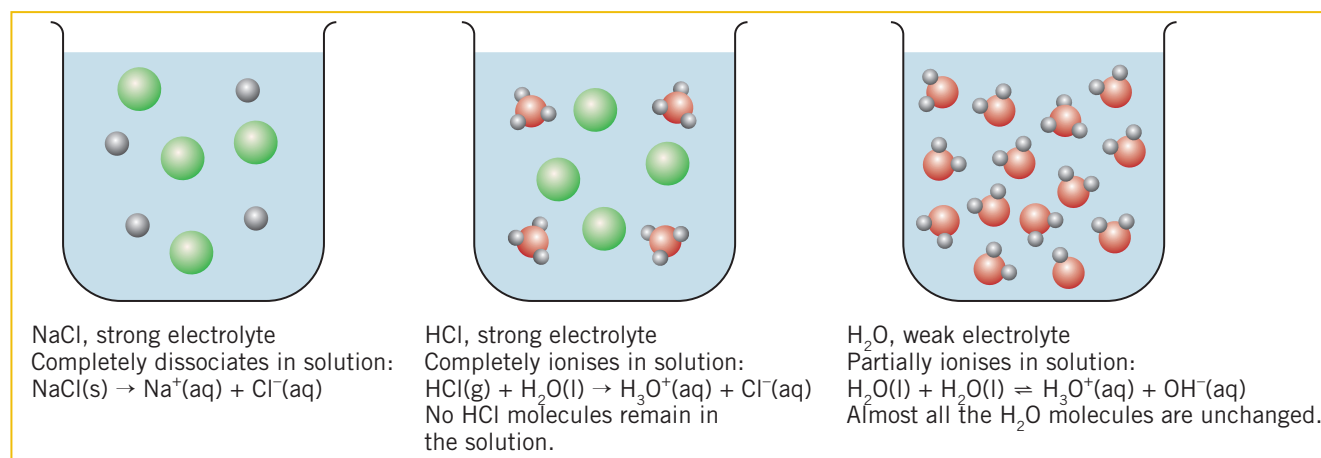


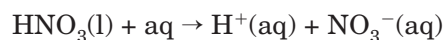
Figure 7.2 Differences between the solutions of strong and weak electrolytes

## Arrhenius acid–base theory

In the 17th century Robert Boyle described acids as a group of substances that tasted sour, and changed the colour of certain dyes (indicators) such as litmus. He also noted that acids were corrosive, but in the presence of certain other substances (now known as bases), the effect of the acid was reduced or reversed.

It was not until over 200 years later that Svante Arrhenius provided a definition of acids and bases in terms of the ions they produce in the presence of water. According to Arrhenius, acids are substances that produce hydrogen ions,  $\text{H}^+$ , when dissolved in water and bases are substances that produce hydroxide ions,  $\text{OH}^-$ , when dissolved in water.

Nitric acid,  $\text{HNO}_3$ , can be classified as an Arrhenius acid. When the pure liquid is dissolved in water, it reacts to produce a solution containing hydrogen ions and nitrate ions:



As a dilute solution, nitric acid is one of the acids present in acid rain.

Calcium hydroxide may be added to water sources to reduce the amount of acid present. When calcium hydroxide is added to water, it dissociates into separate calcium and hydroxide ions. Because it produces hydroxide ions in solution, it is an Arrhenius base:



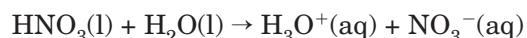


## Brønsted–Lowry acid–base theory

A major limitation to the Arrhenius theory is that the acid–base definition is restricted to aqueous solutions. In 1924 Johannes Brønsted and Thomas Lowry independently came up with a more general definition that is now known as the Brønsted–Lowry theory of acids and bases.

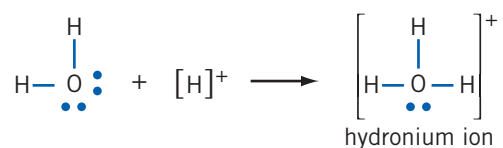
In the Brønsted–Lowry theory an acid is a substance that donates a hydrogen ion,  $\text{H}^+$  (proton), and a base is a substance that accepts a hydrogen ion. This definition links acids with bases and requires that if any substance behaves as an acid, there must also be a base present in the reaction. When an acid reacts with a base, the acid donates its hydrogen ion to the base in the overall chemical reaction.

Thus the reaction of nitric acid with water under the Brønsted–Lowry definition would be represented as:



with the  $\text{HNO}_3$  acting as the acid and the  $\text{H}_2\text{O}$  acting as the base. When the  $\text{HNO}_3$  molecule donates an  $\text{H}^+$  ion it produces the nitrate ion,  $\text{NO}_3^-$ , and when the  $\text{H}_2\text{O}$  molecule accepts the  $\text{H}^+$  ion, it forms the hydronium ion,  $\text{H}_3\text{O}^+$ .

The hydronium ion,  $\text{H}_3\text{O}^+$ , forms when the  $\text{H}^+$  from the acid interacts with the non-bonding electrons on an  $\text{H}_2\text{O}$  molecule to form a new covalent bond in which both of the electrons in the bond are provided by the oxygen, as shown in the following electron dot diagram:



The hydronium ion can also hydrogen bond strongly to other water molecules, so formulas such as  $\text{H}_5\text{O}_2^+$  and  $\text{H}_9\text{O}_4^+$  represent ions that may also be present in solutions of an acid in water.

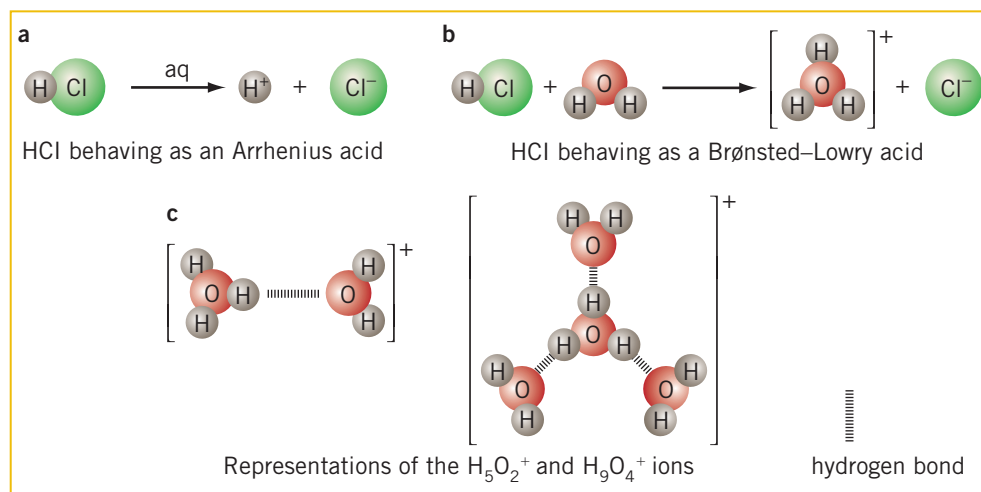


Figure 7.3 (a) An Arrhenius acid; (b) a Brønsted–Lowry acid; (c) the hydrated hydrogen ion in water

The self-ionisation reaction of water introduced earlier is another example of an acid–base reaction according to the Brønsted–Lowry definition:



In this reaction, one  $\text{H}_2\text{O}$  molecule has acted as the Brønsted–Lowry acid and donated an  $\text{H}^+$  ion to the second  $\text{H}_2\text{O}$  molecule. This second  $\text{H}_2\text{O}$  molecule has acted as a Brønsted–Lowry base in accepting the  $\text{H}^+$  ion.

The Brønsted–Lowry theory allows reactions that do not take place in water, but do involve a hydrogen ion transfer, to be classified as acid–base reactions. When ammonia gas and hydrogen chloride gas are brought together, a white solid of ammonium chloride is obtained. The formation of ammonium chloride in this reaction is an acid–base reaction.

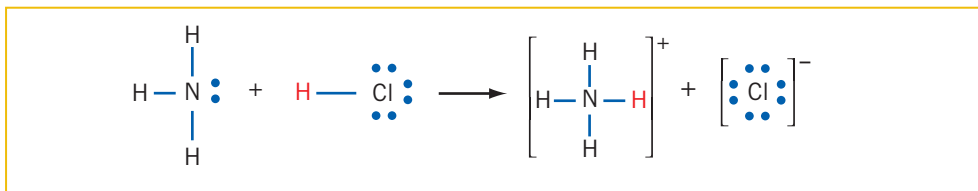
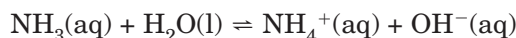


Figure 7.5 Equation for the reaction between ammonia and hydrogen chloride

The HCl molecule has transferred an  $\text{H}^+$  to the lone pair of electrons on the nitrogen to form a new covalent bond in the  $\text{NH}_4^+$  ion. Because HCl has donated an  $\text{H}^+$ , it has acted as the Brønsted–Lowry acid.  $\text{NH}_3$  has accepted this  $\text{H}^+$  and so has acted as the Brønsted–Lowry base.

Ammonia can also accept a hydrogen ion from water in a Brønsted–Lowry acid–base reaction:



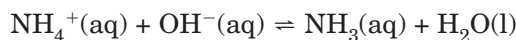
The equilibrium arrows,  $\rightleftharpoons$ , show that in this case the reaction is not complete and most of the ammonia molecules remain unreacted; they are just simply dissolved in the water. In this reaction, ammonia is the base and water is the acid. (Equilibrium reactions of acids and bases in aqueous solution are discussed in more detail in section 7.2.)



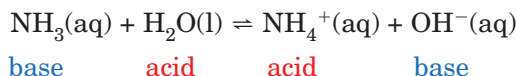
Figure 7.4 Reaction of ammonia gas with hydrogen chloride gas, diffusing from the bottles, to give a white smoke of ammonium chloride. (Note that the name ammonium hydroxide on the bottle is usually written as ammonia solution.)

## Conjugate acids and bases

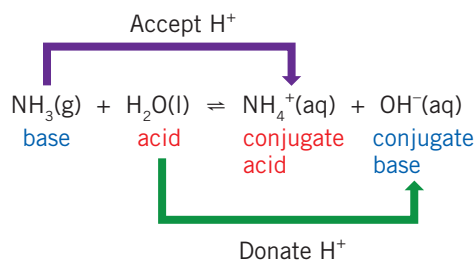
The last equation showing the reaction of ammonia with water shows that the reverse of a Brønsted–Lowry acid–base reaction is also an acid–base reaction. If a base such as sodium hydroxide is added to a solution of an ammonium salt, ammonia is produced. The ammonium ion donates a hydrogen ion to the hydroxide ion to produce ammonia and water:



The two acids and two bases present in the reaction are shown in the equation below:



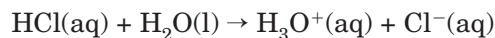
Ammonia,  $\text{NH}_3$ , and the ammonium ion,  $\text{NH}_4^+$ , differ by an  $\text{H}^+$  ion and are called a conjugate acid–base pair. Similarly, the water and the hydroxide ion are a conjugate acid–base pair. The term ‘conjugate acid–base pair’ is given to any pair of substances whose formulas differ by one hydrogen ion,  $\text{H}^+$ :



## Strength of acids and bases

The strength of an acid or a base is indicated by the position of equilibrium when the acid or base is added to water. If the equilibrium constant for the production of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  is large, then the substance is described as a strong acid or base.

Hydrogen chloride is a strong acid because the reaction of hydrogen chloride with water is complete (the equilibrium constant is very large):



There is no evidence that any HCl molecules remain as neutral dissolved molecules in the solution. Since the reverse reaction involving the  $\text{Cl}^-$  ion behaving as a base does not occur to any significant extent, the  $\text{Cl}^-$  ion, which is the conjugate base of HCl, is regarded as a very weak base.

In general, the more readily an acid donates a hydrogen ion, the less likely its conjugate base will accept a hydrogen ion, so a strong acid will have a very weak conjugate base. Similarly, a strong base, such as the hydroxide ion,  $\text{OH}^-$ , accepts hydrogen ions readily so its conjugate acid ( $\text{H}_2\text{O}$ ) is an extremely weak acid.

The strong acids include hydrochloric acid, nitric acid and sulfuric acid, while the strong bases include the oxides and hydroxides of groups 1 and 2 metals.

Figure 7.6 shows the relative strengths of a number of common acids and bases. While a strong acid or base will have a conjugate that is very weak, it is not true that a weak acid or base necessarily has a conjugate that is strong. For example, ammonia,  $\text{NH}_3$ , is a weak base and its conjugate acid,  $\text{NH}_4^+$ , is also weak. Acetic acid,  $\text{CH}_3\text{COOH}$ , is a weak acid and the acetate ion,  $\text{CH}_3\text{COO}^-$ , its conjugate base, is also weak.

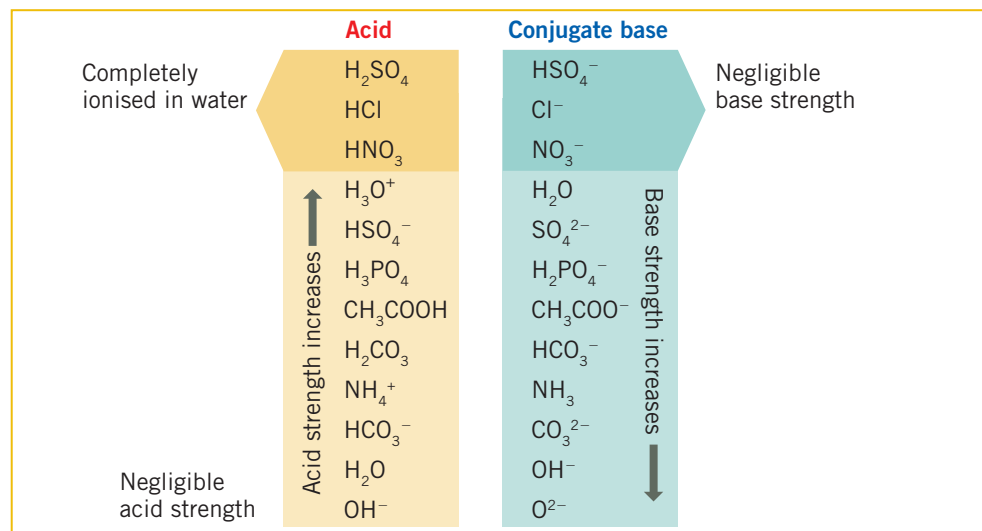
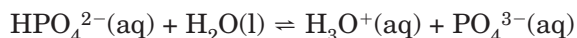
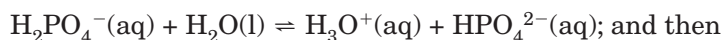
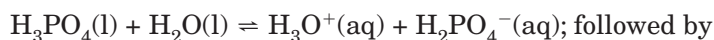
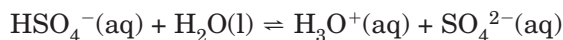
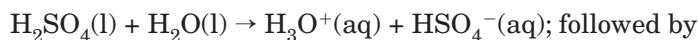


Figure 7.6 Relative strengths of some common acid–base conjugate pairs

If the relative strengths of two acids or bases are known, then the relative strengths of their conjugate pairs can be determined. Since acetic acid is a stronger acid than the ammonium ion, it follows that ammonia must be a stronger base than the acetate ion. Similarly, if the hydrogencarbonate ion is a stronger base than the sulfate ion, then the hydrogensulfate ion must be a stronger acid than carbonic acid ( $\text{H}_2\text{CO}_3$ ).

Acids such as hydrochloric acid and nitric acid that only donate one hydrogen ion (a proton) in an acid–base reaction are called monoprotic acids. However, there are other acids, such as sulfuric acid,  $\text{H}_2\text{SO}_4$ , and phosphoric acid,  $\text{H}_3\text{PO}_4$ , that can donate more than one hydrogen ion. These acids are referred to as multiprotic acids.



Sulfuric acid is an example of a diprotic acid, while phosphoric acid is triprotic. The number of hydrogen ions an acid can donate does not relate to the strength of the acid. Sulfuric acid is a strong acid because the first hydrogen ion is completely donated to water. In other words, every molecule of sulfuric acid that is added to water will react to produce a hydronium ion and a hydrogensulfate ion in solution.

However, the hydrogensulfate ion is a weak acid and so the reaction involving the donation of the second hydrogen ion is not complete. Phosphoric acid is an example of a weak acid because its reaction with water is not complete (the equilibrium constant is not large), as shown by the equilibrium arrows in the equations above.

### \* Review exercise 7.1

- Predict and explain the difference in the electrical conductivity of a solution of  $1 \text{ mol L}^{-1}$  potassium nitrate and a solution of  $1 \text{ mol L}^{-1}$  glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ .
- The acidic nature of carbonic acid,  $\text{H}_2\text{CO}_3$ , can be explained by both the Arrhenius and Brønsted–Lowry theories. Using relevant equations, explain how carbonic acid can be classified as an acid according to both of these theories.
- Hydrogen chloride,  $\text{HCl}$ , is a gas at room temperature while hydrogen nitrate,  $\text{HNO}_3$ , is a liquid. However, the two aqueous solutions of these different compounds have similar properties.
  - Explain the similarities between the two solutions.
  - In terms of their intermolecular bonding, explain why hydrogen chloride is a gas at room temperature, but hydrogen nitrate,  $\text{HNO}_3$ , is a liquid.
- Write an equation for the following substances behaving as an:
  - Arrhenius base in water
    - $\text{LiOH}(\text{s})$
    - $\text{Ba}(\text{OH})_2(\text{s})$
  - Arrhenius acid in water
    - $\text{H}_3\text{PO}_4(\text{l})$
    - $\text{HNO}_3(\text{l})$

*continued*

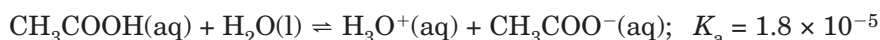
### Review exercise 7.1 — continued

- 5 Write an equation for the following substances behaving as a:
- Brønsted–Lowry acid in water
    - $\text{H}_2\text{PO}_4^-$
    - $\text{H}_2\text{S}(\text{g})$
  - Brønsted–Lowry base in water
    - $\text{NH}_3(\text{g})$
    - $\text{CH}_3\text{COO}^-$
- 6 Write the formula for the conjugate acid of each of the following.
- $\text{HCO}_3^-$
  - $\text{H}_2\text{O}$
  - $\text{OH}^-$
  - $\text{NH}_3$
- 7 Write the formula for the conjugate base of each of the following.
- $\text{H}_2\text{S}$
  - $\text{CH}_3\text{COOH}$
  - $\text{NH}_4^+$
  - $\text{HCO}_3^-$
- 8 Boric acid,  $\text{H}_3\text{BO}_3$ , is a weak triprotic acid. Write the equations to show its behaviour as a triprotic acid in water.
- 9 Hydrogen bromide, HBr, is a stronger acid than hydrogen sulfide,  $\text{H}_2\text{S}$ .
- Identify the following statements as true or false, giving reasons for your answer.
- The equilibrium constant for the hydrolysis reaction of HBr will be larger than that for  $\text{H}_2\text{S}$ .
  - A solution of HBr will always have more  $\text{H}_3\text{O}^+$  ions present than a solution of  $\text{H}_2\text{S}$ .
  - $\text{Br}^-(\text{aq})$  is a stronger base than  $\text{HS}^-(\text{aq})$ .

## 7.2 Hydrolysis reactions of weak acids, bases and salts

As mentioned in section 7.1, the strength of an acid or a base can be described in terms of the position of equilibrium when the substance donates a hydrogen ion to, or accepts a hydrogen ion from, water. This type of reaction with water is called a hydrolysis reaction.

Acetic acid,  $\text{CH}_3\text{COOH}$ , is classified as a weak acid because the equilibrium constant for the hydrolysis reaction is small:

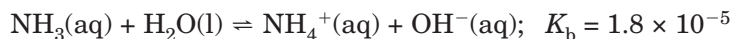


In this equation, acetic acid is behaving as a Brønsted–Lowry acid.  $K_{\text{a}}$  is the symbol given to the equilibrium constant for a hydrolysis reaction of an acid. This equilibrium constant is called the acidity constant. For the hydrolysis reaction of acetic acid, the acidity constant expression would be written as:

$$K_{\text{a}} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

An equilibrium mixture of acetic acid and water contains very few hydronium ions or acetate ions compared to the number of acetic acid molecules. For example, in a  $0.1 \text{ mol L}^{-1}$  acetic acid solution, approximately 99% of the acetic acid molecules are un-ionised.

Ammonia is classified as a weak base because the equilibrium constant for its hydrolysis reaction is small:



In this equation ammonia is behaving as a Brønsted–Lowry base.  $K_b$  is the symbol given to the equilibrium constant for a hydrolysis reaction of a base. This equilibrium constant is called the basicity constant.

(It is only a coincidence that the  $K_a$  value for acetic acid and the  $K_b$  value for ammonia are the same. These values indicate that the extent of hydrolysis in solution is approximately the same for both compounds.)

Table 7.1 lists the hydrolysis reactions for several weak acids and bases together with the equilibrium constants for these reactions.

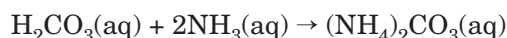
**TABLE 7.1 SOME WEAK ACIDS AND BASES AND THEIR AQUEOUS SOLUTION EQUILIBRIA**

		Hydrolysis equation	Equilibrium constant
Acids	Phosphoric acid	$\text{H}_3\text{PO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{H}_2\text{PO}_4^-(\text{aq})$	$K_a = 7.5 \times 10^{-3}$
	Carbonic acid	$\text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})$	$K_a = 4.3 \times 10^{-7}$
	Ammonium ion	$\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq})$	$K_a = 5.6 \times 10^{-10}$
Bases	Carbonate ion	$\text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{OH}^-(\text{aq})$	$K_b = 1.8 \times 10^{-4}$
	Acetate ion	$\text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOH}(\text{aq}) + \text{OH}^-(\text{aq})$	$K_b = 5.6 \times 10^{-10}$

## Salts

A salt is an ionic compound that contains a negative ion (an anion) other than the oxide ion,  $\text{O}^{2-}$ , or the hydroxide ion,  $\text{OH}^-$ . Sodium fluoride, calcium carbonate, iron(III) sulfate and ammonium nitrate are examples of salts.

A salt can be thought of as a compound whose positive ions (cations) are derived from a base and negative ions from an acid. For the salt potassium chloride, the potassium ions may have come from the base potassium hydroxide and the chloride ions from hydrochloric acid. Ammonium carbonate,  $(\text{NH}_4)_2\text{CO}_3$ , is the salt produced when carbonic acid,  $\text{H}_2\text{CO}_3$ , acting as an acid reacts with ammonia, a base:



## Solutions of salts in water—hydrolysis of ions

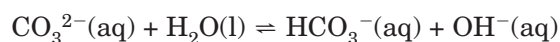
When a salt dissolves in water it dissociates completely into ions. Salts are strong electrolytes.

Sodium carbonate dissociates in water according to the following equation:

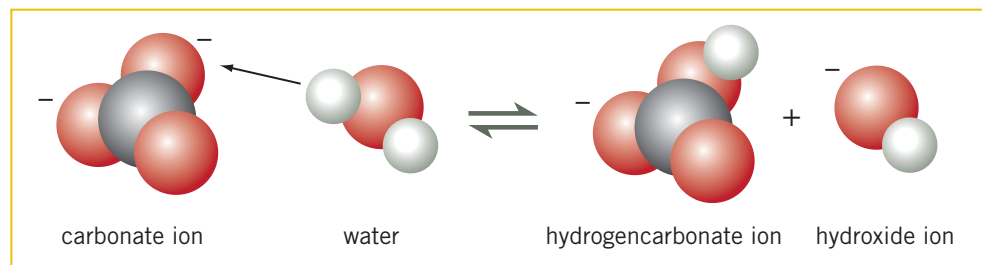


It is then possible that one or both of the ions produced in the dissociation reaction can undergo further reaction with water. This reaction of an ion, obtained from

the dissociation of a salt, with water is an example of a hydrolysis reaction. For example, in a solution of sodium carbonate, the carbonate ion undergoes hydrolysis to produce the hydrogencarbonate ion and a hydroxide ion:



In this reaction the carbonate ion acts as a Brønsted–Lowry base, accepting a hydrogen ion from water to form the hydrogencarbonate ion as the conjugate acid. The formation of hydroxide ions in the reaction explains why a solution of sodium carbonate is basic. (The  $\text{Na}^+$  ions in the solution do not undergo hydrolysis.)



**Figure 7.7** Hydrolysis of the carbonate ion

Depending on which ions,  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$ , are formed in any hydrolysis reaction of this type determines whether the resulting solution will be acidic, basic or neutral. If hydronium ions,  $\text{H}_3\text{O}^+$ , are formed, then the resulting solution is acidic. If hydroxide ions are formed, then the solution of the salt will be basic. The salt solution is said to be neutral if neither of the ions formed, when the salt dissociates, undergoes hydrolysis.

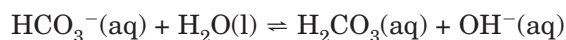
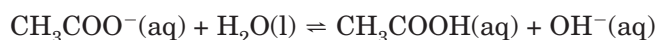
### Neutral salts

The negative ions that are the conjugate bases of strong monoprotic acids are exceptionally weak bases and do not hydrolyse in water. Thus ions such as  $\text{Cl}^-$  and  $\text{NO}_3^-$  do not undergo hydrolysis. Positive ions of groups 1 and 2 metals, formed when the strongly basic oxides and hydroxides of these metals dissociate in water, do not show any acid–base properties, so ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  do not hydrolyse in water.

Therefore, salts formed from the reaction of a strong acid with a strong base are neutral because neither the positive ions nor the negative ions undergo any further hydrolysis reaction in solution. Sodium chloride, potassium nitrate and calcium bromide are examples of neutral salts.

### Basic salts

A negative ion that is the conjugate base of a weak acid such as the acetate ion,  $\text{CH}_3\text{COO}^-$ , from acetic acid, or the hydrogencarbonate ion,  $\text{HCO}_3^-$ , from carbonic acid, undergoes hydrolysis to produce a solution that is basic:



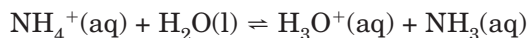
It is the formation of the hydroxide ion in these reactions that causes the solution to be basic. In these cases, the negative ion acts as a Brønsted–Lowry base, accepting a hydrogen ion from water to produce a solution with an excess of hydroxide ions. This means that salts such as sodium hydrogencarbonate, magnesium acetate and potassium carbonate will produce a basic solution in water.

In general, the salt formed from the reaction between a weak acid and a strong base will be composed of a positive ion with no significant acid–base properties

and a negative ion that is a weak base. As a result, when this salt is dissolved in water, the negative ions are able to undergo hydrolysis (to form  $\text{OH}^-$ ) and because of this reaction the solution will be basic.

### Acidic salts

A positive ion that is the conjugate acid of a weak base, such as the ammonium ion, undergoes hydrolysis to produce a solution that is acidic:



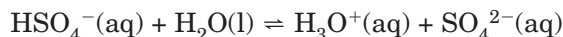
The ammonium ion behaves as a Brønsted–Lowry acid and donates a hydrogen ion to water to produce a solution containing hydronium ions. Salts such as ammonium chloride and ammonium nitrate are therefore classified as acidic salts.

In general, the salt formed from the reaction between a strong acid and a weak base will be composed of a positive ion that is itself a weak acid and a negative ion that has no significant acid–base properties. Consequently, when this salt is dissolved in water, the positive ions will undergo hydrolysis (to form  $\text{H}_3\text{O}^+$ ) and the salt solution will be acidic.

### Salts from multiprotic acids

Sulfuric acid and carbonic acid are both diprotic acids, while phosphoric acid is a triprotic acid. More than one type of negative ion can be produced when these acids react with a base.

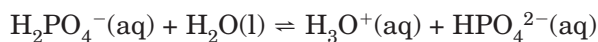
The hydrogensulfate ion,  $\text{HSO}_4^-$ , derived from sulfuric acid, is a weak acid. When salts containing this ion are added to water, an acidic solution is produced, due to the following hydrolysis reaction:



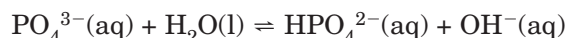
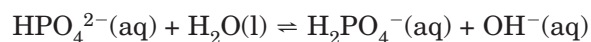
The sulfate ion,  $\text{SO}_4^{2-}$ , is neutral and does not hydrolyse in water.

Both the hydrogencarbonate ion and carbonate ion are basic, so solutions of salts containing these ions are usually basic.

The dihydrogenphosphate ion,  $\text{H}_2\text{PO}_4^-$ , produces a solution that is acidic:



However, the remaining two ions derived from phosphoric acid, the hydrogenphosphate ion,  $\text{HPO}_4^{2-}$ , and the phosphate ion,  $\text{PO}_4^{3-}$ , produce solutions that are basic, since both ions behave as Brønsted–Lowry bases and accept a hydrogen ion from water:



### Salts containing group 13 and transition metal ions

The +3 ions formed from metals in group 13 of the periodic table, as well as many of the +2 and +3 ions of the transition metals, produce salts that are acidic. At first it seems odd that ions, such as  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ , that do not have hydrogen to donate, should behave as acids in aqueous solution. However, these highly charged ions attract water molecules to themselves to form a hydrated or complex ion. These hydrated ions can then react with water molecules to produce a solution that contains excess hydronium ions.

In Figure 7.8 the water molecules are shown arranged around an aluminium ion. The partially charged negative end of the polar water molecule is attracted to the

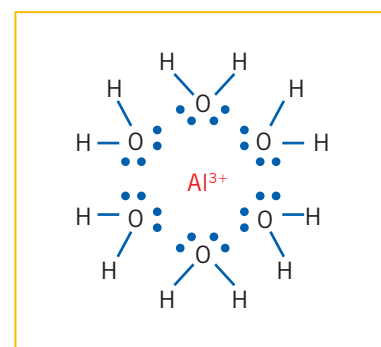


Figure 7.8 Water molecules arranged around an  $\text{Al}^{3+}$  ion, forming a complex ion with the formula of  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$



small, highly charged positive ion. As a result the aluminium ion has six water molecules attached to it by ion–dipole bonds.

The hydrated aluminium ion can then act as a Brønsted–Lowry acid and donate a hydrogen ion from one of the water molecules attracted to it, to another water molecule in the solution:



It is generally the case that +3 ions such as  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  produce solutions that are more acidic than the solutions of +2 ions such as  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ .

Table 7.2 summarises the acid–base nature of commonly encountered ions.

**TABLE 7.2 ACID–BASE NATURE OF A SELECTION OF IONS**

Neutral ions	Ions that form acidic solutions	Ions that form basic solutions
Group 1 and 2 ions, e.g. $\text{Na}^+$ , $\text{K}^+$ , $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ Conjugate negative ions of strong acids, e.g. $\text{Cl}^-$ , $\text{Br}^-$ , $\text{NO}_3^-$ $\text{SO}_4^{2-}$	Conjugate positive ions of weak bases, e.g. $\text{NH}_4^+$ Group 13 and transition metal ions, e.g. $\text{Al}^{3+}$ , $\text{Fe}^{3+}$ $\text{HSO}_4^-$ $\text{H}_2\text{PO}_4^-$	Conjugate negative ions of weak acids, e.g. $\text{CH}_3\text{COO}^-$ , $\text{F}^-$ , $\text{CN}^-$ $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ $\text{HPO}_4^{2-}$ and $\text{PO}_4^{3-}$

### → Example 7.1

When sodium chloride is dissolved in water, the solution obtained does not change the colour of litmus paper. However, a solution formed by dissolving sodium carbonate in water turns litmus paper a blue colour. Explain these observations.

### → Solution

When a salt is dissolved in water, the ions dissociate. Depending on the identity of the ions, some of them then undergo a hydrolysis reaction.

**Sodium chloride:** A sodium chloride solution contains  $\text{Na}^+$  and  $\text{Cl}^-$  ions:



Neither of these ions react with water (that is, undergo hydrolysis). The solution therefore remains neutral and as a result will not change the colour of litmus paper.

**Sodium carbonate:** A sodium carbonate solution contains  $\text{Na}^+$  and  $\text{CO}_3^{2-}$  ions:



The  $\text{Na}^+$  ions do not undergo hydrolysis; however, the  $\text{CO}_3^{2-}$  ions do, according to the following equation:



The hydroxide ions produced in this reaction make the solution basic and basic solutions turn litmus blue.

## \* Review exercise 7.2

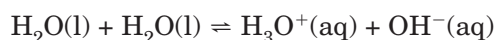
- A solution is labelled  $0.100 \text{ mol L}^{-1}$  hydrochloric acid. What is the concentration of hydronium ions in the solution?
  - Would you expect a  $0.100 \text{ mol L}^{-1}$  acetic acid solution to have the same concentration of hydronium ions in its solution? Explain your answer.
- Aqueous solutions of acetic acid and ammonia are both poor conductors of electricity, although they are both better conductors than water. However, when acetic acid and ammonia solutions are mixed, the resulting solution is a much better conductor. Write equations to support an explanation of these observations.
- Write equations for any hydrolysis reactions that take place after the dissociation of each of the following salts when dissolved in water.
  - $\text{Na}_3\text{PO}_4$
  - $\text{NH}_4\text{NO}_3$
  - $\text{FeCl}_3$
- Predict whether the following salts when dissolved in water will produce neutral, acidic or basic solutions. Explain your reasoning and include relevant equations to support your explanation.
  - $\text{KHSO}_4$
  - $\text{NaHCO}_3$
  - $\text{Ca}(\text{NO}_3)_2$

## 7.3 pH



### Self-ionisation of water

In Figure 7.6 water is listed as a very weak acid as well as a very weak base. A substance that can behave both as an acid or a base is called amphoteric. In any sample of water, some of the water molecules will collide with other water molecules with sufficient energy to enable a transfer of hydrogen ions in a Brønsted–Lowry acid–base reaction:



In this reaction one water molecule behaves as an acid and the other behaves as a base. The equation represents the self-ionisation of water.

The equilibrium constant for this reaction is very small because water is a weak electrolyte and only a few of the water molecules undergo ionisation.

The equilibrium law expression for the self-ionisation of water can be written as:

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K$$

The concentration of water is not included in this expression because the water is shown as a pure liquid in the chemical equation. The value of the concentration of water is very large, compared to the concentrations of the ions, and it is assumed to remain constant.

The equilibrium constant for the self-ionisation of water is known as the self-ionisation constant (or simply the ionisation constant) and is given the symbol  $K_w$ . At 25°C it has a value of  $1.0 \times 10^{-14}$ .

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

Since the self-ionisation reaction produces one hydronium ion for every hydroxide ion, the concentration of each ion in pure water must be the same:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mol L}^{-1} \text{ at } 25^\circ\text{C}$$

Pure water is regarded as neutral in an acid–base context, so in a neutral solution the concentration of hydronium ion must be equal to the concentration of hydroxide ion. When an acid dissolves in water,  $\text{H}_3\text{O}^+$  ions are formed, causing the  $[\text{H}_3\text{O}^+]$  to be greater than the  $[\text{OH}^-]$ . An acidic solution is therefore defined as a solution in which  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ . Similarly when a base dissolves in water,  $\text{OH}^-$  ions are formed, resulting in the  $[\text{OH}^-]$  becoming larger than the  $[\text{H}_3\text{O}^+]$ . A basic solution is therefore one in which  $[\text{OH}^-] > [\text{H}_3\text{O}^+]$ .

The self-ionisation constant,  $K_w$ , for water is the equilibrium constant for a reaction that occurs in all aqueous solutions, so the value of  $[\text{H}_3\text{O}^+][\text{OH}^-]$  for any aqueous solution at 25°C must be  $1 \times 10^{-14}$ . It also follows that, at 25°C, an acidic solution must have a value for  $[\text{H}_3\text{O}^+]$  that is greater than  $1 \times 10^{-7} \text{ mol L}^{-1}$ , while the  $[\text{H}_3\text{O}^+]$  in a basic solution must be smaller than  $1 \times 10^{-7} \text{ mol L}^{-1}$ .

#### → Example 7.2

Calculate the concentration of  $\text{OH}^-$  ions in an aqueous solution that contains  $0.0100 \text{ mol L}^{-1} \text{ H}_3\text{O}^+$ , at 25°C.

#### → Solution

$$\begin{aligned}[\text{H}_3\text{O}^+] &= 1 \times 10^{-2} \text{ mol L}^{-1} \\ [\text{H}_3\text{O}^+][\text{OH}^-] &= 1 \times 10^{-14} \text{ in any aqueous solution at } 25^\circ\text{C} \\ 1 \times 10^{-2} \times [\text{OH}^-] &= 1 \times 10^{-14} \\ \text{so } [\text{OH}^-] &= \frac{1 \times 10^{-14}}{1 \times 10^{-2}} = 1 \times 10^{-12} \text{ mol L}^{-1}\end{aligned}$$

#### → Example 7.3

Calculate the concentration of  $\text{H}_3\text{O}^+$  ions in a solution of  $0.0235 \text{ mol L}^{-1}$  barium hydroxide,  $\text{Ba}(\text{OH})_2$ , at 25°C.

#### → Solution

1 mol of  $\text{Ba}(\text{OH})_2$  produces 2 mol of  $\text{OH}^-$  ions.  
The concentration of  $\text{OH}^-$  ions in  $0.0235 \text{ mol L}^{-1} \text{ Ba}(\text{OH})_2$  is therefore  
 $2 \times 0.0235 = 0.0470 \text{ mol L}^{-1}$

$$\begin{aligned}[\text{H}_3\text{O}^+][\text{OH}^-] &= 1 \times 10^{-14} \\ [\text{H}_3\text{O}^+] \times 0.0470 &= 1 \times 10^{-14} \\ [\text{H}_3\text{O}^+] &= \frac{1 \times 10^{-14}}{0.0470} = 2.13 \times 10^{-13} \text{ mol L}^{-1}\end{aligned}$$

#### → Example 7.4

Calculate the concentration of  $\text{H}_3\text{O}^+$  ions in an aqueous solution that contains 1.45 g of NaOH dissolved in 250 mL of solution at 25°C.

#### → Solution

The steps in this calculation are:  
mass NaOH → mole NaOH → mole of  $\text{OH}^-$  →  $[\text{OH}^-]$  →  $[\text{H}_3\text{O}^+]$

**Step 1**  $n(\text{NaOH}) = \frac{m(\text{NaOH})}{M(\text{NaOH})}$   
 $M(\text{NaOH}) = 22.99 + 16.00 + 1.008 = 39.998 \text{ g mol}^{-1}$   
 $n(\text{NaOH}) = \frac{1.45}{39.998} = 0.03625 \text{ mol}$

**Step 2**  $c(\text{NaOH solution}) = \frac{n(\text{NaOH})}{V(\text{NaOH solution})}$   
 $= \frac{0.03625}{0.250} = 0.1450 \text{ mol L}^{-1}$

**Step 3** Because 1 mol of NaOH forms 1 mol of  $\text{OH}^-$   
 $c(\text{OH}^-) = c(\text{NaOH}) = 0.1450 \text{ mol L}^{-1}$

**Step 4**  $[\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}$   
 $[\text{H}_3\text{O}^+] \times 0.1450 = 1 \times 10^{-14}$   
 so  $[\text{H}_3\text{O}^+] = \frac{1 \cdot 10^{-14}}{0.1450} = 6.90 \times 10^{-14} \text{ mol L}^{-1}$

## What is pH?

Examples 7.3 and 7.4 show that the concentration of  $\text{H}_3\text{O}^+$  in a basic solution can be very small. In pure water, at  $25^\circ\text{C}$ , the concentration of  $\text{H}_3\text{O}^+$  is  $1 \times 10^{-7} \text{ mol L}^{-1}$ , while in a solution of a strong acid this concentration could be as high as  $10 \text{ mol L}^{-1}$ .

To simplify the representation of the acidity of a solution, Søren Sørensen developed the concept of pH, which he called the ‘hydrogen ion exponent’. In order to express the acidity of a solution in a set of more convenient numbers, Sørensen defined the pH of an aqueous solution as:

$$\text{pH} = -\log_{10}(\text{concentration of } \text{H}_3\text{O}^+), \text{ or}$$

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

Another way of representing the relationship between pH and the concentration of  $\text{H}_3\text{O}^+$  is:

$$\text{if } [\text{H}_3\text{O}^+] = 1 \times 10^{-x} \text{ then } \text{pH} = x.$$

In pure water, at  $25^\circ\text{C}$ ,

$$[\text{H}_3\text{O}^+] = 1 \times 10^{-7} \text{ mol L}^{-1} \text{ so } \text{pH} = 7.$$

In a  $0.1 \text{ mol L}^{-1}$  solution of the strong acid HCl,

$$[\text{H}_3\text{O}^+] = 1 \times 10^{-1} \text{ mol L}^{-1}, \text{ so } \text{pH} = 1.$$

In a  $0.1 \text{ mol L}^{-1}$  solution of sodium hydroxide, at  $25^\circ\text{C}$ ,

$$[\text{H}_3\text{O}^+] = 1 \times 10^{-13} \text{ mol L}^{-1}, \text{ so } \text{pH} = 13.$$

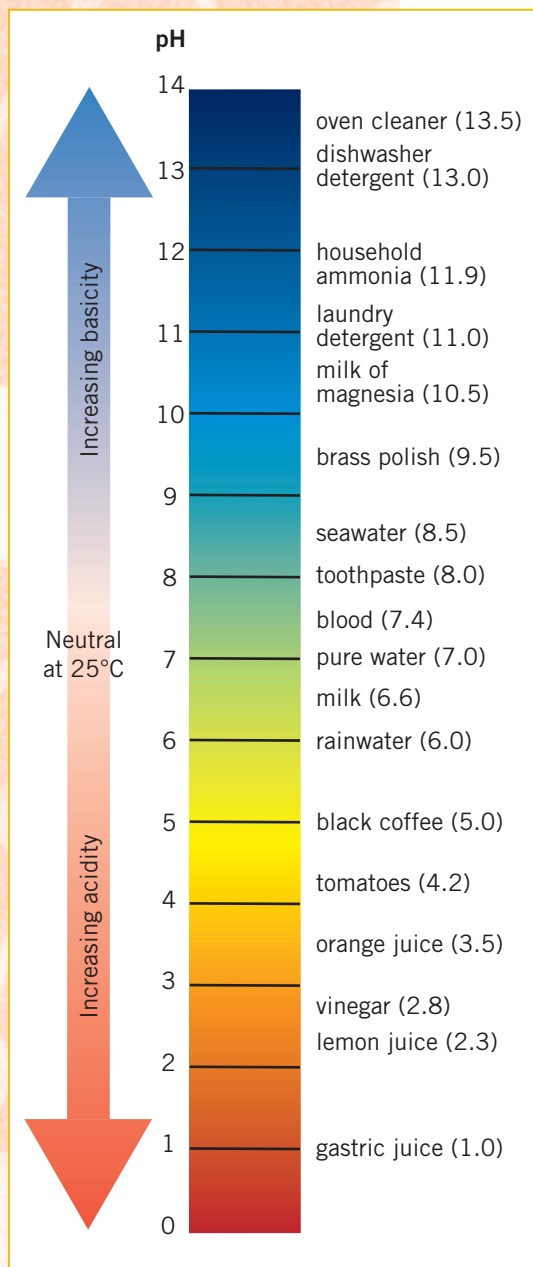
Since it is possible to produce aqueous solutions of strong acids with a concentration close to  $10 \text{ mol L}^{-1}$ , and aqueous solutions of strong bases also close to a concentration of  $10 \text{ mol L}^{-1}$ , the range of pH values can be as large as  $-1$  to  $15$ . However, for most solutions of acids and bases the range of values is from  $0$  (a very acidic solution) to  $14$  (a very basic solution).

Figure 7.9 shows the range of pH values for some common acids, bases and neutral substances that are part of a modern lifestyle. This figure also shows that pH decreases as a solution becomes more acidic and pH increases as a solution becomes more basic.

In summary:

- $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$
- in all aqueous solutions, at  $25^\circ\text{C}$ ,  $[\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}$
- the pH of a neutral solution at  $25^\circ\text{C}$  is 7
- acidic solutions have pH values less than 7 and  $[\text{H}_3\text{O}^+] > 1 \times 10^{-7} \text{ mol L}^{-1}$ , at  $25^\circ\text{C}$
- basic solutions have pH values greater than 7 and  $[\text{H}_3\text{O}^+] < 1 \times 10^{-7} \text{ mol L}^{-1}$ , at  $25^\circ\text{C}$ .

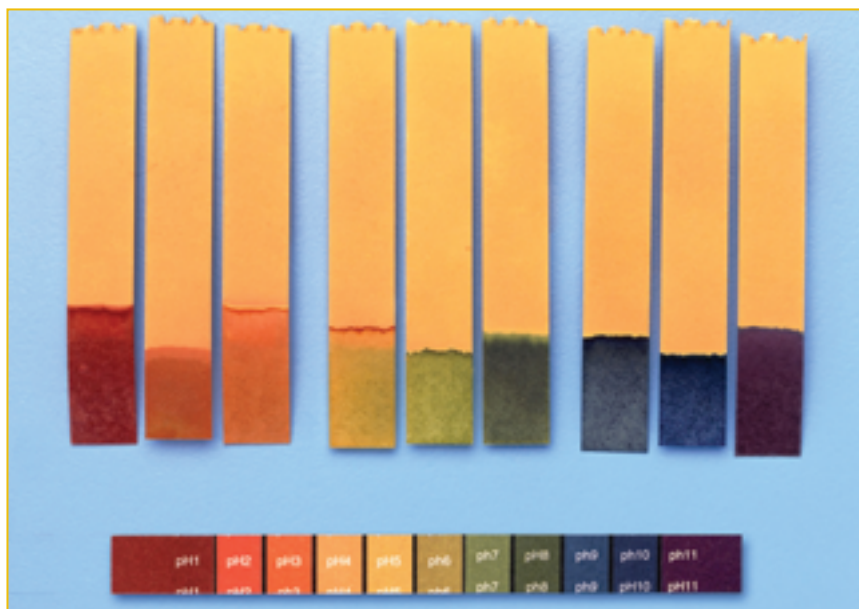
## Measuring pH



**Figure 7.9** The pH values of some common substances. The colours ranging from red to green through to blue are approximate universal indicator colours.

An approximate measure of the pH of a solution can be obtained by using pH paper. This is paper that has been impregnated with a mixture of acid–base indicators, and as a result, it changes to different colours at different pH values. Universal indicator paper can be used to measure pH values in the range from 1 to around 11. More accurate indicator papers for measuring the pH of substances such as saliva, urine, soils and water supplies consist of plastic strips that have small squares of paper, impregnated with different acid–base indicators, along the strip. Comparing the sequence of colours on the test strip with the reference chart on the pH indicator container allows more accurate pH measurement than with universal indicator alone.

For more precise measurement of pH, it is necessary to use a pH meter. A pH meter consists of a pair of special electrodes (see Chapter 8) connected to a meter that is capable of measuring very small voltage differences, of the order of millivolts. The voltage difference between the two electrodes depends on the pH of the solution. Once calibrated against solutions of known pH, the pH meter is capable of measuring pH values to an accuracy of less than 0.1 of a pH unit.



**Figure 7.10** The range of colours for universal indicator pH paper. These paper strips have been soaked in a solution of universal indicator (a mixture of several different indicators). When the paper is dipped into a solution it changes colour, depending on the pH of the solution. The scale at the bottom shows the colours to be expected for pH values ranging from 1 (red) to 11 (violet).



Figure 7.11 A pH meter being used to measure the pH of water containing some dissolved carbon dioxide. Why is the pH lower than 7?

## pH calculations

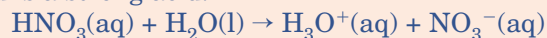
It is possible to calculate the pH of a solution of any strong acid or strong base given the concentration of the solution. A strong acid or base is completely ionised or dissociated in solution, allowing the determination of either the concentration of the hydronium ion or the hydroxide ion in the solution. From the hydronium ion concentration, the pH can be determined directly using the expression  $\text{pH} = -\log[\text{H}_3\text{O}^+]$ . From the hydroxide ion concentration it is possible to use the value of  $K_w$  for the self-ionisation of water to determine the concentration of the hydronium ion, and from this calculate the pH of the solution.

### → Example 7.5

What is the pH of a  $0.001 \text{ mol L}^{-1}$  solution of nitric acid?

### → Solution

Since nitric acid is a strong acid:



1 mol of  $\text{HNO}_3$  forms 1 mol of  $\text{H}_3\text{O}^+$

$$[\text{H}_3\text{O}^+] = 0.001 \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1 \times 10^{-3}) = \mathbf{3}$$

### → Example 7.6

What is the pH of a  $0.1 \text{ mol L}^{-1}$  solution of potassium hydroxide, at  $25^\circ\text{C}$ ?

### → Solution

Since potassium hydroxide is a strong base:



1 mol of  $\text{KOH}$  produces 1 mol of  $\text{OH}^-$

$$[\text{OH}^-] = 0.1 \text{ mol L}^{-1}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] \times 1 \times 10^{-1} = 1 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = \frac{1 \times 10^{-14}}{1 \times 10^{-1}} = 1 \times 10^{-13}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1 \times 10^{-13}) = \mathbf{13}$$

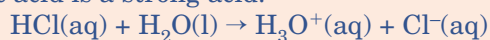
*continued*

→ **Example 7.7**

What is the pH of a  $0.0561 \text{ mol L}^{-1}$  solution of hydrochloric acid?

→ **Solution**

Since hydrochloric acid is a strong acid:



1 mol of HCl forms 1 mol of  $\text{H}_3\text{O}^+$

$$[\text{H}_3\text{O}^+] = 0.0561 \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 0.0561 = \mathbf{1.25}$$

→ **Example 7.8**

What is the pH of a  $0.00750 \text{ mol L}^{-1}$  solution of magnesium hydroxide, at  $25^\circ\text{C}$ ?

→ **Solution**

Since magnesium hydroxide is a strong base:



1 mol of  $\text{Mg}(\text{OH})_2$  produces 2 mol of  $\text{OH}^-$

$$[\text{OH}^-] = 2 \times 0.00750 = 0.0150 \text{ mol L}^{-1}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] \times 0.0150 = 1 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = \frac{1 \times 10^{-14}}{0.0150} = 6.67 \times 10^{-13}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(6.67 \times 10^{-13}) = \mathbf{12.2}$$

When a solution of a strong acid reacts completely with a solution of a strong base in the stoichiometric amounts required by the balanced equation, the resulting solution is neutral. Since the concentration of  $\text{H}_3\text{O}^+$  ion is the same as the concentration of  $\text{OH}^-$ , the pH of the resulting solution, at  $25^\circ\text{C}$ , is 7.

If, however, the strong acid and strong base are not mixed in stoichiometric amounts, then some of either the acid or the base will remain unreacted after the reaction. It is this remaining acid or base that will determine the pH of the final solution.

The steps involved in a calculation of the pH of a mixture of a strong acid and a strong base are:

- 1 Calculate the amount in mole of  $\text{H}_3\text{O}^+$  in the acid solution and the amount in mole of  $\text{OH}^-$  in the base solution, before any reaction occurs.
- 2 Assuming the  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  react in a 1:1 mole ratio,  $\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ , determine which is in excess.
- 3 Calculate the amount in mole of excess  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$ .
- 4 Using the new volume of the mixed solution, calculate the concentration of excess  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$ .
- 5 Determine the pH of the solution from the concentration of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  from step 4.

### → Example 7.9

10.0 g of calcium hydroxide is added to 200 mL of 0.400 mol L<sup>-1</sup> HCl. Calculate the pH of the solution resulting from this reaction. Assume that the volume is not affected by the addition of the calcium hydroxide.

### → Solution

$$n(\text{Ca}(\text{OH})_2) = \frac{m(\text{Ca}(\text{OH})_2)}{M(\text{Ca}(\text{OH})_2)} \quad M(\text{Ca}(\text{OH})_2) = 74.096 \text{ g mol}^{-1}$$
$$= \frac{10.0}{74.096} = 0.1350 \text{ mol}$$

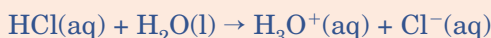


1 mol of Ca(OH)<sub>2</sub> forms 2 mol of OH<sup>-</sup>

mol of OH<sup>-</sup> present before the reaction = 2 × 0.1350 = 0.2700 mol

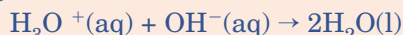
$$c(\text{HCl solution}) = \frac{n(\text{HCl})}{V(\text{HCl solution})}$$

$$n(\text{HCl}) = 0.200 \times 0.400 = 0.08000 \text{ mol}$$



1 mol of HCl will form 1 mol of H<sub>3</sub>O<sup>+</sup>

mol of H<sub>3</sub>O<sup>+</sup> before the reaction = 0.08000 mol



0.08000 mol of H<sub>3</sub>O<sup>+</sup> will react with 0.08000 mol of OH<sup>-</sup>, but there is 0.2700 mol of OH<sup>-</sup>, i.e. H<sub>3</sub>O<sup>+</sup> is the limiting reagent and OH<sup>-</sup> is in excess.

mol of OH<sup>-</sup> remaining after reaction = 0.2700 - 0.08000 = 0.1900

volume of final solution = 0.200 L

$$c(\text{OH}^{-} \text{ in final solution}) = \frac{n(\text{OH}^{-})}{V(\text{final solution})}$$
$$= \frac{0.1900}{0.200} = 0.9500 \text{ mol L}^{-1}$$

$$K_w = [\text{H}_3\text{O}^{+}][\text{OH}^{-}] = 1 \times 10^{-14}$$

$$[\text{H}_3\text{O}^{+}] \times 0.9500 = 1 \times 10^{-14}$$

$$[\text{H}_3\text{O}^{+}] = \frac{1 \times 10^{-14}}{0.9500} = 1.053 \times 10^{-14} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^{+}] = -\log(1.053 \times 10^{-14}) = \mathbf{14.0}$$

## pH and temperature

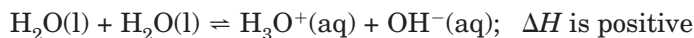
The self-ionisation of water is represented by the equation:



The reaction of an acid with a base is an exothermic reaction. The ionic equation for the reaction of a strong acid with a strong base is:



This is the reverse of the equation for the self-ionisation of water, so this reverse reaction must be endothermic:



For this equilibrium system, an increase in temperature favours the endothermic reaction (the forward direction), and would result in an increase in the equilibrium constant. This means that for the self-ionisation reaction of water, at temperatures above 25°C, the value of  $K_w$  must be greater than  $1 \times 10^{-14}$ . For example, at 40°C the value of  $K_w$  is  $2.916 \times 10^{-14}$ . At temperatures below 25°C,  $K_w$  will be smaller than  $1 \times 10^{-14}$ , for instance, at 10°C, the value is  $2.93 \times 10^{-15}$ .



→ **Example 7.10**

Calculate the pH of pure water at 40°C, given that the  $K_w$  at 40°C is  $2.92 \times 10^{-14}$ .

→ **Solution**

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 2.92 \times 10^{-14}$$

Since the solution is neutral,  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$

$$[\text{H}_3\text{O}^+]^2 = 2.92 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = 1.709 \times 10^{-7} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 1.709 \times 10^{-7} = \mathbf{6.77}$$

While the pH of pure water at 40°C is less than 7, this does not mean that pure water at 40°C is acidic. The value of 7 for the pH of a neutral solution (or pure water) only applies when the temperature is 25°C. Pure water at 40°C is neutral, because the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are equal, but the pH of this neutral water is 6.77.

**\* Review exercise 7.3**

(For these problems assume a temperature of 25°C unless informed otherwise.)

- Calculate the concentration of  $\text{H}_3\text{O}^+$  in each of the following solutions.
  - 0.0125 mol L<sup>-1</sup> HCl
  - 0.0340 mol L<sup>-1</sup> LiOH
  - A solution containing 0.0550 mol of calcium hydroxide dissolved in 250 mL of solution
- Determine the hydronium ion and hydroxide ion concentrations in a solution with a pH of 9.
- Calculate the pH of solutions having the following concentrations of  $\text{H}_3\text{O}^+$ .
    - $5.39 \times 10^{-3} \text{ mol L}^{-1}$
    - $1.43 \times 10^{-9} \text{ mol L}^{-1}$
  - What is the hydronium ion concentration in solutions with the following pH values?
    - 3.21
    - 7.50
    - 12.43
- Calculate the hydronium ion concentration, hydroxide ion concentration and pH of the solutions formed when the following solutions are mixed.
  - 0.100 L of 0.300 mol L<sup>-1</sup> HNO<sub>3</sub> and 0.100 L of 0.300 mol L<sup>-1</sup> KOH
  - 0.500 L of 0.500 mol L<sup>-1</sup> HNO<sub>3</sub> and 0.500 L of 0.250 mol L<sup>-1</sup> KOH
  - 0.500 L of 0.250 mol L<sup>-1</sup> HNO<sub>3</sub> and 0.500 L of 0.250 mol L<sup>-1</sup> Ba(OH)<sub>2</sub>
- Calculate the pH of pure water at 10°C, given  $K_w = 2.93 \times 10^{-15}$  at this temperature.
- Explain why it is acceptable to use universal indicator to test the pH of a sample of garden soil, but a pH meter is preferable to measure the pH of the water in a river system.

- 7 Five colourless 0.1 mol L<sup>-1</sup> solutions of the substances listed below were tested with universal indicator paper.

HCl

KF

Mg(NO<sub>3</sub>)<sub>2</sub>

NH<sub>4</sub>NO<sub>3</sub>

NaOH

The results obtained are shown in Figure 7.12; however, the solution tested for each strip of paper was not recorded.

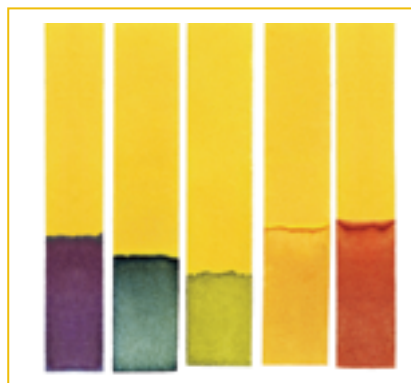


Figure 7.12

- Use the universal indicator colours shown in Figures 7.9 and 7.10 to determine the approximate pH of the solution tested for each strip, and so determine whether each solution contains a strong acid, weak acid, strong base, weak base or neutral substance.
- Identify the solution tested by each strip of indicator paper. Explain your reasoning and give equations to support your answer.

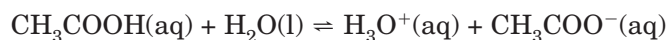
## 7.4 Chemistry of buffer solutions



### What is a buffer?

A buffer is a solution that resists a change in its pH when small amounts of an acid or base are added. Consisting of a mixture of a weak acid and its conjugate base, often in equimolar amounts, a buffer solution is able to react with H<sub>3</sub>O<sup>+</sup> introduced by addition of an acid, or with OH<sup>-</sup> introduced by addition of a base.

In a buffer solution prepared by mixing acetic acid and sodium acetate solutions, the following equilibrium is set up:



If a solution of an acid is added to the acetic acid/acetate mixture, the system is put out of equilibrium. To re-establish equilibrium, the acetate ions react with some of the added acid (H<sub>3</sub>O<sup>+</sup>) to shift the position of equilibrium to the left. Since much of the added H<sub>3</sub>O<sup>+</sup> ion is removed in this process, the overall concentration of H<sub>3</sub>O<sup>+</sup> does not alter appreciably.

If a solution of a base is added to this equilibrium mixture, the added OH<sup>-</sup> ions react with the H<sub>3</sub>O<sup>+</sup> present. In response to the decrease in concentration of one of the products, more acetic acid reacts in order to maintain equilibrium. The position of equilibrium shifts towards the right. This results in additional H<sub>3</sub>O<sup>+</sup> being produced, which can react with more of the added OH<sup>-</sup>. This continues until all the added OH<sup>-</sup> is consumed (or the acetic acid is 'used up').

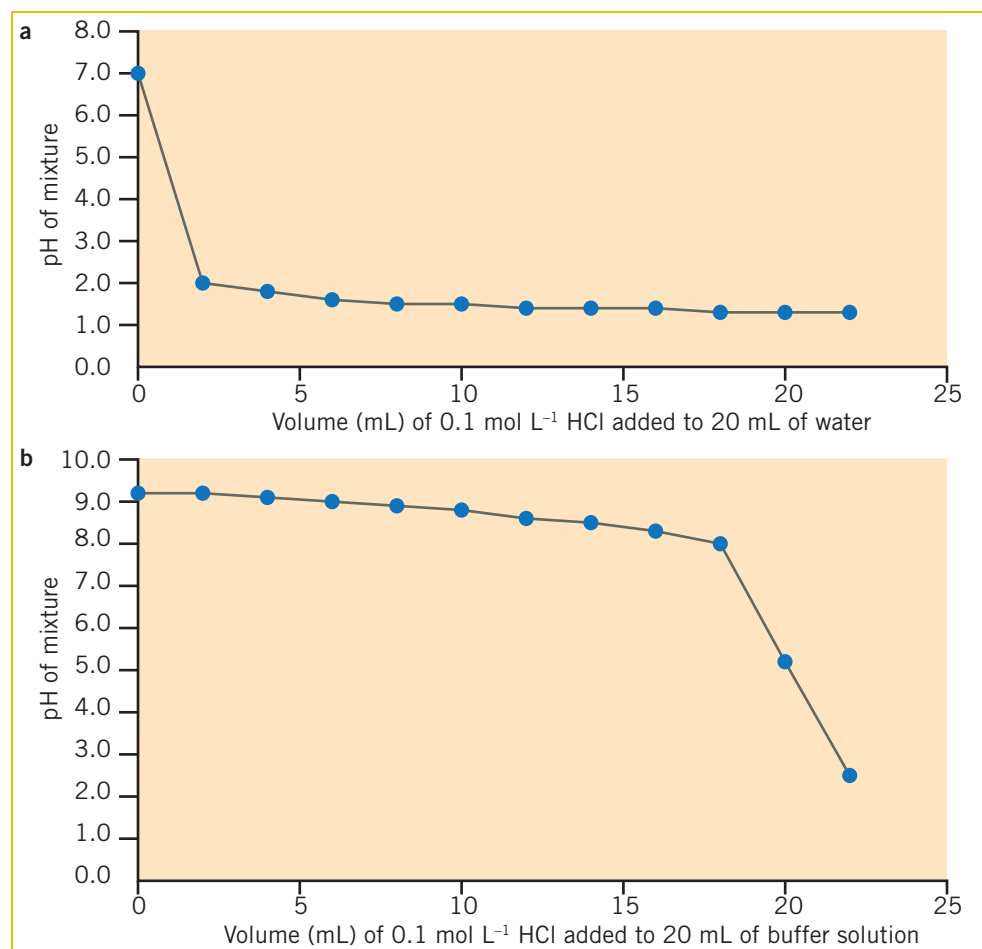
In both of these scenarios, much of the excess acid or base added can be consumed without a great alteration to the concentration of H<sub>3</sub>O<sup>+</sup> in the original mixture. As a result, the pH of the acetic acid/acetate ion buffer does not change much.

For example, a solution that is 1.0 mol L<sup>-1</sup> with respect to both acetic acid and sodium acetate has a pH of 4.74 (the details of the calculation of this pH are beyond the scope of this text). If 0.02 mol of sodium hydroxide is added to 1.0 L

of this acetic acid/acetate buffer, the pH of the resulting solution changes to 4.76. However, if 0.02 mol of sodium hydroxide is added to 1.0 L of pure water, the pH of the solution changes from 7 to 12.3.

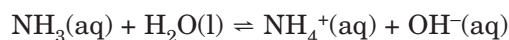
Figure 7.13 shows the buffering effect of an ammonium ion/ammonia buffer when an acid is added, in comparison to the change in pH that occurs when an identical amount of acid is added to distilled water.

When less than 5 mL of 0.1 mol L<sup>-1</sup> HCl solution is added to 20 mL of water, the pH of the mixture decreases over 5 units (graph a). However, with 20 mL of the 0.1 mol L<sup>-1</sup> ammonium ion/0.1 mol L<sup>-1</sup> ammonia buffer solution, even with the addition of up to 15 mL of the HCl solution, the pH has only changed over the range of 1 unit (graph b).



**Figure 7.13** Change in pH when 0.1 mol L<sup>-1</sup> HCl solution is added to water (graph a) or a 0.1 mol L<sup>-1</sup> ammonium ion/0.1 mol L<sup>-1</sup> ammonia buffer (graph b).

The following equilibrium exists in the ammonium ion/ammonia buffer solution:



When some acid is added to this mixture, there is a reaction between the added H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup>, which results in a removal of OH<sup>-</sup> from the ammonia equilibrium mixture. To partially overcome this change, the equilibrium position moves towards the right to replace the OH<sup>-</sup>. The pH of the buffer solution therefore does not alter very much despite the addition of the acid.

Buffer solutions are often prepared by mixing a weak acid or base with a salt of that acid or base. For example, a NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub> buffer solution can be prepared

by dissolving ammonium chloride in a dilute solution of ammonia. By choosing an appropriate acid–base conjugate pair and adjusting their concentrations, a buffer solution of virtually any pH can be prepared.

### Buffer capacity

A buffer solution can act as a ‘shock absorber’, keeping the pH much the same when small amounts of extra acid or base are added to it from another source. The extent to which the buffer can ‘absorb’ the extra acid or base added is called the buffer capacity. The buffer capacity depends on two factors:

- the relative concentrations of the weak acid and its conjugate base. The most effective buffer (the greatest buffer capacity) is one in which the concentrations of the acid and its conjugate base in the buffer are equal
- the concentrations of the weak acid and its conjugate base. The buffer capacity increases with an increase in the concentration of the conjugate pair. The greater the concentration of the conjugate pair, the more likely the buffer will be able to combine with the added acid or base by shifting the position of equilibrium either left or right.

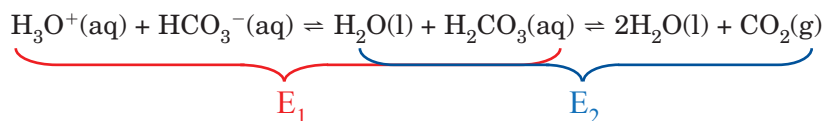
### Blood as a buffer system

A large number of the biochemical reactions that take place in living things are sensitive to changes in pH. In particular, the vast array of enzymes or biological catalysts operate only over a very small range of pH values, so anything that causes the pH of body fluids to alter appreciably can lead to illness or even death.

The pH of blood is normally held between 7.35 and 7.45 and this is achieved with a system of buffers. The three major buffer systems in the bloodstream involve  $\text{HCO}_3^-/\text{H}_2\text{CO}_3/\text{CO}_2$ ,  $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$ , and a more complex system involving proteins.

In the body, the most common metabolic process involving the production of substances that change the pH of blood is respiration. One of the products of respiration, carbon dioxide, is acidic and lowers the pH of body fluids. The buffer system that is most significant in keeping the pH of blood constant during respiration is the carbonic acid/hydrogencarbonate system.

The equilibrium reactions in this buffer system in the blood are shown below:



There are two equilibrium reactions represented here but only one of these,  $\text{E}_1$ , is an acid–base reaction. The second equilibrium reaction,  $\text{E}_2$ , involves the production of carbon dioxide as a gas, which can easily escape from the solution, and so provides a pathway via which the equilibrium can be shifted to the right, consuming excess acid ( $\text{H}_3\text{O}^+$ ).

The actual buffer system in blood plasma is the carbonic acid/hydrogencarbonate reaction represented by  $\text{E}_1$ . This buffer consists of a weak acid,  $\text{H}_2\text{CO}_3$ , and its conjugate base,  $\text{HCO}_3^-$ . While this buffer in its own right could regulate blood pH, the presence of the extra equilibrium reaction involving the production of gaseous carbon dioxide from carbonic acid ( $\text{E}_2$ ) makes the elimination of excess  $\text{H}_3\text{O}^+$  from the bloodstream even more efficient. This latter reaction, the elimination of carbon dioxide from the bloodstream via the lungs, is particularly important during strenuous exercise.



The actual buffer and equilibrium chemistry associated with the provision of adequate supplies of oxygen to muscle tissue and the removal of carbon dioxide produced in respiration via the bloodstream is more complex than presented here. The principles of equilibrium considered in Chapter 6 and the chemistry of buffers introduced in this chapter play a pivotal role in explaining how blood pH is maintained close to the optimum pH of 7.4.

### Calibration of a pH meter

The chemistry of living things is dependent on pH. Small changes in the pH of the cell contents of a plant or animal can have a significant impact on survival. Similarly, small changes in the pH of the aqueous solutions found in the environment can be detrimental to the survival of living things. As a consequence, monitoring of the pH of solutions in and around living things is vital. Accurate monitoring is achieved using a pH meter.

The probe of the pH meter acts like a small electrochemical cell (see Chapter 8) that produces a certain cell potential (voltage) when placed in a solution containing  $\text{H}_3\text{O}^+$  ions. The voltage generated is dependent on the concentration of  $\text{H}_3\text{O}^+$  ions in the solution. This voltage measurement is converted to pH readings by the meter.

For the pH meter to be used to record accurate pH values, it must be first be calibrated. This calibration is achieved by using buffers of known pH values. Two buffers with a pH of 4 and 10 are commonly used. The electrodes of the pH meter are immersed in the pH 4 buffer solution and the scale is calibrated to read 4. The electrodes are cleaned and dried and then placed in the pH 10 buffer and the scale calibrated to read 10. From these two points, the meter is able to produce a linear scale between the two buffer readings and so be ready to measure pH values to an accuracy of 0.1 pH units or less.

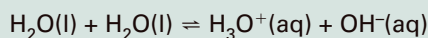
The use of buffers for calibration is not just because the pH of a buffer can be calculated from the concentrations of weak acid and the conjugate base, but also because any contamination of the electrodes resulting from them not being cleaned properly between measurements will not significantly alter the pH of the buffer solution. Also, the pH of the buffer solution remains reasonably constant during storage; for instance, absorption of carbon dioxide from the air will not significantly alter the pH of the buffer.

### \* Review exercise 7.4

- 1 Explain why a mixture of ammonium chloride and ammonia can act as a buffer, but a mixture of hydrochloric acid and sodium chloride solution cannot.
- 2 If a buffer solution is composed of a weak acid and its conjugate base in a 1:1 mole ratio, why does mixing 500 mL of  $1.0 \text{ mol L}^{-1}$  acetic acid with 250 mL of  $1.0 \text{ mol L}^{-1}$  sodium hydroxide produce a buffer solution?
- 3 Write equations to show what happens to a buffer solution containing equimolar amounts of  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  when we add a small amount of:
  - a  $\text{OH}^-(\text{aq})$
  - b  $\text{H}_3\text{O}^+(\text{aq})$
- 4 Why would it be unwise to use tap water to calibrate a pH meter?

## MAJOR IDEAS

- An electrolyte is a substance that produces a solution that conducts electricity when dissolved in water.
- Strong electrolytes completely dissociate or ionise in solution.
- Weak electrolytes only partially ionise in solution.
- Water is a weak electrolyte; it undergoes self-ionisation:



- The equilibrium constant for this reaction at 25°C is  $1 \times 10^{-14}$ .
- According to the Arrhenius theory, acids are substances that produce  $\text{H}^+$  when dissolved in water and bases are substances that produce  $\text{OH}^-$  when dissolved in water.
- In the Brønsted–Lowry theory an acid is a substance that donates  $\text{H}^+$  (proton) and a base is a substance that accepts  $\text{H}^+$ .
- A conjugate acid–base pair is any pair of substances that differ by one hydrogen ion.
- Strong acids and bases have large equilibrium constants for the reaction with water (hydrolysis reaction); weak acids and bases have small equilibrium constants.
- In general, a strong acid will have a weak conjugate base and a strong base will have a weak conjugate acid.
- Strong acids include hydrochloric acid, nitric acid and sulfuric acids; strong bases include the oxides and hydroxides of group 1 and 2 metals.
- Often the conjugate acid or base of a weak base or acid (respectively) is also weak.
- Acids that can donate more than one hydrogen ion (a proton) in an acid–base reaction are called polyprotic acids.
- The acidity constant ( $K_a$ ) of an acid is the equilibrium constant for the hydrolysis of the acid (HA):

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

- A salt is an ionic compound that contains a negative ion (an anion) other than the oxide ion,  $\text{O}^{2-}$ , or the hydroxide ion,  $\text{OH}^-$ .
- Salts dissociate in water. The ions formed may then undergo hydrolysis to produce acidic or basic solutions.
- A solution of an ionic compound is acidic if the hydrolysis reaction of one of its ions forms  $\text{H}_3\text{O}^+$ , and basic if  $\text{OH}^-$  is formed.
- The acid–base properties of ions are summarised in Table 7.2.
- A substance that can behave both as an acid and a base is called amphoteric.
- The equilibrium constant for the self-ionisation of water is the self-ionisation constant,  $K_w$ :

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

- In a neutral solution, at any temperature  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ . In an acidic solution  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$  and in a basic solution  $[\text{OH}^-] > [\text{H}_3\text{O}^+]$ .
- At 25°C,  
in a neutral solution  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mol L}^{-1}$   
in an acidic solution  $[\text{H}_3\text{O}^+] > 1 \times 10^{-7} \text{ mol L}^{-1}$   
in a basic solution  $[\text{OH}^-] > 1 \times 10^{-7} \text{ mol L}^{-1}$
- The value of  $K_w$  changes with temperature. The self-ionisation reaction of water is endothermic, so  $K_w$  increases with increasing temperature and decreases with decreasing temperature.
- $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$
- At 25°C, a neutral solution has a pH of 7, an acidic solution, pH less than 7 and a basic solution, pH greater than 7.
- A buffer is a solution that resists a change in its pH when small amounts of an acid or base are added.
- A buffer solution consists of a mixture of a weak acid and its conjugate base.
- The extent to which the buffer can ‘absorb’ the extra acid or base added is called the buffer capacity.
- The buffer capacity depends on the concentrations of the weak acid and its conjugate base. The best buffering capacity is obtained if the concentrations are large and approximately equal to one another.
- The buffer system in the blood depends on the equilibria:  
$$\text{H}_3\text{O}^+(\text{aq}) + \text{HCO}_3^-(\text{aq}) \rightleftharpoons \text{H}_2\text{O}(\text{l}) + \text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons 2\text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$$
- Buffer solutions are used to calibrate pH meters because the pH of the solution remains approximately the same despite a small degree of contamination.

## QUESTIONS

(Assume all the pH questions refer to solutions at 25°C, unless informed otherwise.)

- 1 Using ammonium chloride and ammonia as examples, explain the meaning of the terms ‘strong electrolyte’ and ‘weak electrolyte’.
- 2 **a** Write an equation to show acetic acid acting as an acid according to the Arrhenius theory.  
**b** Write an equation to show sulfuric acid acting as an acid according to the Brønsted–Lowry theory.  
**c** Write an equation to show magnesium hydroxide acting as a base according to the Arrhenius theory.

- d** Write an equation to show sodium carbonate acting as a base according to the Brønsted-Lowry theory.
- 3 a** Write the formula for the conjugate acid of each of the following.
- $\text{OH}^-$
  - $\text{HPO}_4^{2-}$
  - $\text{H}_2\text{SO}_4$
  - $\text{HS}^-$
  - $\text{CO}_3^{2-}$
- b** Write the formula for the conjugate base of each of the following.
- $\text{OH}^-$
  - $\text{HPO}_4^{2-}$
  - $\text{HCN}$
  - $\text{NH}_4^+$
  - $\text{HSO}_4^-$
- 4** For each of the following equations identify the conjugate acid–base pairs, indicating which is the acid and which the base in each pair.
- $\text{HCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
  - $\text{HSO}_4^-(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{SO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
  - $\text{PH}_3(\text{g}) + \text{HI}(\text{g}) \rightleftharpoons \text{PH}_4^+(\text{s}) + \text{I}^-(\text{s})$
  - $\text{CH}_3\text{NH}_2(\text{l}) + \text{CH}_3\text{CH}_2\text{OH}(\text{l}) \rightleftharpoons \text{CH}_3\text{NH}_3^+(\text{l}) + \text{CH}_3\text{CH}_2\text{O}^-(\text{l})$
  - $\text{O}^{2-}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{OH}^-(\text{aq})$
- 5** Using equations, explain why  $\text{CH}_3\text{COOH}$  is classified as a monoprotic acid, but  $\text{H}_3\text{PO}_4$  is classified as a triprotic acid.
- 6** Phosphoric acid is a triprotic acid but is not as strong an acid as monoprotic hydrochloric acid. Why is this the case?
- 7** Identify the following statements as true or false.
- Comparing 1 L of  $0.1 \text{ mol L}^{-1}$  acetic acid and 1 L of  $0.1 \text{ mol L}^{-1}$  nitric acid:
- Both solutions have the same pH.
  - The acetic acid would contain fewer hydroxide ions than the nitric acid.
  - Both solutions are prepared by adding 0.1 mol of the original pure acid to water and making up to 1 L.
  - The pH of the acetic acid is higher than 7 and that of the nitric acid is lower than 7.
  - Both solutions contain the same mass of original acid.
  - The equilibrium constant for the hydrolysis of acetic acid is smaller than that for the hydrolysis of nitric acid.
- g** Both solutions would require the same volume of  $0.1 \text{ mol L}^{-1}$  sodium hydroxide for complete reaction.
- 8** Identify the following statements as true or false.
- Comparing 1 L of  $0.1 \text{ mol L}^{-1}$  potassium hydroxide and 1 L of  $0.1 \text{ mol L}^{-1}$  ammonia:
- The pH of the potassium hydroxide solution would be higher than the pH of the ammonia solution.
  - The ammonia solution would contain more hydronium ions than the potassium hydroxide solution.
  - The value of  $K_w$  in the ammonia solution is less than the value of  $K_w$  in the potassium hydroxide solution.
  - Both solutions would require the same volume of  $0.1 \text{ mol L}^{-1}$  hydrochloric acid for complete reaction (to equivalence).
- 9** You have been supplied with  $0.001 \text{ mol L}^{-1}$  solutions of four monoprotic acids and asked to measure their pH values.
- The values you obtain are recorded below.
- |            |          |
|------------|----------|
| Solution M | pH = 5.7 |
| Solution N | pH = 3.0 |
| Solution O | pH = 4.5 |
| Solution P | pH = 6.2 |
- Arrange these four solutions in order of increasing acid strength (weakest to strongest)
  - Is any one of these acids a strong acid? Justify your answer.
  - Another student in the class has been given  $0.001 \text{ mol L}^{-1}$  solutions of some bases and records the following pH values.
- |            |         |
|------------|---------|
| Solution X | pH = 11 |
| Solution Y | pH = 9  |
| Solution Z | pH = 13 |
- Comment on the likely acid–base nature of these three solutions and the measurements that this student has made.
- 10** Some solutions of sodium bromide, sodium hydrogensulfate and sodium hydrogencarbonate are found to have the pH values shown below.
- |                          |          |
|--------------------------|----------|
| Sodium bromide           | pH = 7   |
| Sodium hydrogensulfate   | pH = 5.5 |
| Sodium hydrogencarbonate | pH = 8.0 |

Explain these results in terms of any hydrolysis reactions that take place when the salts are dissolved in water.

- 11** Explain the difference between the terms 'ionisation', 'dissociation' and 'hydrolysis'.
- 12 a** Water is a weaker acid than the hydrogenselenate ion,  $\text{HSeO}_4^-$ . Write a balanced ionic equation for the hydrolysis of the hydrogenselenate ion.
- b** Water is a weaker base than the cyanide ion,  $\text{CN}^-$ . Write a balanced ionic equation for the hydrolysis of the cyanide ion.
- 13** The labels have fallen off three bottles, each of which contains white crystals. The bottles are known to contain ammonium nitrate, sodium nitrate and sodium carbonate. Using only pH paper, explain how you would determine the contents of each bottle.
- 14** A dilute solution of ammonia has its pH recorded as 9.5. Determine the hydronium ion and hydroxide ion concentrations in the solution.
- 15** A  $0.100 \text{ mol L}^{-1}$  solution of acetic acid is found to be 1.35% ionised. Determine the pH of this solution.
- 16** Explain the meaning of the following statement with particular reference to the terms 'dilute', 'concentrated', 'strong' and 'weak'.  
A  $10 \text{ mol L}^{-1}$  solution of acetic acid is a concentrated solution of a weak acid, while a  $0.001 \text{ mol L}^{-1}$  solution of sulfuric acid is a dilute solution of a strong acid.
- 17** Calculate the pH of the following solutions.
- a** A solution in which the concentration of hydroxide ions is  $5.38 \times 10^{-3} \text{ mol L}^{-1}$
- b** 45 mL of a  $0.00735 \text{ mol L}^{-1}$  solution of the strong acid HBr
- c**  $3.25 \text{ mol L}^{-1}$  sodium hydroxide solution
- d** A solution prepared by dissolving 4.48 L of hydrogen chloride gas at STP in water to form 0.250 L of solution
- e** The solution formed by reacting 24.0 mL of  $2.00 \text{ mol L}^{-1}$  nitric acid with 0.0532 g of barium hydroxide
- 18** Solution A has a concentration of hydronium ions that is 10 000 times greater than that of solution B. By what factor is the pH of solution A different from the pH of solution B?

**19** Copy and complete the following table

	$[\text{H}_3\text{O}^+]$ ( $\text{mol L}^{-1}$ )	$[\text{OH}^-]$ ( $\text{mol L}^{-1}$ )	pH	Acidic or basic?
Solution 1		$3.45 \times 10^{-4}$		
Solution 2			7.59	
Solution 3	$2.96 \times 10^{-6}$			

- 20** In January 2008 researchers in the USA developed a buffer system that resists pH changes when the temperature changes. In their investigations with biologically active molecules that are very sensitive to pH they discovered that in some buffer systems the pH decreased when the temperature dropped while in other buffer systems the pH increased when the temperature dropped.
- a** Why does the pH of water change when the temperature is changed?
- b** What can you conclude about the buffer systems that caused a decrease in pH when the temperature dropped?
- c** What can you conclude about the buffer systems that caused an increase in pH when the temperature dropped?
- (And the answer to the problem of pH varying with temperature faced by the researchers was to simply mix two of the different types of buffer solution until there was no significant change in pH during the cooling process.)
- 21 a** A  $0.1 \text{ mol L}^{-1}$  solution of acetic acid has a pH of 2.93. This changes to a pH of 4.74 when  $0.1 \text{ mol}$  of sodium acetate is added. Explain why the pH changes in this way.
- b** The mixture of acetic acid and sodium acetate solutions produced in part a has  $0.5 \text{ mL}$  of  $0.1 \text{ mol L}^{-1}$  HCl added to it. Explain why the pH of the solution does not change significantly.
- 22 a i** Using only ammonium chloride and ammonia solution, describe how you could produce a buffer solution.
- ii** Explain how this buffer solution would 'work'.
- b** If you wanted to decrease the pH of the buffer solution produced in part a and you only have access to ammonium chloride and ammonia solution, what would you do? Explain your answer.
- c** If you wanted to produce a solution with a greater buffer capacity than that produced in part a describe the changes you would make to the production of the buffer.



- 23** Strenuous athletic activity can lead to the formation of lactic acid in muscles from the oxidation of glucose in a limited oxygen supply. The presence of the excess acid in the muscle tissue is claimed to interfere with muscular activity and it has been claimed that athletic performance is reduced.

Some athletes involved in short-distance events hyperventilate just before the race starts. Hyperventilation involves rapid, deep breathing. It is argued that hyperventilation increases oxygen flow to the bloodstream and expels carbon dioxide.

- Use the equations involving the two equilibria in the carbonic acid/hydrogencarbonate/ $\text{CO}_2$  buffer system to show what would be the effect of this rapid breathing on the position of equilibrium.
  - What would happen to the pH of blood as a result of hyperventilation?
  - Lactic acid has the formula  $\text{C}_3\text{H}_6\text{O}_3$  and is a weak monoprotic acid. Write an equation to show what will happen to lactic acid when it dissolves in an aqueous medium such as blood.
  - How does hyperventilation help prevent the build up of excess  $\text{H}_3\text{O}^+$  from lactic acid in the muscle tissue?
  - If the race starts later than the athlete anticipated, why might hyperventilation be dangerous?
- 24** One method that can be used to monitor the progress of a reaction or determine the equivalence point of a titration involves measuring the electrical conductivity of the reaction mixture.

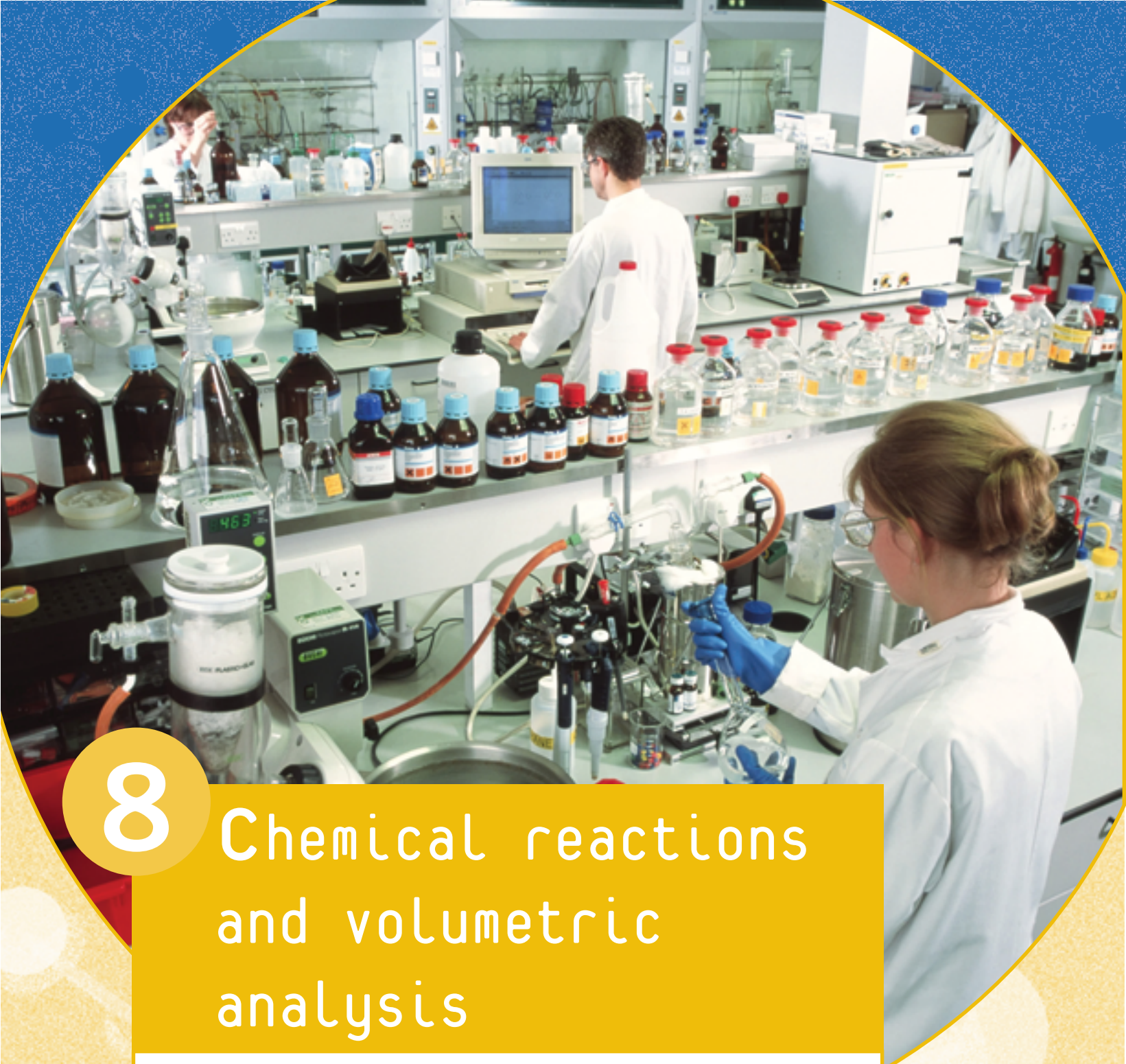
In a solution, the electric current is carried by the anions and cations. The conductance of a solution is therefore a measure of the concentration and type of cations and anions present. Most ions have similar conductances; however, hydrogen ions and hydroxide ions have particularly high conductances, as shown in the table below.

Cation	Relative conductance	Anion	Relative conductance
$\text{H}^+$	349.8	$\text{OH}^-$	198.3
$\text{Na}^+$	50.1	$\text{Cl}^-$	76.3
$\text{K}^+$	73.5	$\text{NO}_3^-$	71.5
$\text{NH}_4^+$	73.5	$\text{SO}_4^{2-}$	159.6
$\text{Ba}^{2+}$	127.3	$\text{CH}_3\text{CO}_2^-$	40.9

When one solution is added to another, the conductivity of the reaction mixture will change as the type and proportion of ions present varies as the reaction proceeds. The changes in conductivity during four titrations are shown in the graphs on the next page. In each titration, the addition of the solution from the burette was continued past the equivalence point.

For each graph (on the next page), explain, in terms of the ions present before, during and after the reaction, why the conductance changes in the way shown. Also explain how you could use the graphs to determine when the equivalence point is reached for titration 1 and titration 2.

Titration number	Solution being titrated, i.e. solution present in the flask at the beginning of the titration	Solution added from the burette	Conductance curve of the reaction mixture
1	20 mL of approximately 0.1 mol L <sup>-1</sup> HCl	0.1 mol L <sup>-1</sup> NaOH	
2	20 mL of approximately 0.1 mol L <sup>-1</sup> HCl	0.1 mol L <sup>-1</sup> NH <sub>3</sub>	
3	20 mL of approximately 0.1 mol L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub>	0.1 mol L <sup>-1</sup> Ba(OH) <sub>2</sub>	
4	20 mL of approximately 0.1 mol L <sup>-1</sup> CH <sub>3</sub> COOH	0.1 mol L <sup>-1</sup> NH <sub>3</sub>	



# 8

## Chemical reactions and volumetric analysis

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

- write ionic equations for the common reactions of acids
- describe the procedures used during a titration
- explain the methods used to minimise experimental error during titrations
- explain the characteristics of primary and secondary standards
- explain the difference between end point and equivalence point in a titration
- explain the choice of indicators in titrations
- perform calculations based on acid–base and redox titrations.

Two questions are at the heart of chemistry: ‘What is the structure of matter?’ and ‘How is matter transformed from one form to another?’ The first has been dealt with, in part, in the chapters on bonding. The second has been introduced in Chapters 4–7 and will be extended in this chapter.

Chemical reactions keep us alive, produce and cook our food, drive our cars, supply our electrical energy directly and indirectly, provide the means to cure our diseases, keep us looking attractive, synthesise and colour the fabrics that make our clothing, colour our world and generate our construction materials, as well as a host of other applications. We are dependent on chemistry and chemicals for our survival and our way of life. As one anonymous source has asked, ‘What in the world isn’t chemistry?’

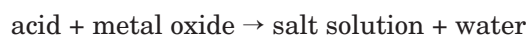
## 8.1 Acid–base and redox: two key chemical reactions

### Acid–base reactions

Some of the properties and reactions of acids and bases were introduced in Chapter 7. In this section, additional reactions of acids and bases will be examined.

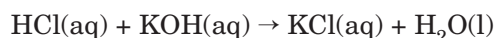
#### Reactions of acids with metal oxides and hydroxides

These two reactions are generally referred to as neutralisation reactions, with the basic hydroxide or oxide neutralising the acid to produce a solution with a pH of approximately 7. The general equations for these two reactions are:

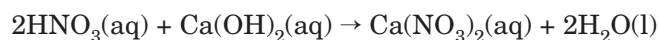


Examples of molecular or overall equations for the first reaction type are given below:

- reaction of hydrochloric acid with a solution of potassium hydroxide

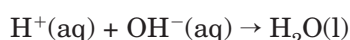


- reaction of nitric acid with a solution of calcium hydroxide



In this chapter, the hydronium ion,  $\text{H}_3\text{O}^+(\text{aq})$ , will be represented as  $\text{H}^+(\text{aq})$  in order to simplify some of the equations.

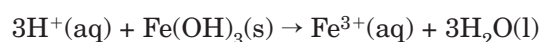
The two molecular equations above have the same ionic equation:



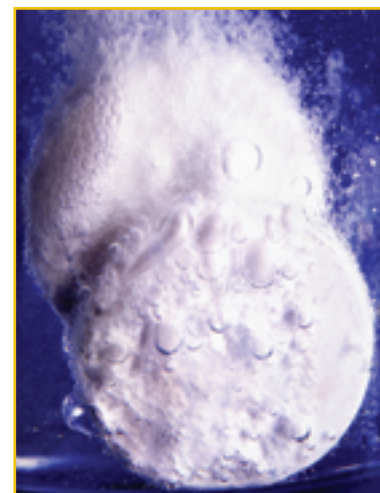
Indeed every reaction of a strong acid with a group 1 or 2 metal hydroxide solution has this same ionic equation. (The ions that have not been changed during the reaction (the spectator ions) are not included in the ionic equation. A method used to determine the spectator ions in a reaction was explained in Chapter 5.)

The hydroxides of group 13 metals and transition metals are generally sparingly soluble, so the ionic equations for these reactions include the formula of the solid metal hydroxide.

For example, for the reaction of hydrochloric acid with iron(III) hydroxide, the ionic equation would be:



( $\text{Cl}^-$  ions act as spectator ions.)



**Figure 8.1** Antacid tablets dissolving in water involve a reaction between an acid and a hydrogencarbonate.



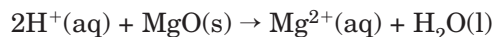
**Figure 8.2** Copper reacting with concentrated nitric acid

This also applies to any solid hydroxide. In the ionic equation they are represented by writing the 'neutral' formula, such as NaOH(s).

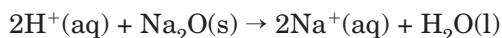
Reactions between acids and metal oxides generally involve the metal oxide in the solid state. Group 1 metal oxides are soluble in water, but the oxide ion is such a strong base that it reacts with the water to produce hydroxide ions. An aqueous solution of the oxide ion is not possible.

Examples of ionic equations for reactions of acids with metal oxides are:

- reaction of nitric acid with magnesium oxide



- reaction of sulfuric acid with solid sodium oxide

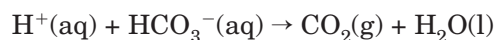
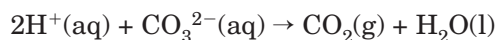


### Reactions of acids with carbonates and hydrogencarbonates

Both of these reactions result in the formation of a salt, carbon dioxide and water:



Group 1 metal carbonates and all hydrogencarbonates are soluble in water so the ionic equations for the reactions of solutions of these compounds are:



Carbonates of the other metals are insoluble in water so their formulas are written as solids. Other carbonates and hydrogencarbonates added to the acid as solids are also shown as the 'neutral' formula. Examples of these ionic equations are:

- reaction of hydrochloric acid with aluminium carbonate



- reaction of nitric acid with solid potassium hydrogencarbonate



The reaction of acid with metal hydroxides, carbonates and hydrogencarbonates is the basis of many antacid tablets on the market.

The lining of the stomach contains cells that produce a solution that is about  $0.1 \text{ mol L}^{-1}$  hydrochloric acid. This acid is a necessary part of the digestion of protein and keeps the stomach at an optimum pH for the enzyme pepsin to begin breaking down protein.

The walls of the stomach are normally protected from the effect of this acid by mucous that is secreted by cells in the stomach wall. Two Western Australian scientists, Barry Marshall and Robin Warren, were awarded the Nobel Prize in 2005 for their discovery that stomach ulcers, holes in the stomach wall that allow acid to attack the unprotected tissue beneath, are caused by a particular bacterium.

Sometimes too much acid is produced in the stomach and this may enter the oesophagus, where the 'burning' condition known as indigestion or heartburn may be experienced. This condition can be easily treated with an antacid powder. This is a substance that contains one or more of a carbonate, hydrogencarbonate or a group 2 or 13 metal hydroxide. Table 8.1 gives the composition of some common antacids.

**TABLE 8.1** INGREDIENTS IN COMMON ANTACIDS

Antacid name	Active ingredient
Alka-Seltzer	$\text{NaHCO}_3$
Mylanta	$\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$
Milk of magnesia	$\text{Mg}(\text{OH})_2$
Roloids	$\text{Mg}(\text{OH})_2$ and $\text{CaCO}_3$

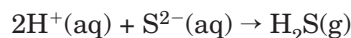
### Reactions of acids with sulfides and sulfites

Other general reactions of acids include their reaction with sulfides and sulfites, as represented in the general equations below:



Examples of ionic equations for reactions involving a sulfide and a sulfite are represented as follows:

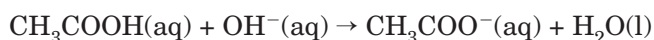
- reaction of nitric acid with a solution of sodium sulfide



- reaction of hydrochloric acid with solid magnesium sulfite

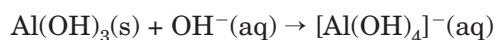


If weak acids are involved in any of the reactions described in this section, they are represented in the ionic equation in their ‘un-ionised’ form. For example, the ionic equation for the reaction of acetic acid with a solution of potassium hydroxide would be:



### Reaction of a base with an amphoteric oxide or hydroxide

In Stage 2 of this chemistry course, the separation of aluminium oxide from bauxite in the Bayer process was discussed. Aluminium oxide and hydroxide are both examples of amphoteric compounds. An amphoteric substance is able to act as both an acid and a base. As well as reacting with acids, aluminium oxide and aluminium hydroxide react with a base such as sodium hydroxide to produce a solution containing the aluminate ion, a complex ion:



## Redox reactions

Whereas acid–base reactions are classified in terms of hydrogen ion (proton) transfer, redox (oxidation–reduction) reactions involve electron transfer.

In redox reactions:

- when a substance loses electrons, it is oxidised
- when a substance gains electrons, it is reduced
- oxidants gain electrons and undergo reduction
- reductants lose electrons and undergo oxidation.

Like acid–base reactions, oxidation and reduction reactions must occur as a pair. In a redox reaction, there is transfer of one or more electrons from a reductant to an oxidant.



**Figure 8.3** Some commonly used antacids

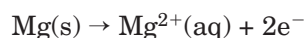
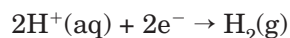
## Reactions of acids with metals

Strong acids such as hydrochloric acid and sulfuric acid react with some metals to produce a salt solution and hydrogen gas:

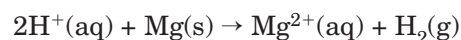


Dilute nitric acid reacts in the same way, but at higher concentrations the reaction with metals is more complex (see Chapter 10). Less reactive metals such as copper, silver and gold will not react with acids to produce hydrogen in this manner.

The electron transfer nature of the reaction of a metal with an acid can be seen in the following example, of magnesium reacting with hydrochloric acid, that has been split into its two component half-reactions:

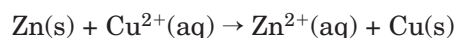


The acid ( $\text{H}^+$ ) has gained electrons and has been reduced to hydrogen gas. The metal has been oxidised to the positive ion (cation), releasing two electrons in the process. The ionic equation for this reaction (obtained by adding the two half-equations together) is then:



## Metal displacement reactions

In the Stage 2 course the reactivity series of metals was introduced, demonstrating that it is possible for some metals to donate electrons to the positive ions of less reactive metals and, in the process, 'displace' that less reactive metal from solution. For example, if zinc metal is placed in a solution containing copper ions, the zinc is oxidised, and donates its electrons to the copper ions. The copper ions are reduced to the metal:

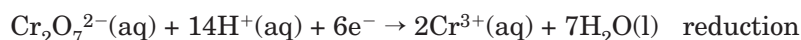


This is an example of a group of redox reactions known as displacement reactions.

## Redox reactions in solution

Some redox reactions that are important for chemical analysis (determining how much of a particular chemical is present in a sample) include those involving solutions of potassium permanganate, potassium dichromate, iron(II) salts and the oxalate ion,  $\text{C}_2\text{O}_4^{2-}$ .

The half-equations for these reactions are:



In addition to the redox reactions considered above, there is a vast array of other redox reactions that are important to our lifestyle. These include combustion reactions, respiration, photosynthesis, corrosion and batteries. Some of these will be considered in detail later in this text.

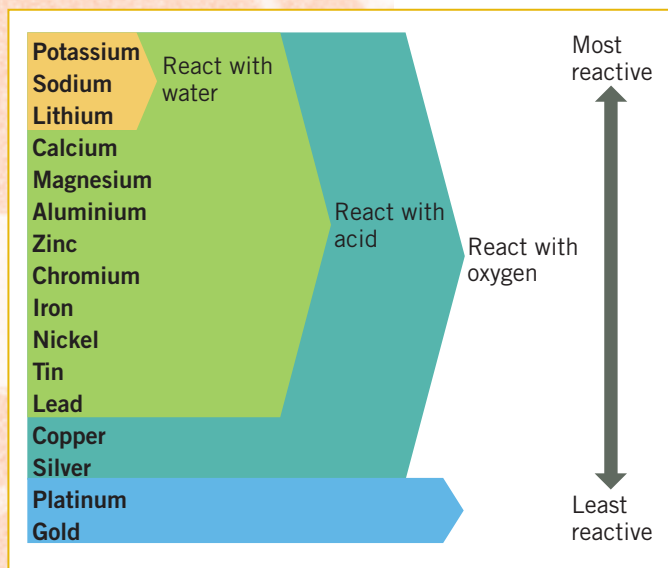


Figure 8.4 The displacement series of metals

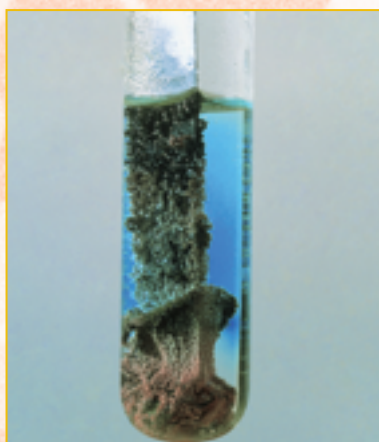


Figure 8.5 Zinc displacing copper from a solution of copper sulfate

### → Example 8.1

Write ionic equations and give observations for the following reactions.

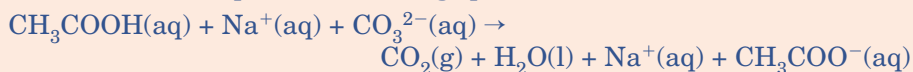
- Acetic acid is added to a solution of sodium carbonate.
- Hydrochloric acid is mixed with solid nickel hydroxide.
- A purple solution of potassium permanganate is added dropwise to an acidified solution of potassium oxalate.

### → Solution

(Guidelines for writing ionic equations and giving observations were given in section 5.1. The colours of ions and gases were given in Table 5.2.)

- a** This is a reaction of an acid with a carbonate, so the products will be carbon dioxide, water and a solution of sodium acetate (the salt).

The unbalanced equation, including spectator ions is:



The spectator ion is  $\text{Na}^+(\text{aq})$ .

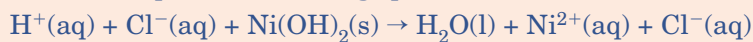
The balanced ionic equation is:



**Observations:** A colourless odourless gas forms and a colourless solution remains.

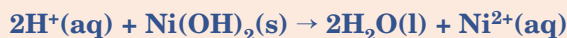
- b** This is a reaction of an acid with a hydroxide, so the products will be water and a solution of nickel chloride (the salt).

The unbalanced equation, including spectator ions is:



The spectator ion is  $\text{Cl}^-(\text{aq})$ .

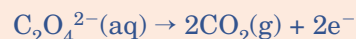
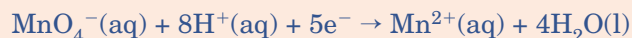
The balanced ionic equation is:



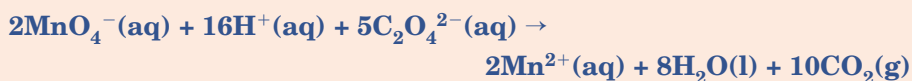
**Observations:** The green solid dissolves to form a green solution.

- c** Ionic equations for redox reactions are normally written by adding the two relevant half-equations together ensuring the electrons ‘cancel out’.

The two relevant half-equations for this reaction are:



So the final equation will show that the number of electrons being gained by  $\text{MnO}_4^-$  is equal to the number of electrons lost by  $\text{C}_2\text{O}_4^{2-}$ , the first equation needs to be ‘multiplied by 2’ and the second one by 5, before adding them together. This gives a balanced ionic equation of:



**Observations:** A colourless odourless gas is produced and the purple solution turns colourless.



## \* Review exercise 8.1

- Write balanced ionic equations, and give observations, for each of the following chemical reactions.
  - Sulfuric acid is added to a solution of lithium hydroxide.
  - Nitric acid is added to solid copper(II) oxide.
  - Iron(II) hydroxide is reacted with a solution of hydrochloric acid.
  - Solid potassium oxide is added to a solution of sulfuric acid.
  - Nitric acid is added to calcium carbonate.
  - A solution of potassium hydrogencarbonate is added to hydrochloric acid.
  - Nitric acid is added to solid ammonium sulfide.
  - A solution of rubidium sulfite is reacted with sulfuric acid.
- Write balanced ionic equations for the following oxidation and reduction reactions.
  - Zinc metal is added to dilute sulfuric acid solution.
  - Copper metal is added to a solution of silver nitrate.
  - Very dilute nitric acid is poured onto a piece of calcium.
  - Acidified potassium permanganate solution is added to a solution of iron(II) sulfate and the colour of the purple permanganate solution is observed to disappear.
  - Acidified potassium dichromate solution is added to a solution of sodium oxalate and the orange colour of the dichromate solution is observed to change to a deep green colour.
- The halogens in group 17 form a displacement series. All the halogens are oxidants, but the oxidant strength decreases down the group. Fluorine is the strongest oxidant while astatine is the weakest. Use this information to predict whether or not the following combinations will react. If there would be no reaction, write 'No reaction'. Write an ionic equation for any predicted reactions.
  - Chlorine gas is bubbled through a solution of potassium iodide.
  - A solution of bromine in water is added to a solution of sodium fluoride.
  - A solution of bromine in water is added to a solution of ammonium iodide.
- Aluminium hydroxide and magnesium hydroxide are both white solids, sparingly soluble in water. What chemical reaction can be used to distinguish between these two metal hydroxides?

## 8.2 Chemical analysis: investigations using reaction stoichiometry

### Gravimetric versus volumetric analysis

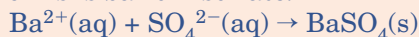
Gravimetric analysis involves determining the mass of a substance produced in a chemical reaction and using this to solve a chemical problem. The technique is often used in chemical reactions where one of the substances is produced as a precipitate.

### → Example 8.2

A chemist is asked to determine the percentage of magnesium hydroxide in a mixture with barium hydroxide. 23.90 g of the mixture is dissolved by the addition of dilute nitric acid and excess of a solution of sodium sulfate is added. The white precipitate formed is filtered and dried. The mass of the dry precipitate is found to be 8.65 g. Determine the percentage, by mass, of magnesium hydroxide in the original mixture.

### → Solution

The precipitate that forms is barium sulfate.



$$\begin{aligned} n(\text{BaSO}_4) \text{ formed} &= \frac{m(\text{BaSO}_4)}{M(\text{BaSO}_4)} & M(\text{BaSO}_4) &= 233.36 \text{ g mol}^{-1} \\ &= \frac{8.65}{233.36} = 0.03707 \text{ mol} \end{aligned}$$

1 mole of  $\text{BaSO}_4$  is obtained from 1 mole of  $\text{Ba}(\text{OH})_2$  in the original sample so 0.03707 mol of  $\text{Ba}(\text{OH})_2$  was present in the mixture.

$$\begin{aligned} n(\text{Ba}(\text{OH})_2) \text{ present} &= \frac{m(\text{Ba}(\text{OH})_2)}{M(\text{Ba}(\text{OH})_2)} \\ M(\text{Ba}(\text{OH})_2) &= 171.316 \text{ g mol}^{-1} \end{aligned}$$

$$m(\text{Ba}(\text{OH})_2) \text{ in original sample} = 0.03707 \times 171.316 = 6.351 \text{ g}$$

$$\text{mass of Mg}(\text{OH})_2 \text{ in the sample} = 23.90 - 6.351 = 17.55 \text{ g}$$

$$\text{percentage of Mg}(\text{OH})_2 \text{ in sample} = \frac{17.55}{23.90} \times 100 = \mathbf{73.4\%}$$

### → Example 8.3

A sample of hydrated copper(II) sulfate has the formula  $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$ . From the following experimental data, determine the value of  $x$ .

0.5861 g of the hydrated copper(II) sulfate was dissolved in water. A solution containing  $6 \text{ mol L}^{-1}$  sodium hydroxide was added and the mixture was boiled for 10 minutes. The black copper oxide precipitate was filtered, washed and dried. The copper(II) oxide had a mass of 0.1867 g.

### → Solution

$$\begin{aligned} n(\text{CuO}) &= \frac{m(\text{CuO})}{M(\text{CuO})} & M(\text{CuO}) &= 79.55 \text{ g mol}^{-1} \\ &= \frac{0.1867}{79.55} = 0.002347 \text{ mol} \end{aligned}$$

1 mol of  $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$  produces 1 mol of CuO.

$$n(\text{CuSO}_4 \cdot x\text{H}_2\text{O}) = 0.002347 \text{ mol}$$

$$n(\text{CuSO}_4 \cdot x\text{H}_2\text{O}) = \frac{m(\text{CuSO}_4 \cdot x\text{H}_2\text{O})}{M(\text{CuSO}_4 \cdot x\text{H}_2\text{O})}$$

$$\text{molar mass of } \text{CuSO}_4 \cdot x\text{H}_2\text{O} = \frac{0.5861}{0.002347} = 249.7 \text{ g mol}^{-1}$$

The sum of the atomic masses of  $\text{CuSO}_4$  is 159.61.

Therefore the sum of the atomic masses of  $x\text{H}_2\text{O}$  is  $249.7 - 159.61 = 90.1$

$$x = \frac{90.1}{18.016} = 5.00$$

Hence, the formula of the hydrated copper(II) sulfate is  **$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$** .

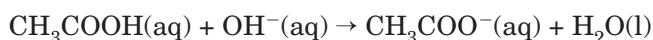
Volumetric analysis involves the use of measured volumes of solutions that undergo chemical reactions. Since much of acid–base and redox chemistry takes place in solutions, volumetric analysis is the most commonly used analytical technique for dealing with these two areas of chemistry.

### Volumetric analysis—a study in concentration

For any chemical reaction with a known equation, taking place in solution, volumetric analysis provides a way to determine the amounts of substances in the solution.

During a typical analysis, a solution of one of the reactants is added to a fixed volume of the other reactant. Provided the concentration of one of these solutions is known, it is possible to determine the concentration of the other solution. However, this analysis depends on the ability to determine the point at which complete reaction of the substances has taken place. This point at which the correct stoichiometric amounts of each substance have reacted is called the equivalence point. The process in which one solution is added progressively to a measured volume of another solution is called a titration.

For example, in the determination of the amount of acetic acid in vinegar the experiment might call for a solution of sodium hydroxide of known concentration to be added to a fixed volume of commercial vinegar:



At the beginning of the titration, the acetic acid will be in excess. As the sodium hydroxide is added, the acetic acid will be consumed. Finally a stage will be reached where sufficient sodium hydroxide has been added to react exactly with all of the acetic acid. The reaction mixture now is a solution of only sodium acetate. This is the point at which the correct stoichiometric amounts of acid and base have been combined—the equivalence point. But in appearance, this stage or point of the reaction will seem no different from any other stage during the titration; colourless solutions are being mixed and colourless solutions are being produced. So some indication of when the equivalence point has been reached will need to be provided.

In acid–base titrations this means of observing the equivalence point is provided by adding an indicator that undergoes a colour change at or near to the equivalence point. The point at which the indicator changes colour is called the end point.

## \* Review exercise 8.2

- For each of the following state whether a gravimetric or volumetric analysis would be the most appropriate.
  - Determining the amount of water of crystallisation in a sample of hydrated barium chloride
  - Calculating the concentration of lead ions in a sample of water using the equation:
$$\text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq}) \rightarrow \text{PbCl}_2(\text{s})$$
  - Determining the percentage of ammonia in a household cleaner by reacting a solution of the cleaner with hydrochloric acid
  - Calculating the amount of sulfur dioxide dissolved in a sample of wine by oxidising it with a solution of potassium permanganate
- A sample of lawn food is known to contain iron as a soluble iron(II) salt. A 0.5479 g sample of the lawn food was dissolved in dilute hydrochloric acid and then a little nitric acid was added. The mixture was boiled and turned an orange-brown colour. An excess of ammonia solution was added and the precipitate of iron(III) oxide,  $\text{Fe}_2\text{O}_3$ , was collected and dried to constant mass. The mass of iron(III) oxide collected was 0.1832 g. Calculate the percentage by mass of iron in the lawn food.
- Using your knowledge of chemical reactions, reactions rates and principles of equilibrium, outline the particular characteristics of a chemical reaction that make it suitable for use in a titration.

## 8.3 Principles of volumetric analysis

### Equipment

Some of the equipment that may be required in volumetric analysis is shown in Table 8.2.

TABLE 8.2 EQUIPMENT USED IN VOLUMETRIC ANALYSES

Pipette	<ul style="list-style-type: none"><li>Used to accurately deliver a specific, measured volume of solution, e.g. 20.00 mL.</li><li>The volume of solution delivered from the pipette is called an aliquot.</li><li>Prior to being used in an analysis, the pipette should be rinsed with a small amount of the solution being delivered from it in the titration.</li></ul>
Burette	<ul style="list-style-type: none"><li>Used to accurately deliver a variable volume of solution.</li><li>The volume of solution delivered from the burette is called the titre.</li><li>Prior to being used in an analysis, the burette should be rinsed with a small amount of the solution that is being delivered for the titre.</li></ul>
Volumetric flask	<ul style="list-style-type: none"><li>Holds an accurately known volume of a solution.</li><li>Used to make up a standard solution.</li><li>Should be rinsed with distilled or de-ionised water prior to use.</li></ul>
Analytical balance	<ul style="list-style-type: none"><li>Used to measure accurate masses of solids that are used to make up standard solutions.</li></ul>
Conical flask	<ul style="list-style-type: none"><li>Used to hold the reaction mixture during the titration.</li><li>Should be rinsed with distilled water before the aliquot is put into it.</li></ul>

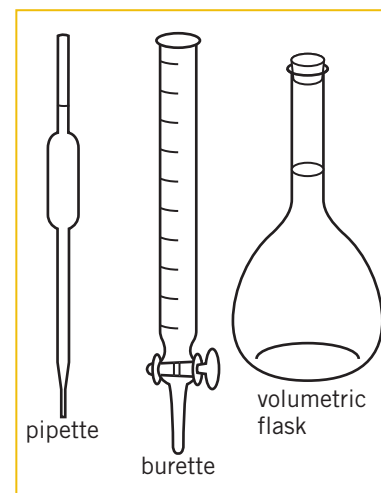


Figure 8.6 Equipment used for volumetric analysis

## Standard solutions

A standard solution has an accurately known concentration. In a titration involving two solutions, one of the solutions must have a known concentration. There are two types of standards that are used in titrations: primary standards and secondary standards.

Many of the substances that are commonly used for acid–base or redox titrations have variable or changing compositions. The concentrated hydrochloric acid and nitric acid used in the laboratory have variable compositions. Concentrated sulfuric acid absorbs water from the atmosphere so its exact composition is not known either. The group 1 hydroxides such as sodium hydroxide and potassium hydroxide also absorb water from the atmosphere, as well as carbon dioxide. Potassium permanganate is such a powerful oxidant that it will react with the small amounts of reducing agents in the atmosphere.

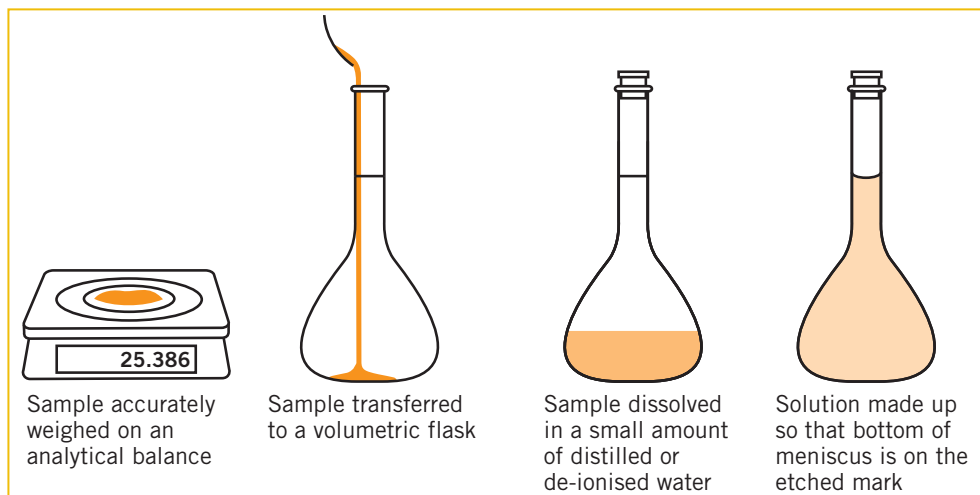
A primary standard is a substance possessing purity criteria that these common acid–base and redox chemicals lack:

- It can be obtained with a high degree of purity and has a known formula.
- It undergoes reactions according to known chemical equations.
- It must be stable. This means its composition does not change on exposure to the atmosphere. Sodium hydroxide is not a suitable primary standard because it absorbs water from the atmosphere (deliquescence) and also reacts with carbon dioxide in the atmosphere. Hydrated sodium carbonate,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , loses water to the atmosphere (hygroscopic).
- It should have a relatively high formula mass to minimise weighing errors. To produce solutions having the same concentration, a greater mass of the substance with the higher molar mass will need to be weighed out. Since the uncertainty in the balance is a fixed value, this fixed value, as a percentage of the larger mass, will be smaller.

Primary standards for acid–base titrations include anhydrous sodium carbonate,  $\text{Na}_2\text{CO}_3$ , oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , and potassium hydrogenphthalate,  $\text{KHC}_8\text{H}_4\text{O}_4$ . Oxalic acid is also a primary standard for redox titrations.

A solution of a primary standard is prepared by dissolving an accurately weighed mass of the primary standard in an accurately known volume of solution, normally contained in a volumetric flask. The steps in the procedure include:

- accurately weighing out a previously calculated mass of the primary standard
- quantitatively transferring the solid to the volumetric flask
- adding a small amount of distilled or de-ionised water to the flask and swirling to dissolve the solid
- adding more distilled or de-ionised water to make the solution up to the calibration mark on the neck of the volumetric flask. The bottom of the meniscus must be just on the mark
- thoroughly shaking the contents to ensure that the solid has dissolved and is evenly spread through the solution (Figure 8.7).



**Figure 8.7** Steps in making a solution of a primary standard

Once a solution of a primary standard has been prepared, it is possible to use this solution of accurately known concentration to titrate a second solution to determine its accurate concentration. This second solution, with its now known concentration, is referred to as a secondary standard solution. It is this process that allows the concentration of a solution of a secondary standard such as hydrochloric acid or sodium hydroxide to be determined.

#### → Example 8.4

10.67 g of anhydrous sodium carbonate was dissolved in distilled water and made up to a 250.0 mL solution in a volumetric flask. What is the concentration of this standard solution?

#### → Solution

$$n(\text{Na}_2\text{CO}_3) = \frac{m(\text{Na}_2\text{CO}_3)}{M(\text{Na}_2\text{CO}_3)} \quad M(\text{Na}_2\text{CO}_3) = 105.99 \text{ g mol}^{-1}$$

$$= \frac{10.67}{105.99} = 0.10067 \text{ mol}$$

$$c(\text{Na}_2\text{CO}_3 \text{ solution}) = \frac{n(\text{Na}_2\text{CO}_3)}{V(\text{Na}_2\text{CO}_3 \text{ solution})}$$

$$= \frac{0.10067}{0.2500} = \mathbf{0.4027 \text{ mol L}^{-1}}$$

### The titration

As discussed previously, a titration involves the addition of one solution to another in a manner that allows a fixed volume of one solution to react completely with a measured volume of the other solution.

A pipette is used to deliver a fixed, accurate volume of one of the reactants to a conical flask. Typically a pipette is used to deliver a specific volume of solution. Pipettes used in school laboratories usually have an accuracy of  $\pm 0.02$  mL. Thus, a 20.00 mL pipette will deliver a volume of solution between 19.98 and 20.02 mL if used correctly.

A burette is used to deliver a variable volume of the second solution. Most school laboratory burettes will deliver up to 50.00 mL with an accuracy of  $\pm 0.05$  mL. The solution in the burette is added carefully to the solution in the conical flask until the reaction is complete (see next section).



**Figure 8.8** Acid being added from a burette to an alkaline solution in the flask. The indicator in this titration is phenolphthalein.



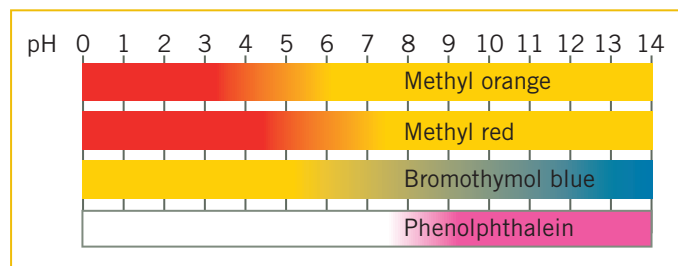
**Figure 8.9** For colourless or pale-coloured solutions, the reading on the burette scale is taken from the bottom of the meniscus. On this burette, the reading is 9.00 mL.

Because the burette is delivering a variable volume of solution, it is generally the case that this volume should not be too small. The uncertainty in the reading is  $\pm 0.05$  mL no matter what volume of solution is delivered. The larger the volume of solution delivered from the burette, the smaller the percentage uncertainty in the result. In general, the volume being delivered from the burette should be approximately the same as the aliquot supplied by the pipette.

The first titration is usually performed quickly to give a rough estimate of the volume that needs to be delivered to achieve complete reaction. After this, the experiment is repeated several times. In each of these titrations, a volume close to that estimated from the first rough experiment is added quickly. Then the volume of solution being delivered from the burette is carefully controlled with drop-by-drop addition and swirling of the conical flask to ensure thorough mixing of the two reactants. The purpose of repeating a titration is to establish two or three results that are concordant. These are results that agree very closely, usually to within 0.1 mL. For subsequent calculations, the average of the concordant titres is used.

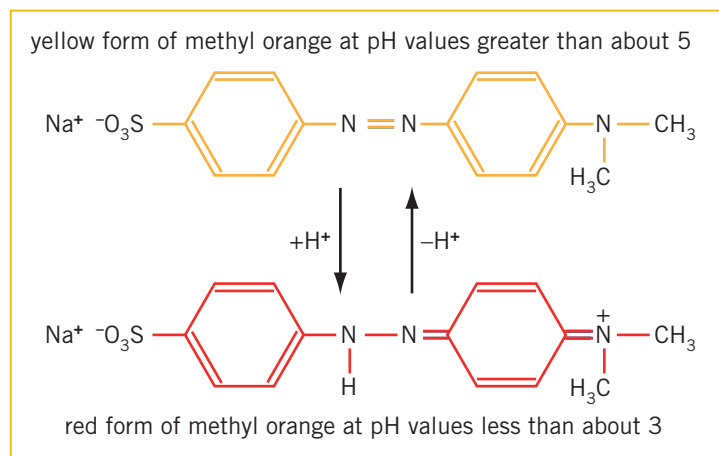
## Indicators

When two colourless solutions undergo a reaction that does not produce a gas or precipitate, it is very difficult to determine when stoichiometric (equivalent) amounts of the two reactants have combined. An indicator is required that produces a colour change at a point very close to the equivalence point.



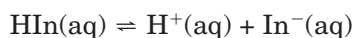
**Figure 8.10** pH colour changes for some common indicators

Acid–base indicators are substances whose colour depends on the pH of the solution in which they are dissolved. By careful choice of an indicator whose colour change takes place at a pH close to the equivalence point for the titration, it is possible to determine when the reaction is complete. The point at which the indicator changes colour is called the end point. So the task of the chemist undertaking the titration is to find an indicator whose end point matches the equivalence point.

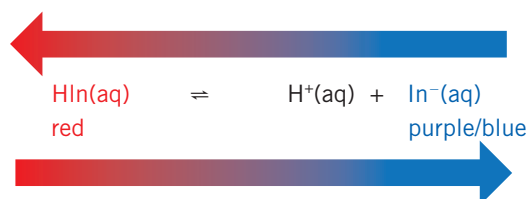


**Figure 8.11** Two forms of methyl orange at different pH values

Indicators for acid–base reactions are themselves weak acids. For an indicator with the general formula HIn, the reaction taking place in an aqueous solution is:



The colour change in the indicator is due to the different colours of HIn and In<sup>−</sup>. For example, litmus is an acid–base indicator that is red in the presence of acid and purple/blue in the presence of base. This can be represented as follows:



Adding H<sup>+</sup> (lowering the pH) causes the position of equilibrium to shift to the left, favouring the red form of the indicator. Removing H<sup>+</sup> by adding OH<sup>−</sup> (raising the pH) shifts the position of equilibrium to the right, favouring the purple/blue form of the indicator.

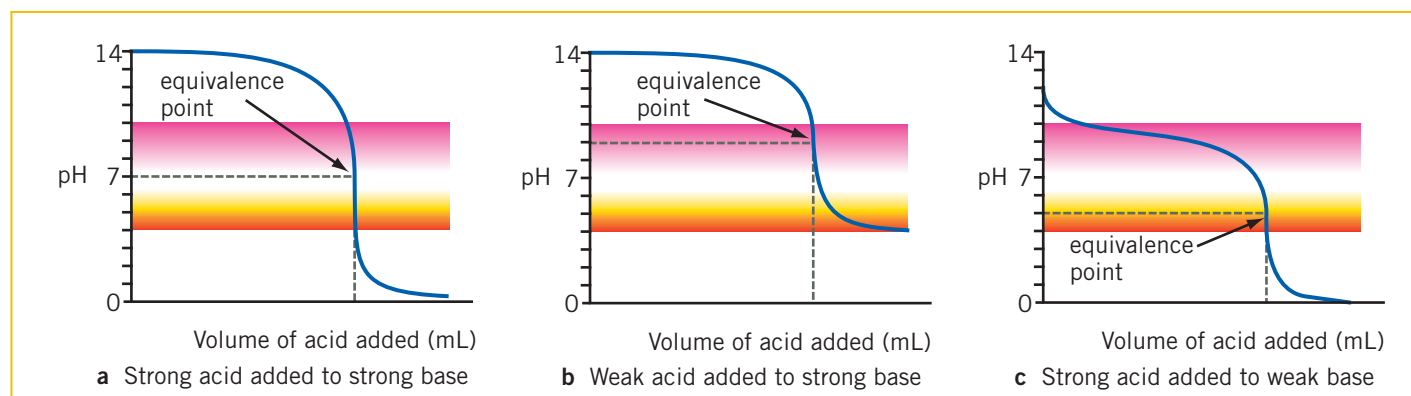
While litmus is not a particularly good indicator for acid–base titrations, the end point would be observed when the concentrations of HIn and In<sup>−</sup> are the same. The colour of the indicator solution at this point would be purple (equal amounts of the red and purple/blue forms).

Acid–base reactions are generally called neutralisation reactions. However, as revealed in Chapter 7, only those reactions that involve a strong acid and a strong base produce a salt that has a pH of 7 (neutral). The salts produced from other combinations involving weak acids or weak bases do not produce solutions with a pH of 7 at the equivalence point. As a result, the choice of indicator for an acid–base titration can be particularly important for obtaining the correct match of end point and equivalence point.

### pH changes in titrations of acids and bases



When an acid solution is added to a base solution, the pH does not change in a linear fashion. Figure 8.12 shows the way in which the pH changes during reactions in which an acid is added from a burette to a fixed aliquot of base. The three titration curves depicted show the change in pH with volume of acid added for (a) strong acid added to strong base, (b) weak acid added to strong base, and (c) strong acid added to weak base.



**Figure 8.12** Acid–base titration curves. The colour changes of indicators methyl orange and phenolphthalein at different pH values are also shown



Initially for each curve, the pH does not change very much while a significant volume of acid is added. Then the pH changes markedly with the addition of only a small volume of acid, followed by another almost horizontal region where the pH does not change very much. The steep section of the curve corresponds to the point where one drop of acid causes the pH to drop from a high pH to a much lower value. This steep section corresponds to the equivalence point of the reaction.

Two indicators commonly used in acid–base titrations are phenolphthalein and methyl orange. Phenolphthalein is colourless at pH values below about 8.3, but changes to pink between pH 8.3 and 9.5. Methyl orange is red at pH values below 3.1, orange between pH 3.1 and 4.4, and above this pH it is yellow. The pH range over which each indicator changes is also shown on the three titration curves in Figure 8.12.



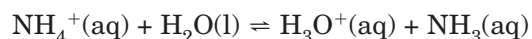
**Figure 8.13** During a titration of hydrochloric acid with sodium carbonate solution, using methyl orange as the indicator, the colours shown from left to right are before the end point, at the end point and after the end point.



**Figure 8.14** During a titration of hydrochloric acid with sodium hydroxide solution, using phenolphthalein as the indicator, the colours shown from left to right are before the end point, at the end point and after the end point.

The key to a successful titration is choosing an indicator that has an end point (colour change) that matches the equivalence point (steep section of the titration curve). For a reaction between a strong acid and a strong base, both methyl orange and phenolphthalein change colour during the addition of the one drop of acid that causes the pH to change dramatically (as shown in Figure 8.12, graph a). As a result, either indicator could be used to determine the equivalence point of a strong acid, strong base titration.

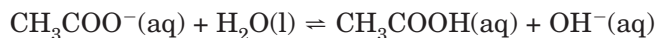
When a strong acid such as hydrochloric acid is added to a weak base such as ammonia, the equivalence point corresponds to the point at which the product is an aqueous solution of ammonium chloride. The ammonium ion is the conjugate acid of a weak base and so produces a solution that has a pH less than 7, due to the hydrolysis reaction given below:



Because the pH of the mixture at the equivalence point has a pH below 7, phenolphthalein is not a suitable indicator for this titration. In the example depicted in Figure 8.12c, where the acid is added to a solution of the weak base, the phenolphthalein would undergo a slow colour change over a large volume

of added acid well before the equivalence point is reached. In general, for the titration of a strong acid and a weak base, methyl orange is the preferred indicator as its end point matches the equivalence point.

On the other hand, when a weak acid such as acetic acid is added to a strong base, such as sodium hydroxide, the solution at the equivalence point contains sodium ions and acetate ions. Acetate ions are the conjugate base of a weak acid and undergo hydrolysis to produce a solution that is basic:

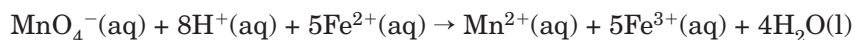


In this case, phenolphthalein changes colour at the equivalence point, but the methyl orange would not begin to change colour until after the equivalence point is reached as shown in Figure 8.12b.

Greater precision can be obtained in acid–base titrations by using a pH meter to monitor the change in pH during the titration. In this course, the reaction of a weak acid with a weak base is not considered. In fact, it is virtually impossible to find an indicator whose end point matches the equivalence point for such a titration as the pH change at the equivalence point is not as marked as it is for the other three scenarios. For titrations between a weak acid and a weak base only a pH meter can accurately monitor the equivalence point.

## Redox titrations

The equivalence point of a titration involving an oxidant and a reductant occurs when one of the oxidant or reductant is completely consumed. For example, in the reaction between acidified potassium permanganate and iron(II) sulfate, the ionic equation for the reaction is:



If the permanganate solution is added from a burette to the solution of iron(II) ions in a conical flask, the equivalence point will occur when all of the  $\text{Fe}^{2+}$  has been consumed.

It is possible to use redox indicators or special voltmeters to determine when the equivalence point has been reached. However, some of the more common redox reactions involve substances that are themselves highly coloured. In these cases, the change in colour when such a substance is consumed, or when it is just present in excess, can be used to determine the equivalence point. In other words, some redox reactions are self-indicating.

The example above of an acidified solution of potassium permanganate being added to a solution of iron(II) sulfate is one such self-indicating redox reaction. The solution of potassium permanganate is a dark purple colour while the iron(II) solution is almost colourless.

As the permanganate solution is added from the burette the purple colour disappears as it is converted to the almost colourless  $\text{Mn}^{2+}(\text{aq})$  ion. The  $\text{Fe}^{3+}(\text{aq})$  ion that is produced at the same time is an orange-brown colour, but the solution is so dilute that this colour is not obvious until later in the reaction (if at all).

Once all of the  $\text{Fe}^{2+}(\text{aq})$  has been consumed, the next drop of permanganate will not react and the solution will now have a pale pink colour due to the excess permanganate ion. This pale pink solution represents the end point (Figure 8.15). Since a slight excess of potassium permanganate has been added to produce the colour change, the end point for these titrations is always just slightly past the equivalence point. With good experimental technique it is possible to reduce this difference to a volume approximately the same as the uncertainty in the burette itself ( $\pm 0.05$  mL).



**Figure 8.15** Redox titration between potassium permanganate and iron(II) sulfate

Potassium permanganate is not a primary standard and so the solution must be previously standardised by titration with a suitable primary standard such as oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ).

### \* Review exercise 8.3

- 1 What is a standard solution?
- 2 Anhydrous sodium carbonate is a primary standard. What are the characteristics of this compound that allow it to be used as a primary standard?
- 3 **a** Two students are arguing over part of an experimental procedure. One claims that the volumetric flask into which the primary standard is to be placed must be dry before use. The other claims that as long as the flask has been thoroughly rinsed with distilled water, it doesn't need to be dry. How would you resolve this argument?  
**b** Later, these same two students argue over whether the conical flask into which the aliquot of a solution of known concentration is added needs to be dry. One states that it must be because any water in the flask would alter the concentration of the material dissolved in the aliquot. The other claims that the presence of water won't make a difference to the final titre. Both students are correct so how do you resolve this argument?
- 4 In preparing a standard solution of oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , in a 250 mL volumetric flask, you record the following measurements.  
Mass of watch glass + oxalic acid = 52.37 g  
Mass of watch glass after transfer to the volumetric flask = 48.98 g  
**a** Why is the weighing procedure described superior to simply recording the mass of the empty watch glass and the mass of watch glass + oxalic acid?  
**b** Calculate the concentration of the oxalic acid solution produced.
- 5 What is the difference between the equivalence point and the end point in a titration?
- 6 In a titration between acetic acid and potassium hydroxide, a student records the following in his laboratory notebook.
  - (i) The burette was rinsed with 5 mL of the acetic acid solution of unknown concentration. This was discarded before the burette was then filled with the acetic acid solution.
  - (ii) The pipette was rinsed with water and then used to transfer 20.00 mL of the standard potassium hydroxide solution to a conical flask. Three drops of methyl orange were added to the flask to produce a yellow coloured solution.
  - (iii) The acetic acid was added to the flask from the burette until the colour of the solution changed from yellow to red. The volume on the burette was recorded and the titre calculated.

The experimental report then goes on to detail the steps in the calculation of the concentration of the acid from this result.

This student has made several mistakes in this procedure. Identify these mistakes.

## 8.4 Calculations in volumetric analysis

The determination of the concentration of vitamin C in orange juice, the amount of 'chlorine' in bleach, the concentration of acetic acid in vinegar, the acid content of wine, and the percentage of active ingredient in an antacid powder are all examples of situations in which a titration might be undertaken to provide the answer. The principles of chemical calculations covered in earlier chapters can now be put to use in an applied situation.

### → Example 8.5

White wine contains a number of weak acids that contribute to the overall character of the wine. However, if too much acid is present, the wine may become 'undrinkable'.

In the analysis of one batch of white wine, a chemist titrates the wine with standard sodium hydroxide solution using phenolphthalein as the indicator.

The results of this experiment are summarised below.

Concentration of standard sodium hydroxide =  $0.1030 \text{ mol L}^{-1}$

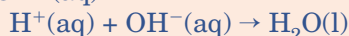
Aliquot of white wine used = 25.00 mL

Average of three concordant titres = 14.78 mL

Determine the amount, in mole, of  $\text{H}^+(\text{aq})$  available for reaction with a base in a 100 mL sample of this wine.

### → Solution

$$\begin{aligned}n(\text{NaOH}) &= c(\text{NaOH}) \times V(\text{NaOH}) \\ &= 0.1030 \times 0.01478 = 1.5223 \times 10^{-3} \text{ mol of NaOH} \\ &= \text{mol of OH}^-(\text{aq})\end{aligned}$$



1 mol of  $\text{OH}^-(\text{aq})$  reacts with 1 mol of  $\text{H}^+(\text{aq})$ .

Amount of  $\text{H}^+(\text{aq})$  in 25.00 mL aliquot =  $1.522 \times 10^{-3} \text{ mol}$

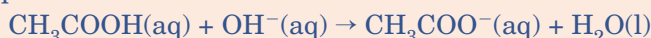
$$\begin{aligned}\text{Amount of H}^+(\text{aq}) \text{ in 100 mL of wine} &= 1.522 \times 10^{-3} \times 4 \\ &= \mathbf{6.09 \times 10^{-3} \text{ mol}}\end{aligned}$$

### → Example 8.6

A particular brand of vinegar was analysed to determine the acetic acid content. A 22.17 g sample of the vinegar was diluted (with distilled water) to 250.0 mL in a volumetric flask. A 20.00 mL aliquot of  $0.1146 \text{ mol L}^{-1}$  sodium hydroxide was placed in a conical flask and titrated with the diluted vinegar solution to a phenolphthalein end point. The average of three concordant titres of diluted vinegar was 33.45 mL. Calculate the percentage by mass of acetic acid in the vinegar.

### → Solution

The ionic equation for the reaction is:



$$\begin{aligned}n(\text{NaOH reacting}) &= c(\text{NaOH}) \times V(\text{NaOH}) \\ &= 0.1146 \times 0.02000 = 2.2920 \times 10^{-3} \text{ mol}\end{aligned}$$

$$n(\text{OH}^- \text{ reacting}) = 2.2920 \times 10^{-3} \text{ mol}$$

1 mol of  $\text{OH}^-$  reacts with 1 mol of  $\text{CH}_3\text{COOH}$

Amount of acetic acid in 33.45 mL titre =  $2.2920 \times 10^{-3} \text{ mol}$

$$\text{Amount of acetic acid in 250 mL} = 2.2920 \times 10^{-3} \times \frac{250.0}{33.45} = 1.7130 \times 10^{-2} \text{ mol}$$

*continued*

$$m(\text{CH}_3\text{COOH in 250 mL solution}) = n(\text{CH}_3\text{COOH}) \times M(\text{CH}_3\text{COOH})$$

$$M(\text{CH}_3\text{COOH}) = 60.052 \text{ g mol}^{-1}$$

$$m(\text{CH}_3\text{COOH in 250 mL solution}) = 1.7130 \times 10^{-2} \times 60.052 = 1.0287 \text{ g}$$

$$\begin{aligned} \text{Percentage of acetic acid in vinegar} &= \frac{m(\text{CH}_3\text{COOH})}{m(\text{vinegar})} \cdot 100 = \frac{1.0287}{22.17} \cdot 100 \\ &= \mathbf{4.640\%} \end{aligned}$$

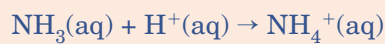
### → Example 8.7

A sample of cloudy ammonia is suspected of having been diluted by an unscrupulous supplier. 100.0 mL of the cloudy ammonia is carefully and quickly transferred to a 500.0 mL volumetric flask and made up to 500 mL with de-ionised water. A 20.00 mL aliquot of this diluted ammonia solution was placed in a conical flask with several drops of methyl orange. The ammonia solution was titrated to the methyl orange end point with 0.0500 mol L<sup>-1</sup> HCl and the average of three concordant titres was 18.42 mL.

- Determine the concentration, in mol L<sup>-1</sup>, of ammonia in the undiluted cloudy ammonia sample.
- When the label on the cloudy ammonia bottle was checked, it claimed that the concentration of ammonia was 10 g of ammonia per 100 g of solution. Was the sample diluted? The density of the cloudy ammonia is 0.90 g mL<sup>-1</sup>.

### → Solution

- The ionic equation for the reaction is:



$$n(\text{HCl}) = c(\text{HCl}) \times V(\text{HCl})$$

$$= 0.0500 \times 0.01842 = 9.210 \times 10^{-4} \text{ mol}$$

$$= n(\text{H}^+)$$

1 mol of H<sup>+</sup> reacts with 1 mol of NH<sub>3</sub>

$$\text{Amount of ammonia in 20.00 mL aliquot} = 9.210 \times 10^{-4} \text{ mol}$$

$$\text{Amount of ammonia in 500 mL} = 9.210 \times 10^{-4} \times \frac{500.0}{20.00} = 0.02302 \text{ mol}$$

$$\text{Concentration of ammonia in the cloudy ammonia} = \frac{n(\text{NH}_3)}{V(\text{NH}_3)}$$

$$= \frac{0.02302}{0.1000}$$

$$= \mathbf{0.230 \text{ mol L}^{-1}}$$

- To enable comparison with the measured values found in part a, the concentration of the cloudy ammonia will need to be calculated in the unit of mol L<sup>-1</sup>:

The label suggests that 100 g of cloudy ammonia contains 10 g of ammonia.

$$100 \text{ g of cloudy ammonia has a volume of } \frac{100}{0.90} = 111 \text{ mL or } 0.111 \text{ L}$$

$$n(\text{NH}_3 \text{ dissolved in this volume}) = \frac{m(\text{NH}_3)}{M(\text{NH}_3)} = \frac{10}{17.034} = 0.587 \text{ mol}$$

$$c(\text{cloudy ammonia}) = \frac{n(\text{NH}_3)}{V(\text{cloudy ammonia})} = \frac{0.587}{0.111} = 5.3 \text{ mol L}^{-1}$$

The cloudy ammonia had been significantly diluted.

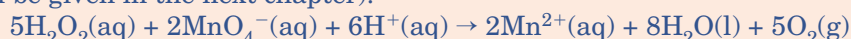
### → Example 8.8

Hydrogen peroxide is used as a mild bleaching agent. Analysis of a sample of hydrogen peroxide can be carried out by using potassium permanganate in a redox reaction.

While checking a sample of commercial peroxide bleach, a chemist transfers 10.00 mL of the peroxide solution to a 250.0 mL volumetric flask and makes it up to the calibrated mark with de-ionised water. A 25.00 mL aliquot of the diluted peroxide solution, mixed with acid, is titrated with a standardised solution of potassium permanganate of concentration  $0.01894 \text{ mol L}^{-1}$ . The average of three concordant titres of permanganate is 28.68 mL. Determine the concentration of hydrogen peroxide in the commercial bleach solution and the percentage by mass. Assume the density of the original peroxide bleach is  $1.00 \text{ g mL}^{-1}$ .

### → Solution

The ionic equation for the reaction is (procedures for balancing these equations will be given in the next chapter):



Amount of  $\text{KMnO}_4$  reacting =  $c(\text{KMnO}_4) \times V(\text{KMnO}_4)$

$$= 0.01894 \times 0.02868 = 5.432 \times 10^{-4} \text{ mol}$$

$$= n(\text{MnO}_4^-) \text{ reacted with } \text{H}_2\text{O}_2$$

From the ionic equation,

2 mol of  $\text{MnO}_4^-$  reacts with 5 mol of  $\text{H}_2\text{O}_2$

so  $5.432 \times 10^{-4}$  mol of  $\text{MnO}_4^-$  reacts with  $5.432 \times 10^{-4} \times \frac{5}{2}$

$$= 1.358 \times 10^{-3} \text{ mol of } \text{H}_2\text{O}_2 = \text{mol of } \text{H}_2\text{O}_2 \text{ in 25 mL aliquot}$$

Amount of  $\text{H}_2\text{O}_2$  in 250.0 mL =  $1.358 \times 10^{-3} \times 10 = 0.01358 \text{ mol}$

= mol of  $\text{H}_2\text{O}_2$  in 10.00 mL of commercial bleach solution

$$c(\text{H}_2\text{O}_2) \text{ in commercial bleach} = \frac{n(\text{H}_2\text{O}_2)}{V(\text{H}_2\text{O}_2)} = \frac{0.01358}{0.01000}$$

$$= \mathbf{1.358 \text{ mol L}^{-1}}$$

Mass of  $\text{H}_2\text{O}_2$  in 10.00 mL of bleach =  $n(\text{H}_2\text{O}_2) \times M(\text{H}_2\text{O}_2)$

$$M(\text{H}_2\text{O}_2) = 34.016 \text{ g mol}^{-1}$$

$$\text{Mass } (\text{H}_2\text{O}_2) = 0.01358 \times 34.016 = 0.4619 \text{ g}$$

$$\text{Percentage of } \text{H}_2\text{O}_2 \text{ in bleach} = \frac{m(\text{H}_2\text{O}_2)}{m(\text{bleach})} \cdot 100 = \frac{0.4619}{10.00} \cdot 100$$

$$= \mathbf{4.62\%}$$

### Back titration

Aspirin is a weak acid that is not soluble in water. Determination of the amount of aspirin in a tablet by a conventional titration procedure is not easy. However, if the aspirin is reacted completely with a measured excess of a base like sodium hydroxide, the excess sodium hydroxide can be determined in a normal titration. Working backwards from the amount of sodium hydroxide remaining, it is possible to calculate how much sodium hydroxide reacted with the aspirin and hence the amount of aspirin in the tablet. This type of procedure is called a back titration.

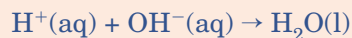
→ **Example 8.9**

Aspirin (acetylsalicylic acid) is a weak monoprotic acid. A 300 mg aspirin tablet was crushed and placed in a conical flask together with 25.00 mL of 0.1000 mol L<sup>-1</sup> sodium hydroxide and the mixture allowed to react completely until the tablet had dissolved. Three drops of phenolphthalein were added to the solution and a pink colour was produced indicating that sodium hydroxide was in excess.

The excess sodium hydroxide in the flask was titrated with 0.0500 mol L<sup>-1</sup> HCl and the titre required to reach the phenolphthalein end point was 16.90 mL.

Calculate the percentage purity of the aspirin tablet if the formula of acetylsalicylic acid is C<sub>9</sub>H<sub>8</sub>O<sub>4</sub>.

→ **Solution**



$$\begin{aligned}n(\text{HCl}) \text{ used in titration} &= c(\text{HCl}) \times V(\text{HCl}) \\ &= 0.0500 \times 0.01690 = 8.450 \times 10^{-4} \text{ mol} \\ &= \text{mol of H}^+ \text{ reacting with OH}^- \text{ in titration}\end{aligned}$$

1 mol of H<sup>+</sup> will react with 1 mol of OH<sup>-</sup>

so  $n(\text{OH}^-)$  in conical flask after reaction with aspirin =  $8.450 \times 10^{-4}$  mol

$$\begin{aligned}n(\text{OH}^-) \text{ originally added to the aspirin} &= c(\text{NaOH}) \times V(\text{NaOH}) \\ &= 0.1000 \times 0.02500 \\ &= 2.500 \times 10^{-3} \text{ mol}\end{aligned}$$

$$n(\text{OH}^-) \text{ reacted with aspirin} = 2.500 \times 10^{-3} - 8.450 \times 10^{-4} = 1.655 \times 10^{-3} \text{ mol}$$

Because acetylsalicylic acid in aspirin is monoprotic,

1 mol of OH<sup>-</sup> will react with 1 mol of acetylsalicylic acid (C<sub>9</sub>H<sub>8</sub>O<sub>4</sub>)

$$n(\text{C}_9\text{H}_8\text{O}_4) \text{ in 1 tablet} = 1.655 \times 10^{-3} \text{ mol}$$

$$m(\text{C}_9\text{H}_8\text{O}_4) = n(\text{C}_9\text{H}_8\text{O}_4) \times M(\text{C}_9\text{H}_8\text{O}_4)$$

$$M(\text{C}_9\text{H}_8\text{O}_4) = 180.154 \text{ g mol}^{-1}$$

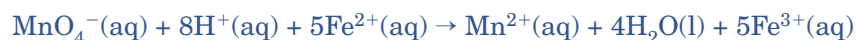
$$m(\text{C}_9\text{H}_8\text{O}_4) = 1.655 \times 10^{-3} \times 180.154 = 0.2982 \text{ g}$$

$$\begin{aligned}\text{Percentage purity of aspirin} &= \frac{m(\text{C}_9\text{H}_8\text{O}_4)}{m(\text{tablet})} \cdot 100 \\ &= \frac{0.2982}{0.300} \cdot 100 = \mathbf{99.4\%}\end{aligned}$$

## \* Review exercise 8.4

- 1 Some photographic developing agents contain a base that provides hydroxide ions. A 10.00 mL sample of developer was diluted to 100.0 mL in a volumetric flask. 20.00 mL of this diluted solution was titrated with 0.0900 mol L<sup>-1</sup> sulfuric acid and required 21.40 mL to reach a methyl orange end point. Calculate the concentration, in mol L<sup>-1</sup>, of the hydroxide ions in the original developer. (Hint: Sulfuric acid is diprotic.)
- 2 A patient suffering from indigestion provides a sample of gastric juices for analysis. A 40.00 mL sample of gastric juice was titrated with 0.1050 mol L<sup>-1</sup> sodium hydroxide to a phenolphthalein end point. The volume of sodium hydroxide solution required was 17.25 mL. Calculate the pH of the gastric juice in the patient.
- 3 A sample of iron ore having a mass of 4.60 g was treated in sulfuric acid to convert the iron in the ore to a mixture of soluble Fe<sup>2+</sup> and Fe<sup>3+</sup> ions. A solution of tin(II) chloride was carefully added to just convert all the Fe<sup>3+</sup> ions to Fe<sup>2+</sup>. Excess Sn<sup>2+</sup> was removed before the next step.

The resulting solution, assumed to be a solution containing Fe<sup>2+</sup>(aq), was diluted to 250.0 mL in a volumetric flask. A 25.00 mL sample of the diluted iron(II) solution was titrated with 0.0278 mol L<sup>-1</sup> potassium permanganate and required 35.6 mL of the permanganate solution to reach the end point:



Calculate the percentage of Fe<sub>2</sub>O<sub>3</sub> present in the ore, assuming that this is the only iron-containing compound present.

- 4 A 4.674 g sample of limestone (impure CaCO<sub>3</sub>) was treated with 375 mL of 0.261 mol L<sup>-1</sup> hydrochloric acid. After the reaction was over, the mixture was filtered and a 25.0 mL sample of the filtrate was titrated with 0.0517 mol L<sup>-1</sup> Ba(OH)<sub>2</sub> to the phenolphthalein end point. The volume of the barium hydroxide solution required was 17.62 mL.

Calculate the percentage, by mass, of CaCO<sub>3</sub> in the limestone sample.





## MAJOR IDEAS

- Some reactions of acids are:
  - acid + metal hydroxide → salt solution + water
  - acid + metal oxide → salt solution + water
  - acid + carbonate → salt solution + carbon dioxide + water
  - acid + hydrogencarbonate → salt solution + carbon dioxide + water
  - acid + sulfide → salt solution + hydrogen sulfide
  - acid + sulfite → salt solution + sulfur dioxide + water
  - acid + metal → salt solution + hydrogen
- In ionic equations, only the species undergoing a change are included. Spectator ions are not included.
- Acid–base reactions are classified in terms of hydrogen ion (proton) transfer but redox reactions involve electron transfer.
- In a redox reaction, there is transfer of one or more electrons from a reductant to an oxidant.
- An equation for a redox reaction can be written by combining the half-equations for the oxidation and reduction reactions, ensuring the electrons ‘cancel out’.
- Gravimetric analysis involves determining the mass of a substance produced in a chemical reaction and using this to solve a chemical problem.
- Volumetric analysis involves the use of measured volumes of solutions to analyse mixtures.
- The process in which one solution is added progressively to a measured volume of another solution is called a titration.
- The equivalence point in a titration is the point at which the correct stoichiometric amounts of each reactant have combined.
- In acid–base titrations the means of observing the equivalence point is provided by adding an indicator that undergoes a colour change at or near to the equivalence point.
- The end point is the point in a titration at which the indicator changes colour.
- A measured volume of solution, usually from a pipette, is called an aliquot.
- Prior to being used in an analysis, the pipette should be rinsed with a small amount of the solution being delivered.
- The volume of solution delivered from the burette is called the titre.
- Prior to being used in an analysis the burette should be rinsed with a small amount of the material that is being delivered for the titre.
- A volumetric flask should be rinsed with distilled water prior to use.
- A standard solution is a solution with an accurately known concentration.
- A primary standard is a substance that can be obtained pure, has a known formula, is stable and has a relatively high formula mass.
- Examples of primary standards for acid–base titrations are anhydrous sodium carbonate,  $\text{Na}_2\text{CO}_3$ , and oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .
- A solution of a primary standard is prepared by dissolving an accurately weighed mass of the primary standard in an accurately known volume of solution.
- A secondary standard does not possess one or more of the characteristics of a primary standard.
- The concentration of a secondary standard solution is determined using a solution of a primary standard, or a solution of known concentration.
- Concordant results are results that agree very closely to one another, e.g. in a titration concordant titres result are normally within 0.1 mL of one another.
- Acid–base indicators are substances whose colour depends on the pH of the solution in which they are dissolved.
- In a titration, an indicator is chosen so that the end point and equivalence point are as close as possible together.
- The pH of the titration mixture at the equivalence point is determined by the salts present in the mixture.

Titration between	Approximate pH of solution at equivalence point	Indicator should have an end point of approximately	Example of an appropriate indicator
Strong acid + weak base	Weak basic pH values, e.g. 9	8–10	Phenolphthalein
Weak acid + strong base	Weak acidic pH values, e.g. 5	3–6	Methyl orange
Strong acid + strong base	7	7 (a reasonably broad pH range of 4–10 is fine)	Phenolphthalein or methyl orange

- In a redox titration involving potassium permanganate an indicator is not required because potassium permanganate is a dark purple colour while its product is almost colourless.
- Potassium permanganate is not a primary standard but the primary standard oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) can be used to standardise its solution.
- In a back titration, a known volume of an excess reactant is added to the reactant being analysed. A titration is then carried out to determine the amount of the excess reactant remaining after the reaction.

## QUESTIONS

- Write ionic equations for the following reactions.
  - A solution of sulfuric acid is added to solid magnesium oxide.
  - Ammonia gas is bubbled through hydrochloric acid.
  - Aluminium oxide is added to a solution of nitric acid.
  - A solution of potassium sulfite is mixed with hydrochloric acid.
  - Solid lithium hydroxide is added to a solution of sulfuric acid.
  - A solution of nitric acid is added to solid iron(III) sulfide.
  - A solution of acetic acid is added to solid calcium carbonate.
  - Aluminium oxide is warmed with a solution of potassium hydroxide.
  - Acidified potassium permanganate solution is added to a solution of sodium oxalate.
- For each of the following write observations and provide an ionic equation if relevant. For those combinations that do not result in a chemical reaction, write 'no reaction'.
  - A solution of ammonia is added to a solution of acetic acid.
  - A solution of calcium hydroxide is added to a solution of sodium hydroxide.
  - Zinc is added to a dilute sulfuric acid solution.
  - Nitric acid is added to solid copper(II) carbonate.
  - Copper is added to a solution of silver nitrate.
  - Solid chromium(III) oxide is added to hydrochloric acid.
  - Sulfuric acid is added to a solution of potassium hydrogencarbonate.
- DDT (from its non-IUPAC name, dichlorodiphenyltrichloroethane) is a pesticide that was banned from general use several decades ago because of its effects on animals further up the food chain. A soil sample is known to be contaminated with DDT and was treated to convert all of the chlorine in the sample to chloride ions. These chloride ions can then be reacted with a solution of silver nitrate to produce solid silver chloride that can be determined gravimetrically.
 

A 25.0 kg sample of soil is treated to convert all of the chlorine in the DDT to chloride ions. A solution containing the dissolved chloride ions is separated from the soil mixture and reacted with excess silver nitrate solution. The precipitate was collected and dried. The mass obtained was 42.9 mg.

  - Write the ionic equation for the reaction of silver nitrate with the solution containing chloride ions.
  - What amount, in mole, of solid was obtained?
  - What amount, in mole, of chloride ions must have been present in the solution obtained from the soil sample?
  - From the non-IUPAC name for DDT, deduce how many chlorine atoms are present in one molecule of DDT and hence determine the amount, in mole, of DDT in 1 kg of soil.
  - If the molar mass of DDT is  $354.49 \text{ g mol}^{-1}$ , calculate the amount of DDT in the soil in ppm (parts per million, or mg per kg).
- How does a primary standard differ from a secondary standard?
- There are a number of steps involved in the preparation of 250.0 mL of a  $0.050 \text{ mol L}^{-1}$  solution of sodium carbonate. From the list below choose those steps that would be included in the preparation of such a solution and list them in the correct order.
  - Dry the inside of the volumetric flask.
  - Weigh out 3.577 g of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ .
  - Wash a 250.0 mL volumetric flask with de-ionised water.
  - Dissolve some sodium carbonate in water.
  - Weigh out 1.325 g of anhydrous sodium carbonate.
  - Transfer the sodium carbonate to a 250 mL conical flask.
  - Rinse the volumetric flask with the sodium carbonate solution.

- Swirl the contents of the volumetric flask until the solid dissolves.
- Fill the volumetric flask with de-ionised water until the top of the meniscus is level with the calibration mark.
- Weigh out 1.325 g of hydrated sodium carbonate.
- Shake the volumetric flask with your thumb over the end to prevent the solution from escaping.
- Transfer all of the solid sodium carbonate to the 250.0 mL volumetric flask.
- Put a stopper on the flask and shake gently to distribute the solution.
- Add some de-ionised water to the flask.
- Fill the volumetric flask with de-ionised water until the bottom of the meniscus is level with the calibration mark.
- Add several drops of phenolphthalein indicator to the solution in the flask.

- 6** For each of the following descriptions of the preparation of a standard solution, explain why the procedure is not accurate, and state, with reasons, whether the actual concentration of the solution would be higher or lower than that calculated using the data given.

**Solution 1:** A clean, dry 250 mL volumetric flask is placed on an analytical balance and weighed. To this flask is added 2.500 g of a solution of concentrated ammonia labelled as 'ammonia—25 g per 100 mL'. The ammonia is diluted with de-ionised water and made up to the calibration mark on the flask before the solution is stoppered and gently shaken.

**Solution 2:** A watch glass is placed on an analytical balance and 5.70 g of potassium hydroxide pellets are weighed. The potassium hydroxide is transferred to a 500.0 mL volumetric flask and de-ionised water is added to make the solution up to the calibration mark.

**Solution 3:** Into an empty beaker on an analytical balance is weighed 2.905 g of hydrated sodium carbonate,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . The solid is transferred to a 1000 mL volumetric flask and is then made up to the calibration mark with de-ionised water.

- 7**
- Why is it unnecessary to have the solution in the burette adjusted to the 0.00 mL 'mark' on the scale at the beginning of any titration?
  - The reading of the meniscus on a 50 mL burette scale after a titration is 36.44. The previous titration required 18.58 mL. One of

the members of a practical group suggests that the burette needs to be 'topped up' with more solution before proceeding to the next titration. The other member of the group suggests that they add the remaining solution to the 50.00 mL mark and then top up the burette to complete the experiment. Whose suggestion is better and why?

- 8** A standard solution of sodium carbonate is prepared by adding an accurately weighed amount of anhydrous sodium carbonate to a 250.0 mL volumetric flask and making the solution up to the calibration mark with distilled water. Measured aliquots of this standard solution are then titrated with a hydrochloric acid solution of unknown concentration.

What will be the effect on the calculated concentration of hydrochloric acid (compared to its actual concentration) of each of the following? (Assume the only factor being altered is the one specifically identified and all other parts of the experiment are performed correctly.)

- The solution in the volumetric flask has water added to a point just above the calibration mark.
  - The pipette is rinsed with water prior to measuring out an aliquot.
  - The chemist performing the titration is colour blind and consistently adds more acid from the burette than needed.
  - The insides of the conical flask are washed down with de-ionised water during the titration.
  - The burette was rinsed with de-ionised water prior to being filled with the acid used for the titration.
- 9** An unknown acid has the general formula  $\text{H}_x\text{A}$ , where all of the hydrogen atoms in the formula are acidic. A 0.432 g sample of this acid was dissolved in water and made up to 250.0 mL in a volumetric flask. A 25.00 mL aliquot of the acid solution was placed in a conical flask together with a few drops of phenolphthalein, and the whole titrated with a solution of 0.0400 mol  $\text{L}^{-1}$  potassium hydroxide. The end point of the titration occurred when 20.00 mL of base had been added.

If the molar mass of the acid is 108 g  $\text{mol}^{-1}$ , what is the value of  $x$ ?

- 10** The percentage of ammonia in a commercial cleaner was determined by volumetric analysis.

A 18.73 g sample of the cleaner was diluted to 250.0 mL in a volumetric flask and 25.00 mL aliquots of the diluted solution were titrated with a previously standardised solution of hydrochloric acid using methyl orange as the indicator. The concentration of the acid solution was  $0.115 \text{ mol L}^{-1}$ .

The following titres were obtained.

Volume of HCl added				
Final burette reading (mL)	46.75	37.35	36.85	43.50
Initial burette reading (mL)	27.80	18.30	16.95	24.35

- a What would you use to rinse the following equipment just prior to the titration?
- pipette
  - volumetric flask
  - burette
  - conical flask
- b Determine the percentage by mass of ammonia in the cleaner showing details of all steps in the calculation.
- 11 A titration of a solution of potassium hydroxide of unknown concentration is to be performed. The solution is going to be titrated with a standardised solution of hydrochloric acid, added from a burette. The following indicators have been provided.

Indicator	Colour		pH range of indicator
	Acid	Base	
Methyl violet	yellow	violet	0.0–1.6
Methyl orange	red	yellow	3.2–4.4
Litmus	red	blue	5.0–8.0
Bromothymol blue	yellow	blue	6.0–7.6
Phenol red	yellow	red	6.6–8.0
Phenolphthalein	colourless	pink	8.2–10.0
Alizarin yellow	yellow	red	11.1–12.0

- a Which indicators would you not consider for this titration? Give reasons for your choice.
- b For each indicator chosen in part a explain what the effect of that choice would be on the calculated concentration of the potassium hydroxide.
- c The potassium hydroxide solution, once standardised, is to be used to determine the concentration of a solution of citric acid, a

weak acid found in citrus fruits. Which of the indicators would be suitable for this titration? Once again, justify your answer.

- 12 Compare the titration of a strong monoprotic acid with that of a weak monoprotic acid, using sodium hydroxide as the base, with respect to:
- pH at the beginning of the titration
  - pH after a slight excess of base has been added
  - amount of base required to reach the equivalence point if equal molar amounts of the two acids are compared
  - pH at the equivalence point
  - indicator that should be used for the titration.
- 13 The graph in Figure 8.16 shows the titration curve for the reaction of two different bases with a standard solution of hydrochloric acid.

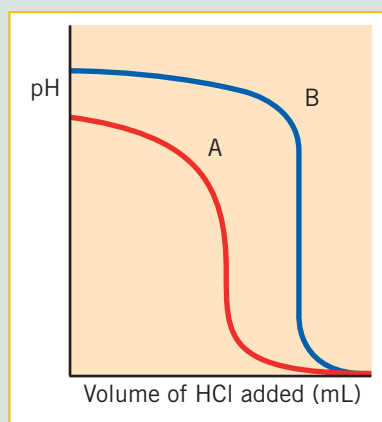
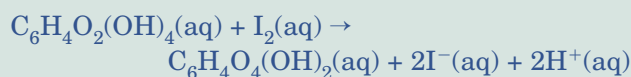


Figure 8.16 Titration curves for reaction of two different bases with HCl

- a Which of these curves is with the strong base and which one is with the weak base?
- b What is the approximate pH at the equivalence point for each titration?
- c Why do the pH values of both solutions eventually reach approximately the same value when they start off at such different pH values?
- d If 20.0 mL of each of the bases A and B was present at the beginning of the titration, provide two possible reasons for the difference between the volume of acid required to reach the equivalence point in each titration.
- 14 A mixture of sodium chloride and anhydrous potassium carbonate with a mass of 0.260 g was made up to 25.00 mL with de-ionised water. This solution required 13.2 mL of  $0.0995 \text{ mol L}^{-1}$  hydrochloric acid to reach the equivalence point.
- What volume of  $0.0500 \text{ mol L}^{-1} \text{ AgNO}_3$  solution would be required to precipitate all of the chloride

ions (including any chloride ions introduced with the hydrochloric acid) from the resulting solution?

- 15** A sample of pure iron weighing 0.835 g is dissolved in sulfuric acid, causing all of the iron to be oxidised to iron(II) ions. The resulting solution is titrated with a solution of potassium dichromate containing  $12.5 \text{ g L}^{-1}$  of  $\text{K}_2\text{Cr}_2\text{O}_7$ . What volume of potassium dichromate solution is required?
- 16** A sample of lawn food is known to contain  $\text{Fe}^{2+}$  as iron(II) sulfate. A 2.000 g sample of lawn food is dissolved in  $0.1 \text{ mol L}^{-1}$  sulfuric acid in a conical flask. The contents of the flask are quickly titrated with a solution of  $0.0200 \text{ mol L}^{-1}$  potassium permanganate. The first permanent pink colour of the solution appears after 13.20 mL of permanganate has been added. Calculate the percentage by mass of iron in the lawn food sample.
- 17** Vitamin C tablets contain ascorbic acid,  $\text{C}_6\text{H}_4\text{O}_2(\text{OH})_4$ . A tablet with a mass of 320 mg is crushed and dissolved in 30 mL of water in a conical flask. The contents of the flask are titrated with a  $0.0458 \text{ mol L}^{-1}$  solution of iodine. Ascorbic acid reacts with iodine according to the equation:



Starch indicator is added to the titration mixture as it turns a deep blue colour when iodine is in excess. The starch indicator changes colour after 24.6 mL of iodine solution has been added.

Determine the mass of ascorbic acid in the tablet and hence the percentage by mass of ascorbic acid in the vitamin C tablet.

- 18** The major acid present in a sample of wine is tartaric acid,  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ , which is a weak diprotic acid. A 25.00 mL aliquot of wine was added to 20.0 mL of  $0.180 \text{ mol L}^{-1}$  potassium hydroxide solution.

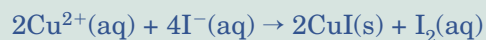
The resulting solution was basic due to excess hydroxide and required 19.85 mL of  $0.100 \text{ mol L}^{-1}$  nitric acid to reach a methyl orange end point.

Calculate the mass of tartaric acid, in  $\text{g L}^{-1}$ , in the wine sample. What assumption has been made in this calculation?

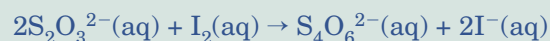
- 19** It is possible to determine the percentage by mass of copper in a copper ore by converting the copper ions into a soluble form, and using them to oxidise

iodide ions to iodine. The iodine produced in this reaction can then be titrated with a standard solution containing thiosulfate ions.

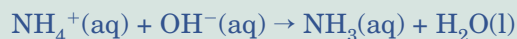
A concentrated sample of a copper ore having a mass of 0.450 g was treated with nitric acid to dissolve all of the copper ions as  $\text{Cu}^{2+}(\text{aq})$ . To the conical flask containing the copper ions was added 3.5 g of potassium iodide, KI. The following reaction took place:



The iodine produced was then titrated with  $0.110 \text{ mol L}^{-1}$  sodium thiosulfate solution using starch indicator to establish the end point. The volume of thiosulfate solution required was 21.65 mL:



- a** Determine the percentage of copper, by mass, in the ore sample.
- b** What assumptions have been made in this calculation?
- 20** 0.132 g of an ammonium salt was dissolved in water and enough potassium hydroxide was added to convert all of the ammonium ions to ammonia:



The mixture was warmed and the ammonia gas, together with some water, was distilled into a flask containing 40.00 mL of  $0.100 \text{ mol L}^{-1}$  hydrochloric acid:



The excess acid was titrated with  $0.0500 \text{ mol L}^{-1}$  sodium hydroxide and required 40.00 mL for neutralisation.

- a** What amount, in mole, of acid was originally present in the flask?
- b** How much acid was left over in the flask after the ammonia had reacted?
- c** What amount, in mole, of ammonia was generated in the first reaction?
- d** What was the percentage, by mass, of ammonium ions in the original salt?
- e** If the negative ion in the ammonium salt has a charge of  $-2$ , what amount, in mole, of the salt was present in the 0.132 g and what is the formula mass of the negative ion? What ion might this be?

- 21** 1.010 g of a hydroxide of iron,  $\text{Fe}(\text{OH})_x$ , was mixed with 20.00 mL of 2.000 mol  $\text{L}^{-1}$  nitric acid and the mixture made up to 200.0 mL in a volumetric flask with distilled water. A 25.00 mL aliquot of this solution was placed in a conical flask and required 14.56 mL of 0.1000 mol  $\text{L}^{-1}$  sodium hydroxide to reach the equivalence point. What is the value of  $x$ ?
- 22** Lindane,  $\text{C}_6\text{H}_6\text{Cl}_6$ , is an insecticide that has been used in the treatment of head lice. On combustion, lindane produces, among other compounds, hydrogen chloride gas. An impure sample of lindane having a mass of 1.200 g was burnt in oxygen. The hydrogen chloride produced was bubbled through 50.00 mL of 0.946 mol  $\text{L}^{-1}$  lithium hydroxide. The resulting solution was titrated with a standard solution of 0.500 mol  $\text{L}^{-1}$  sulfuric acid and a titre of 26.55 mL was required. Calculate the percentage, by mass, of lindane in the impure sample.
- 23** Sulfur dioxide is used in wine as a preservative and antimicrobial agent. It is suggested that wine should contain no more than 125 ppm of free sulfur dioxide. An investigation into the sulfur dioxide content of a sample of imported white wine involves the following titration.
- 50.00 mL of wine was placed in a conical flask together with 5 mL of a 25% sulfuric acid solution and 2–3 mL of starch indicator solution. The mixture was titrated with a standard solution of 0.0110 mol  $\text{L}^{-1}$  iodine solution. The volume of iodine required to just turn the starch indicator blue was 9.85 mL. Determine whether this sample of wine exceeded the 125 ppm limit.
- $$\text{SO}_2(\text{aq}) + \text{I}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{I}^-(\text{aq})$$
- 24** 24.92 g of a certain lead ore consisting of lead carbonate and lead sulfate was heated gently with 50.0 mL of 2.44 mol  $\text{L}^{-1}$  nitric acid. The mixture was then filtered and the filtrate diluted to a volume of 500.0 mL. 25.00 mL aliquots of the diluted filtrate required 22.7 mL of 0.151 mol  $\text{L}^{-1}$  sodium hydroxide to neutralise the unreacted nitric acid. Calculate the percentage, by mass, of lead carbonate in the ore.
- 25** 1.50 g of an acid was dissolved in water and its solution was made up to 250 mL. If 40.0 mL of this acid solution neutralised 25.0 mL of 0.120 mol  $\text{L}^{-1}$  KOH solution, and if the acid is diprotic (that is, each acid molecule can donate two hydrogen ions to a base), find its relative formula mass.



# 9

## Oxidation and reduction

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

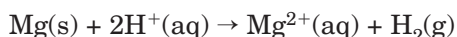
- describe oxidation and reduction in terms of electron transfer and oxidation number
- identify and name common oxidants and reductants
- write ionic equations for oxidation and reduction reactions in an acidic environment
- describe the operation of an electrochemical cell
- explain what standard reduction potentials are and how they can be used to predict redox reactions and the operation of electrochemical cells.

Our lives and our lifestyles depend on redox (oxidation and reduction) chemistry. Respiration and photosynthesis are both redox reactions. The combustion reactions that drive everything from our cars to our power stations are redox reactions. The extraction of metals from their ores and the corrosion of these same metals are also examples of the application of redox chemistry. Any portable electronic device that is run by a battery is deriving its energy from redox reactions.



## 9.1 Review of oxidation and reduction concepts

Oxidation and reduction are electron transfer reactions. In a simple example such as the reaction of magnesium with an acid, the electron transfer from the metal to the hydrogen ion is obvious:



This reaction can be split into its two component parts, known as half-reactions:



Oxidation is defined as a loss of electrons, while reduction is a gain of electrons. In Stage 2 the mnemonic OIL RIG (Oxidation Is Loss, Reduction Is Gain) was presented as a simple tool to assist in memorising these two processes.

The reactivity series of metals studied in earlier chemistry courses involves these same electron transfer reactions. For example, if a piece of zinc is placed in a solution of copper(II) sulfate, the zinc undergoes oxidation and transfers electrons to the copper ions that are then reduced to metallic copper (Figure 9.1):

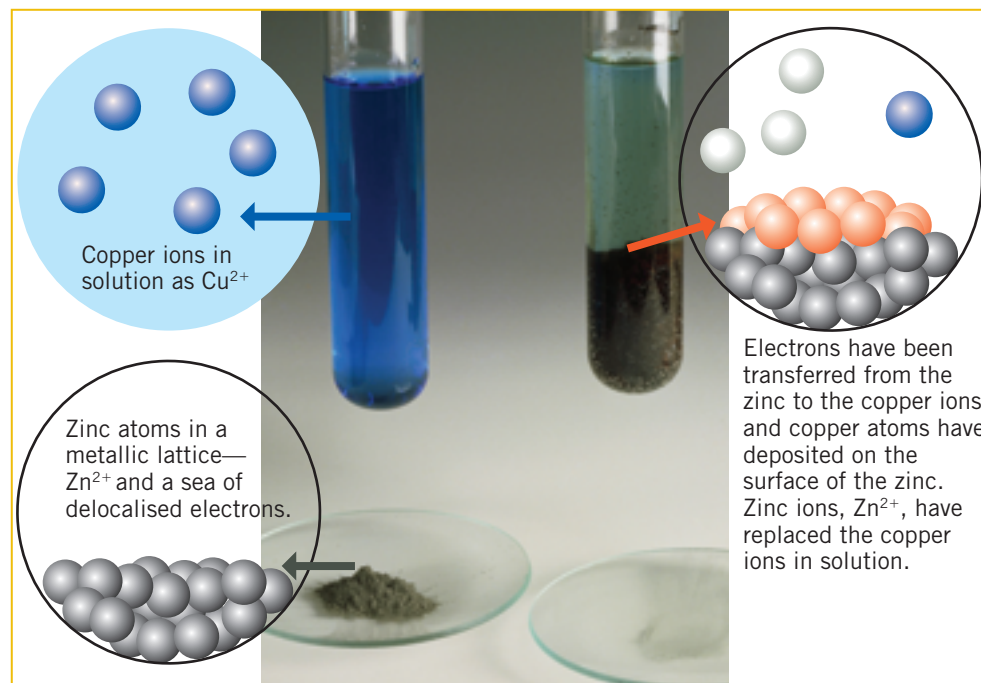
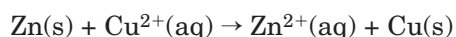


Figure 9.1 Real and molecular view of the reaction between zinc and copper ions in solution



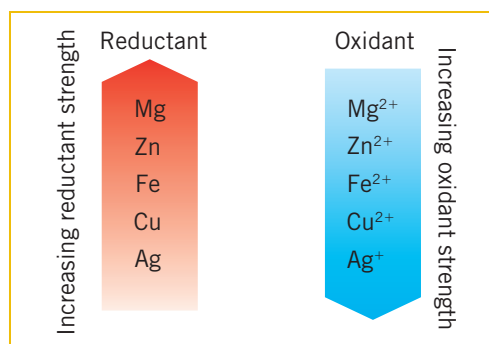
The metals in these redox reactions always lose electrons and are oxidised. Substances that behave in this manner are called reductants (or reducing agents). Reductants undergo oxidation. The substance undergoing reduction is called an oxidant (or oxidising agent).

Table 9.1 summarises these features of redox reactions.

**TABLE 9.1 SUMMARY OF REDOX DEFINITIONS**

Oxidation	Loss of electrons
Reduction	Gain of electrons
Oxidant (oxidising agent)	Gains electrons and undergoes reduction
Reductant (reducing agent)	Loses electrons and undergoes oxidation

The reactivity or displacement series of metals shows that some reductants (and hence some oxidants) are more reactive than others. For example zinc will displace (form) copper from solutions containing copper ions, but copper will not react with a solution containing zinc ions. Figure 9.2 lists some common metals and metal ions in order of reductant strength and oxidant strength. Note that the positive ions of metals that are strong reductants are themselves weak oxidants, while the positive ions of the metals that are weak reductants are quite strong oxidants.



**Figure 9.2** Relative strengths of some reductants and oxidants



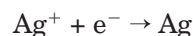
### The spectacle of redox

Some of the earlier transition lenses in spectacles that go dark in the presence of sunlight and then revert back to normal when taken out of the sun were based on a reversible redox reaction involving silver and copper.

The lenses for these spectacles (known as photochromic glass) are made by combining the glass with a silver halide and a small amount of copper(I) chloride. In simple terms, when the lens is exposed to sunlight, specifically UV light, the copper(I) ions are oxidised:



The liberated electrons then reduce the silver ions to silver:



Eventually enough tiny silver crystals form to cause the glass to go darker.

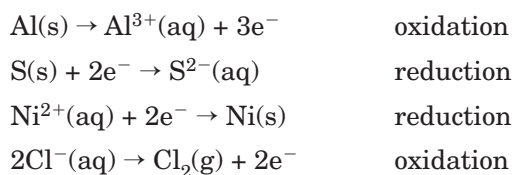
As long as the glass is exposed to UV light, the copper(II) ions and silver remain in the solid matrix of the glass. However, when the UV light source is removed, the copper(II) ions react with the silver. Copper(II) ions are reduced to copper(I) and the silver is oxidised back to silver ions and the glass becomes colourless again.

## \* Review exercise 9.1

- Which of the following equations represent redox reactions? For those that are redox, identify the oxidant and the reductant.
  - $\text{Na(l)} + \text{Cl}_2\text{(g)} \rightarrow \text{NaCl(s)}$
  - $\text{Cu}^{2+}\text{(aq)} + 2\text{OH}^-\text{(aq)} \rightarrow \text{Cu(OH)}_2\text{(s)}$
  - $\text{Mg(s)} + \text{S(s)} \rightarrow \text{MgS(s)}$
  - $\text{Br}_2\text{(aq)} + 2\text{I}^-\text{(aq)} \rightarrow 2\text{Br}^-\text{(aq)} + \text{I}_2\text{(s)}$
- Use the information in Figure 9.2 to write the two half-equations and the overall ionic equation for any reaction that takes place when the two substances named are combined.
  - Iron is placed into a solution of silver nitrate.
  - Magnesium is added to a copper(II) sulfate solution.
  - Zinc chloride solution is poured into an iron vessel.
  - A solution of silver nitrate is placed in a copper container.

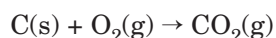
## 9.2 Oxidation number

In a reaction where a metal loses electrons or a non-metal gains electrons to form ions, it is easy to decide which substance has been reduced and which has been oxidised. Similarly, when metal ions gain electrons or non-metal ions lose electrons, the redox nature is obvious.



However, there are many redox reactions in which the electron transfer process is not evident, particularly those reactions that involve the oxidation and reduction of substances with covalent bonds.

For example, when carbon is heated in the presence of oxygen, it burns to produce carbon dioxide:



The atoms in the reactants and product are joined by covalent bonds so it is very difficult to follow the transfer of electrons in this reaction. The carbon has been oxidised in this reaction and, according to the definition of oxidation, must have 'lost electrons'. Some of the electrons that originally 'belonged' to the carbon are now being shared with oxygen atoms, but there has been no complete transfer. To track the electron transfer process in such reactions, chemists have introduced the concept of oxidation number.

An oxidation number is a number that is assigned to each atom in a substance to indicate its oxidation state. For monatomic ions, for example, the oxidation number is simply the ionic charge (including the sign). For other atoms, the oxidation number is a hypothetical charge assigned to an atom by assuming the electrons in each covalent bond are only held by one of the bonded atoms rather than shared between them.

The rules for assigning oxidation numbers are as follows:

- 1 The oxidation number of any element is zero. Whether the element is monatomic (like the noble gases), composed of molecules or a covalent network substance (as in diamond), the oxidation number of each atom is zero. Thus the oxidation number of each atom in Ne, H<sub>2</sub>, O<sub>3</sub>, P<sub>4</sub> or C(diamond) is assigned a value of 0.
- 2 The oxidation number of an atom in a monatomic ion is the same as the charge on the ion. For example, Na<sup>+</sup> has an oxidation number of +1, O<sup>2-</sup> has an oxidation number of -2. All the group 1 metal ions have an oxidation number of +1, and the group 2 metal ions have an oxidation number of +2.
- 3 The oxidation number of oxygen in its compounds is -2. The major exceptions to this rule are fluorine oxide, F<sub>2</sub>O where the oxygen has an oxidation number of +2, and in a group of oxides known as peroxides in which the oxidation number of oxygen is -1. Sodium peroxide, Na<sub>2</sub>O<sub>2</sub>, is an example of a compound in which the oxidation number of oxygen is -1.
- 4 The oxidation number of hydrogen in its compounds is +1. The major exception to this rule is the metal hydrides, such as lithium hydride, LiH, where the oxidation number assigned to hydrogen is -1.
- 5 The sum of the oxidation numbers of the atoms in a neutral compound is zero. In carbon dioxide, CO<sub>2</sub>, the oxidation number of carbon must be +4 to balance the -2 oxidation number on each oxygen atom. In ammonia, NH<sub>3</sub>, the oxidation number on nitrogen must be -3 to balance the +1 oxidation numbers on each hydrogen atom.
- 6 The sum of the oxidation numbers of the atoms in a polyatomic ion must equal the ionic charge. In the sulfate ion, SO<sub>4</sub><sup>2-</sup>, each of the oxygen atoms has an oxidation number of -2, giving a total of -8. To end up with a -2 charge on the ion, the oxidation number of sulfur must be +6.

### → Example 9.1

Determine the oxidation number of nitrogen in each of the following.

- |                    |                                 |
|--------------------|---------------------------------|
| a N <sub>2</sub>   | b N <sup>3-</sup>               |
| c NO <sub>2</sub>  | d N <sub>2</sub> H <sub>4</sub> |
| e HNO <sub>3</sub> | f N <sub>2</sub> O              |
| g NH <sub>3</sub>  | h NaNO <sub>2</sub>             |

### → Solution

- a The oxidation number of the atoms in an element is zero. The oxidation number of each N atom is **0**.
- b The oxidation number of an atom in a monatomic ion is the charge on the ion. The oxidation number of N is **-3**.
- c The oxidation number of each oxygen atom in compounds is -2. The sum of the oxidation numbers in a neutral molecule is zero. The oxidation number of nitrogen is **+4**. (+4 + (2 × -2) = 0)
- d The oxidation number of each hydrogen atom in compounds is +1. The sum of the oxidation numbers in a neutral molecule is zero. The two nitrogen atoms combined must sum to -4, so each nitrogen atom has an oxidation number of **-2**. ((2 × -2) + (4 × +1) = 0)

- e** The sum of the oxidation numbers must be zero and the hydrogen atom is +1 while each oxygen atom is -2. The hydrogen and three oxygen atoms sum to -5, so the oxidation number on nitrogen must be +5.  
 $((+1) + (+5) + (3 \times -2) = 0)$
- f** The sum of the oxidation numbers in a neutral molecule is zero. The oxidation number on the oxygen atom is -2, so the oxidation number on the nitrogen must be +1.  $((2 \times +1) + (-2) = 0)$
- g** The sum of the oxidation numbers in a neutral molecule is zero. The oxidation number on each hydrogen atom is +1 so the oxidation number on nitrogen must be -3.  $((-3) + (3 \times +1) = 0)$
- h** Sodium nitrite is an ionic compound composed of  $\text{Na}^+$  and  $\text{NO}_2^-$  ions. The charge on the sodium ion is +1 and the nitrite ion has a charge of -1. The oxygen atoms in the nitrite ion each have an oxidation number of -2, so the oxidation number on nitrogen must be +3.  $((+3) + (2 \times -2) = -1)$

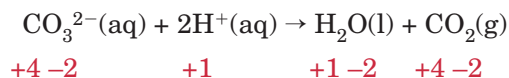
Oxidation and reduction can be defined using the oxidation number concept as an alternative to the electron transfer definition.

An atom undergoes oxidation if its oxidation number increases during a chemical reaction.

An atom undergoes reduction if its oxidation number decreases during a chemical reaction.

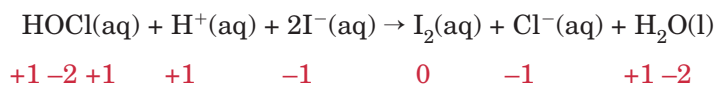
Oxidation numbers can be used to determine whether a reaction is redox or not. Reactions between acids and bases often involve ions, as do precipitation reactions. However, in these reactions the oxidation numbers of the atoms do not change and so there is no redox process involved.

For example, the reaction between an acid and a carbonate can be represented as:



Assigning oxidation numbers to the atoms involved quickly establishes that there has been no change in any of the oxidation numbers of the atoms.

For a redox reaction, oxidation numbers can also be used to identify which substances have been oxidised or reduced. The reaction between hypochlorous acid, HOCl, and a solution of sodium iodide can be represented as:



Obviously the chlorine in HOCl has been reduced from +1 to -1, while the two iodide ions have been oxidised from -1 to 0. This also means that HOCl has acted as the oxidant and  $\text{I}^-$  has acted as the reductant in this reaction.

However, the oxidation number concept is not without its disadvantages. Even though the atoms in covalent molecular substances are assigned an oxidation number that includes a '+' or a '-' sign, these atoms do not have a charge in the same way that the charge on a sodium ion is +1. The thiosulfate ion,  $\text{S}_2\text{O}_3^{2-}$ , might be assumed to have two sulfur atoms with an oxidation number of +2 if the oxidation number rules are applied. However, as Figure 9.3 shows, the structure of the thiosulfate ion is identical to the sulfate ion. One of the oxygen atoms in the sulfate ion has been replaced by sulfur (also a group 16 element).



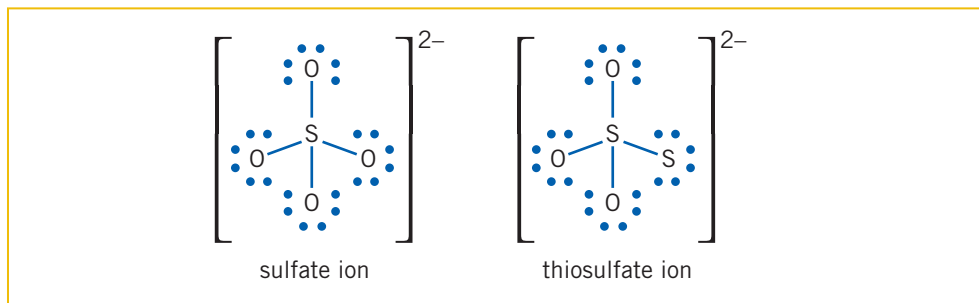
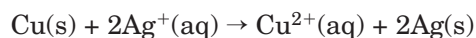


Figure 9.3 Structures of the sulfate and thiosulfate ions

The central sulfur atom in both ions has an oxidation number of +6, while the other sulfur atom in the thiosulfate ion has an oxidation number of  $-2$ . Similar ambiguities arise in assigning oxidation numbers to carbon atoms in some organic compounds, and to various other group 15 to 17 elements.

### Using oxidation number to write redox equations

Simple redox equations involving, for example, metals and their ions, can be easily separated into their component oxidation and reduction half-equations. For example:



The electron transfer process is obvious in such reactions and so the identification of the individual oxidation and reduction half-equations and the overall ionic equation for the reaction is straightforward.

However, a more complex reaction such as the reaction of an acidified solution of potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , with a solution of sodium oxalate,  $\text{Na}_2\text{C}_2\text{O}_4$ , to produce carbon dioxide and a solution containing, among other things, sodium ions, chromium(III) ions and potassium ions, is not as easy to represent as either the separate half-equations, or the overall ionic equation.

The use of oxidation numbers to determine which atom has undergone oxidation and which reduction, coupled with some simple rules, allow the half-equations for more complex reactions in an acidic environment ( $\text{H}^+$ ) to be derived.

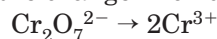
The solution of potassium dichromate described above formed a solution containing  $\text{Cr}^{3+}$ . In the dichromate ion,  $\text{Cr}_2\text{O}_7^{2-}$ , the chromium has an oxidation number of +6, so the reaction of dichromate ion to produce chromium(III) ions is a reduction.



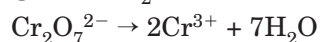
Figure 9.4 The different colours of the various oxidation states of chromium. The solutions from left to right are  $\text{CrCl}_3$ ,  $\text{Cr}(\text{NO}_3)_3$ , potassium chromate and potassium dichromate.

The half-equation for this reaction can be written using the following rules.

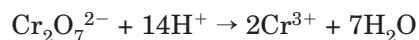
- 1 Balance the atom undergoing the change in oxidation number.



- 2 Balance oxygen atoms by adding water,  $\text{H}_2\text{O}$ , where needed.



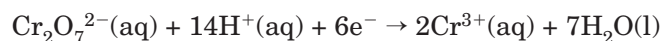
- 3 Balance hydrogen atoms by adding  $\text{H}^+$  where needed.



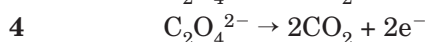
- 4 Balance the charge by adding electrons where needed.



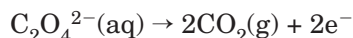
Finally, check that the number of electrons added corresponds to the change in the oxidation number of the atom(s) undergoing reduction or oxidation (the oxidation number of each Cr atom has changed from +6 to +3 and there are two Cr atoms, resulting in a total change in oxidation number of 6), and add state symbols if necessary:



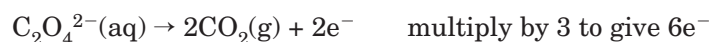
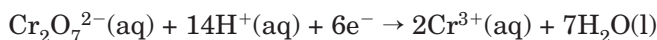
The solution containing the oxalate ion,  $\text{C}_2\text{O}_4^{2-}$ , has produced carbon dioxide, so the oxidation number of carbon has changed from +3 to +4. Applying the same set of rules as for the reduction of the dichromate ion:



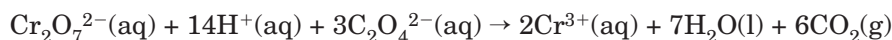
The half-equation, including state symbols, then becomes:



The two half-equations can be added together by ensuring that the electrons lost in the oxidation half-equation are all gained in the reduction half-equation. This may require that one or both equations be multiplied by an integer.



When the electrons in the two half-equations are balanced these half-equations can be added together, and the electrons ‘cancelled out’:



As a final check, make sure that the number of each atom, and the charge, on the left-hand side of the equation balances the number of each atom, and the charge, on the right-hand side. (The  $\text{K}^+$  and  $\text{Na}^+$  ions and the negative ions from the acid act as spectator ions in this reaction and are not shown in the ionic equation.)

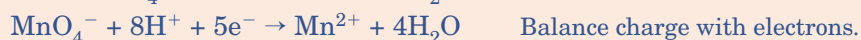
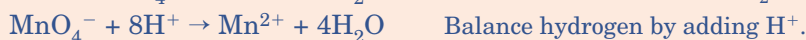
### → Example 9.2

Write the half-equations for the oxidation and reduction reactions and the overall ionic equation for the reaction in which an acidified potassium permanganate solution reacts with a solution of hydrogen peroxide to produce a solution containing manganese(II) ions and oxygen gas.

### → Solution

$\text{MnO}_4^-$  becomes  $\text{Mn}^{2+}$ . The oxidation number of manganese has changed from +7 to +2 so this is the reduction half-equation.

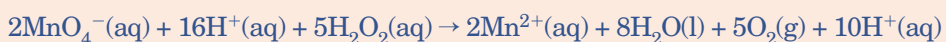
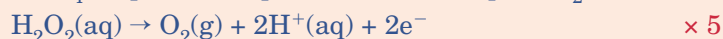
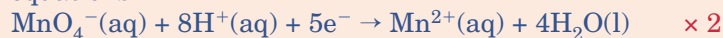
*continued*



$\text{H}_2\text{O}_2$  becomes oxygen,  $\text{O}_2$ . The oxidation number of oxygen has changed from  $-1$  (peroxide) to  $0$  so this will be the oxidation half-equation.



The overall ionic equation for the reaction can be obtained by adding the two half-equations



Since  $\text{H}^+$  is present on the left- and right-hand sides, the equation can be simplified further to give:

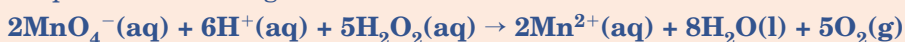


Table 9.2 lists some common oxidants and reductants, together with the product of the reaction and the relevant half-equation.

**TABLE 9.2 SOME COMMON OXIDANTS AND REDUCTANTS**

Reactant	Product	Half-equation
<b>Oxidants</b>		
$\text{O}_2$	$\text{H}_2\text{O}$	$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$
$\text{Cl}_2$	$\text{Cl}^-$	$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$
$\text{MnO}_4^-$ purple	$\text{Mn}^{2+}$ pale pink	$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
$\text{Cr}_2\text{O}_7^{2-}$ orange	$\text{Cr}^{3+}$ green	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$
$\text{ClO}^-$	$\text{Cl}^-$	$\text{ClO}^-(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
$\text{H}^+$	$\text{H}_2$	$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$
$\text{H}_2\text{SO}_4$	$\text{SO}_2$	$\text{H}_2\text{SO}_4(\text{l}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
$\text{HNO}_3$	$\text{NO}_2$ brown gas	$\text{NO}_3^-(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
<b>Reductants</b>		
Zn	$\text{Zn}^{2+}$	$\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$
C	$\text{CO}_2$	$\text{C}(\text{s}) + 2\text{O}^{2-}(\text{s}) \rightarrow \text{CO}_2(\text{g}) + 4\text{e}^-$
$\text{H}_2$	$\text{H}^+$	$\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$
$\text{Fe}^{2+}$ pale green	$\text{Fe}^{3+}$ orange	$\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^-$
$\text{C}_2\text{O}_4^{2-}$	$\text{CO}_2$	$\text{C}_2\text{O}_4^{2-}(\text{aq}) \rightarrow 2\text{CO}_2(\text{g}) + 2\text{e}^-$

## \* Review exercise 9.2

- What is the oxidation number of sulfur in each of the following?
  - $\text{H}_2\text{S}$
  - $\text{S}_8$
  - $\text{H}_2\text{SO}_3$
  - $\text{SO}_3$
  - $\text{Na}_2\text{SO}_4$
  - $\text{CS}_2$
- Write formulas for compounds in which nitrogen has the following oxidation numbers.
  - 3
  - 0
  - +1
  - +2
  - +3
  - +5
- As shown in Figure 9.5 when ammonium dichromate is ignited a spectacular explosive reaction occurs to produce dark green flakes of chromium(III) oxide, nitrogen gas and steam. Write an equation for this decomposition reaction and use oxidation numbers to determine if it is a redox reaction.

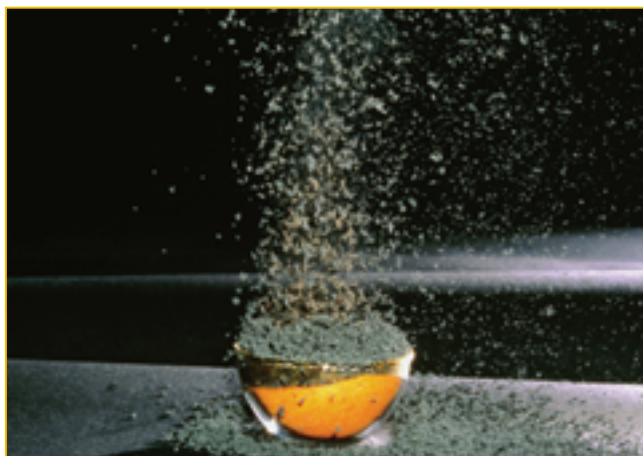


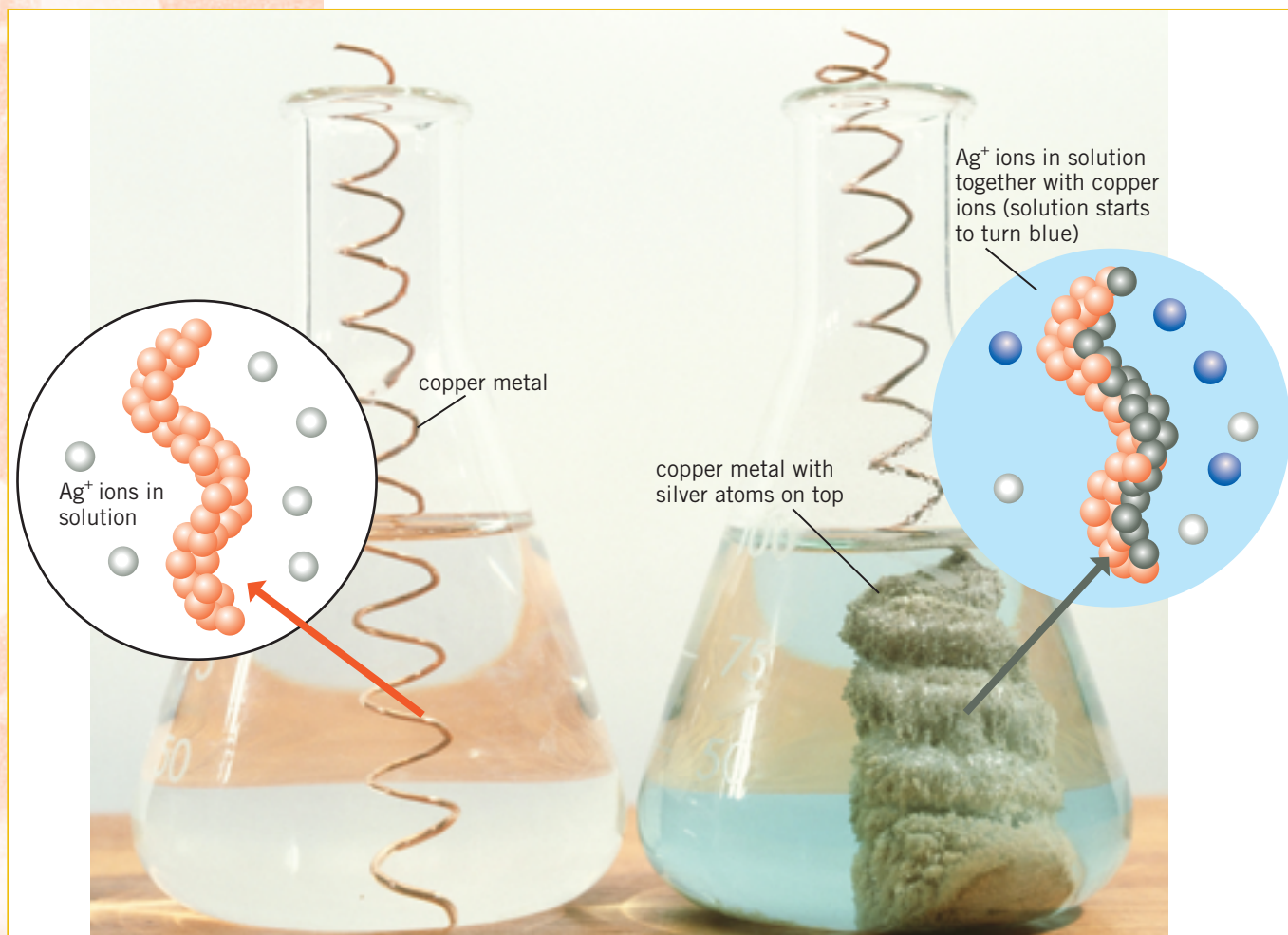
Figure 9.5 Decomposition of ammonium dichromate

- Write the individual oxidation and reduction half-equations and the balanced overall ionic equation for the following reactions carried out in an acidic solution.
  - $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{SO}_3^{2-}(\text{aq}) \rightarrow \text{Cr}^{3+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$
  - $\text{Cu}(\text{s}) + \text{NO}_3^-(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{NO}_2(\text{g})$
  - $\text{Br}^-(\text{aq}) + \text{MnO}_4^-(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + \text{Br}_2(\text{aq})$
- Write balanced ionic equations for the following reactions.
  - When sulfur dioxide is bubbled through an acidified solution of potassium permanganate the sulfur dioxide is converted to sulfate ions and a pale pink solution forms.
  - When a solution of iron(II) sulfate is added to an acidified solution of sodium dichromate a green solution forms.
  - Zinc metal is added to concentrated sulfuric acid and sulfur dioxide is produced.



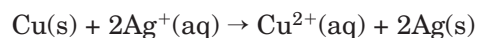
## 9.3 Electrochemical cells

When a piece of copper is placed in a solution of silver nitrate, the formation of silver crystals on the copper and the gradual change of the solution from colourless to blue can be observed. Figure 9.6 shows this change on the macro- as well as the micro-scale.



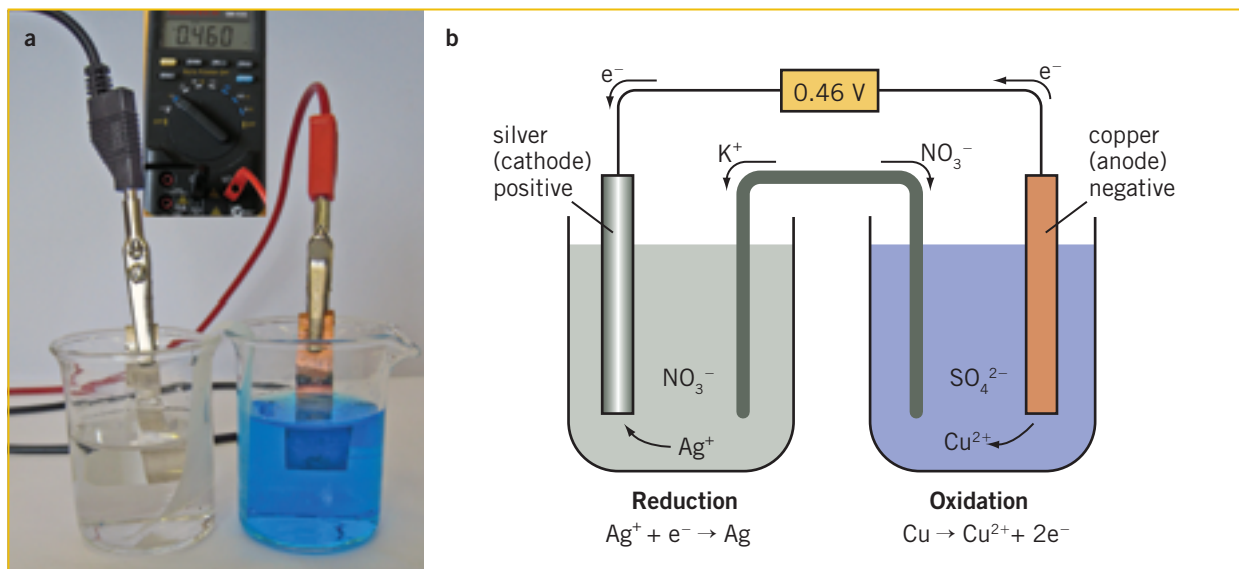
**Figure 9.6** Changes to copper when placed in a solution containing silver ions

The changes taking place in this reaction can be summarised in the equation:



The redox reaction involves electron transfer from a reductant (copper) to an oxidant (silver ions). Because of this electron transfer, the energy released in a redox reaction can be used to do electrical work. In other words, a redox reaction can produce electrical energy rather than simply heat energy.

To produce the energy of the exothermic redox reaction as electrical energy it is necessary to construct an electrochemical or galvanic cell. This cell transfers the electrons through a wire (known as the external circuit) from the reductant to the oxidant, rather than allowing the reactants to come into direct contact with one another. In Figure 9.7 an electrochemical cell that converts chemical potential energy of the reacting copper and silver ions into electrical energy is shown.



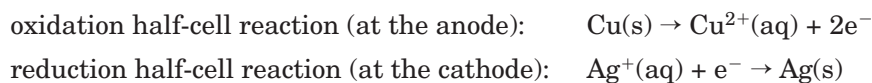
**Figure 9.7** (a) An electrochemical cell involving copper and silver ions. (b) Schematic representation of the changes in the electrochemical cell

The two pieces of metal (copper and silver) in the separate beakers are called electrodes and are linked by a conducting wire (the external circuit). The copper electrode is placed in a solution of copper(II) sulfate, while the silver electrode is in a solution of silver nitrate. To complete the circuit, a salt bridge joins the two beakers. The salt bridge contains an electrolyte solution, usually a saturated solution of a salt such as potassium nitrate whose ions will not react with the contents of either of the beakers.

In the external circuit, the electric current is a flow of electrons in the wire and the electrodes. The circuit is completed in the beakers and salt bridge with a flow of positive and negative ions.

The electrode at which oxidation occurs is called the anode and the electrode at which reduction occurs is called the cathode. In the copper/silver electrochemical cell only one of the electrodes (the cathode) takes part in the reaction. However, every electrochemical cell needs two electrodes, even if neither actually takes part in the reaction.

The two beakers and contents that make up the electrochemical cell are called half-cells. The beaker containing the copper electrode is the half-cell in which oxidation takes place and the beaker with the silver electrode is the one in which the reduction takes place. These half-reactions are:



The electrons that are produced in the oxidation of the copper move through the wire of the external circuit to the cathode where they are picked up by the silver ions. The silver ions are then reduced to metallic silver. As a result of these two half-reactions, the mass of the copper electrode will decrease while that of the silver electrode will increase. The concentration of copper ions in the oxidation half-cell will increase, and the concentration of silver ions in the reduction half-cell will decrease.

The oxidation half-cell reaction only requires the presence of copper. However, to ensure that there is a complete circuit, the solution in this half-cell needs to contain an electrolyte. Using a copper(II) salt such as copper sulfate ensures that the solution will conduct an electric current and that the ions in the solution will

not interfere with the oxidation of the copper. Similarly, the reduction half-cell only requires the presence of a dissolved silver salt such as silver nitrate. The use of silver as the electrode provides the necessary conductor and also ensures that the electrode material will not interfere with the reduction of the silver ions.

As the copper anode is oxidised, the newly formed copper ions,  $\text{Cu}^{2+}$ , enter the solution of the half-cell. The increased positive charge in this half-cell containing the anode is neutralised by negative ions migrating from the salt bridge into the beaker. This migration of negative ions (anions) through the salt bridge is shown in Figure 9.7b. Similarly, at the cathode, silver ions are removed from the solution and the 'missing' positive charge must be replaced. To do this, positive ions (cations) migrate through the salt bridge into the cathode half-cell.

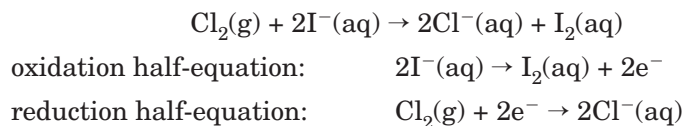
When an electrochemical cell is operating, there is a flow of electrons from the anode to the cathode in the wires of the external circuit, and a flow of ions through the salt bridge. Anions (negative ions) migrate through the salt bridge to the half-cell containing the anode and cations (positive ions) migrate through the salt bridge to the half-cell containing the cathode.

Since the electrons in the wire are flowing from the anode to the cathode, the anode is regarded as the negative electrode (the source of the electrons). The cathode in an electrochemical cell is the positive electrode.

### Summary

- Oxidation takes place at the anode.
- Reduction takes place at the cathode.
- In an electrochemical cell the anode is negative—electrons are produced at this electrode.
- In an electrochemical cell the cathode is positive—electrons are consumed at this electrode.
- Electrons flow from the anode to the cathode through a wire in the external circuit.
- Anions are negative ions and migrate through the salt bridge towards the anode.
- Cations are positive ions and migrate through the salt bridge towards the cathode.
- Both the oxidant and its 'conjugate' reductant are normally present in a half-cell.

Redox reactions are not limited to those between metals and metal ions. As a result, it is necessary to construct half-cells that can accommodate other types of reactions if electrical energy is to be obtained from these reactions. For example, chlorine gas,  $\text{Cl}_2$ , will react with a solution of potassium iodide to form iodine,  $\text{I}_2$ , in a redox reaction:

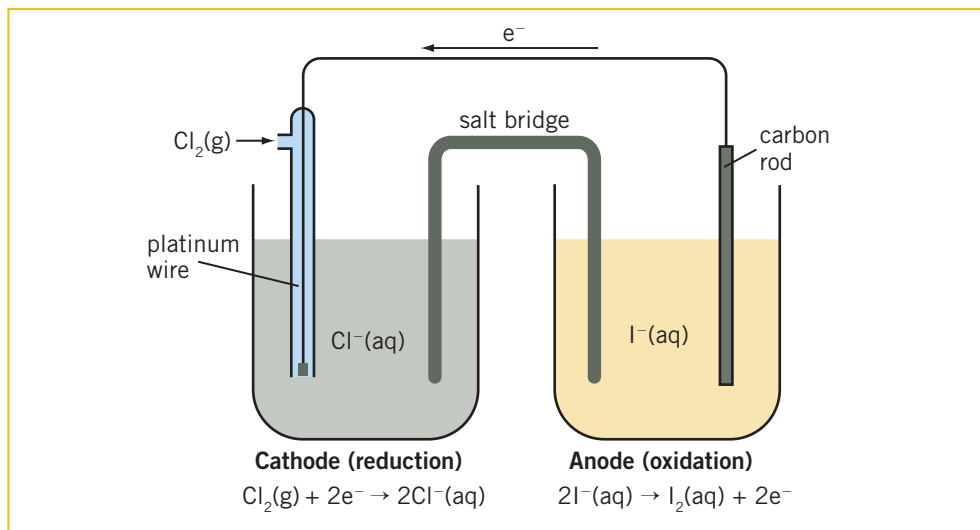


In an electrochemical cell, electrons produced by the oxidation of iodide ions need to flow through an inert electrode (an electrode that will not react with anything in the anode half-cell) to the wire in the external circuit. The electrons then must be transferred to the chlorine gas by another inert electrode.

The most common inert electrodes are carbon (graphite) and platinum (often with a surface coating so that it will adsorb gases). An electrochemical cell that

produces electrical energy from the reaction between chlorine and iodide ions is shown in Figure 9.8.

Electrons produced by the oxidation of iodide ions move up the graphite electrode (anode) to the conducting wire. Some of the chlorine gas bubbling through the reduction half-cell is adsorbed onto the platinum surface (cathode). The adsorbed chlorine molecules combine with the electrons provided from the graphite anode and are reduced to chloride ions.



**Figure 9.8** An electrochemical cell based on the reaction between chlorine and iodide ions

The contents of the half-cell containing the anode change from a colourless solution to a brown solution as iodine is formed. There is no obvious change in the contents of the half-cell containing the cathode. In the salt bridge, the positive ions will flow towards the chlorine half-cell (the half-cell containing the cathode) and the negative ions will flow towards the iodine half-cell (the half-cell containing the anode).

In summary, the nature of the electrodes that can be used for particular half-cell combinations are as follows (Figure 9.9).

- Reactions that involve a metal and a metal ion—the metal becomes the electrode and it is placed in a solution containing its ions. For example, copper metal placed in a solution of copper(II) ions.
- Reactions that involve metal ions in different oxidation states—graphite or platinum is placed in a solution containing both of the metal ions. For example, a graphite electrode placed in a solution containing iron(III) and iron(II) ions.
- Reactions that involve a dissolved non-metal and its ions—graphite or platinum is placed in a solution containing both the non-metal and its ions. For example, a graphite electrode placed in a solution containing bromine and dissolved bromide ions.
- Reactions that involve a gaseous non-metal and its ions—the gas is bubbled over a platinum electrode immersed in a solution of the non-metal ions. For example, hydrogen gas bubbling over a surface of platinum placed in a solution containing hydrogen ions.

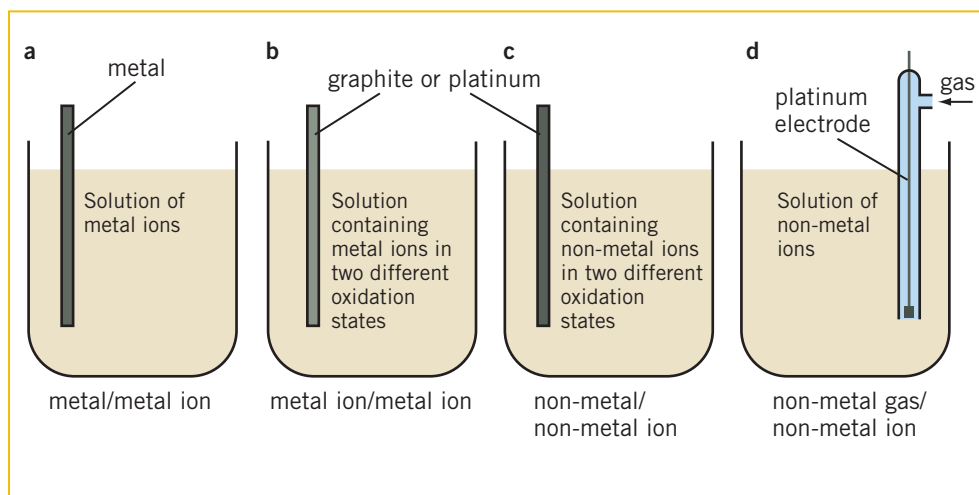


Figure 9.9 Four different types of half-cell arrangement

### \* Review exercise 9.3

- 1 Draw and label an electrochemical cell that produces electrical energy from the reaction:



Your diagram should include the anode and cathode, the half-equations for each electrode, the nature of the electrolyte in each half-cell, the direction of electron flow and the direction of ion migration. In which half-cell does the oxidation reaction take place and in which does the reduction reaction occur?

- 2 For an electrochemical cell, explain why anions in the salt bridge migrate towards the half-cell containing the anode.
- 3 Account for the observation that a piece of copper placed in a beaker with a solution of sodium sulfate, connected by a salt bridge to a solution of silver nitrate in another beaker containing a piece of graphite, will produce electrical energy in the same way as the cell depicted in Figure 9.7. (Assume the copper and graphite are connected by a wire in the external circuit.)
- 4 The redox reaction:



can be used to convert chemical energy into electrical energy.

- a Draw and label an electrochemical cell in which this energy transformation can take place.
- b Identify the anode and cathode.
- c Give the half-equation that occurs at each electrode.
- d Identify the electrolyte in each half-cell.
- e Show the direction of electron flow and the direction of ion migration.
- f In which half-cell does the oxidation reaction take place and in which the reduction reaction?
- g Describe what you would expect to see in each of the half-cells during the operation of the electrochemical cell.
- h If the half-cells remain connected to one another for a long period of time, what will finally happen? Why?

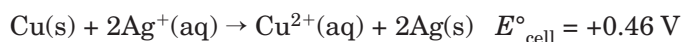
## 9.4 Electric potential and standard reduction potentials

In each of the electrochemical cells considered in the previous section (and in all electrochemical cells) the electrons flow from a reductant in one half-cell to an oxidant in the other half-cell. This can be thought of as the oxidant in one half-cell ‘pulling’ electrons, through the wire, from the reductant in the other half-cell. As established earlier, different oxidants have different strengths. Some such as fluorine,  $F_2$ , are strong oxidants, but others such as sodium ions,  $Na^+$ , are very weak oxidants. It therefore follows that if a half-cell containing a strong oxidant is connected to a half-cell containing a weak oxidant, the electrons in the external circuit wire will be ‘pulled’ towards the half-cell with the stronger oxidant. A measure of the electron-attracting ‘power’ of an oxidant in a half-cell is sometimes referred to as the ‘electric potential’ or the ‘potential’ of the half-cell.

The ‘driving force’ causing the flow of electricity in an electrochemical cell is therefore due to the difference in ‘electric potentials’ of its two half-cells. This driving force or ‘pull’ of electrons in an electrochemical cell is called the cell potential, or the electromotive force, emf, or voltage of the cell. It is also referred to as the potential difference of the cell. The unit of electric potential and cell potential is the volt (V).

In the copper/silver ion electrochemical cell in Figure 9.7 a voltmeter is shown measuring the cell potential (voltage). The reading on the meter is about 0.46 V. The cell potential of an electrochemical cell is given the symbol  $E_{\text{cell}}$  ( $E$  is the symbol used for electric potential).

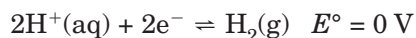
The cell potential of an electrochemical cell not only depends on the nature of the oxidants and reductants in each half-cell, but also depends on the concentrations of the electrolytes, the pressure of any gases involved in the reaction and the temperature at which the cell operates. When the conditions in the cell are  $1 \text{ mol L}^{-1}$  concentration of dissolved substances, 101.3 kPa (1 atm) pressure of gases, and  $25^\circ\text{C}$ , the cell potential of the cell is written as  $E^\circ_{\text{cell}}$ , and is known as a standard cell potential. For example, the standard cell potential for the reaction between copper and a solution containing silver ions is written as:



### Standard reduction potentials

It would be convenient to have numerical measures of the electric potentials or reduction potentials of half-cells, for example to enable comparisons of relative oxidant strengths. However, because each electrochemical cell involves two half-cells, it is not possible to directly measure the reduction potential for only one half-cell. Nonetheless, by assigning one specific half-cell as a reference, it is possible to determine the reduction potentials of other half-cells with respect to that reference.

The chosen reference half-cell is one containing hydrogen gas and hydrogen ions. The concentration of hydrogen ions in this half-cell is  $1 \text{ mol L}^{-1}$ , the pressure of hydrogen gas is 101.3 kPa and the temperature is  $25^\circ\text{C}$ . Under these conditions the reduction potential of this half-cell is defined as zero volts:



The half-cell that produces this half-reaction is called the standard hydrogen half-cell or the standard hydrogen electrode (Figure 9.10).

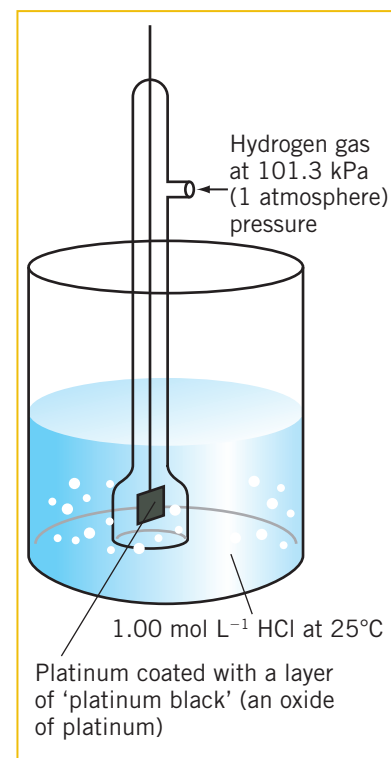


Figure 9.10 Diagram of a standard hydrogen half-cell

(Note: In this textbook,  $E^\circ_{\text{oxidant}}$  and  $E^\circ_{\text{reductant}}$  always refer to the standard electric potential of the reduction reaction; that is, they are the symbols for standard reduction potentials given in Table 9.3.)

IUPAC has a set of rules for assigning standard cell potentials and half-cell reduction potentials. Some of these rules differ from those that may be used in older texts (particularly those from the USA) to determine cell potentials.

According to IUPAC suggestions, the standard cell potential, or the potential difference of a cell, can be calculated in the following way:

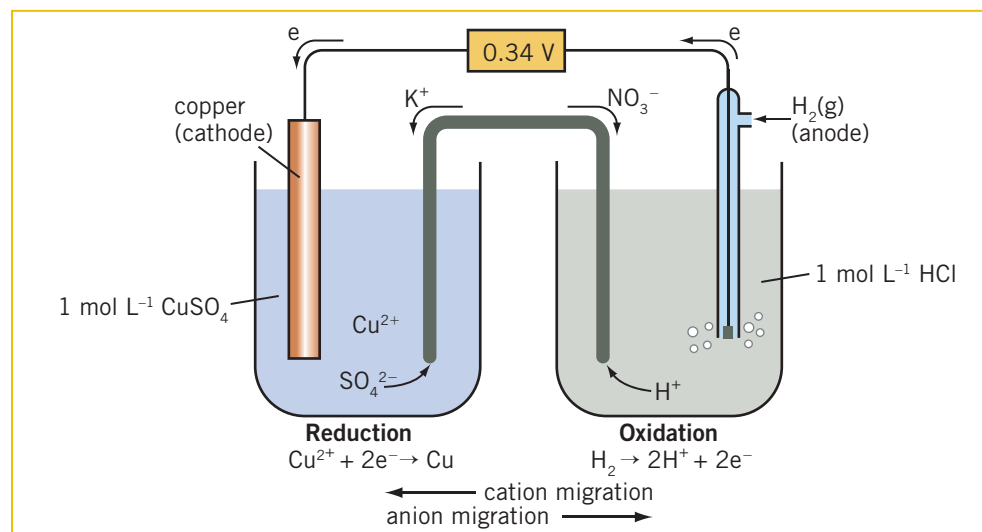
$$\text{standard cell potential} = \begin{array}{l} \text{standard reduction} \\ \text{potential of the half-cell} \\ \text{containing the reacting} \\ \text{oxidant} \end{array} - \begin{array}{l} \text{standard reduction} \\ \text{potential of the half-} \\ \text{cell containing the} \\ \text{reductant} \end{array}$$

or  $E^\circ_{\text{cell}} = E^\circ_{\text{oxidant}} - E^\circ_{\text{reductant}}$

where  $E^\circ_{\text{oxidant}}$  and  $E^\circ_{\text{reductant}}$  are the standard reduction potentials of the half-cells containing the reacting oxidant and the reacting reductant, respectively.

Using this information, the standard reduction potential ( $E^\circ$ ) of a half-cell can be determined by connecting the relevant half-cell to the standard hydrogen half-cell and measuring the cell potential.

For example, the standard reduction potential of the  $\text{Cu}^{2+}/\text{Cu}$  ion half-cell can be determined by setting up an electrochemical cell under standard conditions as shown in Figure 9.11.



**Figure 9.11** Measuring the standard reduction potential ( $E^\circ$ ) for the  $\text{Cu}^{2+}/\text{Cu}$  half-cell

From the activity series of metals it is known that copper does not react with acid under normal circumstances and so in the presence of the standard hydrogen half-cell it is not anticipated that the copper will be oxidised to copper(II) ions. However, at this stage, the only certain way to determine in which half-cell oxidation occurs and in which reduction occurs is to set up the cell and make measurements.

As shown in Figure 9.11, the voltmeter registers a value of 0.34 volts under standard conditions and the electrons flow from the hydrogen electrode to the copper. This means the oxidation half-reaction occurs in the hydrogen half-cell (the anode) and the reduction half-reaction occurs in the copper half-cell (the cathode).

Anode:  $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$  hydrogen is the reductant

Cathode:  $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$  copper ions are the oxidant

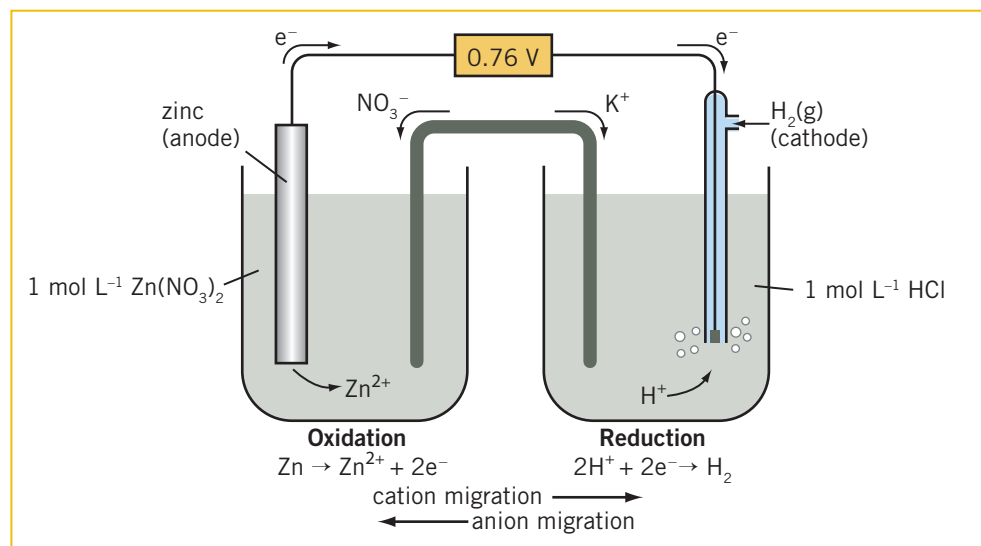
Since  $E^\circ_{\text{cell}} = E^\circ_{\text{oxidant}} - E^\circ_{\text{reductant}}$   
 $0.34 = E^\circ_{\text{oxidant}} - 0$

$$E^\circ_{\text{copper half-cell}} = \text{standard reduction potential of the copper half-cell} \\ = +0.34 \text{ V}$$

Showing the standard reduction potential, this half-cell reaction is written as:



When a more reactive metal such as zinc is set up as a standard half-cell and connected to the standard hydrogen half-cell (Figure 9.12) the zinc becomes the anode, producing electrons that travel through the external circuit to the standard hydrogen electrode where hydrogen ions pick up the electrons and are reduced to hydrogen (at the cathode). The standard cell voltage, as measured with a voltmeter, is 0.76 V.



**Figure 9.12** Measuring the standard reduction potential for the  $\text{Zn}^{2+}/\text{Zn}$  half-cell

Anode:  $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$  zinc metal is the reductant

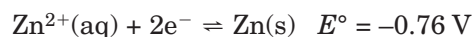
Cathode:  $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$  hydrogen ions are the oxidant

Since  $E^\circ_{\text{cell}} = E^\circ_{\text{oxidant}} - E^\circ_{\text{reductant}}$

$$0.76 = 0 - E^\circ_{\text{reductant}}$$

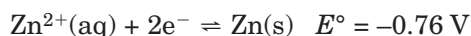
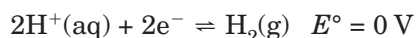
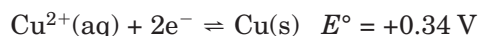
$$E^\circ_{\text{zinc half-cell}} = -0.76 \text{ V}$$

Showing the standard reduction potential, this half-cell reaction is written as:



The negative  $E^\circ$  value indicates that hydrogen ions have a greater tendency to gain electrons (i.e. are a stronger oxidant) than zinc ions.

The three standard reduction potentials previously considered can be placed in order from strongest oxidant to weakest:



Oxidants that are stronger than  $\text{H}^+(\text{aq})$  under standard conditions have a standard reduction potential that is positive, while oxidants that are weaker than  $\text{H}^+(\text{aq})$  have a negative standard reduction potential.

Table 9.3 lists the standard reduction potentials at 25°C for a range of oxidising agents and reducing agents.



**TABLE 9.3 STANDARD REDUCTION POTENTIALS ( $E^\circ$ ) AT 25°C**

Half-reaction	$E^\circ$ (volts)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.78
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	+1.69
$2HClO(aq) + 2H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O(l)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
$HClO(aq) + H^+(aq) + 2e^- \rightleftharpoons Cl^-(aq) + H_2O(l)$	+1.48
$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l)$	+1.46
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	+0.52
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(aq)$	+0.14
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0 exactly
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	-0.13
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	-0.14
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	-0.26
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	-0.28
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$	-0.36
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	-0.40
$2CO_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons HOOCCOOH(aq)$	-0.43
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	-0.73
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.83
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	-1.18
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	-1.66
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.37
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	-2.76
$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	-2.89
$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	-2.91
$K^+(aq) + e^- \rightleftharpoons K(s)$	-2.93

The following generalisations can be made from this table.

- Oxidants are on the left-hand side and reductants are on the right.
- The more positive the reduction potential, the stronger the oxidant.
- The more negative the reduction potential, the stronger the reductant.
- Equilibrium arrows are used to represent the half-cell reactions because these reactions can proceed in both directions, depending what is present in the other half-cell.
- The cell potential of any combination of these half-cells is calculated from the half-cell reduction potentials using the expression:

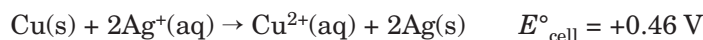
$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{half-cell containing the oxidant}} - E^{\circ}_{\text{half-cell containing the reductant}}$$

- Oxidants generally only react with reductants that have a more negative  $E^{\circ}$  (standard reduction potential) value.
- The greater the difference in  $E^{\circ}$  values between the oxidant and reductant the more likely the reaction is to proceed in the direction predicted. Differences in reduction potentials are related to equilibrium constants. The greater the difference in  $E^{\circ}$  values, the larger the equilibrium constant for the reaction.
- Even when there may be a large difference in standard reduction potentials between the oxidant and reductant, the cell potential does not predict how fast the reaction will take place. It is possible that the rate of reaction at  $25^{\circ}$  is very slow.

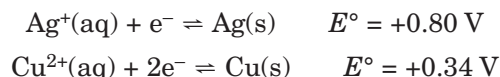
### Using standard reduction potentials to predict cell reactions and cell potentials



Earlier it was noted that the electrochemical cell constructed from a  $\text{Cu}^{2+}/\text{Cu}$  half-cell and an  $\text{Ag}^{+}/\text{Ag}$  half-cell produced a voltage of 0.46 V and that the electrons flowed from the copper anode (negative electrode) to the silver cathode (positive electrode):



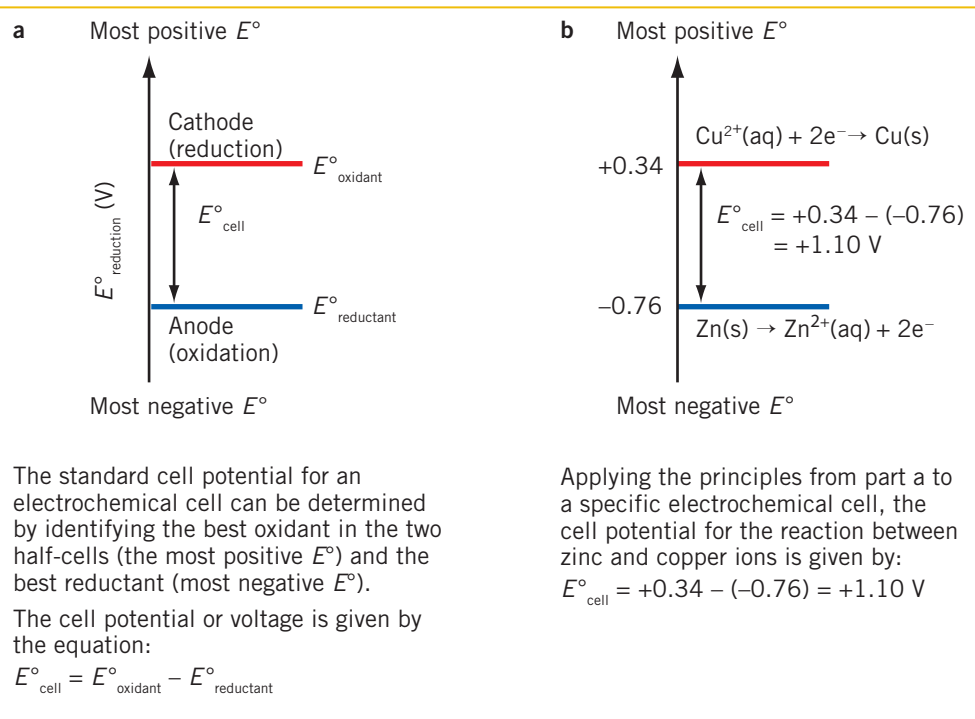
In this electrochemical cell, the silver ions act as the oxidant and the copper as the reductant. The relevant standard half-cell reduction potentials for this cell are:



The cell potential of 0.46 V can be seen to be the difference between the standard reduction potential for silver (+0.80 V) and that for copper (+0.34 V). The silver is the positive electrode in the electrochemical cell, and also has the most positive standard reduction potential:

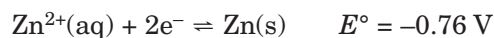
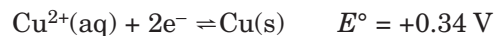
$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{oxidant}} - E^{\circ}_{\text{reductant}} = E^{\circ}_{\text{silver half-cell}} - E^{\circ}_{\text{copper half-cell}} \\ 0.46 &= +0.80 - (+0.34) \end{aligned}$$

(The value of +0.80 V for the standard reduction potential of silver ions does not alter irrespective of the number of silver ions involved in a balanced cell equation. Changing the stoichiometric coefficients in any half-cell equation does not alter the value of the standard reduction potential for that half-cell.)

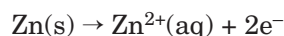
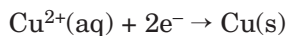


**Figure 9.13** Determining standard cell potentials: (a) for any general combination of half-cells; (b) for the reaction between zinc and copper ions

Figure 9.13a indicates how the values for the standard reduction potentials given in Table 9.3 can be used to predict the cell potential (or potential difference) of an electrochemical cell. The example shown in Figure 9.13b refers to an electrochemical cell made up of a standard copper half-cell and a standard zinc half-cell (as shown in Figure 9.14). Using the values for the individual standard reduction potentials of copper ions and zinc ions:



it is predicted that since  $\text{Cu}^{2+}$  is a stronger oxidant than  $\text{Zn}^{2+}$ , the electrons will flow in the wire towards the copper half-cell. As a result, the copper ions will undergo reduction (gain electrons) and the zinc will undergo oxidation (lose electrons):

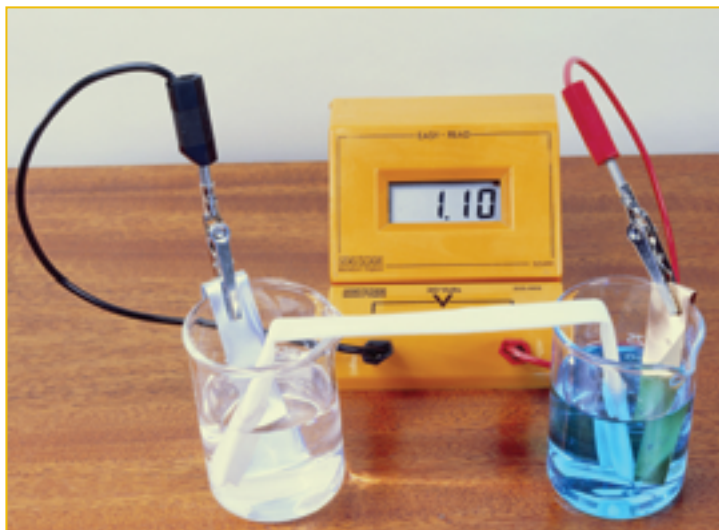


The oxidant in the cell is therefore the copper ions and the reductant is the zinc.

The cell potential (or potential difference) of the cell can be determined by:

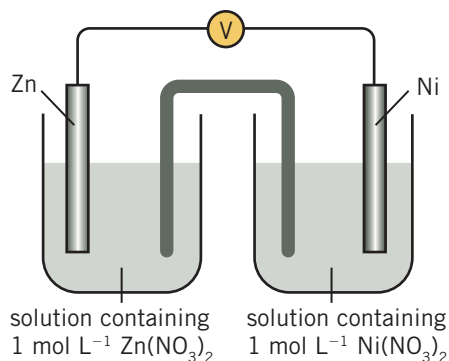
$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{oxidant}} - E^\circ_{\text{reductant}} \\ &= E^\circ_{\text{copper half-cell}} - E^\circ_{\text{zinc half-cell}} \\ &= +0.34 - (-0.76) \\ &= 1.10 \text{ volts} \end{aligned}$$

This is confirmed by the reading on the voltmeter shown in Figure 9.14.



**Figure 9.14** An electrochemical cell based on the reaction between zinc and copper ions

For another example showing how the reactions and standard cell potential of an electrochemical cell can be predicted, a cell composed of a standard zinc/zinc ion half-cell and a standard nickel/nickel(II) ion half-cell will be considered:



The relevant standard reduction potentials for this cell are:



From these values it can be predicted that:

- because  $\text{Ni}^{2+}$  is the stronger oxidant (has the larger reduction potential ( $E^{\circ}$ )), the electrons in the wire will flow towards the nickel half-cell
- $\text{Ni}^{2+}$  will gain electrons; that is, undergo reduction:  

$$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Ni}(\text{s})$$
- $\text{Ni}^{2+}$  will act as the oxidant
- Zn will lose electrons; that is, undergo oxidation:  

$$\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$$
- Zn will act as the reductant
- the Ni electrode will be the cathode and the Zn electrode the anode
- the cell potential can be calculated as follows:

$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{oxidant}} - E^{\circ}_{\text{reductant}} \\ &= E^{\circ}_{\text{nickel half-cell}} - E^{\circ}_{\text{zinc half-cell}} \\ &= -0.26 - (-0.76) \\ &= 0.50 \text{ volts} \end{aligned}$$

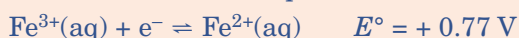
### → Example 9.3

An electrochemical cell is made up of a standard  $\text{Fe}^{3+}/\text{Fe}^{2+}$  half-cell and a standard  $\text{Ni}^{2+}/\text{Ni}$  half-cell.

- Draw this electrochemical cell.
- Use the relevant standard reduction potentials to determine the direction of electron flow and the equations for half-cell reactions and the overall cell reaction.
- Calculate the standard cell potential (potential difference) of the cell.
- On your cell diagram show the anode and cathode and the direction of electron, cation (positive ion) and anion (negative ion) flow.
- Explain what will happen to the cell potential if the cell is 'connected' for a long time.

### → Solution

- See d below.
- The relevant standard reduction potentials are:

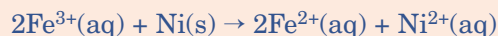


$\text{Fe}^{3+}$  is the stronger oxidant, so electrons will flow towards the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  half-cell (and away from the nickel half-cell).

$\text{Fe}^{3+}$  will gain electrons (undergo reduction):  $\text{Fe}^{3+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Fe}^{2+}(\text{aq})$

Ni will lose electrons (undergo oxidation):  $\text{Ni}(\text{s}) \rightarrow \text{Ni}^{2+}(\text{aq}) + 2\text{e}^{-}$

The overall equation for the cell will be:



- $\text{Fe}^{3+}$  acts as the oxidant and Ni acts as the reductant:

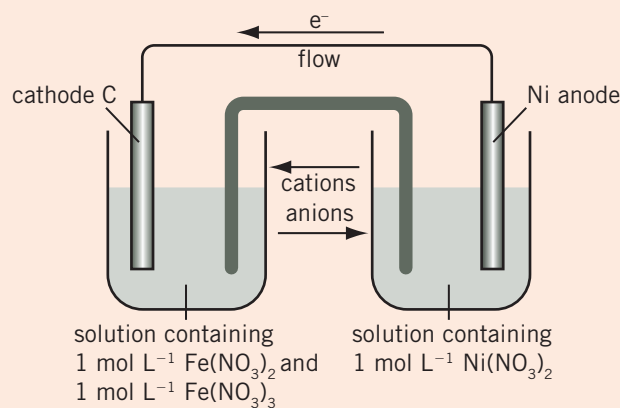
$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{oxidant}} - E^{\circ}_{\text{reductant}} \\ &= E^{\circ}_{\text{iron ions half-cell}} - E^{\circ}_{\text{nickel half-cell}} \\ &= +0.77 - (-0.26) \\ &= 1.03 \text{ volts} \end{aligned}$$

(Note: Despite the half-equation for the reduction of  $\text{Fe}^{3+}$  being multiplied by 2 in order to balance the ionic equation, the value for its standard reduction potential is not changed when calculating the cell potential.)

- Reduction occurs at the cathode, so the electrode in the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  half-cell is the cathode. Oxidation occurs at the anode, so the nickel electrode is the anode.

In the internal part of the cell, the cations flow towards the cathode and the anions towards the anode.

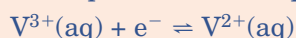
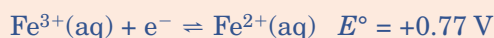
(An alternative way of determining this is recognising that the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  half-cell is becoming more negative (or less positive) because of the flow of electrons into it and the formation of  $\text{Fe}^{2+}$  ions from  $\text{Fe}^{3+}$  ions. Positive ions (cations) will therefore need to move out of the salt bridge into this half-cell to maintain neutrality. Similarly, electrons are flowing away from the nickel half-cell, leaving behind positive  $\text{Ni}^{2+}$  ions. Negative ions (anions) will therefore need to move out of the salt bridge into this half-cell, again to maintain neutrality.)



- e The cell will finally 'go flat'. That is, the cell potential (voltage) will drop to 0 volts. When the two half-cells are first connected, the concentration of the  $\text{Fe}^{3+}$  ions is  $1 \text{ mol L}^{-1}$ , but as this reactant is consumed in the half-cell reaction, its concentration will decrease. This will result in a decrease in the cell potential.

#### → Example 9.4

An electrochemical cell is set up using the two half-cells expressed in the following half-equations:

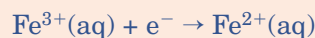


The cell potential of the cell combination under standard conditions is found to be 1.03 V. The voltmeter connections also reveal that the positive electrode (cathode) is in the half-cell containing the iron(III) and iron(II) combination. Determine the standard reduction potential for the conversion of vanadium(III) to vanadium(II).

#### → Solution

In any electrochemical cell the positive electrode is the cathode.

The reaction at the cathode is reduction so the half-equation for the reaction taking place in the iron(III)/iron(II) half-cell is:



That is,  $\text{Fe}^{3+}$  is the oxidant. In the other half-cell an oxidation reaction must occur, so in this half-cell the  $\text{V}^{2+}(\text{aq})$  is the reductant and is oxidised.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{oxidant}} - E^{\circ}_{\text{reductant}}$$

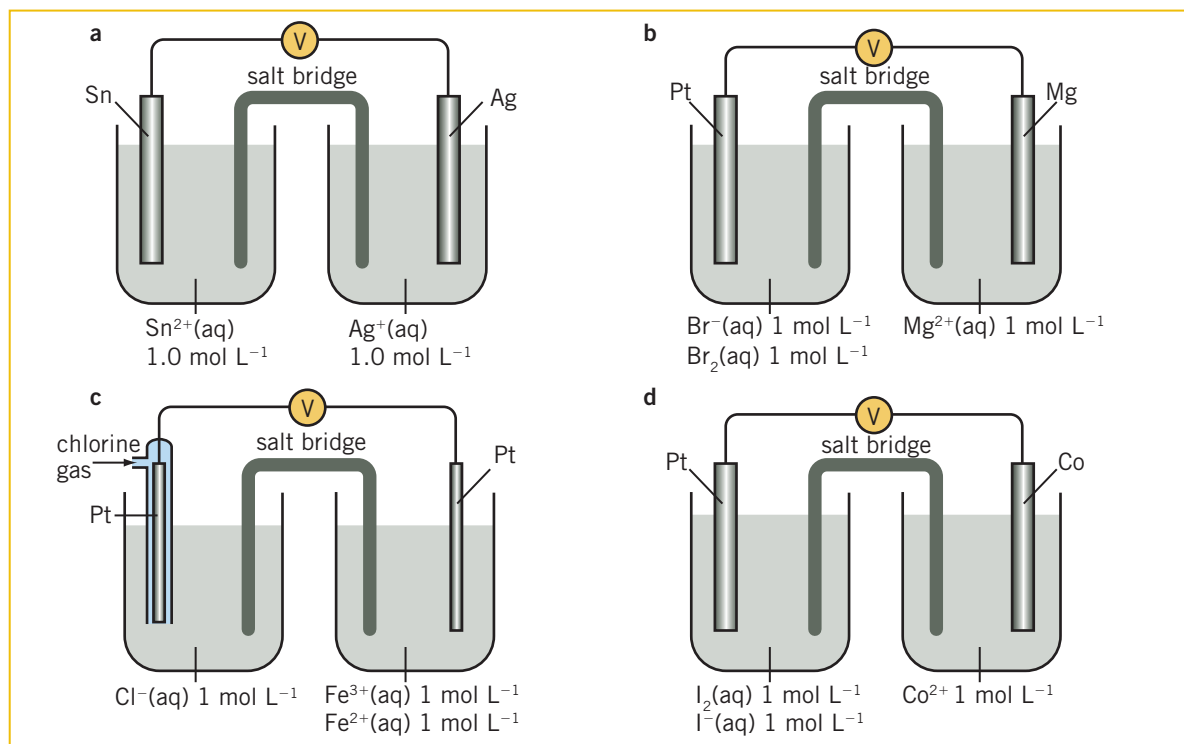
$$1.03 = +0.77 - E^{\circ}_{\text{reductant}}$$

$$\begin{aligned} E^{\circ}_{\text{reductant}} &= +0.77 - 1.03 \\ &= -0.26\text{V} \end{aligned}$$

The standard reduction potential for  $\text{V}^{3+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{V}^{2+}(\text{aq})$  is **-0.26 V**.

## \* Review exercise 9.4

- An electrochemical cell is composed of a  $\text{Pb}^{2+}(\text{aq})/\text{Pb}(\text{s})$  half-cell, a  $\text{Ag}^{+}(\text{aq})/\text{Ag}(\text{s})$  half-cell and a potassium nitrate salt bridge.
  - Draw and label a diagram of the electrochemical cell and indicate the direction of electron flow in the external circuit.
  - Label the anode and the cathode, and write the reaction that occurs at each electrode.
  - What is the overall ionic equation for the cell reaction?
  - Describe the movement of ions within the solutions and the salt bridge.
  - Calculate the voltage (cell potential) produced by the cell under standard conditions.
  - During the operation of the cell the silver electrode changes in mass by 1.19 g. Will this be an increase or decrease in the mass of the electrode? Explain your answer.
- For each of the cells drawn below determine the:
  - strongest oxidising agent in the electrochemical cell
  - direction of the electron flow through the wire
  - half-equations for the half-reactions that will occur in the cell
  - equation for the overall reaction for the electrochemical cell
  - anode and the cathode
  - cell potential (assume standard conditions)
  - direction of flow of the positive ions and the negative ions.



- If the reaction  $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Cu}(\text{s})$  had been chosen as the standard reference half-cell and had been assigned an  $E^{\circ}$  of 0 V.
  - How would the table of standard reduction potentials differ?
  - How would the values of cell potentials for complete electrochemical cells differ?

4 You have been provided with the following materials:

- strips of nickel, lead, tin, copper, a graphite rod and material to construct a salt bridge
  - 1 mol L<sup>-1</sup> solutions of the following: HCl, CuSO<sub>4</sub>, Fe(NO<sub>3</sub>)<sub>2</sub>, NiSO<sub>4</sub>, Sn(NO<sub>3</sub>)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>
- a Draw a diagram of the electrochemical cell that would give the greatest voltage (cell potential) if constructed from these materials.
- b What would be the cell potential recorded under standard conditions?
- c On the cell diagram label the following:  
anode, cathode, direction of electron movement, direction of movement of anions, half-cell in which oxidation takes place, half-cell in which reduction takes place, half-cell reactions.

## 9.5 Predicting whether redox reactions will take place



Standard reduction potentials can be used to predict whether or not a redox reaction will occur when two substances are mixed.

A spontaneous redox reaction will be expected to occur if the following requirements are satisfied:

- One reactant is an oxidant and the other is a reductant
- The oxidant has a larger standard reduction potential ( $E^\circ$ ) than the reductant. Another way of stating this is that an oxidant higher on the table of standard reduction potentials will react with a reductant lower down on the table.

From the following standard reduction potential values:

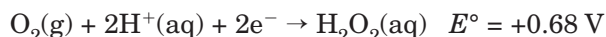
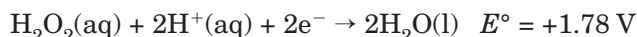


it can be predicted that:

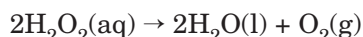
- i chlorine will react with iron because Cl<sub>2</sub> is a stronger oxidant than Fe<sup>2+</sup>  
$$\text{Cl}_2(\text{g}) + \text{Fe}(\text{s}) \rightarrow 2\text{Cl}^-(\text{aq}) + \text{Fe}^{2+}(\text{aq})$$
- ii a solution of iron(II) nitrate will not react with a solution of sodium chloride because Fe<sup>2+</sup>(aq) is not a sufficiently strong oxidant to react with Cl<sup>-</sup>(aq).

As mentioned previously, the table of standard reduction potentials can be used to predict the extent of a chemical reaction. The greater the difference between the  $E^\circ$  values for the oxidant and the reductant, the larger the equilibrium constant for the reaction. However, a large value for the equilibrium constant,  $K$ , does not mean that the reaction rate will also be large.

According to the table of standard reduction potentials, hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, should react with itself to produce water and oxygen:



The overall equation for this reaction is:





In fact, hydrogen peroxide decomposes very slowly at room temperature even though the difference in reduction potentials (1.1 V) suggests that the reaction has a large equilibrium constant.

The standard reduction potentials are also measured under standard conditions. If the conditions for a chemical reaction differ from the standard 25°C, 101.3 kPa pressure of gases and 1 mol L<sup>-1</sup> concentrations, then the use of the table as a predictive tool may not be reliable.

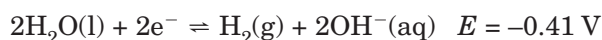
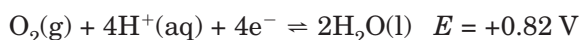
Standard reduction potentials can be used to explain reactions such as:

- metal displacement reactions—to predict which metals are strong enough reductants to react with solutions containing other metal ions
- halogen displacement reactions—to predict the order of oxidant strength of the halogens and which halogens will react with solutions containing halide ions
- reactions of metals with water—any metal with a reduction potential less than around -0.4 V will react with water (even if it is very slow)
- reactions of metals with acids—metals with a reduction potential ( $E^\circ$ ) less than 0.0 V will react with hydrochloric acid and dilute sulfuric acid to form H<sub>2</sub>. Metals with a reduction potential ( $E^\circ$ ) less than 0.95 V will react with reasonably concentrated nitric acid to form NO(g) (which will immediately oxidise to brown NO<sub>2</sub>(g) in the presence of air).

Other aspects of the use of the table of standard reduction potentials include the following:

- Many substances will only react if an acid is present. For example, MnO<sub>4</sub><sup>-</sup>(aq) and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>(aq) both require the presence of H<sup>+</sup>(aq) in their reactions as illustrated in the specific half-equations.
- In an aqueous solution the very weak oxidant metal ions will not participate in a redox reaction. Cations of group 1 and 2 metals together with Al<sup>3+</sup>(aq) can be ignored when predicting redox reactions involving aqueous solutions.
- Nitrate ions and sulfate ions will not participate in redox reactions unless they are present as reasonably concentrated nitric acid or sulfuric acid:
  - Nitric acid—when a metal reacts with the concentrated acid, nitrogen dioxide is formed:
 
$$\text{NO}_3^-(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$$
  - When a metal reacts with less concentrated acid (4–6 mol L<sup>-1</sup>), nitrogen monoxide forms:
 
$$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$$
  - Sulfuric acid—when a metal reacts with concentrated sulfuric acid, sulfur dioxide forms:
 
$$\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$$
- Water can act as both an oxidant and a reductant. Table 9.3 only provides the  $E^\circ$  values for standard conditions.

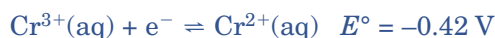
Water can also behave as an oxidant and a reductant in a neutral solution and in the absence of gases at 101.3 kPa pressure. While the reduction and oxidation half-equations remain the same, the values of the reduction potentials change. For example in an aqueous neutral solution (10<sup>-7</sup> mol L<sup>-1</sup> H<sup>+</sup>(aq) and OH<sup>-</sup>(aq)) the relevant reduction potentials are:



However, for this course of study the differences in these values from those in the table of standard reduction potentials will not be important.

## \* Review exercise 9.5

- 1 a List the following in increasing strength (from weakest to strongest) as oxidants.
- i  $\text{I}_2(\text{aq})$
  - ii  $\text{Pb}^{2+}(\text{aq})$
  - iii  $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+(\text{aq})$
  - iv  $\text{Fe}^{2+}(\text{aq})$
- b List the following in order of decreasing tendency to undergo oxidation.
- i  $\text{Fe}^{2+}(\text{aq})$
  - ii  $\text{Ag}(\text{s})$
  - iii  $\text{H}_2\text{O}_2(\text{aq})$
  - iv  $\text{Mg}(\text{s})$
- c List the following in order of decreasing tendency to gain electrons in a redox reaction.
- i  $\text{Cu}^{2+}(\text{aq})$
  - ii  $\text{Br}_2(\text{aq})$
  - iii concentrated nitric acid
  - iv  $\text{H}^+(\text{aq})$
- 2 For each of the following predict whether a redox reaction would occur. If a reaction does take place write the overall ionic equation and give any observations that would be made.
- a Chlorine gas is bubbled through a solution of potassium iodide.
  - b A solution of cobalt sulfate is added to a solution of magnesium chloride.
  - c Aluminium is added to a solution of silver nitrate.
  - d An acidified solution of potassium permanganate is added to a solution of iron(II) sulfate.
  - e Hydrogen sulfide gas is bubbled through a solution of concentrated nitric acid.
- 3 The standard reduction potentials for two different chromium-containing species are given below:



Which one or more of the following would convert an acidified solution of sodium dichromate to chromium(III) ions but not to chromium(II) ions?

- a  $\text{Zn}(\text{s})$
- b  $\text{I}^-(\text{aq})$
- c  $\text{Au}(\text{s})$
- d  $\text{Fe}^{2+}(\text{aq})$

## MAJOR IDEAS

- Oxidation is defined as a loss of electrons, while reduction is a gain of electrons.
- Reductants undergo oxidation. Oxidants undergo reduction.
- An oxidation number is a number that is assigned to each atom in a substance to indicate its oxidation state.
- The general rules for assigning oxidation number are:
  - For monatomic ions the oxidation number is the ionic charge.
  - The oxidation number of an atom in any element is zero.
  - The oxidation number of oxygen in its compounds is  $-2$  (exceptions:  $F_2O$  and peroxides ( $O_2^{2-}$ )).
  - The oxidation number of hydrogen in its compounds is  $+1$  (exception  $H^-$ ).
  - The sum of the oxidation numbers of the atoms in a neutral compound is zero.
  - The sum of the oxidation numbers of the atoms in a polyatomic ion must equal the ionic charge.
- In a reaction, oxidation is an increase in oxidation number and reduction is a decrease in oxidation number.
- A half-equation for an oxidation or reduction reaction can be written using the following rules:
  - Write the formula of the oxidant or reductant, and the product it forms.
  - Balance the atom undergoing the change in oxidation number.
  - Balance oxygen atoms by adding water,  $H_2O$ , where needed.
  - Balance hydrogen atoms by adding  $H^+$  where needed.
  - Balance the charge by adding electrons where needed.
- An ionic equation for a redox reaction can be written by adding the two relevant half-equations, ensuring the electrons cancel out.
- Common oxidants include  $O_2$ ,  $Cl_2$ ,  $MnO_4^-$ ,  $Cr_2O_7^{2-}$ ,  $ClO^-$ ,  $H^+$ , concentrated  $H_2SO_4$  and  $HNO_3$ .
- Common reductants include  $Zn$ ,  $H_2$ ,  $Fe^{2+}$  and  $C_2O_4^{2-}$ .
- In an electrochemical cell a spontaneous redox reaction occurs and chemical energy is converted to electrical energy.
- The electrochemical cell comprises two half-cells, one containing the reductant and the other the oxidant. The half-cells are connected by a wire (the external circuit) and a salt bridge (part of the internal circuit).
- In each half-cell there is an electrode and an electrolyte.
- The cell potential of an electrochemical cell is measured in volts and it depends on the nature of the half-cell reactions and the concentrations/gas pressures of the reacting substances.
- In an electrochemical cell, oxidation occurs at one electrode called the anode. It is the negative electrode. Reduction occurs at the other electrode, called the cathode. It is the positive electrode.
- When an electrochemical cell is discharging (producing electrical energy), electrons flow in the external circuit and ions move internally in the electrolyte between the electrodes.
- In the salt bridge in an electrochemical cell, the positive ions (cations) flow towards the positive electrode (cathode) and the negative ions (anions) flow towards the negative electrode (anode).
- Standard reduction potentials ( $E^\ominus$ ) are a measure of the tendency of a substance to be reduced under standard conditions. They are measured in volts. The hydrogen half-cell is the standard reference with an  $E^\ominus$  of  $0.00\text{ V}$ .
- The strongest oxidants have the highest reduction potentials. The strongest reductants occur at the bottom right of the table of standard reduction potentials.
- In an electrochemical cell, the electrons flow through the external circuit towards the cell with the stronger oxidant (from anode to cathode).
- The cell potential (potential difference or voltage) of an electrochemical cell is the difference in the reduction potentials of the half-cells comprising the cell:
$$E_{\text{cell}} = E_{\text{oxidant}} - E_{\text{reductant}}$$
- A spontaneous redox reaction will occur between two substances if:
  - one reactant is an oxidant and the other is a reductant
  - the oxidant has a more positive standard reduction potential ( $E^\ominus$ ) than the reductant.

## QUESTIONS

- 1 Vanadium, being a typical transition metal, exhibits different oxidation states in its compounds. Four vanadium compounds are shown in solution in Figure 9.15. Determine the oxidation number of vanadium in each.

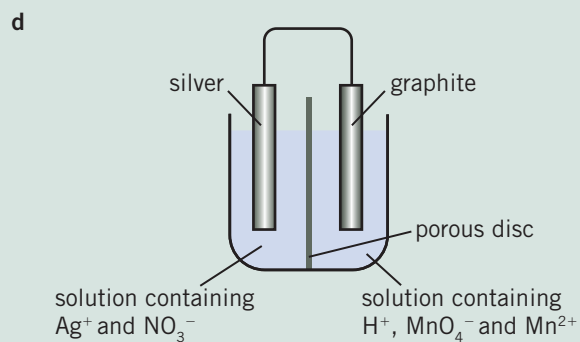
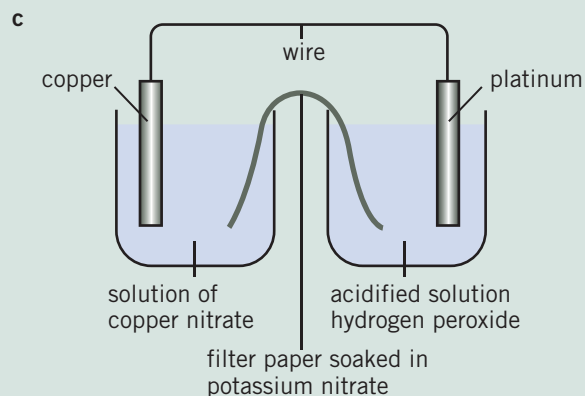
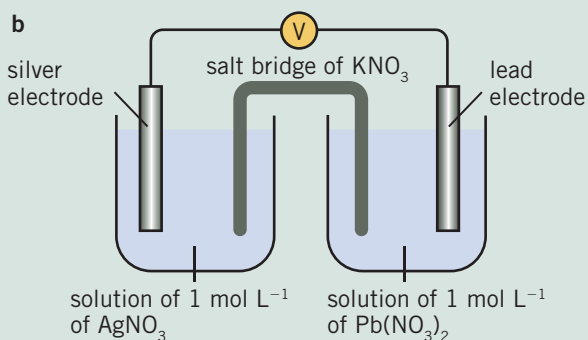
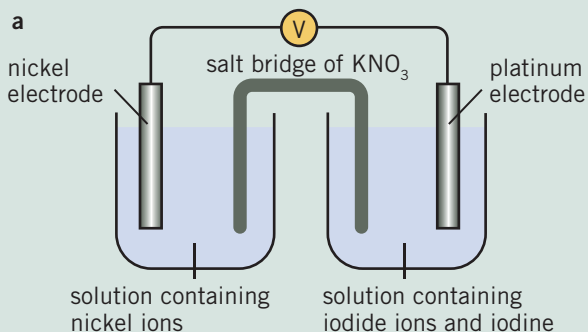


Figure 9.15 The test tubes from left to right contain solutions of  $VO_2Cl$ ,  $VOCl_2$ ,  $VCl_3$  and  $VSO_4$

- 2 For each of the following reactions, identify which reactant has been oxidised and which has been reduced. If the reaction is not redox, then state that it is 'NR'.
- a  $\text{Zn(s)} + 2\text{H}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$   
 b  $\text{Sn}^{4+}(\text{aq}) + \text{Mg(s)} \rightarrow \text{Sn}^{2+}(\text{aq}) + \text{Mg}^{2+}(\text{aq})$   
 c  $\text{Br}_2(\text{aq}) + \text{Ni(s)} \rightarrow 2\text{Br}^-(\text{aq}) + \text{Ni}^{2+}(\text{aq})$   
 d  $\text{Cu}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{CuCO}_3(\text{s})$   
 e  $\text{Cl}_2(\text{g}) + 2\text{Br}^-(\text{aq}) \rightarrow 2\text{Cl}^-(\text{aq}) + \text{Br}_2(\text{aq})$   
 f  $10\text{Br}^-(\text{aq}) + 2\text{MnO}_4^-(\text{aq}) + 16\text{H}^+(\text{aq}) \rightarrow$   
 $5\text{Br}_2(\text{aq}) + 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O(l)}$   
 g  $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr(s)}$   
 h  $2\text{Na(s)} + 2\text{H}_2\text{O(l)} \rightarrow$   
 $2\text{Na}^+(\text{aq}) + 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$   
 i  $3\text{SO}_2(\text{g}) + \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow$   
 $3\text{SO}_4^{2-}(\text{aq}) + 2\text{Cr}^{3+}(\text{aq}) + \text{H}_2\text{O(l)}$
- 3 Determine the oxidation number of chlorine in each of the following.
- a HCl  
 b KCl  
 c  $\text{AlCl}_3$   
 d HClO  
 e NaClO  
 f  $\text{HClO}_2$   
 g  $\text{Mg}(\text{ClO}_2)_2$   
 h  $\text{HClO}_3$   
 i  $\text{KClO}_3$   
 j  $\text{HClO}_4$   
 k  $\text{NaClO}_4$   
 l  $\text{Cl}_2\text{O}$   
 m  $\text{SnCl}_4$   
 n  $\text{Cl}_2$
- 4 Balance the following equations by first writing the two half-equations.
- a  $\text{Al(s)} + \text{Sn}^{4+}(\text{aq}) \rightarrow \text{Al}^{3+}(\text{aq}) + \text{Sn}^{2+}(\text{aq})$   
 b  $\text{MnO}_4^-(\text{aq}) + \text{H}^+(\text{aq}) + \text{Fe}^{2+}(\text{aq}) \rightarrow$   
 $\text{Mn}^{2+}(\text{aq}) + \text{H}_2\text{O(l)} + \text{Fe}^{3+}(\text{aq})$   
 c  $\text{Cu(s)} + \text{NO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow$   
 $\text{Cu}^{2+}(\text{aq}) + \text{NO}_2(\text{g}) + \text{H}_2\text{O(l)}$   
 d  $\text{MnO}_4^{2-}(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow$   
 $\text{MnO}_4^-(\text{aq}) + \text{MnO}_2(\text{s}) + \text{H}_2\text{O(l)}$   
 e  $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{I}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow$   
 $\text{Cr}^{3+}(\text{aq}) + \text{IO}_3^-(\text{aq}) + \text{H}_2\text{O(l)}$   
 f  $\text{ClO}_3^-(\text{aq}) + \text{MnO}_4^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow$   
 $\text{MnO}_2(\text{s}) + \text{ClO}_4^-(\text{aq}) + \text{H}_2\text{O(l)}$   
 g  $\text{As}_2\text{O}_3(\text{s}) + \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{H}_2\text{O(l)} \rightarrow$   
 $\text{H}_3\text{AsO}_4(\text{aq}) + \text{N}_2\text{O}_3(\text{g})$
- h  $\text{H}_2\text{SO}_3(\text{aq}) + \text{MnO}_4^-(\text{aq}) \rightarrow$   
 $\text{Mn}^{2+}(\text{aq}) + \text{H}_2\text{O(l)} + \text{SO}_4^{2-}(\text{aq}) + \text{H}^+(\text{aq})$   
 i  $\text{CuS(s)} + \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \rightarrow$   
 $\text{Cu}^{2+}(\text{aq}) + \text{S(s)} + \text{NO(g)} + \text{H}_2\text{O(l)}$   
 j  $\text{H}_2\text{C}_2\text{O}_4(\text{aq}) + \text{MnO}_2(\text{s}) + \text{H}^+(\text{aq}) \rightarrow$   
 $\text{CO}_2(\text{g}) + \text{Mn}^{2+}(\text{aq}) + \text{H}_2\text{O(l)}$
- 5 Write balanced ionic equations for the following.
- a When nickel is added to a dilute solution of nitric acid, gaseous NO is evolved and the solution becomes pale green.  
 b Acidified potassium permanganate solution is de-colourised by oxalic acid.  
 c When  $\text{SO}_2$  gas is bubbled through an acidified solution of potassium dichromate, the  $\text{SO}_2$  is oxidised to  $\text{SO}_4^{2-}$ .  
 d Oxygen gas is formed when a solution of hydrogen peroxide is added to an acidified solution of potassium permanganate.
- 6 Around 50 years ago the first compounds of the noble gases of group 18 were made. Today there are quite a few examples of these compounds and they have significant redox properties.
- A compound with the formula  $\text{H}_4\text{XeO}_6$  is added to a solution of hydrobromic acid, HBr. The solution turns orange and an unreactive gas (Xe) is produced. Write the half-equations for the oxidation and reduction reactions taking place and also the ionic equation for the overall reaction.
- 7 The active constituents of household bleach are chloride ions ( $\text{Cl}^-$ ) and hypochlorite ions ( $\text{ClO}^-$ ), which react in the presence of acid to form chlorine.
- a Write a half-equation for the reduction of  $\text{ClO}^-$  to  $\text{Cl}_2$ .  
 b Write a half-equation for the oxidation of  $\text{Cl}^-$  to  $\text{Cl}_2$ .  
 c Hence write an overall ionic equation for the reaction between chloride and hypochlorite ions to produce chlorine.
- 8 For each of the cells drawn on the next page determine the:
- i strongest oxidant in the electrochemical cell  
 ii direction of the electron flow through the wire  
 iii half-equations that will occur in the cell  
 iv ionic equation for the overall reaction for the electrochemical cell  
 v anode and the cathode

vi cell potential (assume the solutions are  $1.0 \text{ mol L}^{-1}$ )

vii direction of flow of the positive ions and the negative ions.



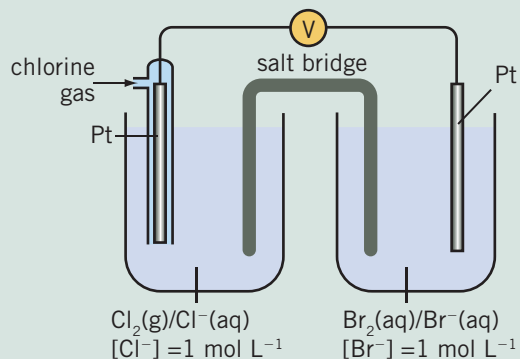
9 An electrochemical cell consisting of  $\text{Cr}^{3+}(\text{aq})/\text{Cr}(\text{s})$  and  $\text{Fe}^{3+}(\text{aq})/\text{Fe}^{2+}(\text{aq})$  half-cells is connected to a voltmeter. For this cell:

a draw a diagram, labelling the anode and cathode and indicating the direction of charge flow through the circuit

b write the separate half-equations, indicating which electrode each occurs at, and the equation for the overall cell reaction

c calculate the standard cell potential.

10 Consider the following electrochemical cell.



a Write the equation for the cathode reaction.

b In which direction do the electrons flow (towards  $\text{Cl}_2/\text{Cl}^-$  or towards  $\text{Br}_2/\text{Br}^-$ )?

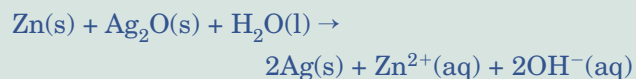
c In which direction do the positive ions flow (towards  $\text{Cl}_2/\text{Cl}^-$  or towards  $\text{Br}_2/\text{Br}^-$ )?

d What is the oxidant in the cell reaction?

e Write the overall cell reaction.

f Calculate the cell potential of the cell under standard conditions.

11 A useful electrochemical cell for small articles such as watches makes use of silver oxide and zinc as described by the equation:



The cell produces  $1.50 \text{ V}$ .

a Write half-equations for the reactions occurring at the anode and the cathode.

b Name the oxidant and the reductant in the cell.

c What is the standard reduction potential for the half-cell containing  $\text{Ag}_2\text{O}(\text{s})$ ? What has been assumed in this calculation and is it a reasonable assumption? Explain your answer.

12 Electrochemical cells can be represented using a 'shorthand' method. For example, the copper/silver ion cell is represented as:



In this representation, the electrode at which oxidation takes place is written on the left and

the electrode at which reduction takes place is written on the right.

This representation of the contents of the cell can be generalised as follows:

anode/anode solution//cathode solution/cathode

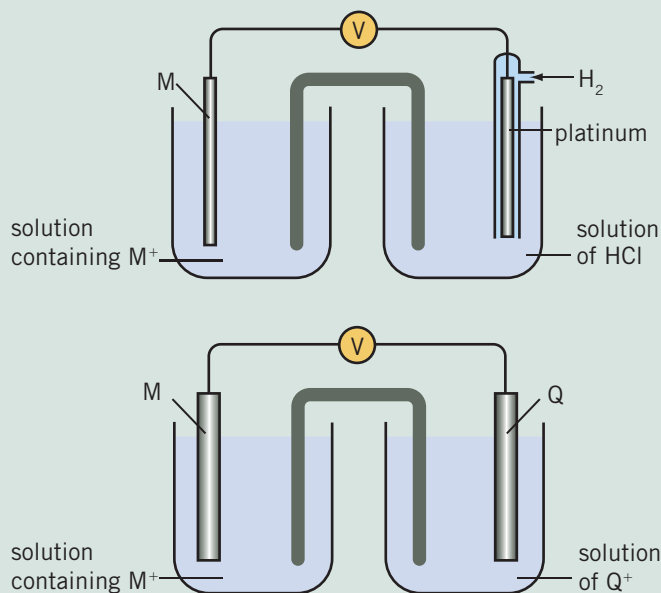
The single slash '/' represents a change in phase, usually between a solid electrode and a solution. The double slash '//' represents a salt bridge or similar porous barrier through which ions can move.

- Sketch the cell represented by  $\text{Zn}/\text{Zn}^{2+}//\text{Co}^{2+}/\text{Co}$ . Identify the anode and cathode, write the half-cell equations and determine the cell potential under standard conditions.
  - Using this way of representing an electrochemical cell, the standard hydrogen half-cell is written as  $\text{Pt}/\text{H}_2/\text{H}^+$ . Draw a diagram of this particular half-cell and use it to explain this representation.
  - A more complex electrochemical cell has the representation  $\text{Cu}/\text{Cu}^{2+}//\text{ClO}_3^-, \text{Cl}^-/\text{Pt}$ . Assuming that the anode and cathode are correctly identified, write the two half-equations that contribute to this cell and the ionic equation for the overall cell reaction.
- 13** A half-cell is made by placing a copper electrode in a solution of copper sulfate. Another half-cell is constructed using a graphite rod in a mixture containing iodine dissolved in a solution of potassium iodide. A salt bridge is used to connect the two solutions and a wire to connect the electrodes. All solution concentrations are  $1 \text{ mol L}^{-1}$ .

- Write the half-equation for each half-cell and the ionic equation for the full cell reaction.
- What is the direction of electron flow (which particular half-cell is the electron source and which half-cell receives the electrons)?
  - In which direction do anions flow in the salt bridge?
  - Which electrode is the cathode?
- What is the overall cell potential (assuming standard conditions)?
- What is the purpose of the graphite electrode?
  - What would happen if the graphite was replaced by iron?
  - What would happen if the graphite was replaced by silver?

- What changes in the electrodes and the solutions would be observed over a period of time while the cell is producing an electric current?

- 14** Two electrochemical cells were set up as shown in the following diagram.

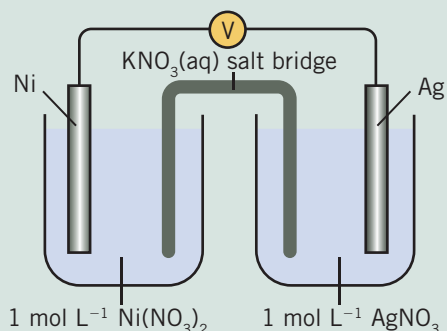


In the first cell the electrons flow from platinum to M and the cell potential is 0.11 V.

In the second cell the electrons flow from M to Q and the cell potential is 1.61 V.

Determine the standard reduction potentials for  $\text{M}^+ + \text{e}^- \rightarrow \text{M}$  and for  $\text{Q}^+ + \text{e}^- \rightarrow \text{Q}$  and explain how you obtained your answer.

- 15** The following problem has been set on an examination paper.



'For the following electrochemical cell determine the standard cell potential and the overall equation for the reaction taking place. Use the table of standard reduction potentials provided.'

In answering this question one student writes the following:

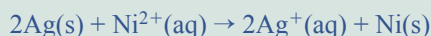
Oxidation takes place at the anode which is the electrode that has the most positive  $E^\circ$  value. In this case this is the silver as it has an  $E^\circ$  of +0.80 V while the nickel has the lower value at -0.26 V. So the oxidation reaction is:



This means that the reduction reaction is at the nickel electrode so:



The overall reaction is:



The cell potential is calculated using the expression:

$$E^\circ = E^\circ_{\text{oxidation}} - E^\circ_{\text{reduction}}$$

Since the half-equation for the oxidation of silver has to be doubled to balance the electrons, the  $E^\circ$  for the half-cell has to be doubled as well.

$$\text{So } E^\circ = +1.60 - (-0.26) = 1.86 \text{ V}$$

The cell potential is 1.86 V.

What (if anything) is wrong with the answer given by the student?

- 16** The University of New South Wales has developed an electrochemical cell, based on the redox chemistry of vanadium, that has been used as a small-scale energy source (battery). One half-cell contains two vanadium-containing ions,  $\text{VO}_2^+(\text{aq})$  and  $\text{VO}^{2+}(\text{aq})$ , while the other half-cell is a mixture of solutions of vanadium(II) and vanadium(III) sulfate.

- What are the oxidation numbers of vanadium in the two ions in each half-cell?
- Write the half-equation for the possible reduction reaction in each half-cell.

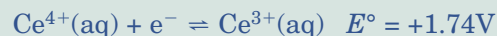
When this cell is delivering an electric current it is observed that the concentration of  $\text{V}^{3+}(\text{aq})$  increases.

- What is the ionic equation for the overall cell reaction?

The cell produces a voltage of 1.26 V when operating under standard conditions. When the half-cell comprising vanadium(II) and vanadium(III) is connected to a standard hydrogen half-cell it generates a cell potential of 0.26V, and in this cell the hydrogen ions are reduced.

- What is the standard reduction potential ( $E^\circ$ ) for the  $\text{VO}_2^+(\text{aq})/\text{VO}^{2+}(\text{aq})$  half-cell?

- 17** Consider the following standard reduction potentials:



Using just these half-cells, draw a diagram of an electrochemical cell that would generate a voltage closest to 1.50 V. On your diagram mark the anode, cathode, direction of electron flow and the direction in which the cations will migrate in the cell.

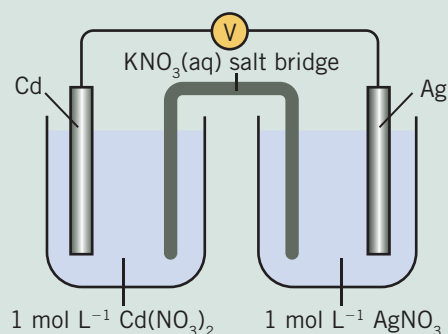
- 18** A standard hydrogen half-cell is connected to a half-cell in which oxygen gas is bubbled over platinum immersed in a solution of  $1 \text{ mol L}^{-1} \text{ HCl}$ .
- Draw a diagram of the cell labelling the anode, cathode, direction of electron flow and direction in which anions migrate.
  - What is the cell potential of this cell under standard conditions?
  - What happens to the pH in each half-cell?
- 19** Two hypothetical metals, A and D, have the following standard reduction potentials:



An electrochemical cell is constructed from these two metals, immersed in a  $1 \text{ mol L}^{-1}$  solution of the sulfate of each metal.

- What would be the reading on a voltmeter placed in the external circuit?
- In which direction would electrons flow in this cell?

- 20** An electrochemical cell is set up as shown in the diagram below.



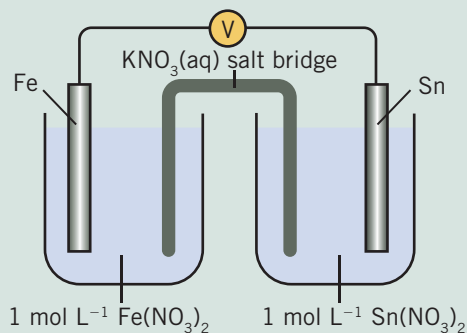
- What is the cell potential produced by this cell if standard conditions are used?

**b** Write the half-reactions for each half-cell.

Some of the chemicals in the two half-cells can be removed and the cell will still produce approximately the same voltage.

**c** What can be replaced in each half-cell and still allow it to operate as the same cell in the diagram above, and what could you use to replace each substance?

**21** An electrochemical cell is set up as shown using tin and iron electrodes.



**a** What is the cell potential for the cell under standard conditions?

A piece of magnesium is placed in the solution containing the tin electrode, but not touching the tin.

**b** What would be observed in the tin half-cell?

**c** What would be observed on the voltmeter as the magnesium was placed in the tin(II) solution?

**22** The first electrochemical cell was constructed by Count Alessandro Volta in 1880. In this cell Volta placed cardboard or porous paper soaked in a solution of sulfuric acid between a sheet of zinc and copper.

**a** What is the likely anode reaction?

**b** What observation, made over a long period of time, would confirm this prediction?

**c** The other electrode did not change during the operation of the cell, even for very long periods of time. Explain this observation.

**d** When Volta replaced the zinc by tin the power of the cell decreased, but when he used silver to replace the copper there was no change in the power of the cell. Explain this observation.

**e** If the porous paper was soaked in water rather than sulfuric acid, the cell did not produce any electricity. Explain.

**f** After some period of time the cell ceased to operate as effectively as it did at the beginning.

However, if the plates were removed from the porous paper and then returned a short time later, the cell operated as it did at the beginning. How can this observation be explained?

**23** Write the ionic equations for any reaction that occurs in the following procedures.

In each case describe in full what you would observe, including any colours, odours, precipitates and gases evolved.

**a** Chlorine gas is bubbled into a solution of potassium bromide.

**b** Hydrogen sulfide is bubbled into an aqueous solution of bromine.

**c** Concentrated nitric acid is added to zinc metal.

**d** Potassium metal is placed in water.

**e** Very dilute nitric acid is added to zinc solid.

**f** Potassium permanganate solution is added to acidified hydrogen peroxide solution.

**g** Aluminium metal is rubbed with abrasive and then placed in a solution of copper(II) sulfate.

**h** Silver metal is warmed with concentrated nitric acid.

**i** Acidified potassium dichromate solution is added to a solution of sodium oxalate.

**j** Bromine is added to a 1 mol L<sup>-1</sup> solution of potassium chloride.

**k** Copper is added to a solution containing silver nitrate.

**l** Zinc is added to a solution of iron(III) nitrate.

**m** A solution of zinc nitrate and sodium chloride are mixed.

**24** Briefly explain the following situations. Support your answers with the appropriate equations.

**a** A solution of nickel nitrate can be satisfactorily stored in a copper pot, but a solution of silver nitrate can not.

**b** If left in an open container, a solution of hydrogen peroxide will slowly decompose.

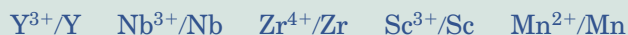
**c** Copper metal will not react with hydrochloric acid, but it will react with nitric acid.

**d** An acidified solution of potassium permanganate is a strong oxidising agent. However, hydrochloric acid cannot be used to acidify the solution of potassium permanganate.

**e** Sodium metal cannot be prepared by adding a reductant to an aqueous solution of sodium chloride.



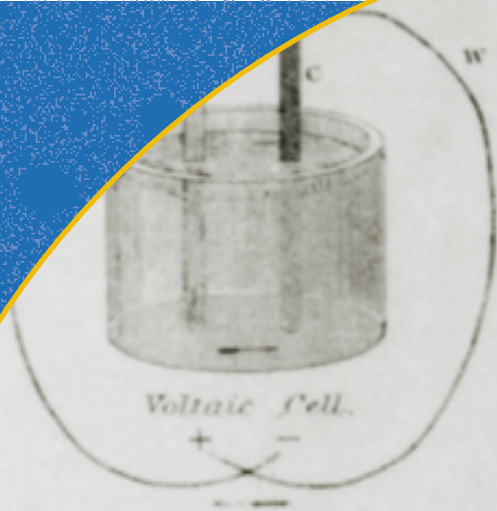
**25** A chemist investigating the redox reactions of transition metals sets up the following half-cells:



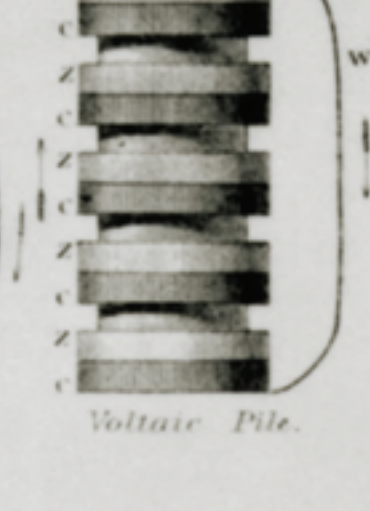
She then tested some combinations of two half-cells and tabulated her results. The values in the boxes indicate the cell potentials, in volts, obtained from the combinations, and the metal that acts as the anode is in brackets.

	$\text{Y}^{3+}/\text{Y}$	$\text{Nb}^{3+}/\text{Nb}$	$\text{Zr}^{4+}/\text{Zr}$	$\text{Sc}^{3+}/\text{Sc}$	$\text{Mn}^{2+}/\text{Mn}$
$\text{Y}^{3+}/\text{Y}$		1.27 (Y)	0.82 (Y)	<b>i</b>	1.19 (Y)
$\text{Nb}^{3+}/\text{Nb}$			0.45 (Zr)	0.93 (Sc)	0.08 (Mn)
$\text{Zr}^{4+}/\text{Zr}$				<b>ii</b>	<b>iii</b>
$\text{Sc}^{3+}/\text{Sc}$					<b>iv</b>
$\text{Mn}^{2+}/\text{Mn}$					

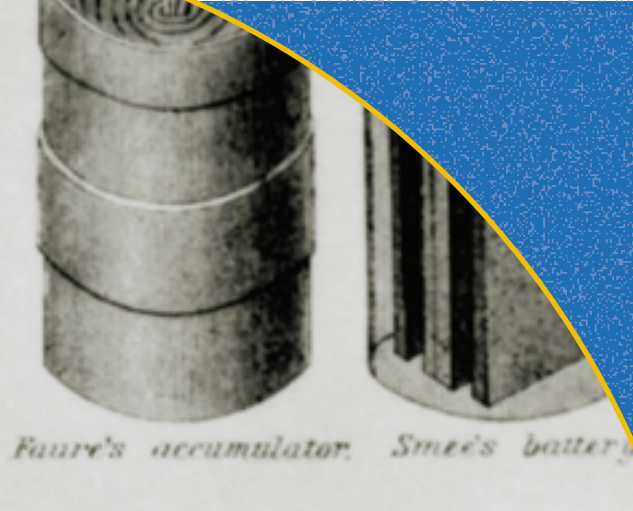
- a** What are the missing values **i**, **ii**, **iii** and **iv**? Which metal would act as the anode in each case?
- b** If the standard reduction potential ( $E^\circ$ ) for the  $\text{Sc}^{3+}/\text{Sc}$  standard half-cell is  $-2.03 \text{ V}$ , list the standard reduction potential ( $E^\circ$ ) for the other four half-cells.



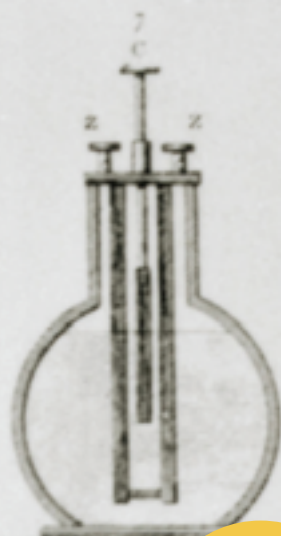
*Voltaic Cell.*



*Voltaic Pile.*



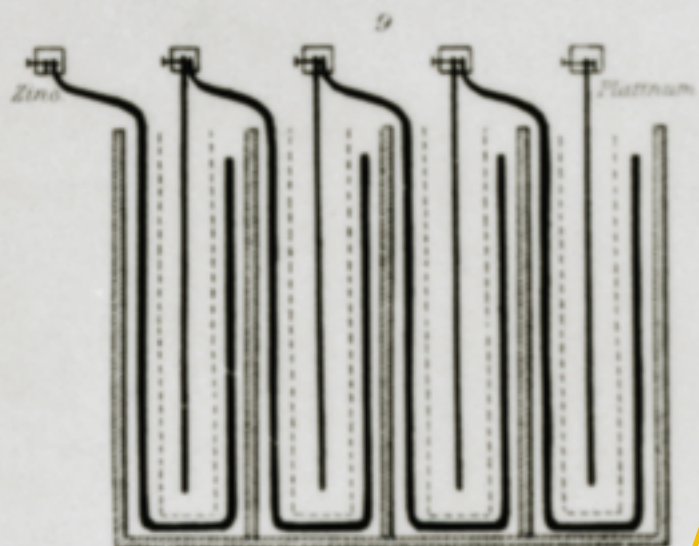
*Faure's accumulator. Smeed's battery.*



*Bichromate*



*Daniell's battery.*



*Grove's battery.*

10

## Application of redox chemistry to modern lifestyles

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

- apply your understanding of oxidation and reduction in investigations concerning commercial electrochemical cells and corrosion of metals.

## 10.1 Commercial electrochemical cells

Much of our modern lifestyle is structured around mobility. As we have become more mobile, we have also found new ways to take the 'comforts of home' with us. When away from home, we can communicate via mobile phones, we can watch video clips or live sporting telecasts, we can check our emails or update a Facebook page. These and many other activities that we undertake daily are made possible because of batteries. The word 'battery' has become widely accepted in our society to mean a portable source of electrical energy. Technically, a battery is defined as a combination of 'electrochemical cells'.



Figure 10.1 An assortment of cells

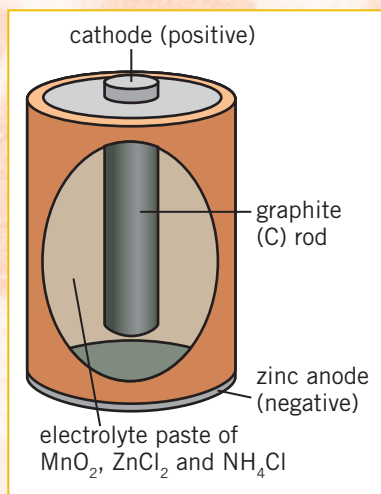


Figure 10.2 Cut away-section of a dry cell showing the anode and cathode

### The dry cell

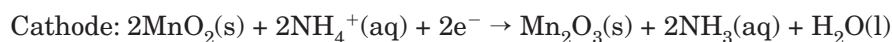
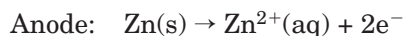
A cell or a battery is an electrochemical cell that stores useful energy in the form of an oxidant and a reductant that are capable of releasing energy when required. While any redox reaction could be harnessed as an energy source for a cell, in practice there are certain limitations, such as cost, portability and lifetime, that restrict the choice of materials.

The two major types of cells are primary cells (in which the spontaneous redox reaction only occurs once and cannot be reversed) and secondary cells (that can be recharged by passing a current through them to convert products back to reactants).

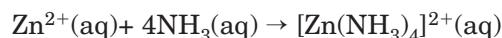
The most familiar primary cell is the dry cell (or Leclanché cell, after its inventor, Georges Leclanché). The anode consists of a zinc container while the cathode is

a graphite rod surrounded by powdered manganese dioxide,  $\text{MnO}_2$ . The space between the electrodes is filled with the electrolyte, which is commonly a moist paste of  $\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2$  (Figure 10.2).

The electrode reactions are complex but may be simply represented as:



The ammonia that is produced forms a complex ammine ion with the zinc ions:



This dry cell has a limited shelf life since the ammonium chloride provides an acidic environment that eventually corrodes the zinc can.

The dry cell produces a cell potential (voltage) of around 1.5 V. It cannot be recharged (because the zinc ions are removed from the vicinity of the anode).

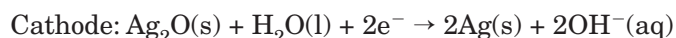
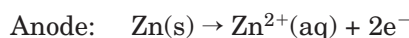


Figure 10.3 A silver oxide button cell

### Silver oxide cell

The silver oxide cell is a primary cell that has long life and can be used as a small, portable energy supply. Its major disadvantages are the cost to produce it and the environmental hazards associated with leakage.

The electrode reactions involved in this cell are:



The 'button' cells are commonly used in cameras, calculators, watches and other appliances that require a steady current and a long service life. Recent research has developed rechargeable versions of these cells with characteristics that are claimed to rival those of lithium cells.



### The lead–acid accumulator

The cells considered above were designed to deliver relatively small currents of electricity. However, to start a car engine requires a very large current to be delivered in a relatively short period of time. To produce the current necessary, a large amount of the oxidant and reductant needs to be available for reaction.

The lead–acid accumulator, the most commonly used battery to start cars, is made up of cells each consisting of an anode that is a grid of lead alloy packed with finely divided spongy lead and a cathode that is a similar lead alloy grid but packed with lead(IV) oxide powder,  $\text{PbO}_2$ . The finely divided materials provide the large surface area necessary to deliver the electric current required. The electrolyte is a solution that is about 35% sulfuric acid by volume. The cells are connected in series.

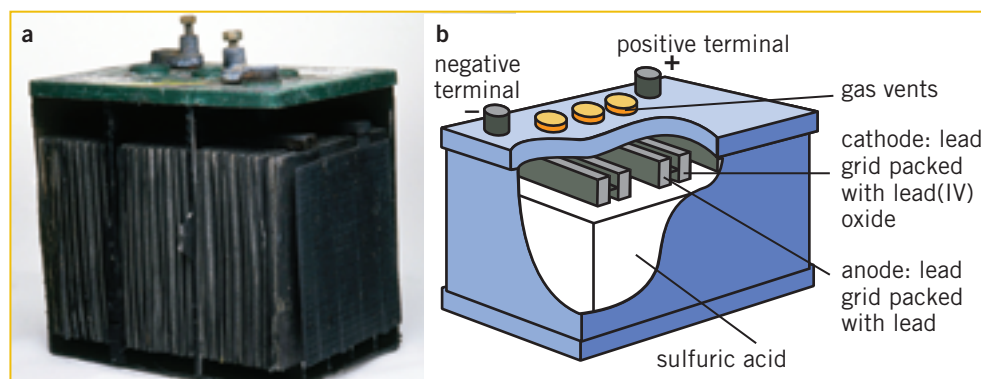
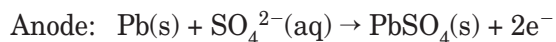


Figure 10.4 (a) Car battery cut open to reveal lead plates. (b) Cut-away view of a lead–acid cell

During the discharging process, chemical energy is changed to electrical energy by the battery. At the anode (the negative electrode), lead is oxidised to form  $\text{Pb}^{2+}$  ions. These ions combine with the sulfate ions in solution to form insoluble  $\text{PbSO}_4$  that sticks to the anode surface:



At the cathode (the positive electrode),  $\text{PbO}_2$  is reduced to  $\text{Pb}^{2+}$  ions and again  $\text{PbSO}_4$  is produced:



The overall discharging reaction is:



Lead sulfate is formed at each electrode, and this forms a coating on the electrodes.

Sulfuric acid is consumed in the cathode reaction and, as a result, the acid becomes less concentrated (and less dense since a solution of sulfuric acid has a higher density than that of water). The cell potential falls during the operation of the battery. Since sulfuric acid is denser than water, measuring the density of the electrolyte can be used to check the extent to which the battery has been discharged.

Most lead–acid accumulators are composed of six cells, each giving a cell potential of 2 V. Therefore, a fully charged car battery has a total cell potential of about 12 V.

Unlike the dry cell, the lead–acid battery can be recharged since the products of the cell reaction ( $\text{PbSO}_4$ ) adhere to the electrodes. Consequently, the lead–acid accumulator is regarded as a secondary cell. In the recharging process, electrical energy is converted into chemical energy. If an external voltage that is larger than the cell potential is applied to the cell, the electrode reactions can be reversed with  $\text{PbSO}_4$  being reduced to Pb at one electrode and oxidised to  $\text{PbO}_2$  at the other.

The lead electrode (the negative electrode in the electrochemical cell) is connected to the negative terminal of the charging power source, and the lead/lead(IV) oxide electrode (the positive electrode in the electrochemical cell) is connected to the positive terminal of the charging power source.

The cell reaction that occurs during the recharging or charging process is the reverse to the reaction that occurs spontaneously during discharging:

Recharging reaction:



If a lead–acid battery is recharged too rapidly, it may produce hydrogen and oxygen at the electrodes. Not only is there the danger of an explosion, but also the electrolysis of water causes water to be lost from the battery and so requires that the battery be topped up from time to time with distilled water.

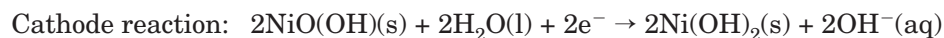
### Nickel–cadmium cell

The nickel–cadmium cell is a lightweight, portable, rechargeable cell. The products of the anode and cathode reactions stick to the electrodes and so the electrode reactions can be reversed.



Figure 10.5 A nickel–cadmium cell and some NiMH cells (see research investigation at end of chapter)

In this cell, the anode is cadmium metal surrounded by a paste containing hydroxide ions (usually potassium hydroxide). The cathode is constructed from nickel oxyhydroxide.



A cell potential of around 1.2–1.3 V is produced by this cell so it is not always a suitable replacement for a 1.5 V dry cell. However, the voltage delivered by the battery does not alter significantly during the discharging process and in electronic devices where multiple cells are used, the lower cell potential of the nickel–cadmium cell may not be a significant problem.

The major disadvantage of the nickel–cadmium cell is the toxicity of cadmium and the resulting environmental issues associated with disposal of these cells.

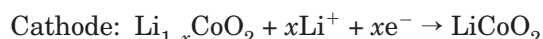
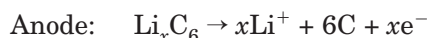
## Lithium ion cell

This is the cell now most common in mobile phones and laptop computers. Lithium is a very reactive metal with the standard reduction potential ( $E^\circ$ ) for the reaction  $\text{Li}^+ + \text{e}^- \rightarrow \text{Li(s)}$  being around  $-3$  V. Lithium is also a very light element so the amount of energy from a given mass of metal is considerably higher than for the same mass of other metals that might be used in cells. The amount of energy that can be provided per gram is known as the energy density and for lithium this is around 40 kJ per gram. For zinc, the value is around 2 kJ per gram.

The lithium ion cell is different from the earlier described lithium cell that used an anode of lithium metal. The more recently developed lithium ion cell uses an anode of carbon (graphite) into which the lithium ions can be inserted and converted into a reductant equivalent to lithium. In the presence of the delocalised electrons in the graphite, the lithium ion can be made to behave like a lithium atom, a strong reductant. The reductant is assigned the formula  $\text{Li}_x\text{C}_6$ , or more simply  $\text{Li(C)}$ . The value of  $x$  ranges from 0 to 0.9.

Research has revealed that lithium ions can also be incorporated into the layers of cobalt oxides and can produce a reversible electrochemical process in which the cobalt ion in the complex oxide changes back and forth between  $\text{Co}^{4+}$  and  $\text{Co}^{3+}$ . This material forms the cathode of the lithium ion cell.

In simple terms, the electrode processes are (in an ideal cell the value of  $x$  is 1):



A pictorial representation of this cell is given in Figure 10.7.



Figure 10.6 Lithium ion cell from a laptop computer

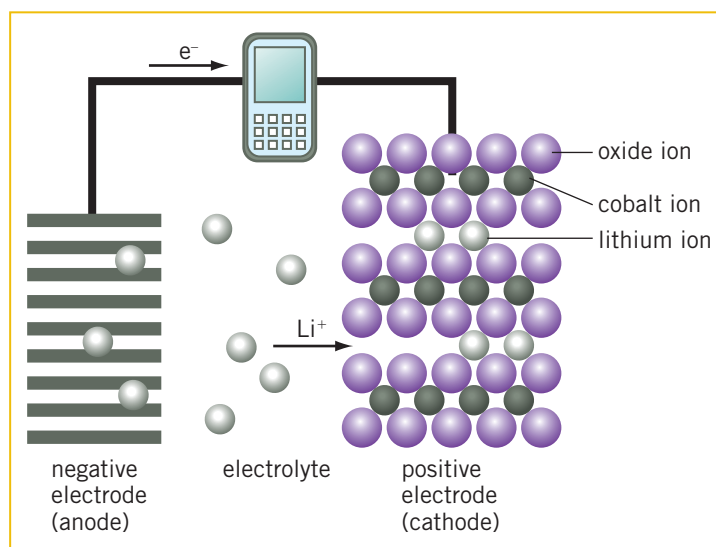


Figure 10.7 Representation of the discharging process in a lithium ion cell. Lithium ions migrate from the anode to the cathode through the electrolyte.

The discharging and charging processes involve lithium ions being transported to and from the cathode. Because the lithium in the cell behaves like the reactive element, the electrolyte solution through which the ions move cannot contain water. This can be achieved by dissolving lithium salts in polar solvents that do not have hydrogen attached to oxygen or nitrogen (these solvents are called aprotic solvents). Flammability concerns with some of these solvents have led to the use of solid polymer electrolytes along which the lithium ions can be transported.

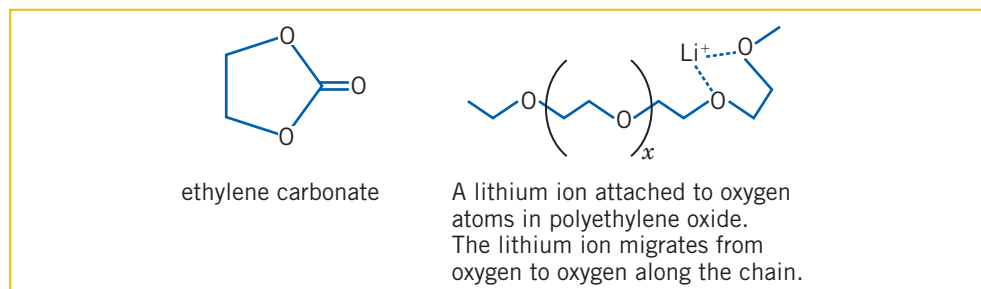


Figure 10.8 An aprotic solvent and an example of a solid polymer electrolyte

## Fuel cells

While recharging can regenerate the oxidants and reductants in secondary cells, it is possible to produce a cell in which the reactants are supplied continuously to (and the products removed continuously from) the electrodes. Such a cell is called a fuel cell. The most common fuel cell is based on the reaction between hydrogen and oxygen to form water.

The electrodes are porous, compressed carbon containing a suitable catalyst. The electrolyte may be either hydrochloric acid or potassium hydroxide solution.

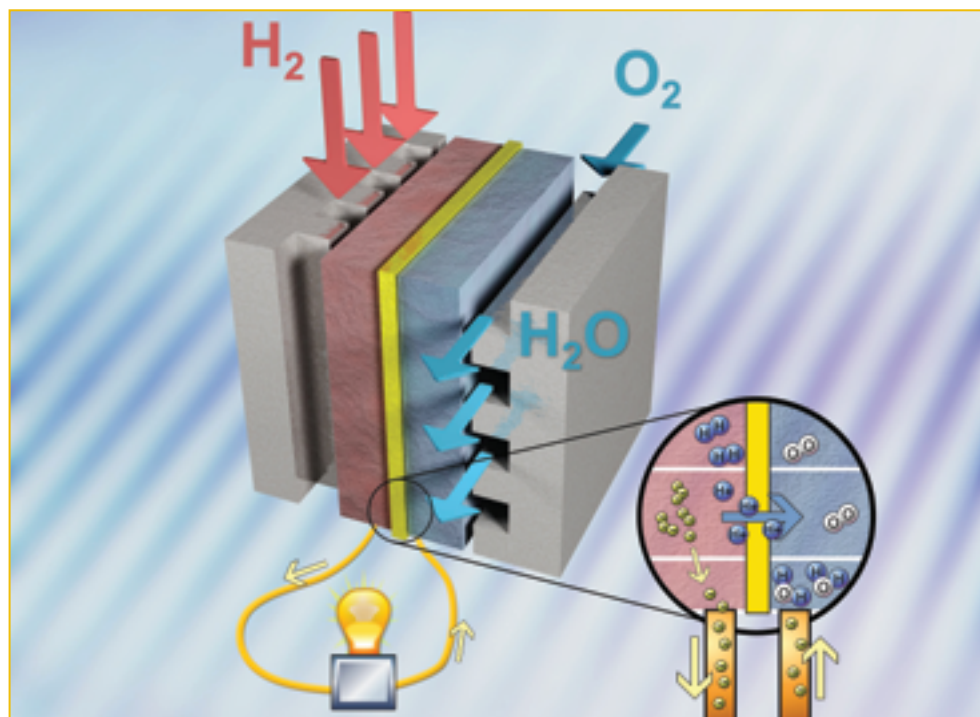
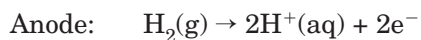


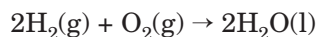
Figure 10.9 Schematic of the electrode reactions taking place in a fuel cell. Hydrogen at the anode (red) is oxidised to hydrogen ions (see insert). The hydrogen ions migrate through the porous anode material into the electrolyte region (yellow). Oxygen diffuses through the cathode (blue) and is reduced to water in the presence of the hydrogen ions (see insert).

At the anode, hydrogen is oxidised to hydrogen ions (in acid electrolyte) or water (in alkaline electrolyte). At the cathode, oxygen is reduced to water (in acid electrolyte) or hydroxide ions (in alkaline media).

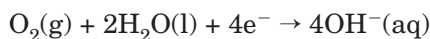
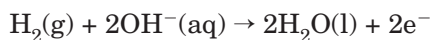
With an acid electrolyte



The overall reaction, for both electrolytes, is:



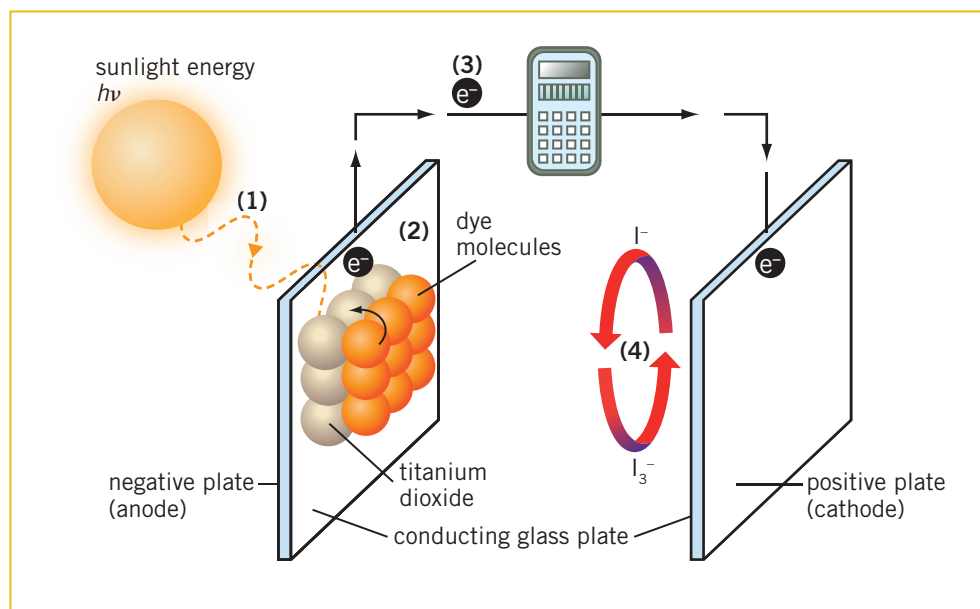
With an alkaline electrolyte



Such cells operate continuously as long as the reactants are provided. Because it converts the energy of the redox reaction directly to electricity, the fuel cell is much more energy efficient than conventional large-scale methods of producing electricity, such as a coal- or gas-fired power station. However, the major disadvantage of such cells is their expense, and while they have been successfully incorporated into some special applications such as spacecraft, they are presently not used in large-scale electricity generation.

### Dye-sensitised solar cells

These cells rely on the energy from sunlight to excite the electrons in a dye (in a process similar to the action of sunlight on chlorophyll in plants) into a higher energy state where they become free to move into the external circuit of the cell. The circuit is completed at the cathode where triiodide ions ( $\text{I}_3^-$ ) are reduced to iodide ions ( $\text{I}^-$ ). The iodide ions migrate to the anode where they regenerate the dye. The two electrodes are made from glass that has had a thin film of platinum deposited on the surface so that it is transparent to light, but is also a conductor.



**Figure 10.10** The operation of a dye-sensitised solar cell. Sunlight (1) is absorbed by the dye and an electron is released to the titanium dioxide. This electron then moves onto the conducting glass plate (2) and through the external circuit (3). At the cathode the added electrons reduce  $\text{I}_3^-$  to  $\text{I}^-$  (4). Iodide ions migrate to the anode where they regenerate the dye and are oxidised back to  $\text{I}_3^-$ .

Research is ongoing to uncover the role of titanium dioxide in the process, and whether there are better electrolytes. Researchers also wish to establish whether there are better dyestuffs with greater solar efficiency—that is, dyes that are capable of converting more of the solar spectrum into electricity. At present only the visible and part of the ultraviolet region of the spectrum are used. The infrared region remains an untapped source of energy in this process. A watch manufacturer has produced a prototype of a watch with a face made from such a solar cell. The cell is so thin and transparent that the face of the watch can be seen through the cell. The cell generates the electricity to run the watch during the day and presumably has a secondary cell to allow the watch to operate at night.



## \* Review exercise 10.1

- 1 Give the equations for the anode and cathode half-cell reactions in the following cells for which the cell reactions are given.
  - a Dry cell:  $\text{Zn(s)} + 2\text{MnO}_2\text{(s)} + 2\text{H}^+\text{(aq)} \rightarrow \text{Zn}^{2+}\text{(aq)} + \text{Mn}_2\text{O}_3\text{(s)} + \text{H}_2\text{O(l)}$
  - b Lead–acid accumulator:  $\text{Pb(s)} + \text{PbO}_2\text{(s)} + 4\text{H}^+\text{(aq)} + 2\text{SO}_4^{2-}\text{(aq)} \rightarrow 2\text{PbSO}_4\text{(s)} + 2\text{H}_2\text{O(l)}$
  - c Hydrogen/oxygen fuel cell:  $2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(l)}$  (acidic conditions)
- 2 Electron transfer reactions produce a cell potential of about 1.48 V in the commercially available Eveready dry cell.

The equation for the reduction half-cell reaction occurring in the dry cell is:



- a What is the equation for the oxidation half-cell reaction in the dry cell? What is the standard reduction potential for this half-cell?
  - b Assuming standard conditions, calculate the reduction potential for the reduction reaction of  $\text{MnO}_2$ .
  - c State one advantage and one disadvantage of using a dry cell in electrical appliances.
  - d It is observed that the paste in the dry cell becomes less acidic as the cell operates. Suggest a reason for this.
  - e Why is the dry cell described above called a primary cell?
- 3 The lead–acid accumulator, or car battery, uses a redox reaction to produce a steady voltage of about 12 V. The lead–acid accumulator is composed of six cells that are each made up of a lead electrode and a lead(IV) oxide electrode,  $\text{PbO}_2$ , in a sulfuric acid solution. Assume standard conditions are present.
    - a The following reaction occurs at the lead(IV) oxide electrode:
$$\text{PbO}_2\text{(s)} + 4\text{H}^+\text{(aq)} + \text{SO}_4^{2-}\text{(aq)} + 2\text{e}^- \rightarrow \text{PbSO}_4\text{(s)} + 2\text{H}_2\text{O(l)} \quad E^\circ = +1.69 \text{ V}$$
Write the half-equation for the reaction occurring at the other lead electrode, and quote its standard reduction potential, which is  $-0.36 \text{ V}$ .
    - b Which electrode is the anode and which is the cathode?
    - c Calculate the theoretical voltage for a car battery cell.
    - d The actual voltage produced by each of the six cells in the car battery is about 2.2 V. Suggest a reason for the difference between this value and the voltage calculated in part c.
    - e Write the equation for the reaction that occurs during the charging of a discharged battery.
    - f Explain why measuring the density of the sulfuric acid in the battery can indicate how ‘charged’ the battery is. (Liquid sulfuric acid is more dense than water.)
  - 4 Some time ago button cells were based on a mercury/mercury(II) oxide reaction rather than the silver/silver(I) oxide reaction.
    - a Write the equations for the anode and cathode reactions for a mercury button cell, assuming the only difference between this cell and the silver oxide cell is the presence of mercury in place of silver.
    - b Why do you think this type of cell been replaced by silver oxide button cells?
  - 5 It is possible to construct a fuel cell based on the oxidation, by oxygen, of methanol,  $\text{CH}_3\text{OH}$ .
    - a Assuming the cell operates using an acid electrolyte, write the equations for the anode and cathode reactions for this fuel cell. (Carbon dioxide and water are formed during the oxidation of methanol.)

- b How does this cell differ from a dry cell or nickel–cadmium cell?
  - c In what ways are fuel cells similar to other types of electrochemical cells?
  - d What advantage does a methanol/oxygen fuel cell have over a hydrogen/oxygen fuel cell?
  - e Compare the environmental impact of the products of the methanol/oxygen fuel cell with those from a hydrogen/oxygen fuel cell.
- 6 Calculate and compare the mass of each element that needs to be oxidised at the anode in a dry cell, a lead–acid accumulator and a lithium cell in order to produce 1 mole of electrons. Why does this information make the lithium cell such a popular choice as a cell?

## 10.2 Corrosion of metals



All metals (except perhaps gold and platinum) react with oxygen. Some, like sodium, react vigorously while others, such as copper, need to be strongly heated to react.

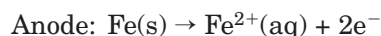
While aluminium is quite a reactive metal, its reaction with oxygen produces a continuous and impervious coating of aluminium oxide that prevents further reaction, even at the high temperatures used in cooking. Stainless steel also forms a similar protective oxide coating (chromium oxide dominates, but other metals in the steel alloy such as nickel also play a part).

Iron and copper are somewhat less reactive than aluminium, but they will oxidise, particularly on heating. Unlike aluminium, however, the oxide coating of these two metals allows further reaction of the metal. The oxide coating is ‘flaky’ and exposes fresh metal to the air and water, and so allows further oxidation.

### Rusting of iron

The most common example of corrosion, rusting of iron, differs from dry corrosion (reaction of iron with air, in the absence of water) in a number of respects. The major requirement for ‘wet’ corrosion or rusting is the presence of oxygen and water, although other factors, such as impurities in the iron and the presence of electrolytes dissolved in the water, enhance the rate of the rusting process. ‘Wet’ corrosion also has an electrochemical nature because the oxidation and reduction processes can take place at different points on the metal. In addition, because the metal is an electrical conductor, it promotes the flow of electrons from the anode to the cathode.

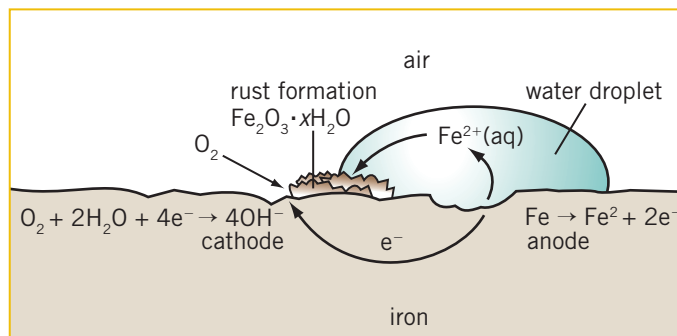
In the rusting process, the iron acts as the anode where oxidation of Fe takes place, initially to form  $\text{Fe}^{2+}$ .



The cathode may be an impurity, such as carbon, in the iron, or a region of high oxygen concentration.

The reduction reaction may be represented as:



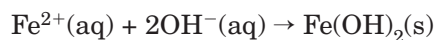


**Figure 10.11 Corrosion of iron in the presence of water and air**

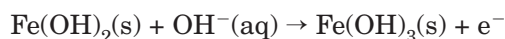
The rusting process occurs most rapidly when iron or steel is exposed to the atmosphere and is covered with a film of water for a considerable period. The solid rust (see Figure 10.11) usually forms near the cathode where the hydroxide ions are produced. Since this reduction reaction takes place where there is an abundance of air (oxygen), the actual pitting or loss of iron (the anode reaction) is more likely to occur where there is a deficiency of air. This differential aeration effect can lead to the iron corroding below paintwork or where two metal surfaces are in contact.

In the presence of other electrolytes, for example salts near the ocean, or pollutants such as  $\text{SO}_2$  and  $\text{NO}_2$ , solutions of greater conductivity are produced and so the rate of rusting will increase.

The iron(II) ions and the hydroxide ions produced diffuse towards each other and precipitate as iron(II) hydroxide, according to the following equation:



The iron(II) hydroxide is very easily oxidised by air (more readily than the original iron) to form iron(III) hydroxide:



The iron(III) hydroxide is then partially dehydrated to give rust,  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ .

The  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$  are only sparingly soluble (the latter being the least soluble) and their formation removes  $\text{Fe}^{2+}$  from solution. This in turn shifts the position of equilibrium in favour of the rusting process.

The overall equation for the rusting of iron is:



### Prevention of corrosion

The formation of rust on iron and steel can be slowed down or stopped by a number of methods.

- i Application of a surface coating, either metal or non-metal, which prevents oxygen and water from coming in contact with the iron. Examples include painting and plating with tin, chromium or silver.

If a less reactive metal is used as the coating, then any scratch on the surface will lead to an increase in corrosion of the more reactive metal, namely the iron. For example, for an iron can coated on the inside with tin, if the tin coating is scratched, the iron will become the anode and will oxidise quicker than a piece of uncoated iron. Most cans today are coated on the inside with a plastic material. This increase in corrosion rate of iron also occurs in any situation where the piece of iron is in contact with any other metal less active than itself, for example, copper.

- ii Galvanising the surface of the metal with a coating of a more reactive metal. For example, if a layer of zinc is coated onto an iron surface, the more reactive zinc will give up its electrons, i.e. it will oxidise more readily than the iron, even if the surface coating is scratched.
- iii Connecting the iron or steel, by a conducting wire, to a piece of more reactive metal such as zinc, magnesium or aluminium. The more reactive metal is sacrificially oxidised instead of the iron being oxidised, i.e. the more reactive metal acts as the anode. The method is very similar to that in point ii, except that the reactive metal can be replaced easily after it has been consumed. The more reactive metal in this process is often called the sacrificial anode.
- iv Making the iron or steel the cathode of an electrolytic cell. The cell consists of a DC (direct current) power source, an anode of scrap metal and the iron or steel cathode. The applied voltage makes the iron (steel) object negatively charged and so prevents its oxidation. The scrap metal anode must be replaced from time to time (or it can be made of an inert material if scrap metal is not available). This process is called cathodic protection.

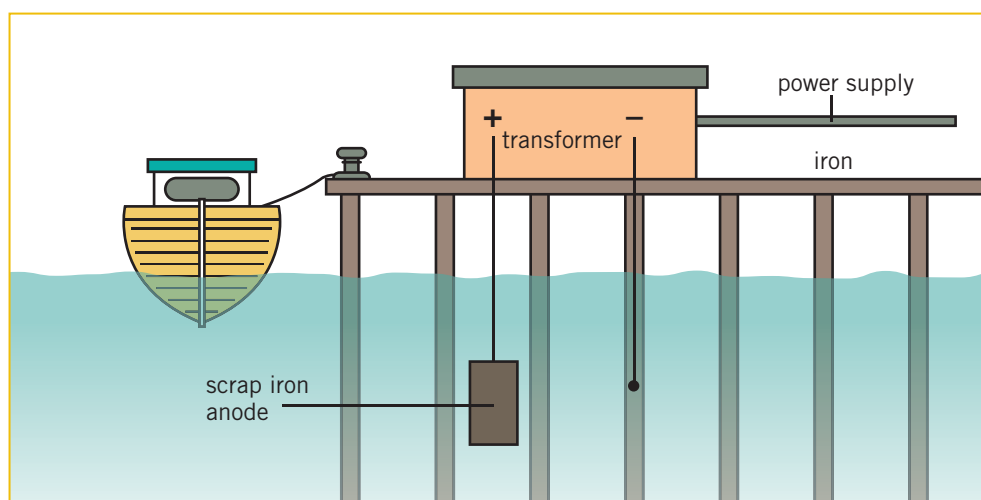
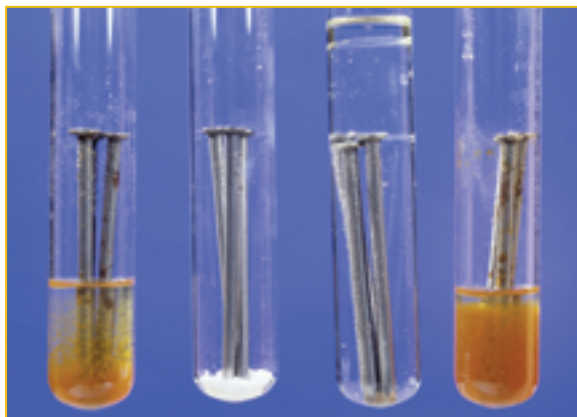


Figure 10.12 Cathodic protection of an iron wharf



## \* Review exercise 10.2

- 1 Iron is corroded by the action of certain substances in the atmosphere.



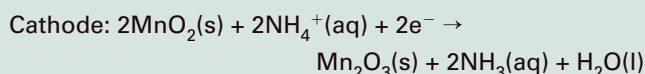
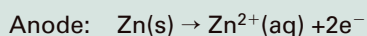
**Figure 10.13** Rust experiment: The four test tubes originally contained, from left to right: nails, water and air; nails with calcium oxide (absorbs water); nails under water that has had the dissolved air removed; and nails in salt water.

- a** Four test tubes were set up to demonstrate the conditions necessary for rusting. The results of this experiment are shown in Figure 10.13. From these results, decide which two substances cause the corrosion of iron. Explain how you decided on your answer.
- b** Write equations to show that the oxidation of iron metal by these substances causes a precipitate of iron(II) hydroxide to form.
- c** Use the equations you wrote in part b to explain why the corrosion process is slowed under conditions of high pH.
- d** If a copper pipe is used to replace a section of iron pipe, a plastic washer (a ‘separator’) must be used to separate the iron and copper. Explain why.
- 2 The supporting posts of some jetties are made of iron and are connected to zinc bars below the waterline to protect the iron from corrosion by seawater. Use standard reduction potentials to explain:
- a** how zinc protects the iron against corrosion
- b** whether a lead bar would be effective in protecting the iron from corrosion
- c** whether sodium metal would be a suitable alternative for protecting iron.
- 3 Chemical engineers are developing alloys that can be used in combination with iron. One of the issues faced is the possibility of increased corrosion rate when two different metals are combined. Alloy X is found to have a standard reduction potential ( $E^\circ$ ) of around +0.27 V. Alloy Y has a standard reduction potential of -0.59 V. From this information, predict the issues with corrosion facing the engineers if they place these two alloys in contact with an iron structure in a moist environment.
- 4 In a car, the negative terminal of the battery is usually connected to the body of the car. It is claimed that this protects the body of the car from rusting.
- a** Discuss whether this claim is reasonable.
- b** What would be the consequences of attaching the positive terminal of the battery to the body of the car, instead of attaching the negative terminal?
- 5 A block of cadmium and a block of copper are joined together and the combined block is placed in a solution of dilute hydrochloric acid. It is observed that bubbles of gas are only evolved from the surface of the copper. However, if the two blocks are separated and placed in the same acid, the bubbles only appear on the cadmium surface. Explain this observation.

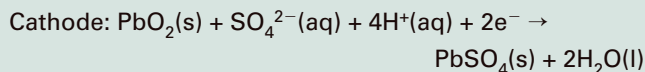
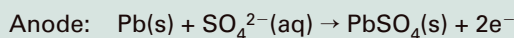
## MAJOR IDEAS

- A cell or a battery is an electrochemical cell that stores useful energy in the form of an oxidant and a reductant that are capable of releasing electrical energy when required.
- Primary cells are cells in which the spontaneous redox reaction cannot be reversed.
- Secondary cells can be recharged by passing a current through them to convert products back to reactants.
- In the dry cell (or Leclanché cell), the anode consists of a zinc container while the cathode is a graphite rod surrounded by powdered manganese dioxide,  $\text{MnO}_2$ . The electrolyte is a moist paste of  $\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2$ .

The electrode reactions are:



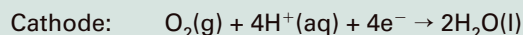
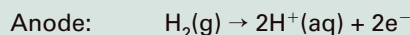
- The dry cell has a limited shelf life, produces a voltage of around 1.5 V and cannot be recharged.
- The lead–acid accumulator, used in vehicles, is an example of a secondary battery.
- The lead–acid accumulator is made up of cells consisting of an anode of lead and a cathode of a lead grid packed with lead(IV) oxide,  $\text{PbO}_2$ . The electrolyte is sulfuric acid.
- During the discharging process, chemical energy is changed to electrical energy in the battery.



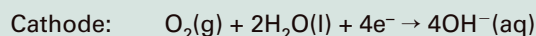
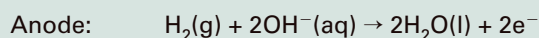
- The overall discharging reaction is:
$$\text{Pb(s)} + \text{PbO}_2(\text{s}) + 4\text{H}^{+}(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$$
- A fully charged car battery has a total cell potential of about 12 V.
- The recharging reaction is:
$$2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)} \rightarrow \text{Pb(s)} + \text{PbO}_2(\text{s}) + 4\text{H}^{+}(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq})$$
- Other commercially available cells include zinc/silver oxide, nickel–cadmium and lithium ion batteries.
- In a fuel cell, the reactants are supplied continuously (and the products removed continuously) to the electrodes.
- The most common fuel cell is based on the reaction between hydrogen and oxygen to form water.
- The electrodes are porous, compressed carbon containing a suitable catalyst. The electrolyte may be either hydrochloric acid or potassium hydroxide solution.

- The electrode reactions in this fuel cell are:

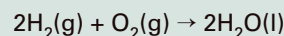
With an acid electrolyte



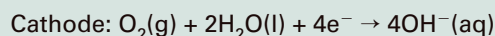
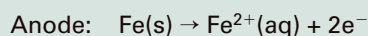
With an alkaline electrolyte



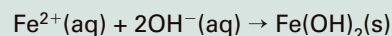
- The overall reaction, for both electrolytes, is:



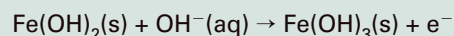
- Some metals such as aluminium are protected from corrosion by impervious oxide layers.
- Rusting of iron occurs in the presence of oxygen and water.
- Factors such as impurities in the iron and the presence of electrolytes dissolved in the water enhance the rate of the rusting process.
- Corrosion in the presence of water has an electrochemical nature because the oxidation and reduction processes can take place at different points on the metal.
- In the corrosion of iron, the half-reactions are:



The iron(II) ions and hydroxide ions diffuse towards each other and precipitate as iron(II) hydroxide:



The iron(II) hydroxide is oxidised by air to form iron(III) hydroxide:

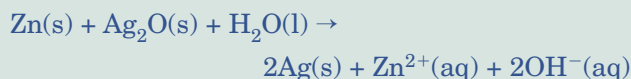


The iron(III) hydroxide is then partially dehydrated to give rust,  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ .

- The overall equation for the rusting of iron is:
$$4\text{Fe(s)} + 3\text{O}_2(\text{g}) + 2x\text{H}_2\text{O(l)} \rightarrow 2\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O(s)}$$
- The following methods can be used to prevent rusting:
  - application of a surface coating that prevents oxygen and water from coming in contact with the iron. If a less reactive metal is used, the rusting process increases if the coating is scratched
  - galvanising the surface of the metal with a coating of a more reactive metal that is oxidised more readily than the iron
  - connecting the iron or steel, by a conducting wire, to a piece of more reactive metal
  - making the iron or steel the cathode of an electrolytic cell—called cathodic protection.

## QUESTIONS

- 1 AAA- and D-type conventional dry cells both produce about 1.5 V.
- Write the anode and cathode reactions for these cells.
  - Given your answer to part a, what difference is there between these two cells and how would this affect the performance?
  - Why are the contents of the cell in the form of a paste?
- 2 During discharge, a 12 V car battery converts 200 g of lead into  $\text{PbSO}_4$ . What mass of lead(IV) oxide is consumed in the process?
- 3 A useful electrochemical cell for small articles such as watches makes use of silver oxide and zinc as described by the equation:

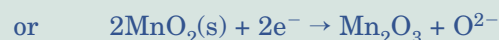
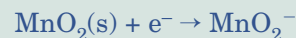


The cell potential of the cell is 1.50 V.

- Write half-equations for the reactions occurring at the anode and the cathode.
  - Name the oxidant and the reductant in the cell.
  - What is the standard reduction potential for the half-cell containing  $\text{Ag}_2\text{O(s)}$ ?
- 4 When a 'flat' lead accumulator (car battery) is being charged, the following overall reaction occurs:
- $$2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)} \rightarrow \text{Pb(s)} + \text{PbO}_2(\text{s}) + 4\text{H}^{+}(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq})$$
- Give the half-equations for the cathode and anode reactions during charging.
  - Does the density of the electrolyte increase or decrease as the battery is charged? Explain your answer.
- 5 Lithium–manganese dioxide batteries are used in portable electronic devices that need to deliver significant currents for short intervals of time. Such devices include cameras with inbuilt flash units. They can also be used for operating an external flash unit. The anode is made from lithium foil and the cathode is made from manganese dioxide and carbon. The electrolyte is lithium perchlorate,  $\text{LiClO}_4$ , dissolved in an organic solvent.
- What is the half-equation for the most likely reaction occurring at the anode?

- From a table of standard reduction potentials (see Appendix 4), what is the standard reduction potential ( $E^\circ$ ) for this anode reaction?

The cathode reaction has been variously proposed as:



- Other than starting with  $\text{MnO}_2$ , what is common about these two reactions?

The battery produces an initial voltage around 3.3 V.

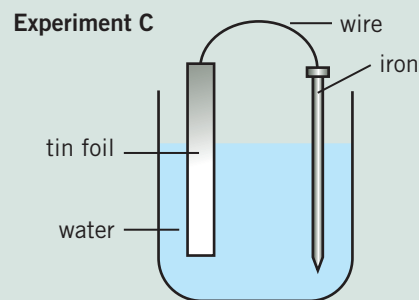
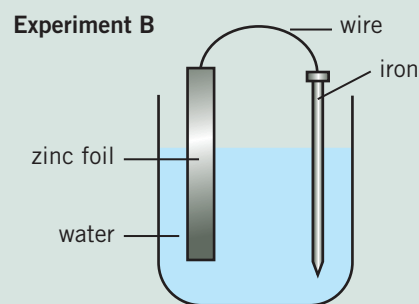
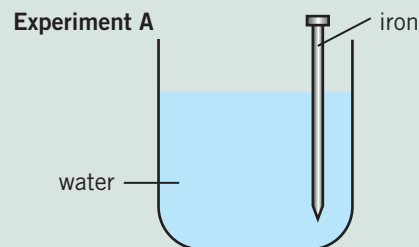
- What is the standard reduction potential of the cathode reaction?
  - Why would standard reduction potentials not be a particularly good way of predicting the cell potential of this battery?
  - The electrolyte is an organic solvent. How is it possible for this battery to produce an electric current without water being present? Why is it not possible to use an aqueous electrolyte in this battery?
- 6 Dry cells that have been operating for some time and have 'gone flat' are often also observed to be leaking. Using the electrode reactions as a guide, explain why these cells often leak.
- 7 In a dry cell, the anode is the zinc casing. In an alkaline cell, the anode is powdered zinc. The cathode reaction is the same in both types of cell. How would this difference in zinc affect the:
- voltage of the cell? Justify your answer
  - current delivered by the cell? Justify your answer. (Hint: The current is a measure of the rate of electron flow.)
- 8 One of the first attempts to develop an alternative energy source for the operation of a heart pacemaker was the construction of a biobattery. This biobattery operated by inserting a zinc electrode and platinum electrode into body tissue. Using the electrolytes in the bloodstream and other body fluids it was hoped that a voltage would be produced by the combination.
- What is the equation for the most likely anode reaction in this biobattery?
  - Assuming platinum is an inert electrode, what is likely to be the equation for the cathode reaction? (Hint: What does blood transport around the body?)

- c What voltage would this combination produce in theory?
- d Why is the voltage obtained in practice significantly less than this predicted value?
- e From a health point of view, what questions would you want answered about such a biobattery?
- 9 In 2007 the Sony Corporation announced the development of a biobattery based on glucose and using biological catalysts (enzymes) to promote the reaction. The cell consists of porous carbon electrodes, a cellophane sheet to separate the anode and cathode compartments and a solution of glucose in a pH 7 buffer of sodium phosphate.

When the cell is operating, it is observed that glucose,  $C_6H_{12}O_6$ , is converted to gluconolactone,  $C_6H_{10}O_6$ , at one electrode. There is no evidence of gas production at the other electrode.

- a Write the half-equation for the reaction of glucose. Is this oxidation or reduction and at which electrode will this reaction take place?
- b What will happen to the other product (apart from gluconolactone) of this reaction of glucose?
- c What property must the cellophane sheet have for this cell to operate?
- d Given the observation at the other electrode of 'no evidence of gas production', predict the likely reaction occurring here. (Hint: What common substance in the environment could be acting as the other half of the redox combination?)
- e What is the purpose of having carbon electrodes that are porous?
- f What is the purpose of the sodium phosphate buffer?
- g The glucose cell produces a voltage of around 0.8 V. Using a table of standard reduction potentials, predict the standard reduction potential of the glucose/gluconolactone half-cell.
- h Why is this estimate of the standard reduction potential only approximate?
- 10 A normal AA dry cell produces a cell potential or voltage of around 1.5 V. Theoretically, an external voltage of slightly more than 1.5 V should be able to recharge this battery. However, in practice the advice from manufacturers and others is that recharging these batteries is dangerous, and could result in an explosion.

- a If a voltage of 1.6 V was applied to the electrodes of a dry cell, what are the most likely products of the reaction? (Consult a table of standard reduction potentials for this.)
- b Comment on the statement that attempting to recharge a dry cell could result in an explosion.
- 11 In which of the following experiments would the nail rust quickest, and in which will the nail rust slowest? Explain your reasoning.



- 12 Some preventative methods used to protect iron from rusting are:
- cathodic protection
  - sacrificial anodes
  - exclusion of air/water.

Which of these three methods is used to protect the following iron objects from corrosion?

For each object, briefly describe what is done to achieve the protection.

- a A sheet of iron roofing
- b A large iron water pipe buried underground
- c A 'tin' (coated) can
- d A car body



- e An iron wharf
- f The hull of a ship

- 13** In an experiment, a nail with copper wrapped around it and a nail with zinc wrapped around it were placed on an agar plate. The agar gel had phenolphthalein and cyanide ions ( $\text{CN}^-$ ) in it. The results of this experiment are shown in Figure 10.14.

Explain these results.

(Hint: Phenolphthalein turns pink in the presence of  $\text{OH}^-$  ions and  $\text{CN}^-$  ions combine with  $\text{Fe}^{2+}$  ions to form the dark blue coloured complex ions,  $[\text{Fe}(\text{CN})_6]^{4-}$ .)



Figure 10.14

- 14** Deep-sea divers sometimes report that the metal on vessels they find on the seabed does not appear to have been corroded. What property or properties of this deep-sea environment might contribute to this lack of corrosion?
- 15** A farmer decides it is time to remove an old rusty iron fence from his property. As he attempts to remove an iron pole from the ground, it snaps just below where it meets the ground. He finds that the pipe below ground level is much more corroded than that above the ground. Explain this observation.
- 16** The black coating that forms on silverware over time is silver sulfide,  $\text{Ag}_2\text{S}$ . This black coating (tarnish) can be removed by rubbing with a mild abrasive, but this also removes some of the silver.

Some street traders try to sell an ‘expensive’ remedy that does not involve removing any silver. They demonstrate that a tarnished silver object when placed on the ‘magic metal’ in a solution of warm sodium bicarbonate (sodium hydrogencarbonate) ‘magically’ turns the silver surface back to the bright lustre. Bubbles of gas may be observed on the silver surface during the demonstration.

You decide that you are not going to spend \$10 on the ‘magic metal’ and that you should be able to use your knowledge of chemistry to clean the silver.

- a Write the half-equation for the corrosion of silver in the presence of sulfide ions.
- b What type of reaction will be necessary to reverse this corrosion?
- c What is the general name given to the type of chemical substance that will produce the reaction in part b?
- d Using your knowledge of chemistry and the substances that may be present in the family home, suggest what might be used as the ‘magic metal’.
- e Write equations to explain how your ‘magic metal’ converts the tarnished silver back into the shiny metal.
- f If a warm salt solution is used in place of the sodium hydrogencarbonate, a smell of rotten eggs can be noticed. Write an equation to explain where this rotten egg smell might be coming from.
- g There is no noticeable smell when sodium hydrogencarbonate is used in the solution with the ‘magic metal’ but bubbles of gas are observed on the silver. Write an equation to explain the bubbles of gas and the lack of the rotten egg smell.

## 17 ▷ RESEARCH

- a The most common batteries used for portable electronic appliances are nickel–cadmium batteries, nickel metal hydride (NiMH) batteries and lithium ion batteries. Investigate the chemistry and properties of these three battery types under the following headings:
  - Cell components (chemicals)
  - Electrode reactions—charging and discharge
  - Variations in the electrolytes used (if any) and chemical reasons for these variations
  - Variations in the nature of the electrodes with reasons for these variations
  - Advantages and disadvantages of each battery
  - The chemical principles that relate to factors such as the voltage of the battery, the total amount of energy it can deliver and how fast it can deliver that energy
  - Precautions to be taken when handling and/or disposing of these batteries

- Environmental impacts (if any) associated with the use of these batteries
- b** There are five basic types of hydrogen/oxygen fuel cells. These are alkaline fuel cells, molten carbonate fuel cells, phosphoric acid fuel cells, polymer electrolyte membrane fuel cells and solid oxide fuel cells. Using the headings in part a as a guide, complete an investigation of the chemistry and properties of these fuel cells.
- c** The Toyota Prius and Honda Civic HEVs (hybrid electric vehicles) both use rechargeable batteries and conventional petroleum-based fuels to operate more efficiently than conventional cars. The batteries used in these HEVs are relatively heavy nickel–metal hydride batteries that recharge during braking. These batteries have a driving range of about 30 km, so there are times when the battery is recharged by burning fuel to run a small generator.

Work is ongoing to explore the use of single-cell lithium ion alternatives for the heavy modules of NiMH batteries used at the moment. In particular, the focus is on the production of a plug-in hybrid battery system (PHEV).

On the other side of this issue is the fact that the production of battery systems for PHEV cars would increase the demand for electricity generated by power stations. Power plants use a large amount of water that has to be turned into steam to generate electricity. The amount of water required to operate a PHEV is about three times that required for the production of petrol for a conventional vehicle. In addition, a conventional power station will consume fossil fuels and produce greenhouse gases.

Research the nature of the batteries that are currently used in HEVs and explain why a shift to lithium ion batteries is being contemplated. In your analysis of these issues, also consider other issues of sustainability and the environmental impact of using PHEVs in terms of water supplies, fossil fuel use and greenhouse gases.

Finally, explore the issues associated with the use of fuel cells and solar-generated electricity in the automobile of the future.

**18** ↻ **RESEARCH** Engineers need to be aware of a variety of situations in which corrosion can occur. Among these systems, the following are included:

- dry corrosion
- galvanic corrosion
- concentration cells

- stress cells
  - ‘concrete cancer’.
- a** Research the chemistry associated with these types of corrosion, explaining the chemical principles that are associated with each.
- b** What is the environmental impact of each type of corrosion?
- c** Finally, discuss the chemistry associated with the various strategies that are used to reduce the impact of each type of corrosion. This discussion could include reference to the following:
- coating the metal surface with paint, oil or a less reactive metal
  - galvanising
  - sacrificial anodes
  - external voltage
  - materials that could be used in place of steel for reinforcing concrete.



# 11

## Organic chemistry 1 Hydrocarbons

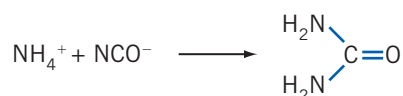
**BY THE END OF THIS CHAPTER YOU SHOULD BE ABLE TO:**

- draw and name structural isomers of alkanes
- use the concepts of bonding to explain the physical properties of hydrocarbons
- draw and name structural and geometrical isomers of alkenes
- write balanced equations for the substitution reactions of alkanes
- write balanced equations for the addition reactions of alkenes
- write balanced equations for the combustion reactions of hydrocarbons.

The term 'organic' has been used over the past 30 or so years to describe anything from art and architecture, through bedding, coffee, gardening, food and even, recently, solar cell electrodes. 'Organic' has become a popular adjective to label something that is natural or derived from nature.

Not surprisingly, the term 'organic chemistry' was used in the 1800s to describe those compounds that were obtained from or found in living things. Inorganic chemistry was then the study of those substances that were obtained from non-living things such as rocks.

Once it was discovered that compounds previously classified as 'organic' could be made from inorganic compounds (see Figure 11.1), the definition of organic chemistry was broadened and today the 'organic' in organic chemistry has a much different meaning from that used in advertising and elsewhere. Organic chemistry is simply the chemistry of the millions of known compounds of carbon. There are a few exceptions such as the carbonates, and the oxides of carbon that are generally classified as inorganic.

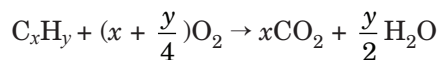


**Figure 11.1** Synthesis of urea (an organic compound) from ammonium cyanate (an inorganic compound)

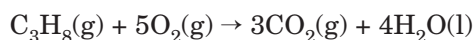
## 11.1 Hydrocarbons

As the name suggests, these compounds contain only carbon and hydrogen. All hydrocarbons can be represented by the formula  $\text{C}_x\text{H}_y$ , where  $x$  and  $y$  are whole numbers. Hydrocarbons undergo combustion or oxidation when ignited in the presence of air or oxygen.

The general equation for the combustion of a hydrocarbon can be written as:



For example, the equation for the combustion reaction of propane,  $\text{C}_3\text{H}_8$ , is:



If hydrocarbons are burnt in a limited supply of air, as in a car engine, carbon monoxide rather than carbon dioxide may form.

The hydrocarbons are often divided into groups or families depending on the nature of the bonds present between the carbon atoms or how the carbon atoms are arranged. For example, if the bonds between the carbon atoms are all single covalent bonds then the hydrocarbons are known as alkanes. If these alkanes form cyclic structures rather than chain structures, then they are called cycloalkanes (Figure 11.3).



**Figure 11.2** Fireball from a liquefied petroleum gas (LPG) explosion

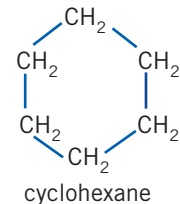
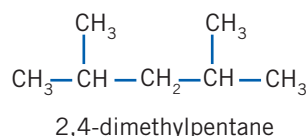
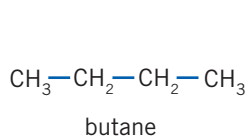


Figure 11.3 Straight chain, branched chain and cyclic alkanes

Another important group of hydrocarbons is the alkenes. These contain at least one carbon–carbon double bond.

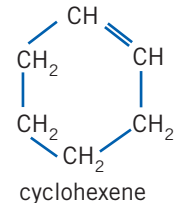
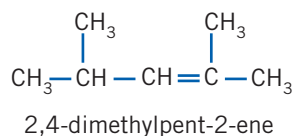
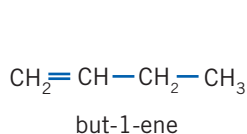


Figure 11.4 Straight chain, branched chain and cyclic alkenes

The hydrocarbons that do not contain a benzene ring are often collectively called aliphatic hydrocarbons.



## 11.2 Alkanes

The general features of the straight chain and branched chain alkanes include the following:

- They consist only of carbon and hydrogen.
- They have only single bonds between the carbon atoms, e.g. propane  $\text{CH}_3-\text{CH}_2-\text{CH}_3$ .
- They have the general formula  $\text{C}_n\text{H}_{2n+2}$ , where  $n = 1, 2, 3$  etc.
- They are colourless and may be gases, liquids or solids at room temperature depending on their relative formula mass.
- They are insoluble in water.

The structural formulas and boiling points of the first eight straight chain alkanes are shown in Table 11.1.

TABLE 11.1 THE FIRST EIGHT STRAIGHT CHAIN ALKANES

Name of alkane	Number of carbon atoms in straight chain	Structural formula	Molecular formula	Boiling point ( $^{\circ}\text{C}$ )
Methane	one	$\text{CH}_4$	$\text{CH}_4$	-161.5
Ethane	two	$\text{CH}_3-\text{CH}_3$	$\text{C}_2\text{H}_6$	-88.6
Propane	three	$\text{CH}_3-\text{CH}_2-\text{CH}_3$	$\text{C}_3\text{H}_8$	-42.1
Butane	four	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$	$\text{C}_4\text{H}_{10}$	-0.5
Pentane	five	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	$\text{C}_5\text{H}_{12}$	36.1
Hexane	six	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	$\text{C}_6\text{H}_{14}$	68.7
Heptane	seven	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	$\text{C}_7\text{H}_{16}$	98.4
Octane	eight	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	$\text{C}_8\text{H}_{18}$	125.7

Many alkanes are composed of branched chains; that is, a straight chain to which side-chains are joined. For example, butane,  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$ , is a straight chain alkane, but methylbutane,  $\text{CH}_3\text{-CH}(\text{CH}_3)\text{-CH}_2\text{-CH}_3$ , is a branched chain alkane.

The names of the branched chain alkanes are based on the names of the straight chain alkanes from which they are derived.

The rules that are used to name alkanes are as follows. (The naming conventions used here are those recommended by the International Union of Pure and Applied Chemistry—IUPAC.)

- i** Choose the longest carbon chain, and name it, as an alkane, according to the number of carbon atoms present (often called the parent chain).
- ii** Number this longest chain from one end, so that the side-chains present have the smallest numbers possible.
- iii** Identify the side-chains (see below) ‘joined’ onto this parent chain and write them, in alphabetical order, as prefixes to the parent name.
- iv** Write the number used to indicate the position of the side-chain before the side-chain name.
- v** If two identical side-chains are present, use ‘di-’ as a prefix to the side-chain name; if three identical side chains are present, then include ‘tri’ as a prefix to the side-chain name; if four identical side-chains are present, use ‘tetra’ as a prefix etc.
- vi** In names of organic compounds, hyphens are placed between words and numbers, and commas are used between two numbers.

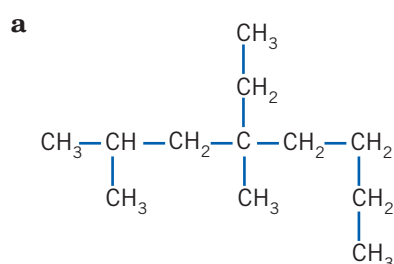
Some of the common side-chains are:

$\text{CH}_3\text{-}$  methyl

$\text{CH}_3\text{CH}_2\text{-}$  or  $\text{C}_2\text{H}_5\text{-}$  ethyl

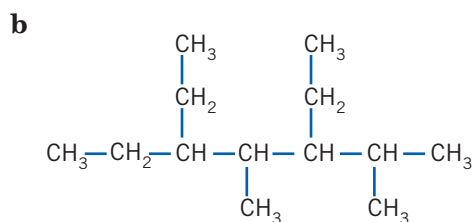
$\text{CH}_3\text{CH}_2\text{CH}_2\text{-}$  or  $\text{C}_3\text{H}_7\text{-}$  propyl

For example:



The longest chain is 8 carbons long, and so the parent chain is octane. The side-chains on this parent chain are two methyl groups (on carbons 2 and 4) and an ethyl group (on carbon 4).

So the name is 4-ethyl-2,4-dimethyloctane.



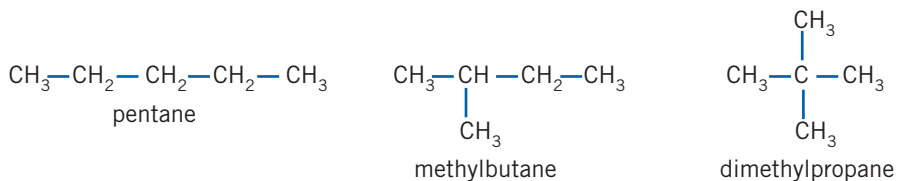
The longest chain contains 7 carbons, so the parent chain is heptane. The side-chains on this parent chain are two ethyl groups on carbons 3 and 5, and two methyl groups on carbons 2 and 4. Note that the numbering of the carbon chain starts from the opposite end to example (a) in accordance with the second rule above.

So the name is 3,5-diethyl-2,4-dimethylheptane.

## Structural isomers of alkanes

Structural isomers are compounds that have the same molecular formula but different structural formulas. (Or an isomer has the same molecular formula but a different structural formula compared to another substance.)

For example, the following compounds are the isomers with the molecular formula of  $C_5H_{12}$ :

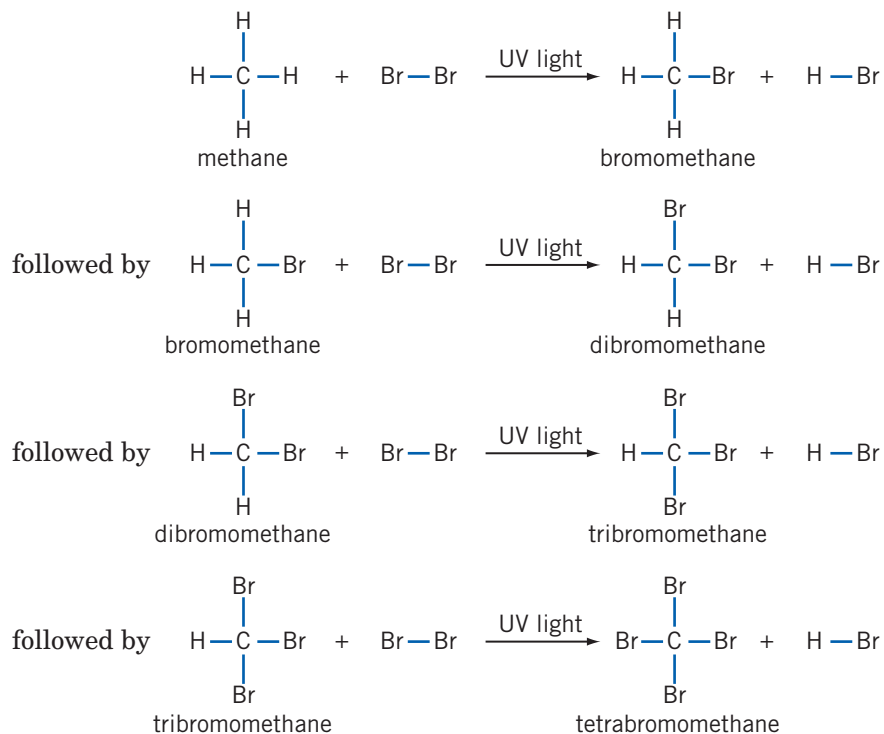


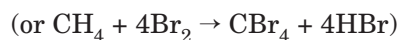
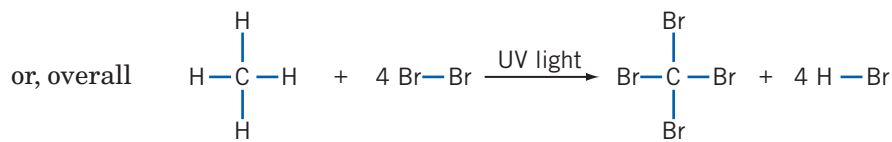
## Substitution reactions of alkanes

A substitution reaction is one in which an atom in a molecule is replaced by a different atom to form a new molecule.

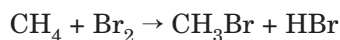
The reactions of alkanes with the halogens (particularly  $\text{Cl}_2$  and  $\text{Br}_2$ ) are examples of substitution reactions. In these reactions, the hydrogen atoms of the alkane are replaced, one after the other, by the halogen atoms. Haloalkanes (compounds that contain carbon and halogen atoms and possibly hydrogen atoms) together with a hydrogen halide are formed in these reactions. The reaction mixture must be exposed to ultraviolet light (or sunlight) for substitution reactions of alkanes to occur. These reactions are often very slow.

For example, when methane is mixed with an excess of bromine, and exposed to ultraviolet light, the following reactions take place:





If a 1:1 molar mixture of methane and bromine was reacted, then the major product formed would be bromomethane. In other words, only one hydrogen atom in each alkane molecule would be substituted by a bromine atom:



However, if an excess of bromine is used, then tetrabromomethane would be the major product. The major organic product formed depends on the amount of reactants present.

Also, if the reaction is carried out in the dark, no substitution reaction occurs.

## Cycloalkanes

One of the bonding properties of carbon that makes it capable of forming so many different compounds is its ability to form cyclic structures or rings. Cycloalkanes are sometimes called alicyclic alkanes. Rings containing from three to 30 or more carbon atoms occur naturally. Many of the organic molecules found in nature contain five or six carbon atoms in the ring.

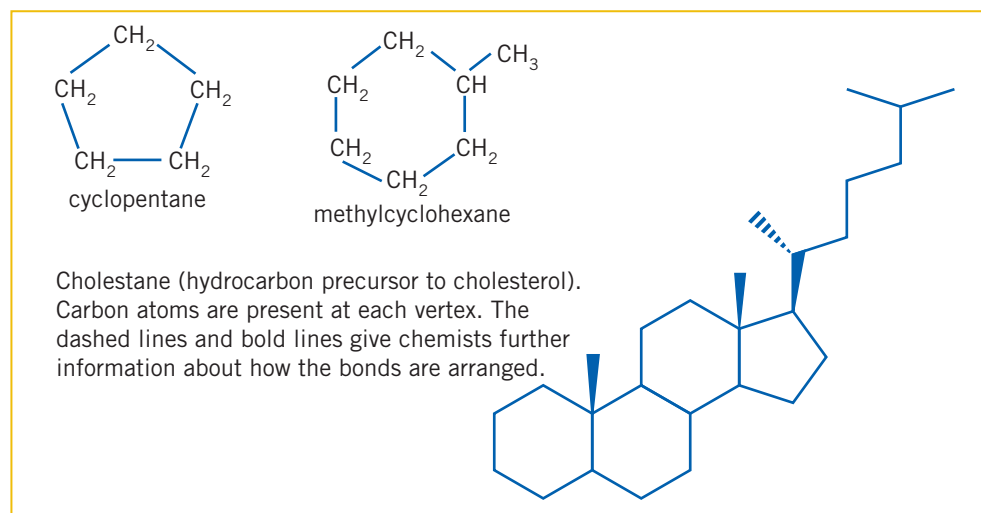
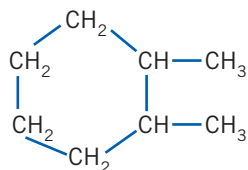


Figure 11.5 Examples of cycloalkanes

The general formula of cycloalkanes is  $\text{C}_n\text{H}_{2n}$ . This is the same as the general formula of alkenes.

In naming cycloalkanes, the ring is regarded as the parent chain and the prefix 'cyclo' is used. The ring is numbered so that the side-chains/groups have the smallest possible number.

For example, the name of the following compound is 1,2-dimethylcyclohexane:

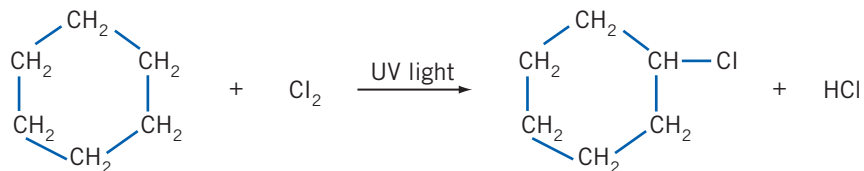




The structural formulas of cycloalkanes can also be written without showing the hydrogen and carbon atoms, for example, cyclohexane can be represented as:



The cycloalkanes, like the alkanes, undergo combustion and substitution reactions. For example, the reaction of cyclohexane with chlorine, in a 1:1 molar ratio, and in the presence of UV light, is:



## 11.3 Alkenes

Alkenes have the following general properties.

- They contain only carbon and hydrogen atoms.
- They have at least one double carbon-carbon bond, for example, propene,  $\text{CH}_2=\text{CH}-\text{CH}_3$ , is an alkene.
- They have a general formula of  $\text{C}_n\text{H}_{2n}$  where  $n = 1, 2, 3$  etc. (Assuming the alkene has only one double bond.)
- They are colourless compounds.
- They have relatively low melting and boiling points.
- They are insoluble in water.

Alkenes are named in much the same way as alkanes, except for the following.

- The longest carbon chain chosen as the parent chain must contain the double carbon-carbon bond.
- This parent chain is numbered from the end that gives the double bond the smallest number possible.
- The suffix '-ene' is used as the ending of the parent name, rather than '-ane'.
- The position of the double bond within the chain is given as the lower number of the two double bonded carbons. The number is placed just before the suffix '-ene'.

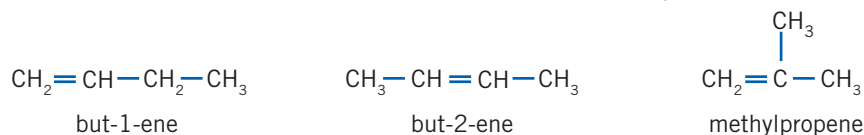
For example:

- a**  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$  The parent chain contains six carbon atoms and the double bond is between carbon 2 and carbon 3, so the name is hex-2-ene.

- b** The parent chain contains seven carbon atoms and the double bond is between carbon 3 and carbon 4. There is an ethyl group on carbon 5 and a methyl group on carbon 6. So, the name is 5-ethyl-6-methylhept-3-ene.

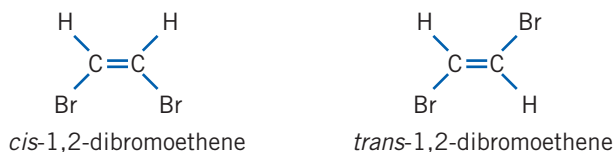
## Structural isomers and geometrical isomers of alkenes

Structural isomerism occurs with alkenes, as it does with alkanes. For example, the structural isomers of alkenes with the formula  $C_4H_8$  are:



Some alkenes can exhibit geometrical isomerism. Geometric isomers have the same molecular formula, but the groups attached to carbon atoms joined by a double bond are arranged differently around the double bond.

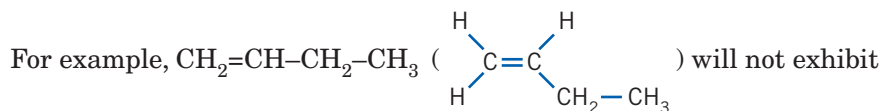
For example, the geometrical isomers of the alkene 1,2-dibromoethene are:



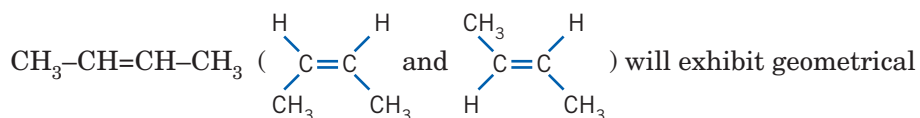
The isomer with the two groups on the same side of the double bond, is called the 'cis' isomer. The isomer with the groups on the opposite side of the double bond is called the 'trans' isomer.

Geometrical isomerism occurs for alkenes because the carbon atoms joined by the double bond are unable to rotate about the double bond. However, if there is only a single bond between two carbon atoms, then the carbon atoms can rotate about the bond. Consequently, geometrical isomerism does not exist for alkanes. (Only structural isomerism exists for alkanes.)

An alkene will exhibit geometrical isomerism if each of the carbon atoms joined by the double bond have different groups attached to them.



geometrical isomerism but

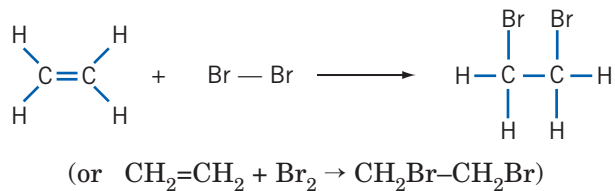


isomerism.

## Reactions of alkenes

Alkenes undergo addition reactions readily with substances such as chlorine, bromine, fluorine, hydrogen, hydrogen halides and water (steam). In an addition reaction, two new atoms are added 'across the double bond' and the double bond becomes a single bond.

Addition reactions normally occur at a much faster rate than substitution reactions. For example, ethene reacts with bromine in the following way:



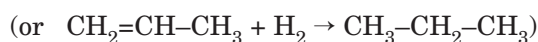
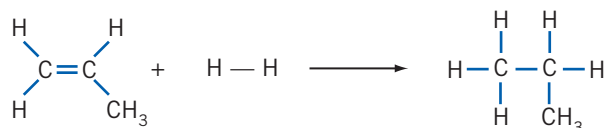


**Figure 11.6** Some orange-coloured bromine water was added to ethene (a colourless gas) in a gas jar. Very rapidly, the bromine solution becomes colourless.



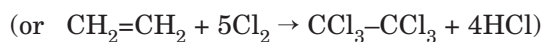
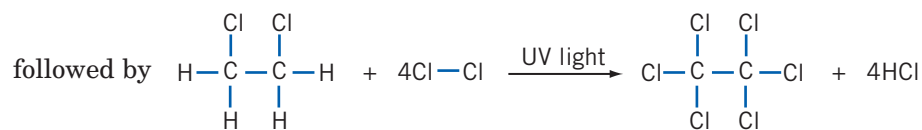
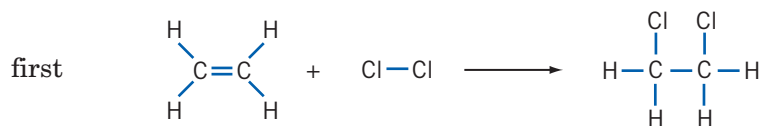
Experimentally, an alkane and an alkene can be distinguished by adding an aqueous solution of bromine. An aqueous solution of bromine is an orange colour and when it reacts with either an alkane or an alkene, a colourless mixture is formed. When an alkene is shaken with an aqueous solution of bromine, the orange colour of bromine disappears almost instantly (Figure 11.6). However, with alkanes, the orange colour of bromine takes a much longer time to disappear, and ultraviolet light is necessary for the reaction to occur.

Another example of an addition reaction is the reaction of propene with hydrogen, as shown below:

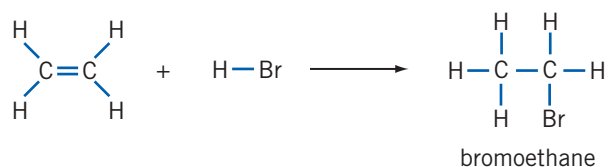


Alkenes can undergo addition reactions followed by substitution reactions with halogens if ultraviolet light is present and if the reaction mixture is allowed to react for sufficient time. Also, for a substitution reaction to occur after an addition reaction, the halogen and alkene need to be initially present in greater than a 1:1 mole ratio mixture. If an alkene is mixed with excess halogen and allowed to react in the dark, then only an addition reaction will occur.

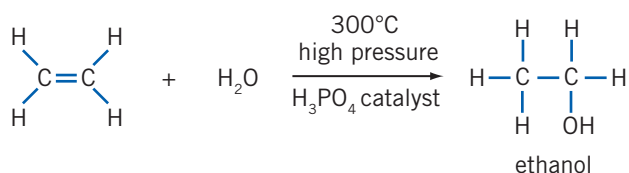
For example, in the presence of ultraviolet light and excess chlorine, ethene will react with chlorine in the following way:



Hydrogen halides such as HCl or HBr will also add to the double bond in an alkene. In this case, the hydrogen adds to one carbon and the halogen to the other to produce a haloalkane. For example, ethene reacts with hydrogen bromide as follows:



Alkenes will also undergo addition reactions with steam in the presence of a suitable catalyst to produce alcohols. For example, ethene will react with steam to produce ethanol. This is a major industrial method of preparation of this important alcohol:



## MAJOR IDEAS

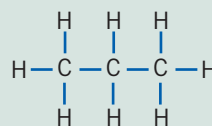
- All hydrocarbons can be represented by the formula  $C_xH_y$ , where  $x$  and  $y$  are whole numbers. Hydrocarbons undergo combustion, in the presence of excess air, to produce carbon dioxide and water.
- Alkanes are hydrocarbons that have only single bonds between their carbon atoms. Both cyclic and chain (aliphatic) alkanes exist.
- Alkanes have the general formula  $C_nH_{2n+2}$ , where  $n = 1, 2, 3$  etc., have low melting and boiling points and are insoluble in water.
- Alkanes and cycloalkanes are named according to IUPAC rules, to give names such as butane, 3-methylheptane and propylcyclohexane.
- Structural isomers are compounds that have the same molecular formula but different structural formulas.
- A substitution reaction is one in which an atom in a molecule is replaced by a different atom to form a new molecule.
- Alkanes undergo slow substitution reactions with halogens in the presence of UV light.
  - As well as haloalkanes forming in these reactions, a hydrogen halide is formed.
  - The composition of the products depends on the relative amounts of alkane and halogen used.
- Alkenes are hydrocarbons with at least one double carbon-carbon bond. Their general formula is  $C_nH_{2n}$ .
- Alkenes have low melting and boiling points and are insoluble in water.
- Alkenes are named by using a suffix of '-ene', e.g. hex-2-ene and 3-methyloct-2-ene.
- Alkenes exhibit both structural and geometrical isomerism.
- Geometric isomers have the same molecular formula, but the groups attached to carbon atoms joined by a double bond are in different positions in space.
- Alkenes undergo addition reactions readily with substances such as halogens and hydrogen halides.
- In an addition reaction, two new atoms are added 'across the double bond' and the double bond becomes a single bond.
- Addition reactions normally occur at a much faster rate than substitution reactions.

## QUESTIONS

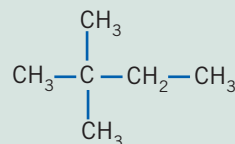
1 Name the following alkanes according to the IUPAC rules.



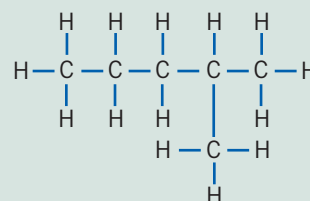
b



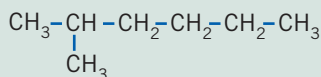
c



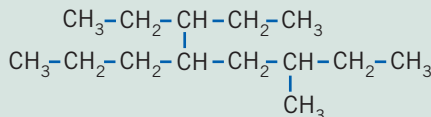
f



g



h



2 Write the structural formulas for the following alkanes.

a hexane

b methylpropane

c 2,3,3-trimethylpentane

d 3-ethyl-2,4-dimethylheptane

3 Give the structural formula of an example of each of the following.

a An aliphatic hydrocarbon

b A straight chain alkane

c A branched chain hydrocarbon

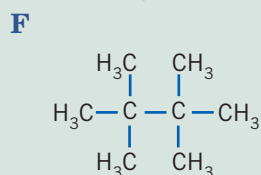
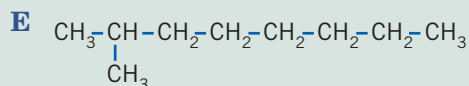
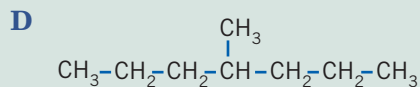
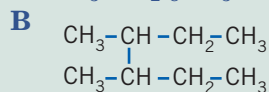
d An alicyclic alkane

4 Draw the structural formulas and name the isomers of the compounds with the following molecular formulas.

a  $C_4H_{10}$

b  $C_6H_{14}$

5 Which of the following substances are isomers?



6 Which of the following substances are isomeric with 2,2-dimethylpentane?

- a pentane
- b methylpentane
- c 2,2-dimethylhexane
- d ethylpentane
- e trimethylbutane
- f 3-methylhexane
- g heptane

7 Give the structural formula of the major organic product formed when the following reaction mixtures are exposed to ultraviolet light. Assume that the reactants are present in a 1:1 mole ratio.

- a  $\text{CH}_4$  and  $\text{Cl}_2$
- b  $\text{CH}_3\text{CH}_3$  and  $\text{Br}_2$
- c  $\text{CH}_3\text{CH}_2\text{CH}_3$  and  $\text{F}_2$
- d dimethylpropane and  $\text{I}_2$

8 Complete each of the gaps in the following equations. Assume each reaction mixture is exposed to sunlight.

- a  $\text{CH}_4 + \text{F}_2 \rightarrow \dots + \text{HF}$
- b  $\text{CH}_4 + 4\text{Br}_2 \rightarrow \dots + 4\text{HBr}$
- c  $\dots + \text{Br}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{HBr}$
- d  $\dots + \dots \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \dots$
- e  $\dots + 6\text{Cl}_2 \rightarrow \text{CCl}_3\text{CCl}_3 + \dots$
- f  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3 + 10\text{Br}_2 \rightarrow \dots + \dots$
- g  $\text{C}_5\text{H}_{12} + \dots \text{O}_2 \rightarrow \dots + \dots$

9 Write balanced equations, using structural formulas, for each of the following reactions.

- a Ethane is mixed with an excess of fluorine, in the presence of UV light.
- b Cyclobutane is burnt in air.
- c A mixture of propane and bromine is placed in a dark cupboard.
- d Tetramethylbutane is mixed with chlorine, in a 1:1 mole ratio, and exposed to sunlight.
- e A mixture of methylcyclopropane and an excess of bromine is exposed to UV light.

10 Which of the following names are correct? If the name is incorrect, give the correct name.

Structural formula	Name. Is it correct or incorrect?
a $\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \end{array}$	Ethylbutane
b $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_3 \\   \\ \text{CH}_3$	5-Methylheptane
c $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	2-Dimethylpentane
d $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{CH}_3-\text{C}-\text{C}-\text{CH}_3 \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	Tetramethylbutane

11 The boiling points of the five isomeric alkanes with formula  $\text{C}_5\text{H}_{12}$  are listed below.

Alkane	Boiling point ( $^\circ\text{C}$ )
Hexane	68.7
3-Methylpentane	63.3
2-Methylpentane	60.3
2,3-Dimethylbutane	58.0
2,2-Dimethylbutane	49.7

Draw the structural formulas of each of these alkanes and explain qualitatively the differences in the boiling points in terms of the intermolecular bonding between the hydrocarbon molecules.

12 Which of the following statements is true about structural isomers?

- A They have the same structural formula but different molecular formulas.
- B They have the same relative formula mass.

- C** Their atoms are connected in the same way.  
**D** They have the same physical properties.
- 13 a** Table 11.1 gave the boiling points for the first eight alkanes. Successive members of the alkane family differ by just  $-\text{CH}_2-$ . Account for the fact that the difference in boiling points between  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  is so much larger than the difference between the boiling points of  $\text{C}_7\text{H}_{16}$  and  $\text{C}_8\text{H}_{18}$ .
- b** Sketch a plot of boiling point vs relative formula mass for the first eight straight-chain alkanes.
- 14** The shiny skin of a fruit such as an apple contains hydrocarbons with between 27 and 30 carbon atoms. Explain why the skin of an apple would help prevent water from being lost from the fruit.
- 15** Name the following alkenes, according to the IUPAC rules:
- a**  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$
- b** 
$$\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_2-\text{C}=\text{CH}-\text{CH}_3 \\ | \qquad \qquad | \\ \text{CH}_2 \qquad \qquad \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$
- c** 
$$\begin{array}{c} \text{CH}_3-\text{CH}=\text{CH}-\text{CH}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$
- d** 
$$\begin{array}{c} \text{CH}_3 \qquad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \qquad \qquad \text{H} \end{array}$$
- e** 
$$\begin{array}{c} \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \\ || \\ \text{CH}-\text{CH}_2-\text{CH}_3 \end{array}$$
- f** 
$$\begin{array}{c} \text{H} \qquad \qquad \text{CH}_2-\text{CH}_3 \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \qquad \qquad \text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$$
- 16** Give the structural formulas of the following compounds.
- a** hex-3-ene  
**b** 2,2-dimethyloct-4-ene  
**c** 1,2,3-trichloro-3-ethylpent-1-ene  
**d** 4-propylhept-1-ene  
**e** dimethylbut-2-ene
- 17** Which of the following compounds are structural isomers of hex-1-ene?
- a**  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$   
**b**  $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$   
**c** 
$$\begin{array}{c} \text{CH}_3-\text{C}=\text{C}-\text{CH}_3 \\ | \qquad | \\ \text{H}_3\text{C} \quad \text{CH}_3 \end{array}$$
- 18** Give the names and structural formulas of the five isomers with the molecular formula  $\text{C}_5\text{H}_{10}$ . Assume that each isomer contains a double carbon-carbon bond.
- 19** Give the structural formulas of the following geometrical isomers.
- a** *trans*-2,3-difluorobut-2-ene  
**b** *cis*-2,3-difluorobut-2-ene  
**c** *trans*-pent-2-ene  
**d** *cis*-1-bromo-2-chloroethene
- 20** Give the IUPAC name of each of the following alkenes (including the appropriate suffix of '*cis*' or '*trans*' in each name).
- a** 
$$\begin{array}{c} \text{H} \qquad \qquad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{CH}_3-\text{CH}_2 \qquad \text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$$
- b** 
$$\begin{array}{c} \text{H}_3\text{C} \qquad \text{Cl} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{Cl} \qquad \qquad \text{CH}_3 \end{array}$$
- c** 
$$\begin{array}{c} \text{CH}_3 \qquad \text{CH}_3 \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \qquad \qquad \text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$$
- 21 a** Draw the two geometric isomers of 1,2-dichloroethene, and name them.  
**b** Draw a structural isomer of 1,2-dichloroethene, and name it.
- 22** Which of the following compounds cannot exist as geometrical isomers?
- a** 
$$\begin{array}{c} \text{F} \qquad \qquad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{F} \qquad \qquad \text{CH}_2-\text{CH}_3 \end{array}$$
- b** 
$$\begin{array}{c} \text{Cl} \qquad \text{Cl} \\ | \qquad | \\ \text{CH}_3-\text{C}-\text{C}-\text{CH}_3 \\ | \qquad | \\ \text{H} \qquad \text{H} \end{array}$$
- c** propene  
**d** but-1-ene  
**e** 2,3-dibromobut-2-ene  
**f** hex-3-ene
- 23** Give the structural formula (showing all bonds including those to hydrogen) of the organic product formed in each of the following reactions.
- a**  $\text{CH}_2=\text{CH}_2 + \text{Cl}_2 \rightarrow$   
**b**  $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{Br}_2 \rightarrow$   
**c**  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 + \text{H}_2 \rightarrow$   
**d**  $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{excess Cl}_2 \xrightarrow{\text{UV light}}$   
**e**  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 + \text{steam} \rightarrow$   
**f**  $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3 + \text{HI} \rightarrow$

- 24** Describe the reaction conditions you could use to carry out the following reactions, for example, in 1:1 mole ratio of reactants, in the dark.
- The formation of 1,2-difluoroethane from ethene
  - The formation of  $\text{CCl}_3\text{-CCl}_2\text{-CCl}_3$  from propene
  - The preparation of 2,3-dibromopentane from pent-2-ene
  - The preparation of hexafluoroethane from ethene
- 25** Give the name and structural formula of the organic compound you could use to form each of the following.
- 1,2-dibromopropane
  - hexachloroethane
  - methylpropane
  - 3,4-difluoroheptane
  - $\text{CBr}_3\text{-CBr}_2\text{-CBr}_2\text{-CBr}_3$
  - $\text{CH}_2\text{Cl-CH}_2\text{Cl}$
- 26** Write a balanced equation, using structural formulas for the following reactions.
- Propene is mixed with fluorine in a 1:1 mole ratio.
  - Methylpropene is mixed with an excess of bromine and the mixture is put in a dark cupboard.
  - Ethene is reacted with hydrogen in the presence of a catalyst.
  - 1 mole of but-1-ene is mixed with 1 mole of chlorine, in the presence of UV light.
  - Pent-2-ene is reacted with an excess of bromine in the presence of UV light.
  - Hex-3-ene is burnt in air.
  - But-2-ene is reacted with hydrogen bromide gas.
- 27** Match each formula, in the following table, with its correct name.

Formula		Name	
a	$\begin{array}{ccccccc} \text{CH}_3 & - & \text{CH} & - & \text{CH} & = & \text{C} & - & \text{CH}_3 \\ & &   & & & &   & & \\ & & \text{CH}_3 & & & & \text{CH}_2 & - & \text{CH}_3 \end{array}$	A	Ethyl-2-methylpentane
b	$\begin{array}{ccccccc} & & & & \text{CH}_2 & - & \text{CH}_3 \\ & & & &   & & \\ \text{CH}_3 & - & \text{CH} & - & \text{CH} & - & \text{CH}_2 & - & \text{CH}_3 \\ & &   & & & & & & \\ & & \text{CH}_3 & & & & & & \end{array}$	B	Pentane
c	$\begin{array}{ccccccc} & & & & \text{CH}_2 \\ & & & &    \\ \text{CH}_3 & - & \text{CH}_2 & - & \text{CH} & - & \text{C} & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH}_3 \\ & & & &   & & & & & & & & \\ & & & & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH}_3 \end{array}$	C	2,4-Dimethylhex-3-ene
d	$\begin{array}{ccccccc} \text{H}_3\text{C} & & \text{CH}_3 \\   & &   \\ \text{H}_3\text{C} & - & \text{C} & - & \text{C} & - & \text{CH}_2 & - & \text{CH} & = & \text{CH}_2 \\   & &   \\ \text{H}_3\text{C} & & \text{CH}_3 \end{array}$	D	Propane
e	$\begin{array}{ccccccc} \text{H} & \text{H} & \text{H} \\   &   &   \\ \text{H} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{H} \\   &   &   \\ \text{H} & \text{H} & \text{H} \end{array}$	E	3-Ethyl-2-propylhex-1-ene
f	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	F	4,4,5,5-Tetramethylhex-1-ene



# 12

## Organic chemistry 2 Functional groups

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

- recognise the functional groups alcohol, aldehyde, ketone, carboxylic acid, ester and amine
- name and draw structural formulas of simple examples of compounds containing these functional groups
- compare and explain the physical properties of compounds with these functional groups
- explain that compounds with the same functional group exhibit similar chemical properties
- explain the difference in structure of primary, secondary and tertiary alcohols
- predict and write equations for the oxidation of alcohols
- recognise the general structure of  $\alpha$ -amino acids, and explain their behaviour in neutral, acidic and basic environments.



A functional group is an atom or a group of atoms that determines the chemical and, in part, physical properties of an organic compound. The presence of a particular functional group in a molecule can be used to predict the type of reactions the molecule will undergo. This predictive ability is very important in the synthesis of new organic molecules.

Figure 12.1 shows some functional groups in simple molecules.

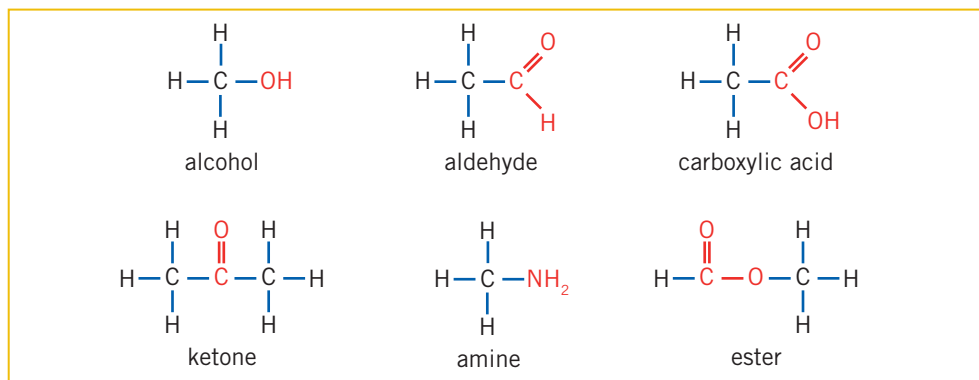


Figure 12.1 Examples of functional groups

Some of the chemistry of functional groups is related to the changing oxidation number of the carbon atom that is part of the group. In methane,  $\text{CH}_4$ , for example, the oxidation number of carbon is  $-4$ , the lowest possible value for carbon. In the alkyl halides, for example  $\text{CH}_3\text{Cl}$ , and alcohols, for example  $\text{CH}_3\text{OH}$ , the oxidation number of the carbon attached directly to the functional group is  $-2$ . Aldehydes, for example  $\text{HCHO}$ , and ketones, for example  $\text{CH}_3\text{COCH}_3$ , have the carbon atom in the functional group with an oxidation number of zero. In a carboxylic acid such as methanoic acid,  $\text{HCOOH}$ , the oxidation number of the carbon has increased to  $+2$ .

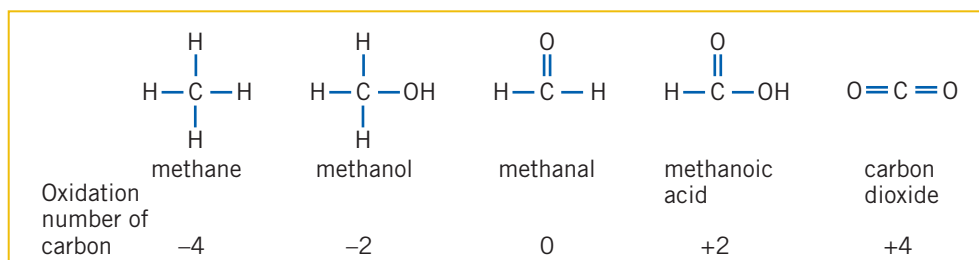


Figure 12.2 Oxidation numbers and functional groups

## 12.1 Alcohols

The functional group present in an alcohol is the  $-\text{OH}$  group attached to a tetrahedral carbon atom. The simplest alcohol is methanol,  $\text{CH}_3\text{OH}$ .

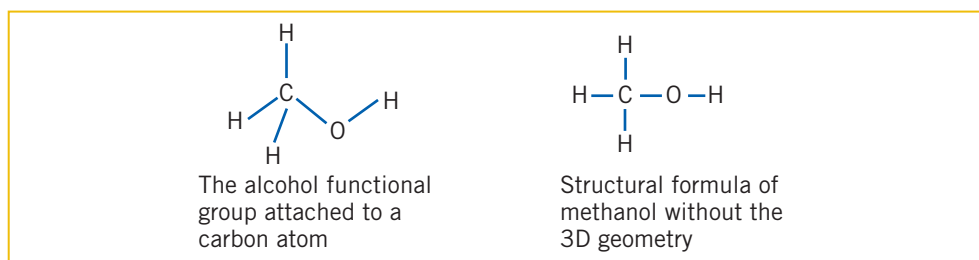


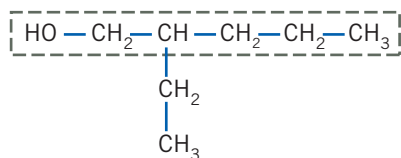
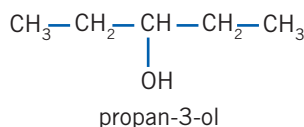
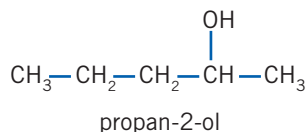
Figure 12.3 Representations of the structure of methanol

## Naming alcohols

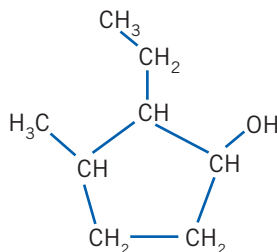
The following steps describe how alcohols are named, as recommended by IUPAC.

- i The alcohol is named by selecting the longest carbon chain that contains the  $\text{-OH}$  functional group. This longest chain becomes the parent alkane and the alcohol is named by adding the suffix 'ol' in the place of the 'e' in the alkane name.
- ii The position of the alcohol functional group is indicated by the use of a number placed before the suffix 'ol'.  
(The prefix 'hydroxy' is used for some compounds where there is more than one functional group present).
- iii The alcohol functional group is given the smallest possible number in the chain and takes priority over any side-chain alkyl groups.
- iv If two alcohol functional groups are present then the suffix 'diol' is used and the 'e' is not dropped from the alkane name.
- v For cyclic alcohols, the numbering begins at the carbon atom attached to the alcohol functional group.

Some examples of alcohols and their names are shown below.



The name of the alcohol shown above is 2-ethylpentan-1-ol. The dotted line shows the longest chain with the alcohol functional group is a pentane, though is a longer carbon chain in the molecule.



The cyclic alcohol shown above is 2-ethyl-3-methylcyclopentanol.



Figure 12.4 All of these products contain an alcohol

## Physical properties of alcohols

The simple alcohols with up to eight carbon atoms in the longest chain are colourless liquids at room temperature. The boiling point of an alcohol is higher than that of the parent alkane. This is due to the presence of hydrogen bonds as well as dispersion forces between the alcohol molecules, compared to only dispersion forces holding the alkane molecules together.

TABLE 12.1 BOILING POINTS OF SOME ALCOHOLS

Number of carbon atoms	Name	Formula	Boiling point (°C)
1	Methanol	CH <sub>3</sub> OH	65
2	Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	78
3	Propan-1-ol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	97
4	Butan-1-ol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	118

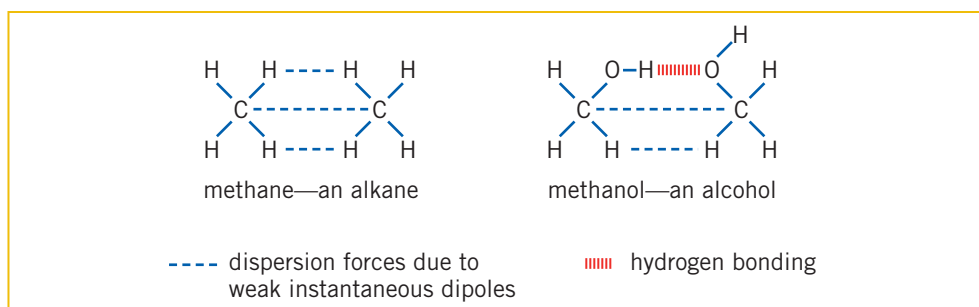


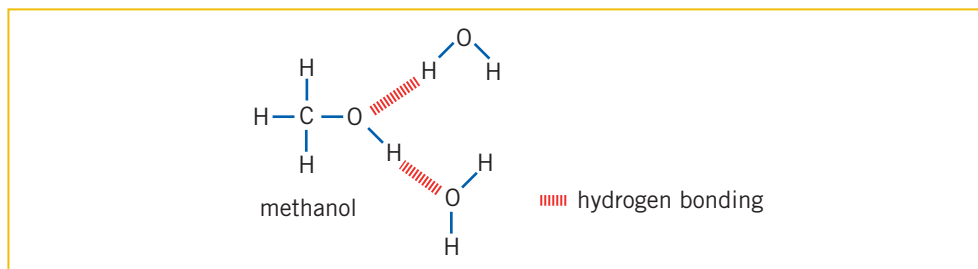
Figure 12.5 Bonding between methane molecules and between methanol molecules

Hydrogen bonding occurs between molecules where a hydrogen atom is bonded to one of the three highly electronegative atoms—nitrogen, oxygen or fluorine. Alcohols have an –OH group so the hydrogen attached to the oxygen in one molecule can hydrogen bond to an oxygen atom in another alcohol molecule as shown in Figure 12.5. However, in the alkanes there are only carbon and hydrogen atoms, so no hydrogen bonding is possible. Only dispersion forces can exist between alkane molecules.

Since hydrogen bonds are stronger than dispersion forces, and because there will be dispersion forces present between the alcohol molecules as well, the alcohols have much higher melting and boiling points than the parent alkanes.

The increasing strength of the dispersion forces as successive –CH<sub>2</sub>– groups are added to the molecule best explains the gradual increase in boiling points of the alcohols. The hydrogen bonding interaction will be much the same for all the alcohols as they contain only one alcohol functional group. However, the strength of dispersion forces increases with increasing number of electrons in the molecule. The alcohol molecules with larger molecular masses have more atoms present in the molecule and so have more electrons.

Alcohols with smaller molecular masses are soluble in water, but as molecular mass increases, the solubility of the alcohol in water decreases. After butanol, the alcohols are essentially insoluble in water.



**Figure 12.6** Interaction between alcohol and water molecules

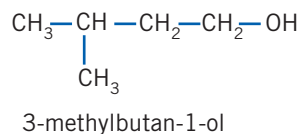
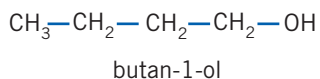
Figure 12.6 shows the hydrogen bonding that can occur between methanol and water molecules. Methanol dissolves in water because this hydrogen bonding is similar in strength to the hydrogen bonding between the water molecules and between the methanol molecules that must be disrupted in the dissolving process. However, for the larger alcohols such as pentan-1-ol, if they were to dissolve, the larger hydrocarbon chain would need to push many water molecules apart, thereby breaking the hydrogen bonds between these molecules. The small number of hydrogen bonds that form between the alcohol functional group on the alcohol and surrounding water molecules is not sufficient to make up for the bonds that have to be broken between water molecules. As a result, pentan-1-ol and similar longer chain alcohols will not dissolve in water. The few hydrogen bonds that form cannot overcome the energy required to break the water molecules apart to fit in the hydrocarbon chain of the alcohol.

## Types of alcohols

Alcohols are often classified as primary, secondary or tertiary. This classification is based on the number of carbon atoms (or hydrogen atoms) attached to the carbon atom to which the  $\text{-OH}$  group is bonded.

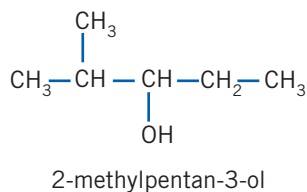
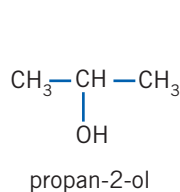
In a primary alcohol, one carbon atom and two hydrogen atoms are attached to the carbon atom to which the  $\text{-OH}$  group is bonded.

For example, two primary alcohols are:



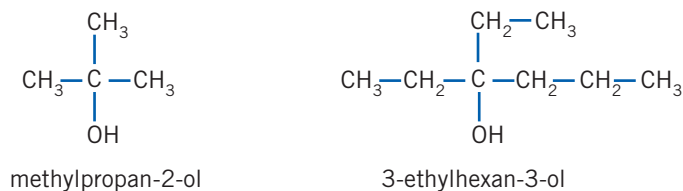
In a secondary alcohol, two carbon atoms and one hydrogen atom are attached to the carbon atom to which the  $\text{-OH}$  group is bonded.

For example, the following compounds are secondary alcohols:

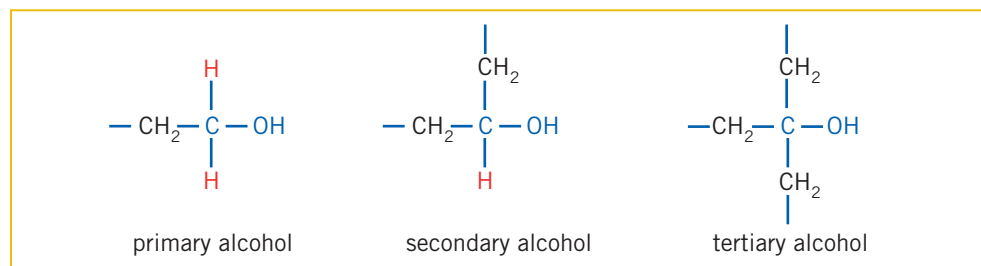


In a tertiary alcohol, three carbon atoms and no hydrogen atoms are attached to the carbon atom to which the  $\text{-OH}$  group is bonded.

Two examples of tertiary alcohols are:



The classification of alcohols as primary, secondary and tertiary is quite important, as each of these types of alcohol behaves in a different fashion chemically.



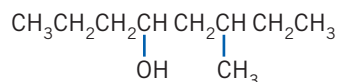
**Figure 12.7** The formulas show the relationship between the type of alcohol and the number of hydrogen and carbon atoms bonded to the carbon atom to which the  $-\text{OH}$  group is bonded.

The alcohols can show structural isomerism in the same way as the alkanes. For example, butan-1-ol (shown on the previous page) and methylpropan-2-ol (shown above) are isomers with the molecular formula  $\text{C}_4\text{H}_{10}\text{O}$ .

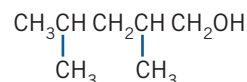
### \* Review exercise 12.1

1 Name the following alcohols according to IUPAC rules.

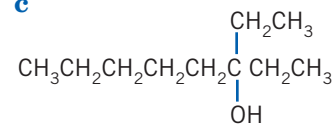
**a**



**b**



**c**



2 Give the structural formulas of the following compounds.

**a** ethanol

**b** butan-2-ol

**c** 3,3,4,4-tetramethylpentan-1-ol

**d** butane-1,2-diol

3 A group of organic compounds called ethers are isomeric with some alcohols. Ethers contain a  $\text{C}-\text{O}-\text{C}$  bond. The simplest ether has the formula  $\text{CH}_3\text{OCH}_3$ .

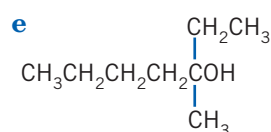
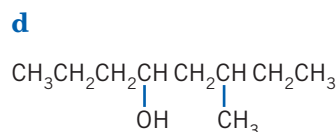
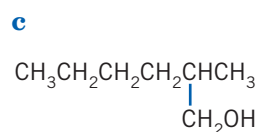
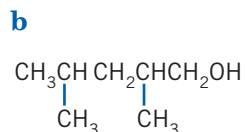
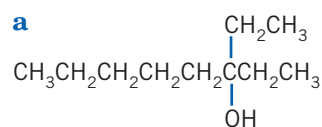
**a** Which alcohol is isomeric with this ether?

**b** Predict how the boiling point and water solubility of the alcohol in part a would compare with this isomeric ether. Justify your prediction.

4 Place the following three molecules in order of increasing boiling point and increasing solubility in water. Explain any similarities in the order of these compounds in the two lists.

- a  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$   
 b  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$   
 c  $\text{CH}_3\text{CH}_2\text{OCH}_3$

5 Identify the following alcohols as primary, secondary or tertiary.

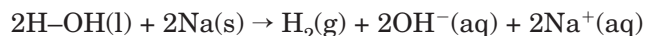


## 12.2 Reactions of alcohols

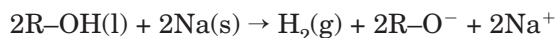
### Reaction with reactive metals

Reactive metals such as sodium and potassium react with water to produce a solution containing the hydroxide ion and liberating hydrogen gas.

For example:

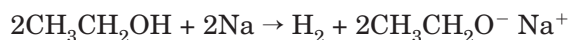


Alcohols behave in a similar fashion with these reactive metals, though not as vigorously as with water. In addition to hydrogen, the other product of the reaction is the alkoxide ion,  $\text{R}-\text{O}^-$ :



(R- represents a hydrocarbon chain.)

When sodium metal is added to ethanol, the products of the reaction are hydrogen and sodium ethoxide:



For alcohols with comparable molecular mass, the order of reactivity is primary > secondary > tertiary. This order of reactivity can be used as a qualitative measure of the type of alcohol group present in a molecule.

Also, as the hydrocarbon chain of the alcohol increases in length, the reactivity of the alcohol decreases as the likelihood of a successful collision between the alcohol functional group and the metal is reduced.



Figure 12.8 Sodium reacting with ethanol

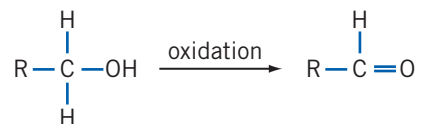
## Oxidation of alcohols

The two most common reactions of alcohols are oxidation and reaction to form another group of compounds called esters.

### Formation of aldehydes

A primary alcohol can be oxidised to form a compound containing the aldehyde functional group or the carboxylic acid functional group, depending on the experimental conditions used for the oxidation.

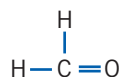
Aldehydes can be prepared by the oxidation of primary alcohols. This reaction can generally be represented as:



The aldehyde functional group is  $\begin{array}{c} \text{H} \\ | \\ -\text{C}=\text{O} \end{array}$  (or  $-\text{CHO}$ ) and it always must be at the end (or beginning) of a carbon chain.

Aldehydes are named using the suffix 'al' to replace the 'e' in the name of the alkane chain. The numbering of the carbon chain begins with the carbon atom of the aldehyde group.

The simplest aldehyde with one carbon atom is given the name methanal,  $\text{HCHO}$ :



Other examples of aldehydes are given in Figure 12.9.

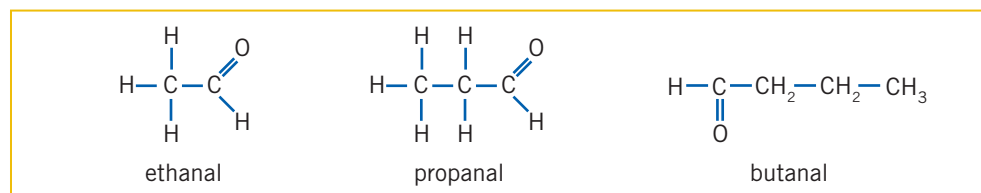
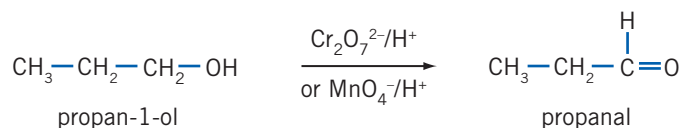


Figure 12.9 Some simple aldehydes

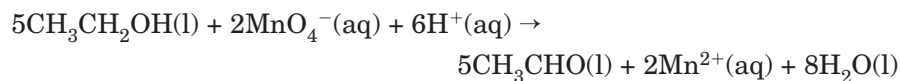
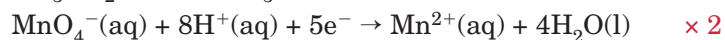
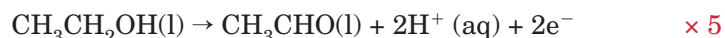
The oxidation of primary alcohols to aldehydes involves the reaction of the alcohol with an oxidising agent such as an acidified solution of potassium dichromate or an acidified solution of potassium permanganate with the aldehyde being carefully removed (often by distillation) from the reaction mixture as it is formed.

For example:



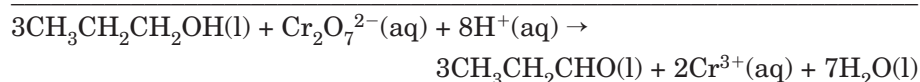
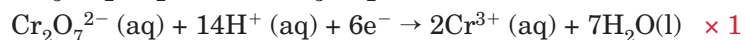
Since this is a redox reaction, it is possible to break the overall equation into the two component oxidation and reduction half-equations, as shown for ethanol and propan-1-ol on the following page.

- i The equation for the reaction of ethanol with an acidified solution of potassium permanganate, to form ethanal, is:



The observation for this reaction would be: the purple-coloured solution turns a very pale pink.

- ii The equation for the reaction of propan-1-ol with an acidified solution of potassium dichromate, to form propanal, is:



The observation for this reaction would be: the orange solution turns green. (The dichromate ion is an orange colour and the chromium ion,  $\text{Cr}^{3+}$ , is a green colour. The alcohol and aldehyde are colourless.)



Figure 12.10 Oxidation of ethanol by an acidified solution of potassium permanganate (a purple compound). The test tube on the left shows the mixture before reaction, the test tube on the right contains the mixture after the reaction.

### Formation of carboxylic acids

The aldehyde functional group can be oxidised further under the conditions used in the examples above and unless care is taken to remove the aldehyde as it is formed, it will react further to produce a compound containing another functional group—the carboxylic acid group.

Carboxylic acids contain the  $\begin{array}{c} \text{OH} \\ | \\ -\text{C}=\text{O} \end{array}$  functional group, which is sometimes written as  $-\text{COOH}$ , or  $-\text{CO}_2\text{H}$ .

As is the case with the aldehydes, the carboxylic acid functional group is always positioned on the end of a carbon chain and the carbon atom in the group is given the first number in the carbon chain.

A carboxylic acid is named by using the suffix 'oic acid' in the place of the 'e' in the name of the parent alkane. Some examples of carboxylic acids and their names are given in Figure 12.11. (According to the IUPAC recommendations, the carboxylic acid  $\text{CH}_3\text{COOH}$  may be known by either its trivial name, acetic acid, or its systematic name, ethanoic acid.)

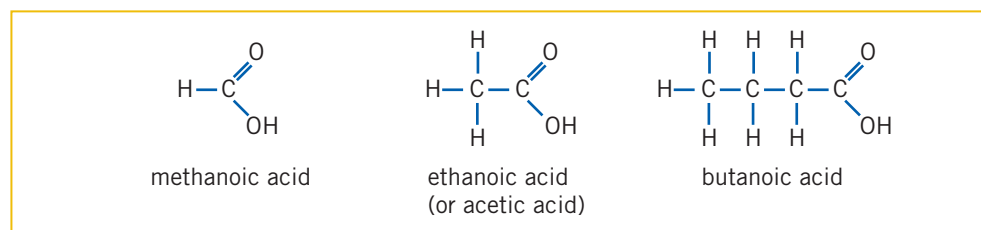


Figure 12.11 The structural formulas of some simple carboxylic acids

Carboxylic acids are prepared by the oxidation of primary alcohols or aldehydes, using acidified dichromate or permanganate solutions (Figure 12.12).





point of a carboxylic acid such as acetic acid can be explained by the formation of dimers (combinations of two molecules joined together), of the type shown in Figure 12.13, in the pure liquid. Also, in general, each carboxylic acid can form hydrogen bonds 'through' two of its atoms.

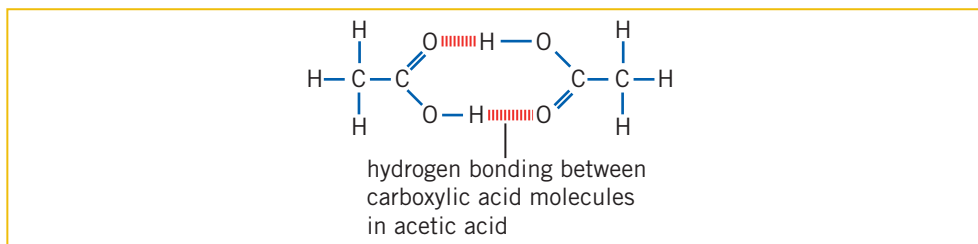


Figure 12.13 Hydrogen bonding between acetic acid molecules in the pure liquid

### Formation of ketones

In secondary alcohols, the  $\text{-OH}$  functional group is not on a terminal or end carbon atom. As a result it is not possible for these alcohols to be oxidised to form an aldehyde or carboxylic acid. Oxidation of secondary alcohols using the same conditions as those used for primary alcohols produces a new functional group—the ketone group.

Ketones contain the carbonyl functional group  $\text{>C=O}$ . Consequently, the ketone group will be found within the chain of carbon atoms and never on an end.

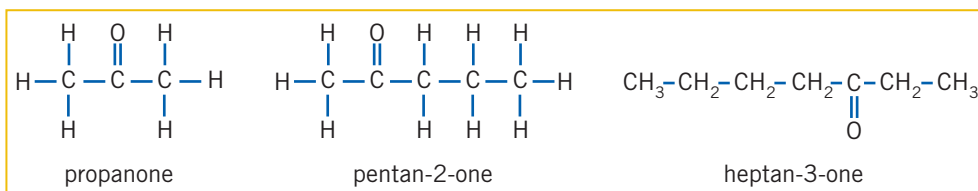
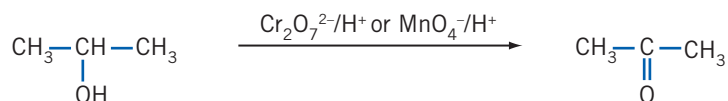


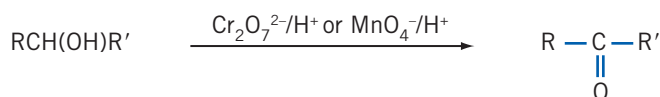
Figure 12.14 Some examples of ketones

Ketones are named by replacing the 'e' in the alkane chain with 'one'. The simplest ketone has three carbon atoms and is called propanone (sometimes also called acetone).

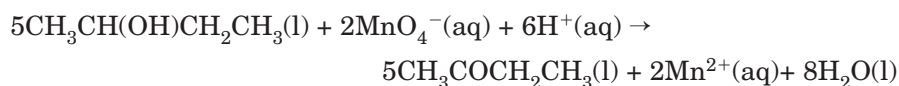
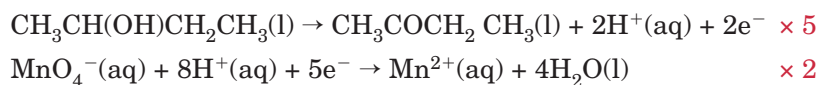
Ketones are formed from the oxidation of secondary alcohols, using acidified dichromate or permanganate solutions. For example:



or the general equation:



As shown earlier, the overall equation for the oxidation of an alcohol can be determined by first writing the two half-equations. For example, the equation for the oxidation of butan-2-ol, using acidified potassium permanganate solution, to form butanone is:

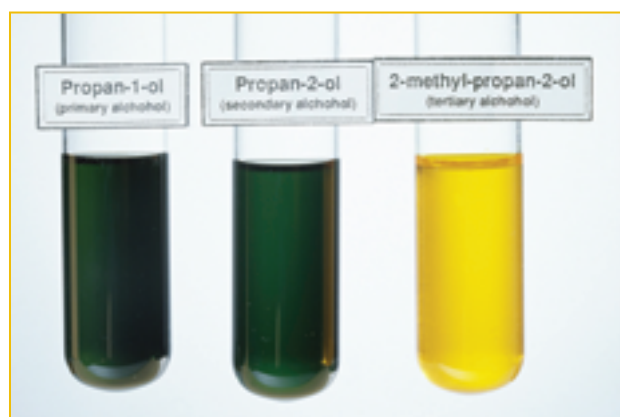


Ketones cannot be oxidised any further by acidified dichromate or permanganate solutions.

Finally, tertiary alcohols will not undergo oxidation with either acidified permanganate or dichromate solution. Table 12.2 summarises the oxidation reactions of alcohols.

**TABLE 12.2 OXIDATION OF ALCOHOLS**

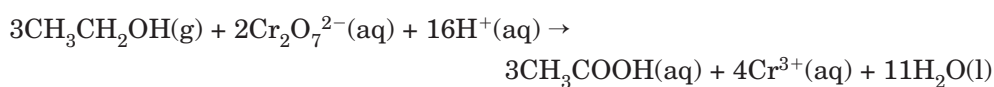
Alcohol type	Oxidant	Product(s)
Primary (RCH <sub>2</sub> OH)	Acidified dichromate or acidified permanganate solution	Mild conditions produce the aldehyde (RCHO), which can be distilled from the reaction mixture. After heating for a period of time, the carboxylic acid (RCOOH) is produced.
Secondary (RCH(OH)R')	Acidified dichromate or acidified permanganate solution	Formation of the ketone (RCOR')
Tertiary	Acidified dichromate or acidified permanganate solution	No reaction



**Figure 12.15** The contents of the test tubes show the result obtained by heating the three alcohols with the yellow-coloured acidified solution of dichromate. If a reaction occurs, the yellow–orange colour of the mixture changes to green due to formation of Cr<sup>3+</sup> ions.

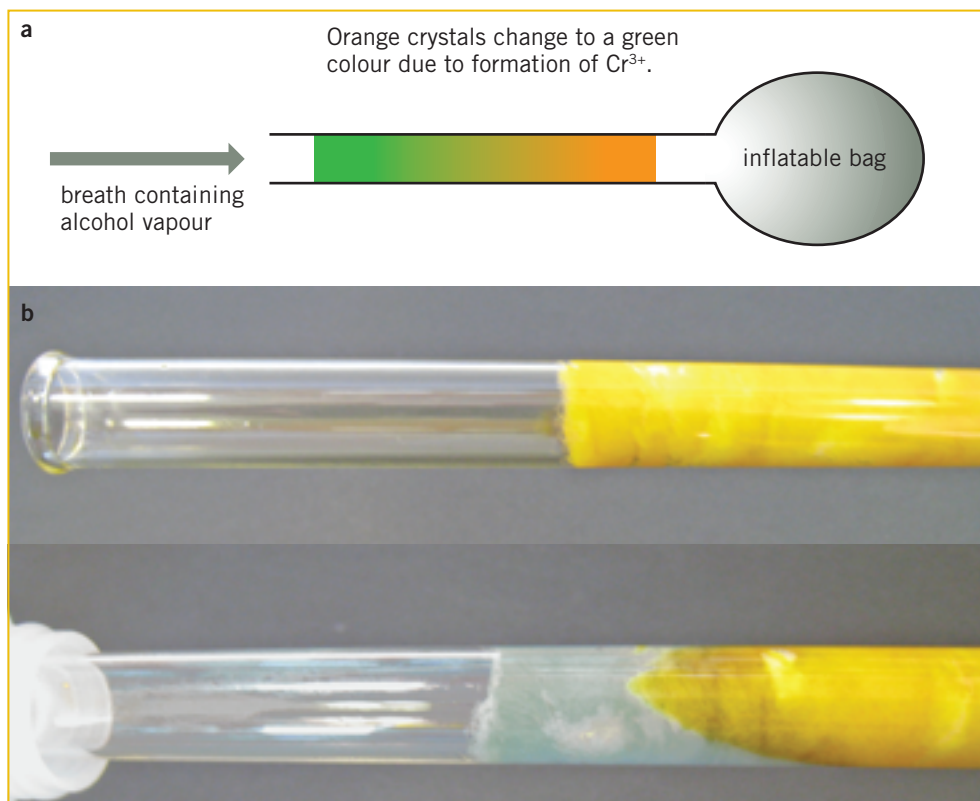
The oxidation of an alcohol with acidified potassium dichromate was the basis of the preliminary breathalyser test that was used in the past to detect the amount of alcohol (ethanol) in the blood of someone who had been drinking. There is a direct relationship between the amount of alcohol in the bloodstream and the amount of alcohol in air breathed out of the lungs. This relationship arises from the equilibrium between ethanol dissolved in the bloodstream and ethanol released as vapour into the lungs.

Early breathalysers consisted of a tube packed with orange potassium dichromate granules and a plastic bag at the end. As the suspect breathed through the tube to fill up the bag, if there was ethanol in the breath, the orange crystals would change to the green colour of chromium(III) ions:



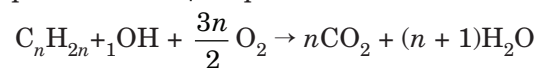
If the volume of exhaled breath is kept constant (by blowing up a bag to a fixed size), then the amount of green colour that forms in the tube of orange dichromate crystals is a direct measure of the amount of alcohol in the breath. If the amount of green colour that formed exceeded a particular distance along the tube then the person was considered to have a sufficiently high reading to warrant a more accurate blood alcohol test being performed.

Figure 12.16b shows the results of an experiment in which ethanol vapour is passed through a tube filled with potassium dichromate moistened with sulfuric acid.



**Figure 12.16** (a) Representation of an early breathalyser. (b) The dichromate in the tube before reaction with alcohol, then the dichromate after alcohol is blown into the tube

Alcohols also undergo oxidation when they are burnt in air or oxygen. The products of the reaction of an alcohol with excess air are carbon dioxide and water. A general equation for the complete combustion of an alcohol is:



**Figure 12.17** An ethanol burner. Some camp stoves such as Trangias also use ethanol (methylated spirits) as their fuel.



## \* Review exercise 12.2

1 Give the name and formula of the organic compound formed in each of the following reactions.

Reaction mixture	Name of product	Formula of product
a $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ is mixed with an acidified solution of potassium permanganate for a short time, and the product is then removed from the reaction mixture by distillation.		
b $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ is boiled with an acidified solution of potassium dichromate.		
c Hexan-3-ol is reacted with an acidified solution of sodium dichromate.		
d 2-Methylbutan-2-ol is boiled with a solution of acidified potassium permanganate.		
e $\begin{array}{c} \text{CH}_2\text{CH}_3 \\   \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COH} \\   \\ \text{CH}_3 \end{array}$ is heated with an acidified solution of potassium dichromate.		
f Pentan-3-ol is mixed with an acidified solution of potassium permanganate and the mixture is heated.		
g A piece of potassium is added to propan-2-ol.		

2 First write the two relevant half-equations, then derive the overall ionic equation for each of the following reactions (use structural formulas for the organic compounds).

- Propan-2-ol is heated with an acidified solution of potassium permanganate.
- Butan-1-ol is mixed for a short time with an acidified solution of sodium dichromate.
- Pentanal is heated with an acidified solution of potassium permanganate.

3 Hexan-1-ol, hexanal and pentanoic acid have approximately the same relative formula mass. Place these three compounds in order of increasing boiling point (lowest to highest) and justify your answer.

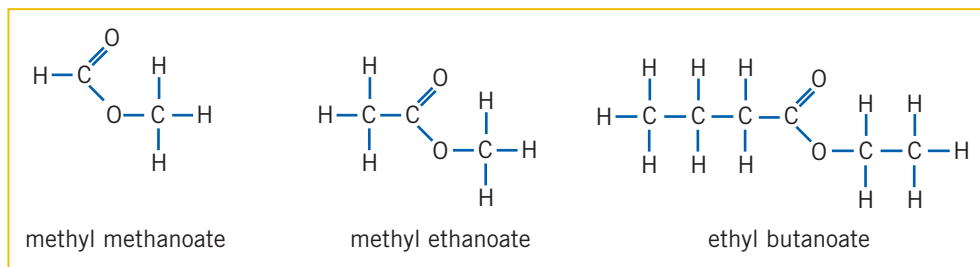
4 Write the equation for the complete combustion of butan-1-ol in excess air.

## 12.3 Esters

Esters are a group of compounds formed in the reaction between a carboxylic acid and an alcohol. They occur naturally in many fruits and are responsible for the 'fruity odour' of many of these. They are also present in fats and vegetable oils. Commercially, esters are used to make food flavours, perfumes, scents, industrial solvents, and as softening agents in the plastics industry.

The functional group present in an ester is  $\begin{array}{c} \text{—C—O—} \\ || \\ \text{O} \end{array}$  or  $\text{—COO—}$ .

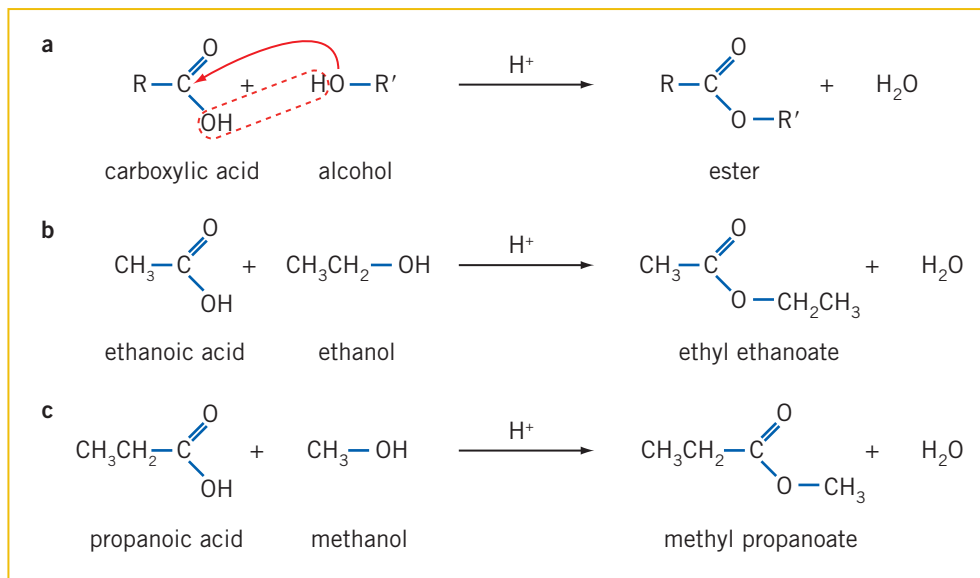
The carbon atom in the ester group can be bonded to a hydrogen atom or an alkyl group, while the oxygen atom is bonded to an alkyl group. Figure 12.18 shows some esters with their names. Try to work out how esters are named from the examples given here.



**Figure 12.18** Examples of simple esters

Esters are formed in the reaction between a carboxylic acid and an alcohol in the presence of an acid catalyst such as concentrated sulfuric acid. The mixture is normally heated for some time, during which a condensation reaction takes place. Such reactions involve the elimination of a water molecule as the acid combines with the alcohol. In this reaction, the hydrogen from the alcohol group combines with the OH from the carboxylic acid to form water.

Figure 12.19a shows the general reaction between a carboxylic acid represented as RCOOH and an alcohol represented as R'OH. The dotted oval drawn around the H on the alcohol and the OH on the carboxylic acid shows the atoms that join together to form the water molecule in this esterification process. The oxygen on the alcohol bonds with the CO carbon atom to form the ester functional group.

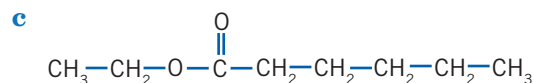
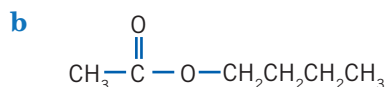
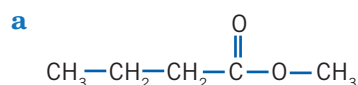


**Figure 12.19** Formation of an ester from a carboxylic acid and an alcohol: (a) general reaction, (b) formation of ethyl ethanoate, (c) formation of methyl propanoate

As can be gathered from the names of the esters above, the nomenclature for an ester is based on the first word being the alkyl group from the alcohol that reacts, and the last word being derived from the carboxylic acid by replacing the '-ic acid' with '-ate'. (The name of an ester comprises two words.)



2 Name the following esters.



3 Give the formulas of the organic compounds formed in the following reactions.

**a** Methyl ethanoate (acetate) is boiled with a solution of hydrochloric acid.

**b** Propyl butanoate is heated with a solution of sodium hydroxide.

4 The reaction of propene with mercuric acetate in the presence of water produces a compound, A, with the formula  $\text{C}_3\text{H}_8\text{O}$ . If propene is reacted with diborane ( $\text{B}_2\text{H}_6$ ) and then water, it produces a compound, B, with the same formula  $\text{C}_3\text{H}_8\text{O}$ .

Both A and B react with a solution of acidified potassium dichromate. A produces a colourless liquid, C, with the formula  $\text{C}_3\text{H}_6\text{O}$  and B produces a colourless liquid, D, with the formula  $\text{C}_3\text{H}_6\text{O}_2$ .

Compound D can react with both A and B in the presence of a trace amount of concentrated sulfuric acid to produce two different compounds with the same molecular formula.

**a** Name and draw the structural formulas of the organic compounds A, B, C and D.

**b** Draw the structural formulas of the two different compounds that D forms with A and B, identifying which comes from A and which comes from B.

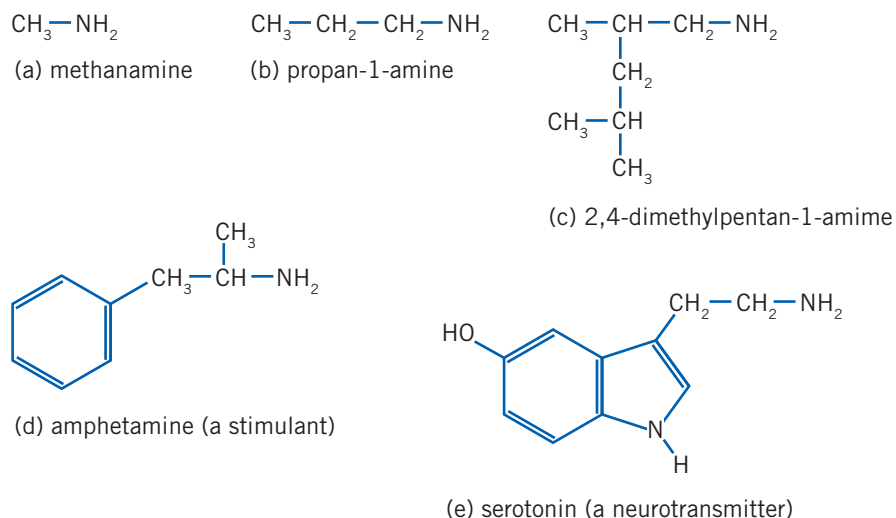
## 12.4 Primary amines and amino acids

From your previous studies of organic chemistry, it is not hard to conclude that carbon, hydrogen and oxygen are the three most common elements found in organic molecules. The fourth most common element is nitrogen. Nitrogen-containing organic compounds are particularly important in biological systems. Among the more important biologically active molecules containing nitrogen are DNA (deoxyribonucleic acid), proteins and various enzymes (which are actually proteins) responsible for catalysing the vast array of biologically important reactions. Many of the pharmaceuticals and drugs that we take also include nitrogen-containing organic compounds.

### Primary amines

Primary amines contain the  $\text{—NH}_2$  functional group where the nitrogen is bonded directly to a carbon atom. Figure 12.21 shows a range of primary amines, some of which are biologically active (but whose structures you do not need to know).



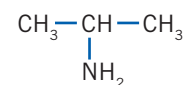


**Figure 12.21** Examples of primary amines

Primary amines are named in a similar fashion to alcohols. In Figure 12.21 the name given to structure (b) is obtained by finding the longest chain containing the amine functional group, removing the 'e' from the alkane and replacing it by 'amine' and then inserting a number in front of 'amine' so that the functional group has the smallest number in the chain. In structure (c), the longest carbon chain has five carbon atoms. The amine functional group is assigned the smallest number on the chain and the two methyl side chains are then numbered relative to the amine group.

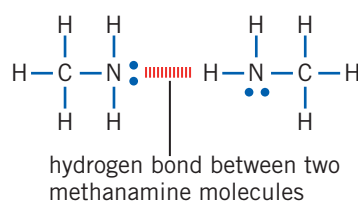
If the amine functional group is not on a terminal carbon atom in the chain, the number in front of 'amine' indicates the position of the functional group.

In the molecule represented by the structural formula on the right, the amine functional group is on the second carbon atom in the chain, so the name given to this molecule is propan-2-amine.



(Propan-2-amine is still a primary amine even though the functional group is not on a terminal carbon atom. Secondary and tertiary amines have different structures and are not considered in this course. IUPAC have recommended a different name for propan-2-amine (and similar structures with  $\text{NH}_2$  groups attached along a chain) to reinforce the idea that it is a primary amine. However, in this course this alternative nomenclature will not be considered.)

Amines are structurally related to ammonia and, like ammonia, are polar molecules, capable of hydrogen bonding to one another and other polar molecules containing oxygen, nitrogen or fluorine.



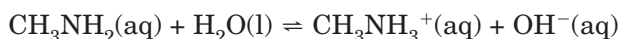
**Figure 12.22** Hydrogen bonding between amine functional groups

The electronegativity difference between nitrogen and hydrogen is less than that between oxygen and hydrogen, so the hydrogen bonding interaction between

amines is weaker than that between alcohols. The relative molecular masses of propane, ethanol and ethanamine are about the same. However, the boiling points for these three compounds are  $-42^{\circ}\text{C}$ ,  $78^{\circ}\text{C}$  and  $17^{\circ}\text{C}$ , respectively. The hydrogen bonding in the amine ensures that it has a much higher boiling point than the alkane of comparable molecular mass. However, the presence of weaker hydrogen bonding interactions between the amine molecules compared to the alcohol molecules results in ethanamine having a lower boiling point than ethanol. Amines with lower molecular masses are usually soluble in water due to their ability to hydrogen bond to the abundant water molecules. However, as was the case with the alcohols, as the molecular mass increases, the non-polar hydrocarbon chain dominates the physical properties of the amine and solubility decreases.

In the same way that ammonia has a pungent smell, so also do the amines, particularly those of lower molecular mass that are more volatile. The smell of rotting animals is often associated with the presence of amines. The common name of butane-1,4-diamine is putrescine, while cadaverine is the name given to pentane-1,5-diamine.

Ammonia is a weak base, and so are the primary amines. Aqueous solutions of amines are basic as a result of a hydrogen atom on a water molecule being donated to the nitrogen atom on the amine. For example, the equation for the reaction of methanamine with water is:



Many prescribed drugs are amines. Because they are often insoluble in water, getting them into body fluids such as blood plasma is difficult. However, by making use of the basic properties of the amine, the molecule can be converted to a soluble salt by reaction of the amine with an acid such as hydrochloric acid.

### $\alpha$ -Amino acids

The name 'amino acid' suggests that these compounds contain an amine and a carboxylic acid functional group. The designation ' $\alpha$ ' is used to show that the two functional groups are attached to the same, terminal carbon atom. The general structural representation of  $\alpha$ -amino acids is shown in Figure 12.23.

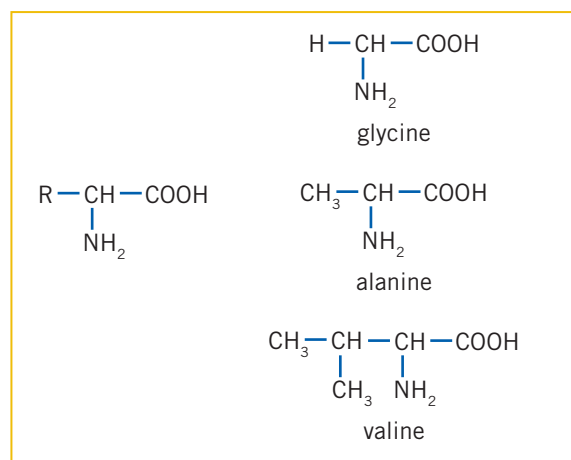


Figure 12.23 General formula of an  $\alpha$ -amino acid and three examples

Amino acids are the individual components (monomers—see Chapter 13) from which proteins are made. While the number of possible  $\alpha$ -amino acids that can be made synthetically is enormous, only 20 are used in nature to construct the proteins and enzymes that are essential for life.



Having both an acidic and a basic functional group means that  $\alpha$ -amino acids are amphoteric—they can behave as either an acid or a base. At high pH values (basic solutions), the carboxylic acid functional group donates its hydrogen ion to produce the carboxylate ion functional group,  $\text{COO}^-$ . At low pH values (acidic solutions), the amine functional group accepts a hydrogen ion to become  $\text{NH}_3^+$ .

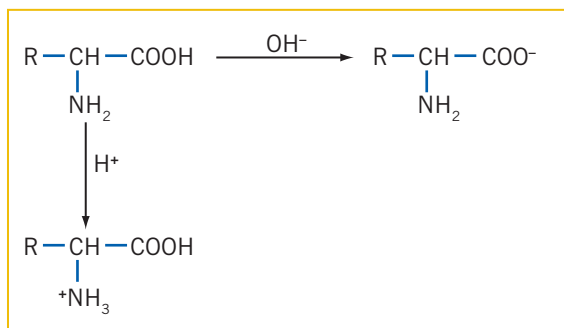


Figure 12.24 Amphoteric nature of  $\alpha$ -amino acids

At room temperature, amino acids are all solids with relatively high melting and boiling points, characteristic of ionic compounds. They are also relatively soluble in water. These observations lead to a conclusion that  $\alpha$ -amino acids in the solid state, as well as in aqueous solution, do not have the amine and carboxylic acid groups present as  $\text{NH}_2$  and  $\text{COOH}$ , but rather their ionic forms,  $\text{NH}_3^+$  and  $\text{COO}^-$ . In Figure 12.25 this ionic form is represented. The general name given to these compounds that have a positive charge on one atom and a negative charge on another is zwitterion. There are no un-ionised  $\alpha$ -amino acids.

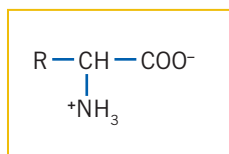


Figure 12.25 Zwitterion form of  $\alpha$ -amino acids

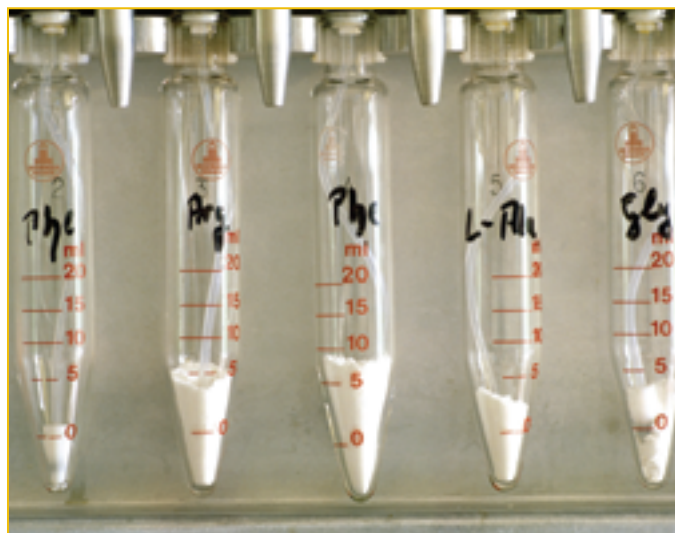


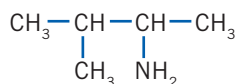
Figure 12.26 Glass tubes containing powdered amino acids used during biological research (from left phenylalanine, arginine, phenylalanine, alanine and glycine)

This characteristic of all amino acids means that not only are they amphoteric, but they are also buffers.

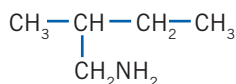
## \* Review exercise 12.4

- 1 Draw the structural formula for each of the following primary amines.
  - a octan-1-amine
  - b 2-methylbutan-2-amine
  - c pentane-1,5-diamine
- 2 There are four primary amines with the formula  $C_4H_{11}N$ . Draw and name each one.
- 3 Name the following primary amines.

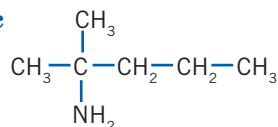
a



b



c



- 4 Using the information in Figure 12.23, draw the structure of glycine in a solution with the following pH values.
  - a pH 10
  - b pH 2
  - c pH 7
- 5
  - a Using the structure of valine given in Figure 12.23, draw the zwitterion form of this amino acid.
  - b What is the evidence for this form of the molecule in the solid state?

## 12.5 Determination of the structural formula of an unknown organic compound



A possible structural formula of an unknown organic compound can be determined in the following way:

- i The qualitative composition is determined experimentally, i.e. the functional groups present are identified.
- ii The quantitative composition is determined experimentally.
- iii The empirical formula is calculated from the quantitative composition.
- iv The relative molecular mass is determined experimentally.
- v The molecular formula is determined from the empirical formula and the molecular mass.
- vi Using data from points i and v, a possible structural formula can be determined.



### → Example 12.1

A compound of C, H and O is burnt in excess oxygen.

- a If 1.243 g of the compound produces 2.48 g of carbon dioxide and 1.01 g of water, find the empirical formula.
- b If 0.524 g of the compound occupies 0.148 L in the gaseous state at 20°C and 98.6 kPa, find the molecular formula.

*continued*

- c The compound dissolves in sodium hydrogencarbonate solution, evolving carbon dioxide. Suggest possible structural formulas.
- d If the compound had not dissolved in the sodium hydrogencarbonate solution, what would be the possible structural formulas?

→ **Solution**

- a Calculation of the empirical formula:

$$\begin{aligned} n(\text{CO}_2) &= \frac{m(\text{CO}_2)}{M(\text{CO}_2)} \\ &= \frac{2.48}{44.01} = 0.05635 \text{ mol} \\ &= \text{mole of C present in the compound} \end{aligned}$$

$$\begin{aligned} n(\text{H}_2\text{O}) &= \frac{m(\text{H}_2\text{O})}{M(\text{H}_2\text{O})} \\ &= \frac{1.01}{18.016} = 0.05606 \text{ mol} \end{aligned}$$

1 mol of  $\text{H}_2\text{O}$  contains 2 mol of H atoms, so

amount of H present in the compound =  $2 \times 0.05606 = 0.1121$  mol

mass of C present in compound =  $0.05635 \times 12.01 = 0.6768$  g

mass of H present in compound =  $0.1121 \times 1.008 = 0.1130$  g

i.e. mass of O present =  $1.243 - (0.6768 + 0.1130) = 0.4532$  g

$$n(\text{O}) \text{ present} = \frac{m(\text{O})}{M(\text{O})} = \frac{0.4532}{16.00} = 0.02832 \text{ mol}$$

	C	H	O
amount in mol	0.05635	0.1121	0.02832
	$\frac{0.05635}{0.02832}$	$\frac{0.1121}{0.02832}$	$\frac{0.02832}{0.02832}$
	= 1.99	3.96	1
	$\approx 2$	4	1

i.e. **empirical formula is  $\text{C}_2\text{H}_4\text{O}$**

- b Calculation of the molecular formula:

$$PV = nRT$$

$$n(\text{compound}) = \frac{PV}{RT} = \frac{98.6 \cdot 0.148}{8.315 \cdot 293.1} = 0.005988 \text{ mol}$$

$$n(\text{compound}) = \frac{m(\text{compound})}{M(\text{compound})}$$

$$\text{molar mass of compound} = \frac{0.524}{0.005988} = 87.5 \text{ g mol}^{-1}$$

$$\text{molecular formula} = (\text{empirical formula}) \times n = (\text{C}_2\text{H}_4\text{O}) \times n$$

$$\text{molecular mass} = \text{formula mass} \times n$$

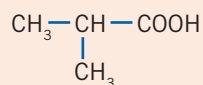
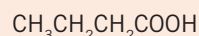
$$\text{i.e. } 87.5 = (24 + 4 + 16) \times n = 44 \times n$$

$$n = \frac{87.5}{44} \approx 2$$

The **molecular formula** is  $(\text{C}_2\text{H}_4\text{O})_2$  or  $\text{C}_4\text{H}_8\text{O}_2$ .

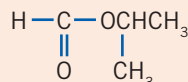
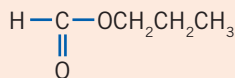
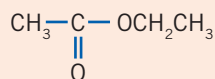
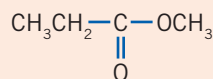
- c Acids react with hydrogencarbonates to form carbon dioxide, so the compound must be a carboxylic acid, that is, it must contain a  $-\text{COOH}$  group.

Possible formulas are:



- d** If the compound had not reacted with  $\text{NaHCO}_3$ , and yet it contains two oxygen atoms, it must be an ester, i.e. contain the group  $-\text{COO}-$ .

Possible formulas are:



### \* Review exercise 12.5

- 1** An organic amine contains the elements carbon, hydrogen and nitrogen only. It was found to contain 54.5% carbon and 13.7% hydrogen by mass. A  $0.106 \text{ mol L}^{-1}$  solution of the amine was prepared. 20.00 mL of this solution was neutralised completely by 23.49 mL of  $0.181 \text{ mol L}^{-1}$  HCl solution.
- Calculate the empirical formula of the amine.
  - Using the titration data, determine the number of amine groups in each molecule of the amine.
  - Determine the molecular formula of the amine.
  - Draw two possible structural formulas for the amine.
- 2** An organic compound on analysis is found to contain 40.0% carbon and 6.67% hydrogen by mass. The remaining element is oxygen. 0.24 mole of the compound has a mass of 14.4 g.
- Determine the empirical and molecular formulas of the compound.
  - Draw and name all of the possible structures for this compound.
- 3** A compound obtained from the hydrolysis of protein with hydrochloric acid is subjected to analysis.
- 2.2274 g of the compound, on complete combustion, produced 3.301 g of carbon dioxide and 1.576 g of water.
- A further 1.782 g of the compound is reacted with sulfuric acid to convert any nitrogen in the compound to  $\text{NH}_4^+$ . This solution containing ammonium ions is then heated with a sodium hydroxide solution to drive off ammonia. The vapour from this reaction is passed into 100.0 mL of  $0.510 \text{ mol L}^{-1}$  HCl. The excess HCl was then titrated with  $1.211 \text{ mol L}^{-1}$  potassium hydroxide and required 25.60 mL to reach the methyl orange end point.
- The only other element that could be present in the compound is oxygen. From this information, determine the empirical formula of the compound.
  - Assuming the empirical formula is also the molecular formula, and knowing the building blocks of protein, suggest a likely structure for this compound.

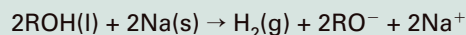
## MAJOR IDEAS

- A functional group is an atom or a group of atoms that determines the chemical and, in part, physical properties of a molecule.
- The formulas, nomenclature and physical properties of organic compounds with different functional groups are given in the table below.

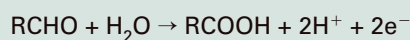
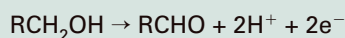
Type of compound	Functional group	IUPAC naming	Main intermolecular forces	Solubility	Boiling points
Alcohol	R-OH	Suffix of 'ol'	Hydrogen bonding	Soluble in water*	Relatively high
Aldehyde	R-CHO	Suffix of 'al'	Dipole-dipole forces	Slightly soluble	Higher than hydrocarbons, lower than alcohols
Ketone	R-CO-R'	Suffix of 'one'	Dipole-dipole forces	Slightly soluble	Similar to aldehydes
Carboxylic acid	R-COOH	Suffix of 'oic acid'	Hydrogen bonding	Soluble in water*	Higher than alcohols
Ester	R-COO-R'	Two words, alkyl then parent name ending in 'oate'	Dipole-dipole forces	Slightly soluble	Higher than hydrocarbons, lower than alcohols
Amine	R-NH <sub>2</sub>	Suffix of 'amine'	Hydrogen bonding	Soluble in water*	Lower than alcohols
Haloalkane	R-X	Prefix of 'chloro', for example	Dispersion and dipole-dipole forces	Not very soluble in water, soluble in non-polar solvents	Low

\*The solubility of the compounds in water decreases with increasing chain length.

- There are three types of alcohols—primary, secondary and tertiary.
  - In a primary alcohol, one carbon atom and two hydrogen atoms are attached to the carbon atom to which the -OH group is bonded, e.g. CH<sub>3</sub>CH<sub>2</sub>OH.
  - In a secondary alcohol, two carbon atoms and one hydrogen atom are attached to the carbon atom to which the -OH group is bonded, e.g. CH<sub>3</sub>CH(OH)CH<sub>3</sub>.
  - In a tertiary alcohol, three carbon atoms and no hydrogen atoms are attached to the carbon atom to which the -OH group is bonded, e.g. (CH<sub>3</sub>)<sub>3</sub>COH.
- Alcohols react with sodium and potassium to form the alkoxide ion and hydrogen gas:



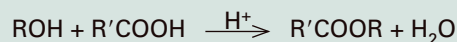
- Primary alcohols can be oxidised by acidified MnO<sub>4</sub><sup>-</sup> or Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> solutions to form aldehydes, which in turn can be oxidised to form carboxylic acids:



- Secondary alcohols can be oxidised to form ketones:

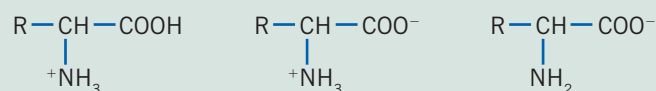


- Tertiary alcohols are not oxidised by acidified MnO<sub>4</sub><sup>-</sup> or Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> solutions.
- Alcohols react with carboxylic acid, in the presence of a catalyst, to form esters, in a condensation reaction:



- Esters undergo hydrolysis in the presence of acid or hydroxide to break the ester bond:
 
$$\text{R}'\text{COOR} + \text{H}_2\text{O} \rightarrow \text{R}'\text{COOH} + \text{ROH} \text{ (in acidic conditions)}$$

$$\text{R}'\text{COOR} + \text{H}_2\text{O} \rightarrow \text{R}'\text{COO}^- + \text{ROH} \text{ (in basic conditions)}$$
- Carboxylic acids are weak acids.
- Amines are weak bases.
- Amino acids are compounds that contain an amine group and a carboxylic acid group.
- For α-amino acids these two functional groups are bonded to the same C atom.
- α-Amino acids are amphoteric because they have both an acidic and a basic functional group.
- The general formulas of amino acids in acidic, basic and neutral solutions are:

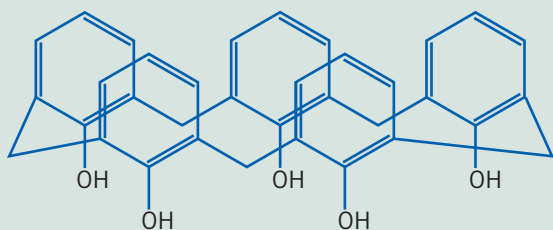


in acidic solutions    in neutral solutions    in basic solutions

- The form of the amino acid under neutral conditions is called a zwitterion. In the solid state, the amino acid is also in this form.
- Structural formulas of a particular compound can be determined from the empirical and molecular formulas of the compound.
- The empirical formula of a compound shows the elements present in the compound, in their simplest ratio.

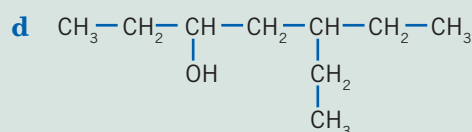
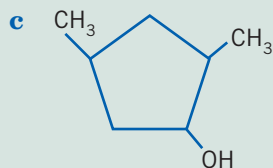
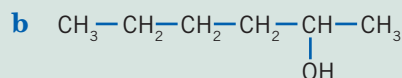
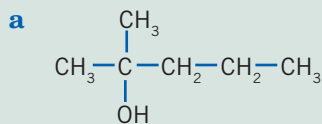
## QUESTIONS

- Using examples of your own choosing, explain the difference in the structure of primary, secondary and tertiary alcohols.
- Use a book of chemical data to tabulate the boiling points of the first nine straight chain alkanes and alcohols.
  - Plot the boiling points against the number of carbon atoms in the chain for both the alkanes and alcohols on the same graph.
  - Explain the similarities and differences between the two plots.
- There have been proposals to use molecules such as that shown below on dams to prevent evaporation.



Explain why such a molecule might be considered for this purpose.

- There are eight isomeric alcohols with the formula  $C_5H_{12}O$ . Draw and name all of these alcohols.
- Name the following alcohols:



- Draw the structural formula and name the alcohol that can be used to prepare each of the following. Describe the reaction conditions that would be chosen for each reaction.
  - pentan-3-one
  - 3,4-dimethylhexanal
  - 3-ethyloctanoic acid
  - ethyl ethanoate (or ethyl acetate)
- Propan-1-ol, propan-2-ol and methylpropan-2-ol are each heated with an acidified solution of potassium permanganate.
  - What observations would be made for each alcohol?
  - Write the individual half-equations and overall equation for any reaction that takes place.
  - Assuming the labels on the containers of each alcohol had been removed, how could you determine the identity of each?
- 2-Methylbutanal is warmed with a solution of acidified sodium dichromate. Copy and complete the table below.

Oxidation half-equation	
Reduction half-equation	
Overall equation	

- Analysis of an unknown compound shows that it contains 62.0% carbon and 10.4% hydrogen, by mass. The remaining element in the compound is oxygen.
  - Determine the empirical formula of this compound.
  - A compound with this empirical formula could be an aldehyde, a ketone, a carboxylic acid or an ester. Draw and name one example of each type of compound having this empirical formula.
  - When the unknown compound is warmed in the presence of sulfuric acid, it produces two new organic compounds. Which functional group must be present in the unknown compound? Write a general equation to justify your answer.
  - The two new compounds, A and B, obtained from the reaction in part c are separated from one another. When A is warmed with an acidified solution of potassium dichromate, it is converted into a compound that is identical to B. Using equations to justify your answer, determine the identity of the unknown compound from the beginning of this question.



**10** Predict the order of reactivity of butan-1-ol, 2-methylpropan-2-ol and butan-2-ol with sodium metal and explain how you reached this conclusion.

**11** A colourless liquid has the molecular formula  $C_6H_{12}O_2$ .

- What are the two general types of functional group that could be present in this substance?
- Describe a simple test that would allow you to distinguish between these two types of compound.

When the liquid was warmed with a solution of sulfuric acid, it decomposed into two different compounds, A and B, that were separated by fractional distillation.

- What must be the functional group present in the original liquid?

Compound A had a distinct smell of vinegar. When potassium metal was added to compound B, there was a very slow reaction with a small amount of gas produced. Compound B did not undergo any observable change when it was treated with an acidified solution of potassium permanganate.

- From this information suggest the structural formula and name for the original liquid at the start of the question.

**12** The field of green chemistry emerged in the early 1990s as the US Environmental Protection Agency urged the development of technologies to 'reduce or eliminate the use or generation of hazardous substances in the design, manufacture and use of chemical products.' A number of 'principles of green chemistry' have been developed including the following.

- Prevention of waste is better than treating or cleaning up waste after use.
- Chemical synthesis should be as efficient as possible with maximum incorporation of the reacting materials in the desired product.
- Synthetic methods should use and generate substances that have little or no toxicity.
- Use of solvents and other auxiliary materials in a chemical reaction should be minimised. If their use is necessary, these materials should not be harmful.
- Energy requirements for chemical reactions should be kept to a minimum.
- Catalytic agents should be used wherever possible.

Methyl esters are commercially important as products in the fragrance industry or as solvents for other chemical reactions.

The formation of methyl ethanoate from ethanol by conventional oxidation requires that the ethanol be heated with a solution of potassium dichromate acidified with sulfuric acid, followed by distillation of the ethanoic acid (acetic acid) from the reaction mixture. The ethanoic acid is then mixed with methanol and heated with methanol in the presence of a small amount of concentrated sulfuric acid in order to convert it to methyl ethanoate.

In 2007 the synthesis of methyl esters using gold/titanium dioxide catalysts was first reported. In this reaction the primary alcohol (for example, ethanol) is reacted with oxygen (air) in methanol as the solvent. The only other product of the reaction is water and the solid catalyst can be recovered from the reaction products.

- Write the two half-equations for the oxidation of ethanol to ethanoic acid in the presence of acidified potassium dichromate.
- What is the overall ionic equation for this reaction?
- What else is present in the reaction mixture after the reaction that is not already shown in the ionic equation?
- Write the equation for the conversion of ethanoic acid to methyl ethanoate.
- What else is present with the reaction product?
- Write the balanced equation for the conversion of ethanol to methyl ethanoate in the presence of methanol and oxygen using the gold-based catalyst.
- Using the green chemistry dot points above, compare the two methods of synthesis of methyl ethanoate with respect to their environmental sensitivity and sustainability.

**13** Describe a chemical test that would allow you to distinguish between the following:

- propanone and propanal
- propanone and propan-1-ol

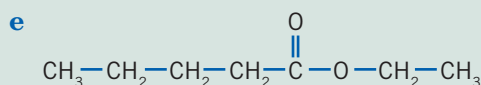
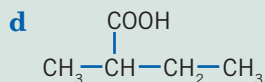
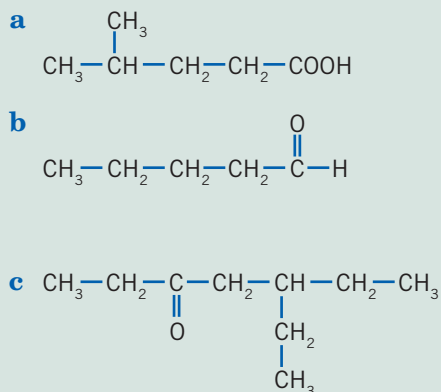
**14** Propanone can form hydrogen bonds to water but not with itself. Explain these observations.

**15** The boiling points of propanone and propan-2-ol are respectively  $56^\circ\text{C}$  and  $82^\circ\text{C}$ . The molecules have approximately the same relative molecular mass, so how can this difference be explained?

16 Draw the structures of the following molecules.

- a octanoic acid
- b 3,3-dimethylpentanoic acid
- c 2-methyl-3-ethylheptanal
- d butyl propanoate

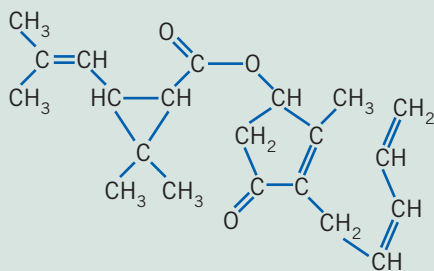
17 Name the following structures:



18 Butanoic acid and ethyl ethanoate are structural isomers. One of these compounds has a boiling point of 77°C and the other has a boiling point of 163°C.

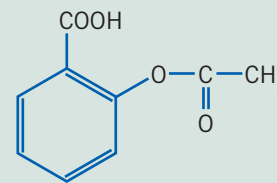
Draw the structural formula of each and identify which compound has which boiling point. Explain how you arrived at your conclusion.

19 The structure of the natural insecticide pyrethrum is shown below.



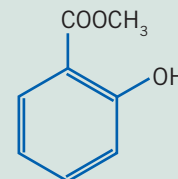
- a What are the two functional groups present in this molecule?
- b One of the compounds used to prepare a sample of pyrethrum is chrysanthemic acid, named after the species of chrysanthemum from which the insecticide is obtained. Draw the structure of chrysanthemic acid.

20 Aspirin has the structure shown in the diagram below.



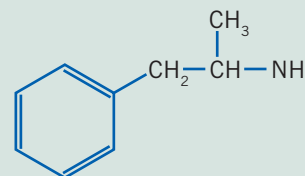
- a Identify the functional groups in the molecule.
- b The synthesis of aspirin usually involves the reaction between two compounds. From the structure given, propose structures for these two organic compounds.
- c Suggest the experimental conditions that might be used to prepare aspirin from these two organic compounds.

Deep Heat is an ointment that is used to relieve muscle pain. The structure of Deep Heat is shown below.



d Deep Heat and aspirin can be formed from the same organic compound. Using your answers from parts b and c, suggest how you would experimentally prepare Deep Heat.

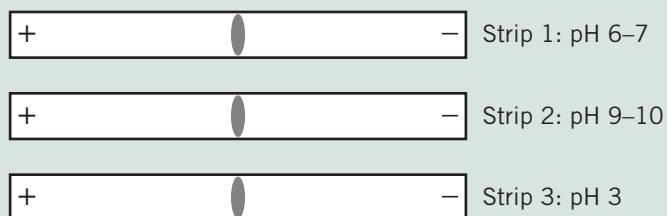
- 21 Butan-1-ol has a boiling point of 117°C while butan-1-amine boils at 78°C. Explain this difference.
- 22 Methanamine, ethanamine and propan-1-amine are very soluble in water. Why are these amines so much more soluble in water than the parent alkanes from which they are derived?
- 23 The structure of amphetamine was given in Figure 12.21 and is given again below.



- a The pH of the digestive juices of the stomach are usually between pH 1 and 2. Draw the structure of amphetamine as it would exist in the stomach.
- b How might this affect the solubility of amphetamine?

- 24** A mixture of hexan-1-ol and hexan-1-amine is placed in a beaker of water.
- Describe the appearance of the resulting mixture.
  - Dilute hydrochloric acid is added to the beaker and the pH drops to 2. Describe and explain any change that is observed when the contents of the beaker are stirred.
- 25** What does the prefix 'α' mean when referring to an α-amino acid?
- 26** Explain why all amino acids are solids at room temperature.
- 27** The structure of the α-amino acid glycine is drawn in Figure 12.23.
- What is wrong with this structural representation?
  - Use equations to show how glycine can act as a buffer in aqueous solution at around pH 7.
- 28** Electrophoresis is a process in which a substance is placed on a piece of porous paper soaked in an electrolyte. The paper has an electrode attached at each end, one of which is connected to the positive terminal of a battery and the other to the negative terminal of the battery. If the substance moves in one direction along the paper, it is possible to establish whether it has an overall positive or negative charge.

The amino acid alanine is placed on three strips of paper as shown in the diagram below. The first strip of paper has been soaked in an electrolyte at a pH 6–7. The second strip has been soaked in an electrolyte with a pH of 9–10 and the third strip has been soaked in an electrolyte with a pH of 3.



Describe how the alanine will move (if at all) on the three strips when an electric current flows, and explain the observations.

A circular inset image showing a microscopic view of biological structures, possibly plant stems or roots, with a prominent white, segmented structure in the foreground and reddish-brown structures in the background. The background of the entire page is a yellow gradient with a faint molecular structure pattern of white circles and lines.

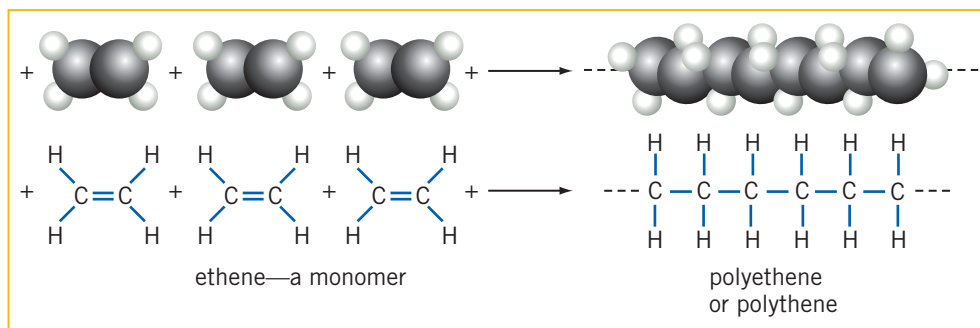
# 13

## Organic chemistry and modern lifestyles

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

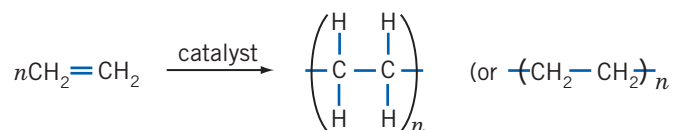
- describe the chemistry of soaps, detergents, amino acids and fats
- apply and explain the concepts of addition and condensation polymerisation, using examples of carbon-based polymers, polypeptides and silicones.





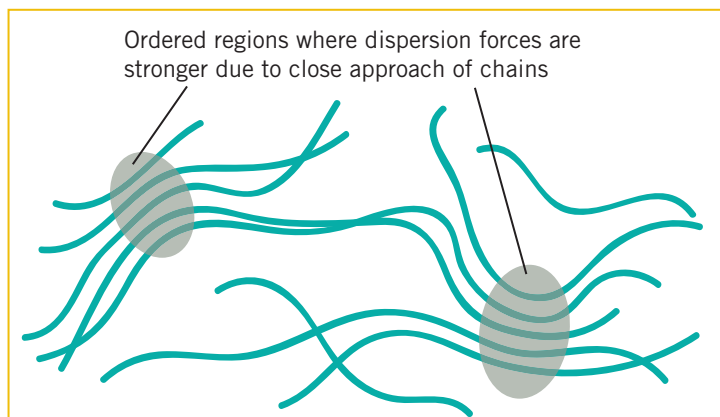
**Figure 13.2** Formation of polyethene from ethene by addition polymerisation

The mechanism of this polymerisation is complex and usually involves the use of a catalyst and a substance known as an initiator (or free radical initiator) to facilitate the reaction. The overall equation for the formation of polyethene from ethene is:



In this equation  $n$  is used to represent a large number of monomer units that have joined together. The value of  $n$  may range from hundreds to thousands. The brackets enclose the repeating unit in the polymer. The name of the addition polymer includes the prefix of 'poly' followed by the name of the monomer. If the monomer name consists of two or more words, it is shown in brackets.

The polymer consists of many chains of varying length and hence molecular mass. These chains interact through dispersion forces and also tangle together in much the same way as strands of spaghetti do in a bowl.



**Figure 13.3** Interactions between polymer chains. In some regions the individual strands can get very close and the dispersion forces are quite strong.

Depending on the conditions used and the catalyst chosen, the polymer chain can form in a predominantly linear fashion, with a relatively high molecular mass, and with little branching of the chain. Polyethene produced under these conditions is known as high density polyethene (HDPE) and it has high mechanical strength. HDPE is used to make bottles and pipes. The other form of this polymer, known as low density polyethene (LDPE), is used to make products like plastic bags, cling wrap and soft toys. LDPE is composed of polymer molecules with a large amount of chain branching. Figure 13.4 shows how the chains are arranged in LDPE and HDPE, illustrating that in the HDPE form the chains are able to approach much closer. This means that the dispersion forces are larger in HDPE than in LDPE.



The arrangement of branched chains in LDPE does not allow close approach of polymer chains, so the chains tend to be further apart. A common use of LDPE is in plastic film such as cling wrap.



The arrangement of unbranched chains in HDPE allows close approach of polymer chains so the chains are held together by stronger dispersion forces. A common use of HDPE is in food storage bottles, such as milk bottles.

**Figure 13.4** The arrangement of carbon chains in low and high density polyethene

There are a number of other addition polymers of commercial importance including poly(vinyl chloride) (PVC), polystyrene, polypropene and poly(methyl methacrylate). Table 13.1 shows the monomer and the repeating unit of the polymer for each of these substances.

**TABLE 13.1** COMMERCIALY IMPORTANT ADDITION POLYMERS

Polymer	Formula and name of monomer	Formula of polymer	Examples of uses
Poly(vinyl chloride), PVC	$\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{Cl} \end{array}$ <p>Vinyl chloride (chloroethene)</p>	$\left( \begin{array}{c} \text{H} & \text{H} \\   &   \\ -\text{C} & - & \text{C}- \\   &   \\ \text{H} & \text{Cl} \end{array} \right)_n$	Pipes, cable insulation, water tanks
Polypropene	$\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{CH}_3 \end{array}$ <p>Propylene (propene)</p>	$\left( \begin{array}{c} \text{H} & \text{H} \\   &   \\ -\text{C} & - & \text{C}- \\   &   \\ \text{H} & \text{CH}_3 \end{array} \right)_n$	Rope, carpet, plastic parts for cars
Poly(methyl methacrylate)	$\begin{array}{c} \text{H} & & \text{CH}_3 \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{COOCH}_3 \end{array}$ <p>Methyl methacrylate (methyl 2-methylpropen-2-olate)</p>	$\left( \begin{array}{c} \text{H} & \text{CH}_3 \\   &   \\ -\text{C} & - & \text{C}- \\   &   \\ \text{H} & \text{COOCH}_3 \end{array} \right)_n$	Plexiglass, paints
Polystyrene	$\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{C}_6\text{H}_5 \end{array}$ <p>Styrene (phenylethene)</p>	$\left( \begin{array}{c} \text{H} & \text{H} \\   &   \\ -\text{C} & - & \text{C}- \\   &   \\ \text{H} & \text{C}_6\text{H}_5 \end{array} \right)_n$	Insulation, packaging



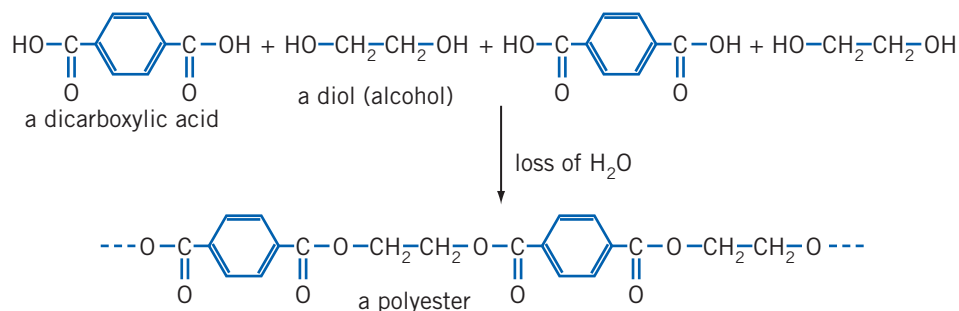
Figure 13.5 Teflon-coated frying pan

## Condensation polymerisation

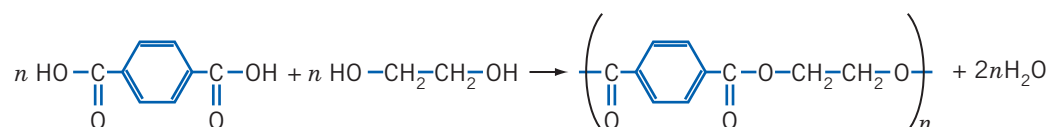
The second general type of polymerisation involves the reaction between monomers that each have two reactive functional groups. When the functional groups on two adjacent monomer molecules react, a larger molecule is formed and a small, stable molecule such as water is eliminated; hence, the name condensation. The reaction takes place in a stepwise fashion but at each stage in the polymerisation there are still two reactive functional groups present at either end of the growing chain.

The reactive functional groups usually involved are carboxylic acid and alcohol or carboxylic acid and amine. The carboxylic acid and alcohol groups combine to form an ester and ultimately a polyester. An amide ( $-\text{NH}-\text{CO}-$ ) is formed when carboxylic acid and amine groups react.

Terylene is an example of a condensation polymer formed from the reaction of one monomer containing two carboxylic acid functional groups and another molecule containing two alcohol functional groups:



A more general representation of the polymerisation is:



The polymer formed in this reaction is called poly(ethylene terephthalate) (PET), more commonly known as terylene. It is an example of a large array of condensation polymers called polyesters.

Nylon belongs to another group of important synthetic polymers known as polyamides. These polymers are formed from the reaction between a dicarboxylic

## CHANCE FAVOURS THE PREPARED MIND

While working on the production of refrigerants in 1938, Roy Plunkett noted that a tank of gaseous tetrafluoroethene,  $\text{CF}_2=\text{CF}_2$ , which was meant to be full, produced no gas when the valve was opened. However, the weight of the tank suggested that the tetrafluoroethene should still be present.

Plunkett sawed the tank in half and discovered that the inside was coated with a white, waxy substance that was extremely unreactive even to the most corrosive of substances known. What Plunkett had discovered, by accident, was the polymer of tetrafluoroethene. We know this today as Teflon.





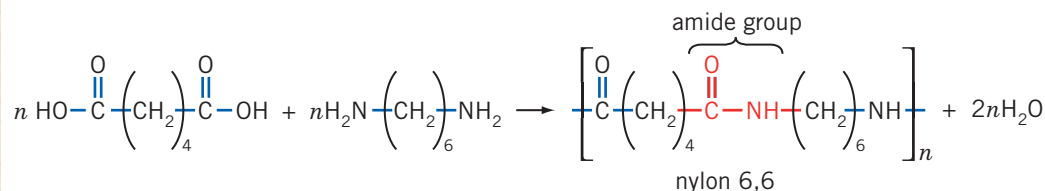
Figure 13.6 Recycling symbols on some containers

## CODE BREAKERS—RECYCLING PLASTIC

On the bottom of many of the plastic containers we use, there is a triangle made from three 'chasing arrows'. Inside the triangle is a number and below the triangle, a letter abbreviation is given (Figure 13.6). The number and abbreviation identify which plastic has been used to make the container and assists in sorting the containers for recycling. The lower the number the easier it is to recycle the container.

Number	Abbreviation	Polymer type
1	PETE (or PET)	poly(ethylene terephthalate)
2	HDPE	high density polyethene
3	V	poly(vinyl chloride) (unplasticised (UPVC) or plasticised (PPVC))
4	LDPE	low density polyethene
5	PP	polypropene
6	PS	polystyrene
7	OTHER	others including nylon and acrylic

acid and a diamine. For example, hexanedioic acid reacts with hexane-1,6-diamine to form nylon 6,6:



The '6,6' in the name for nylon refers to the fact that this form of nylon is made from two monomers each with six carbon atoms in the molecule.

During the manufacture of nylon, the fibres are stretched to assist in the formation of hydrogen bonds between the oxygen of the C=O group on one strand and the hydrogen of the N-H group on an adjacent strand. This increases the strength of the fibres that are formed in the process.

## Natural polyamides—proteins

Amino acids have at least two reactive functional groups in each molecule. As such, these molecules can also form condensation polymers. In living things the naturally occurring amino acids polymerise to form proteins.

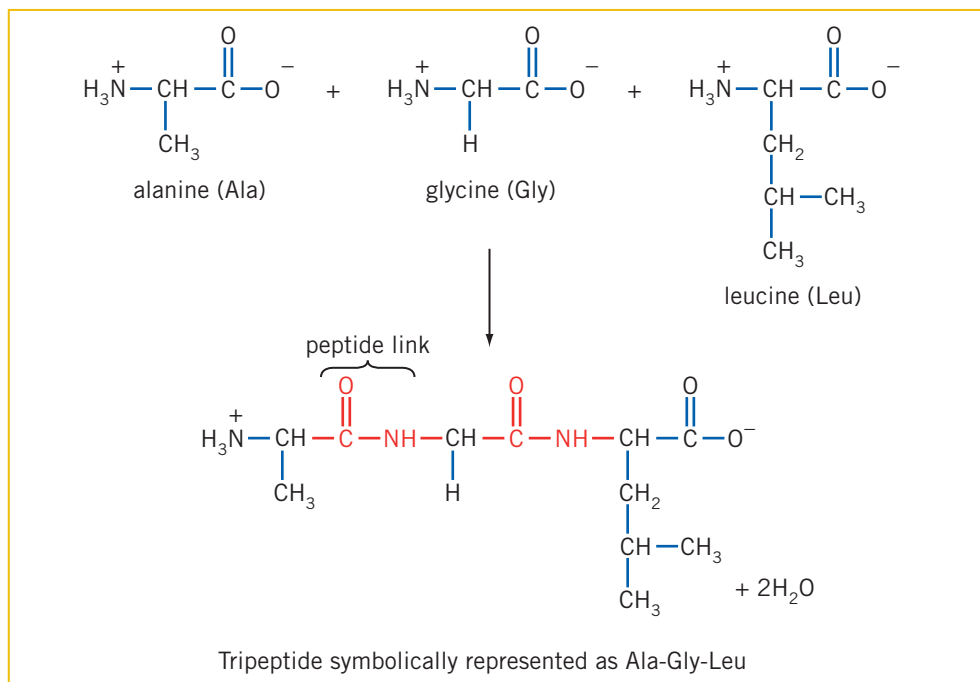
About 50% of the dry weight of every living cell is protein. It is present in skin and muscle and is the major structural component of animal tissue. In addition, proteins are the biological catalysts, or enzymes, that control the chemistry of life.

There are 20 different monomers or amino acids that can combine to form a protein, so the number of possible combinations of these, in a protein chain that might have hundreds or thousands of amino acid components (these components are referred to as amino acid residues), is huge.

The link that forms between the amine functional group of one amino acid and the carboxylic acid functional group of another is an amide group. However, in biological systems these are also called peptide links. When amino acids combine, they form polypeptides and ultimately, when the molecular mass is high enough, proteins. Figure 13.8 shows the combination of three different amino acids to form a tripeptide.



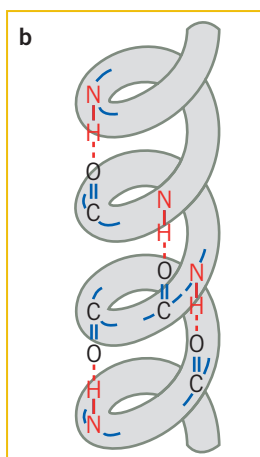
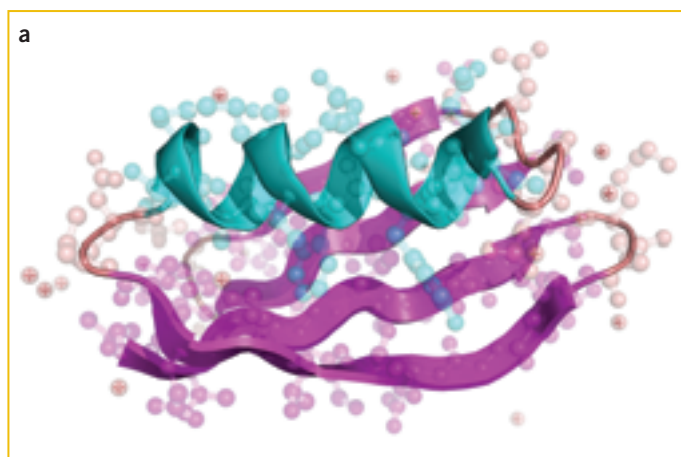
Figure 13.7 Making nylon. The nylon fibre forms at the interface between the two solutions containing the diamine and the dicarboxylic acid.



**Figure 13.8** Formation of a tripeptide from the reaction between alanine, glycine and leucine. Note that there are several other combinations of the three amino acids that could produce a tripeptide.

The sequence of amino acids in the backbone of a protein is called the primary structure of the protein. The primary structure establishes the nature or identity of the particular protein. The amide functional groups in the polypeptide chain of the protein can interact with one another by hydrogen bonding between the oxygen of a C=O group in one part of the chain and the hydrogen of a N-H group elsewhere in the chain. This hydrogen bonding interaction between different parts of the chain results in the secondary structure of the protein, which is often observed as helical or pleated structures (see Figure 13.9).

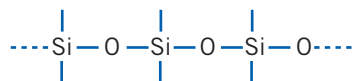
In addition to the primary and secondary structures, proteins also have a tertiary structure that results in a unique folding of the molecule. Part of this tertiary structure is represented in the folding shown in Figure 13.9a. Some proteins have a quaternary structure arising from the interaction of two or more protein structures.



**Figure 13.9** (a) A computer-generated model of a protein chain. The 'ball-and-stick' parts of the chain represent the primary structure. The aqua and pink regions show respectively the helical and pleated arrangements that are held together by hydrogen bonding interactions between amide (peptide) links. (b) Some hydrogen bonding interactions between amide functional groups producing a helical arrangement of the protein chain

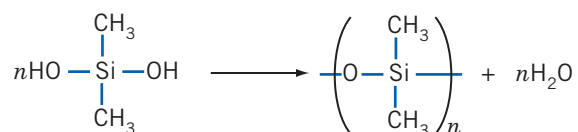
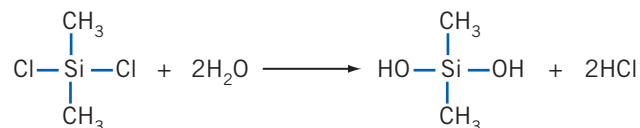
## Silicones

Silicones are a group of polymers that are built on a backbone of silicon and oxygen atoms bonded into long chains:



The two bonds that remain on each silicon atom are usually attached to carbon atoms in alkyl groups (commonly methyl groups,  $-\text{CH}_3$ ).

Silicone polymers are made by reacting chlorosilanes with water to form silanols. These silanols immediately react to produce the polymer chain:



As is the case for condensation polymerisation with carbon-based monomers, the silicon-based monomer must have two reactive functional groups.

Silicones have a range of useful properties including the following. They are:

- excellent electrical insulators
- good lubricants
- very stable to extremes of temperature
- water repellent
- non-toxic
- chemically unreactive
- flexible
- non-stick.



Figure 13.10 A range of silicon-based polymers

A major difference between carbon polymers and the silicones is that the latter are more often liquids and retain these liquid properties over a wide range of temperatures.

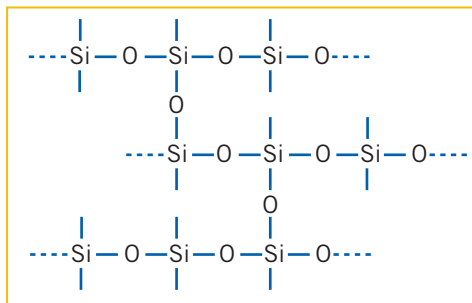
Both the carbon polymers and silicones consist of long linear chains. In the carbon polymers, these chains attract one another with hydrogen bonds (as in the case of nylon), dipole–dipole interactions (for example, polyesters) or by dispersion forces (for example, polyethene). Hydrogen bonding is not possible between most silicone chains, so only dispersion forces and dipole–dipole forces are present.

Dispersion forces depend on the number of electrons present in the substance, but they also depend on the size of the molecules that are involved. The silicon–oxygen bond is much longer than the carbon–carbon bond, so the electrons in the backbone of the silicone chain are spread over a much greater volume. As a result, the instantaneous dipole that exists in the silicone will be weaker than the

instantaneous dipole in the carbon-based polymer. Consequently, the attractive forces between silicone chains are weaker than those between carbon polymer chains.

Silicones can exist as liquids, greases and resins or rubbers. These physical properties can be controlled by the appropriate use of different chlorosilanes in the polymerisation reaction.

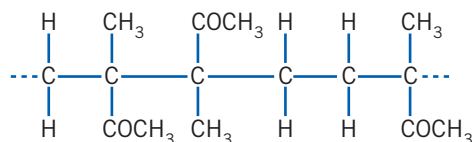
Dichlorosilanes,  $R_2SiCl_2$ , encourage the formation of long-chain silicones. If monochlorosilanes,  $R_3SiCl$ , are added they tend to terminate the chain and so produce smaller (lower boiling point) silicones. Adding trichlorosilanes,  $RSiCl_3$ , adds another functional group permitting one chain to link to another chain (this is known as cross-linking). Cross-linked silicones are more rigid and are often used as resins or rubbers that are better insulators and have greater thermal stability than carbon-based alternatives.



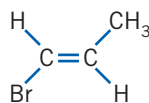
**Figure 13.11** Cross-linking of silicone chains occurs when using monomers with three functional groups.

### \* Review exercise 13.1

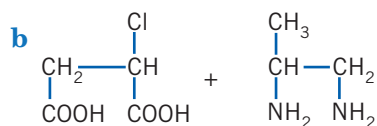
- In what way does the monomer for addition polymerisation differ from the monomer involved in condensation polymerisation? Give examples to support your answer.
- Draw the repeating unit in the polymer made from the polymerisation of but-2-ene.
  - Give the structural formula of the monomer that was used to make the polymer represented in the segment below:



- Substance X has the structure:



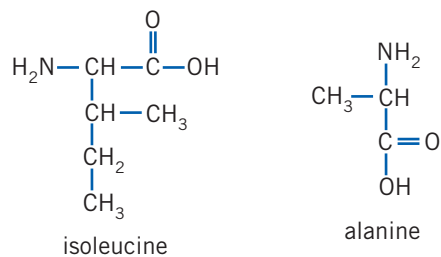
- Draw the structural formula of substance Y, a geometrical isomer of X.
  - X and Y each undergo addition polymerisation. Draw the structure of part of the polymer formed from each, including at least six carbon atoms in the backbone of the chain. How do the addition polymers from these two geometrical isomers compare?
  - Z is a structural isomer of X. Draw the structural formula of Z.
  - Z also undergoes addition polymerisation. Draw the structure of part of the polymer formed from Z, showing at least six carbon atoms in the backbone of the chain.
- Draw the repeating unit in polymers made from the following monomers:



*continued*

### Review exercise 13.1 — continued

5 The structures of the amino acids isoleucine and alanine are shown below:



Draw the structures of the two dipeptides that can be formed from these two substances.

- 6 A 1:1 molar mixture of  $(\text{C}_2\text{H}_5)_2\text{SiCl}_2$  and  $(\text{CH}_3)_2\text{SiCl}_2$  is polymerised in the presence of water.
- If these monomers combine in an 'ideal' fashion on the basis of the 1:1 mole ratio, what would be the formula of the repeating unit?
  - Explain why this 'ideal' polymer structure is not likely to be obtained.

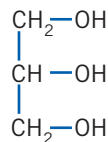
## 13.2 From fats to soap

A balanced diet for a modern lifestyle should contain some fat. The fats that we consume either as animal fats or as vegetable oils are metabolised to form a number of essential compounds that the body cannot produce from other chemicals. These compounds (known as essential fatty acids) play a key role in the production of other biologically significant compounds that are important for our health.



**Figure 13.12** Examples of fats from plants (peanut oil and margarine) and animals (red meat, fish and butter)

Animal fats and plant (vegetable) oils are esters. All share the same alcohol precursor, glycerol, which has three alcohol functional groups. Since each fat molecule usually contains three ester groups formed from the three alcohol groups in glycerol, these fats are known as triglycerides:



glycerol (propane-1,2,3-triol)

The long chain carboxylic acids that combine with glycerol to form the triester fat are called fatty acids. While the alcohol part remains the same, the range of fatty acids that can be involved in the formation of different fats is large. However, there are several characteristics the fatty acids have in common.

- They contain unbranched chains of carbon atoms.
- They usually have between 10 and 20 carbon atoms in the chain and almost invariably consist of an even number of carbon atoms.
- There are no other functional groups present in the carbon chain other than the carboxylic acid group.

An example of a fat molecule is shown in Figure 13.13. In this particular molecule all three fatty acid precursors are the same (stearic acid,  $C_{17}H_{35}COOH$ ). However, in animal fats and vegetable oils it is not necessary for these to be the same.

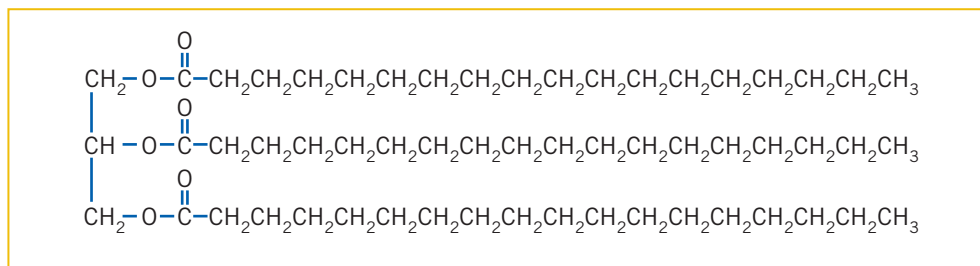


Figure 13.13 An example of a fat, glyceryl tristearate

Figure 13.14 shows the structure of another triglyceride. In this case, the three hydrocarbon chains originating from fatty acids are different and one of them contains a double bond. Triglycerides present in animal fats are usually saturated, meaning they have only single carbon-carbon bonds. Vegetable oils, on the other hand, often have one or more double bonds in one (or more) of the hydrocarbon chains, and are referred to as unsaturated fats.

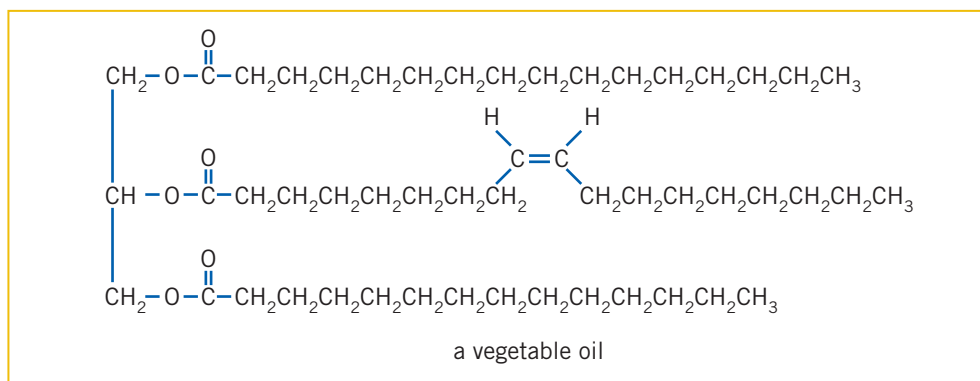
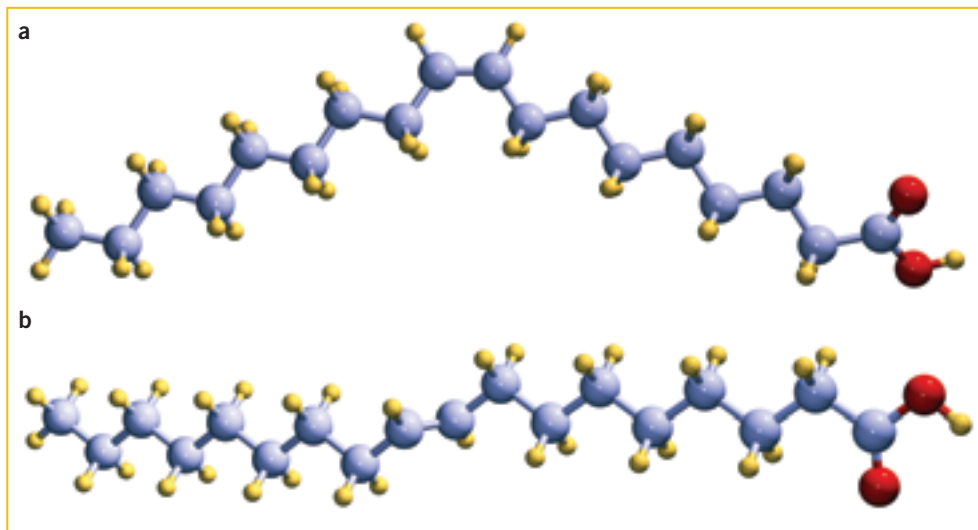


Figure 13.14 A triglyceride with an unsaturated hydrocarbon chain

The long hydrocarbon chains of the triglyceride are essentially non-polar so the attractive forces between fat molecules (at least along the long carbon chains that make up the bulk of the structure) are dispersion forces. The strength of dispersion forces depends, in part, on how close the molecules can get to one another. When a double bond is present in one or more of the chains, the symmetrical shape of the molecule is disrupted and neighbouring molecules cannot get as close as they would if all the hydrocarbon chains were saturated. In addition, fatty acids that have double bonds have this bond present predominantly as the *cis* isomer. Figure 13.15 shows molecular models of two isomeric fatty acids. It is clear that in the *cis* isomer the chains will not be able to pack as close together as for the *trans* isomer.



**Figure 13.15** (a) Oleic acid—the *cis* isomer. (b) Elaidic acid—the *trans* isomer

The decrease in dispersion forces between the triglycerides formed from unsaturated fatty acids is a significant reason why the triglycerides from plants are more likely to be oils than the saturated triglycerides derived from animal fat. For example, olive oil is a liquid at 20°C, but butter is a solid.

The presence of double bonds in the hydrocarbon chains of vegetable oils also makes them more reactive. The vegetable oils can undergo oxidation at the double bond and the oil becomes rancid (the double bond is broken and molecules with a foul taste and odour are produced). Manufacturers of butter substitutes, such as margarine, from vegetable oils endeavour to remove some of the double bonds in the oil by hydrogenation. In the presence of a suitable catalyst, hydrogen adds across the double bond and produces saturated carbon atoms. As a result of this hydrogenation, the oil is converted into a 'soft solid' with a consistency better suited to spreading and cooking than butter.

In the hydrogenation process, a carefully controlled amount of hydrogen is used as a limiting reagent. Not every double bond is saturated in the process, but the conditions that are used for the partial hydrogenation also result in the conversion of *cis* double bonds to *trans* double bonds when the double bond interacts with the metal catalyst during the reaction.

The fats consumed in our diet cannot be absorbed into the bloodstream directly. The triglycerides must first be hydrolysed to produce the fatty acids that are then absorbed through the wall of the small intestine and into the bloodstream. The biochemistry of the digestion of *trans* fats (triglycerides with *trans* double bonds) is not clear. However, there appears to be evidence of a link between the presence of these *trans* fats in the diet and a range of health issues associated with the type of cholesterol produced by the body through to coronary heart disease. Cause and effect is yet to be established, but manufacturers of hydrogenated fats are working towards a reduction in the amount of *trans* fats in their products.

## Soap

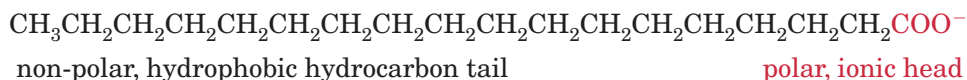
Hydrolysing the ester links in the triglycerides of either animal fats or vegetable oils with a strong base such as sodium hydroxide or potassium hydroxide makes soap. The products of this hydrolysis reaction are glycerol (propane-1,2,3-triol) and the salt of the long chain fatty acid (the soap).





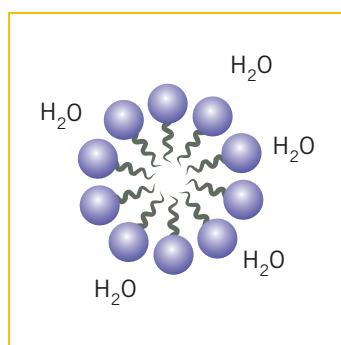
substance that can keep two normally immiscible substances together in the same phase. In simple terms, a soap is capable of keeping oil dissolved in water. The sodium and potassium ions also present in soap are not involved in the cleansing action of the soap.

As the salt of a long chain fatty acid, the soap has both a polar part (the carboxylic acid anion,  $\text{COO}^-$ ) and a non-polar part (the long hydrocarbon chain):



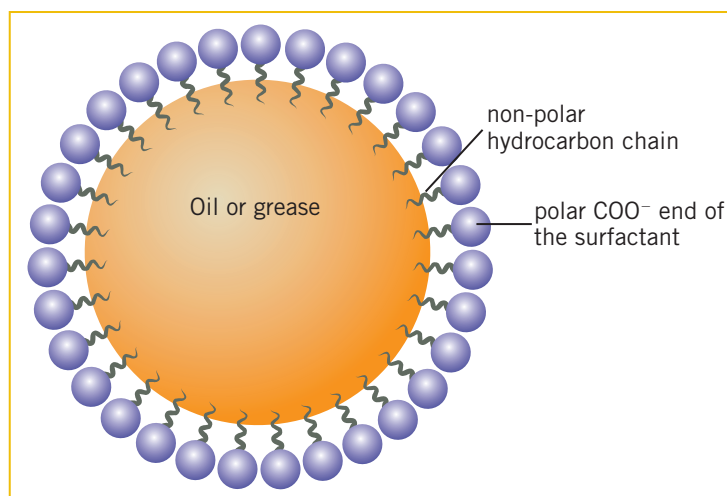
The polar part of the soap molecule is often referred to as the hydrophilic 'end' because it is soluble in water. The non-polar part of the molecule is referred to as the hydrophobic (water-hating) 'end'.

In water, soap forms a cloudy suspension in which the non-polar hydrocarbon chains of the soap molecules are attracted to one another by dispersion forces while the negatively charged carboxylate ends are hydrogen bonded to the surrounding water molecules. The most stable arrangement for this interaction is called a micelle and is depicted in Figure 13.19.



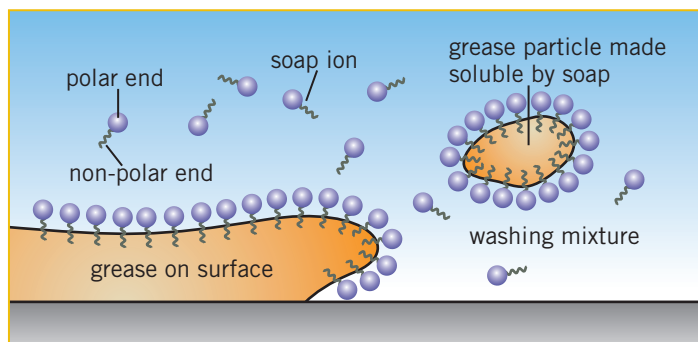
**Figure 13.19** A soap micelle showing the arrangement of the non-polar hydrocarbon tail and the polar  $\text{COO}^-$  head when the soap is mixed in water. Hydrocarbon tails are non-polar and collect together on the inside of the micelle, shielded from the water environment. On the outside, the negative ions are attracted to the surrounding polar water molecules.

Since most grease, oil and stains that are commonly referred to as 'dirt' are non-polar and insoluble in water, the soap micelles are able to rearrange so that the non-polar hydrocarbon tails bury themselves in the 'dirt' as shown in Figure 13.20. With the dirt now captured in the inner region of the micelle, this dirt will behave as a polar substance and mix more readily with the polar water. The soap has therefore effectively 'dissolved' the dirt. When the soapy water is rinsed away it takes the dirt trapped in the micelles with it, leaving a clean surface.



**Figure 13.20** Soap molecules have made a blob of oil or grease 'soluble' so that it can be removed in the rinse water.

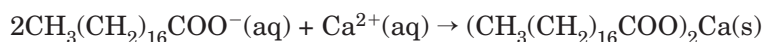
Vigorous agitation of the 'dirty' material in the soapy water increases the rate of the washing process. The surfactant soap molecules that have formed micelles in the soapy water break apart during the vigorous agitation of the washing process and interact more rapidly with the oil or grease on a surface as shown in Figure 13.21.



**Figure 13.21** Simplified representation of the cleaning action of soap during the washing process

In addition, warm water is more likely to promote the cleaning process as it will soften the fats and oils that have accumulated on clothes or other items, making it easier for the surfactant to pull the dirt away from the surface.

Soaps, however, have one significant disadvantage, particularly in Western Australia. In the presence of ions such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$ , the negatively charged soap ions form an insoluble precipitate, a scum, for example:



As a consequence, more soap needs to be used for washing in hard water than in 'soft' water, to obtain a lather. Much of Western Australia's water supply is hard water, containing dissolved calcium ions in particular. When using hard water, the insoluble scum formed by the soap and the  $\text{Ca}^{2+}$  ions is difficult to remove from household areas such as bathrooms and from clothes.



**Figure 13.22** A variety of products containing surfactants

## Detergents

Detergents have been designed with the problems associated with soap scum in mind, the aim being to produce a detergent that has the same non-polar, hydrophobic tail and polar head arrangement as soap, but will not form an insoluble precipitate with the ions in hard water. Chemists soon established that replacing the carboxylate,  $\text{COO}^-$ , with a sulfonate,  $\text{SO}_3^-$ , group provided an effective surfactant ion that would not produce a scum in hard water.

The manufacture of a detergent can be achieved by reacting an alkylbenzene (a product of the petrochemical industry) with concentrated sulfuric acid, followed by sodium hydroxide, as shown in Figure 13.23.

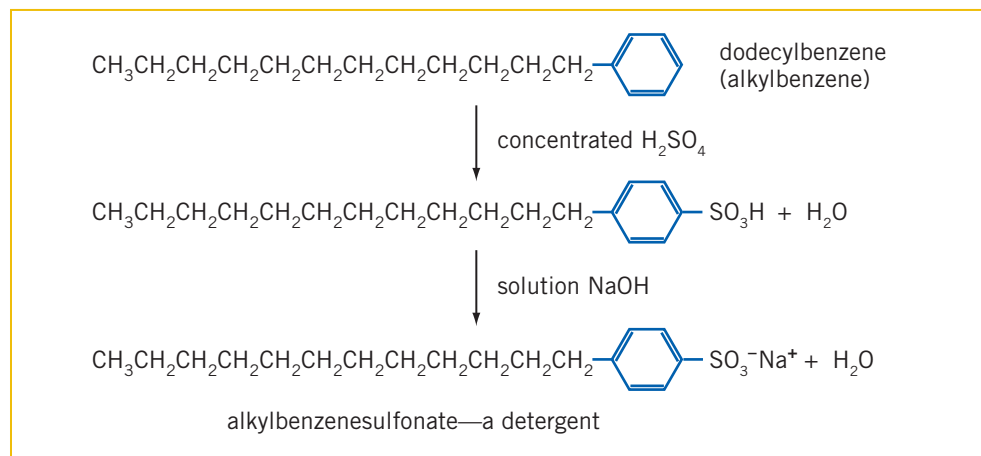


Figure 13.23 Formation of an alkylbenzenesulfonate detergent

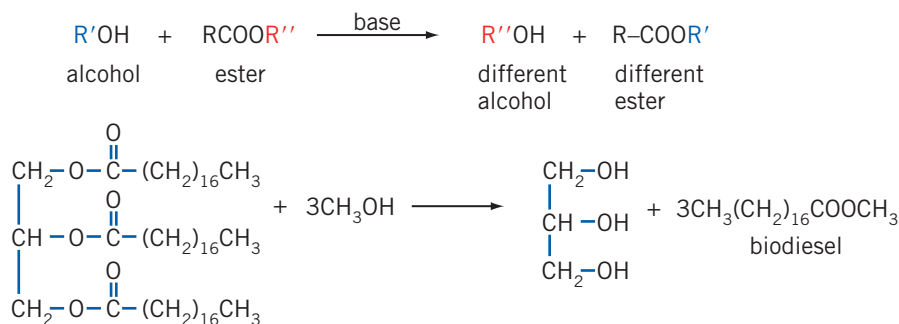
The chemistry of the action of a detergent is essentially the same as that of soap. The non-polar hydrocarbon end attaches itself to the oil or grease while the polar sulfonate end is hydrogen bonded to the water molecules in the aqueous medium.

In addition to the anionic surfactant, modern detergents may also contain enzymes that break down stains including biological stains such as the protein in blood. Brighteners are also sometimes added. These fluoresce in ultraviolet light (which is part of sunlight) and make clothes appear whiter. Some detergents include substances that break down in warm water to produce hydrogen peroxide, a mild bleach.

## Biodiesel

As well as producing soaps from animal and plant fats, a fuel can also be relatively easily produced. Biodiesel is a fuel generally made by converting the fatty acids obtained from animal fats or vegetable oils into esters. The dominant process at present involves vegetable oils (including waste cooking oil). Unlike diesel fuel obtained from petroleum refining, biodiesel is non-toxic, biodegradable and renewable. In addition, biodiesel is regarded as a carbon neutral fuel as its combustion reaction releases the carbon dioxide that was originally used as the source of carbon by the plant from which the fuel was produced.

The saponification of a triglyceride with sodium hydroxide was considered previously (Figure 13.16). If the reaction with sodium hydroxide is performed in the presence of methanol then a process called transesterification takes place:



While there seemed to be great promise associated with biodiesel production, concerns are growing about its limitations. Arable land is required to grow the crops that produce the vegetable oil and this has given rise to large-scale deforestation. Also, it is questionable whether food production should be compromised for fuel production.

Finally, from a green chemistry perspective, where issues associated with hazardous chemicals and waste are of paramount importance, the use of a corrosive substance such as sodium hydroxide for large-scale production is of concern. Also, the reaction does not have a high 'atom economy' since one molecule of glycerol is produced for every three molecules of biodiesel. While there is a market for glycerol, the amount that would be produced during large-scale biodiesel production has no market at present.

## \* Review exercise 13.2

1 Copy and fill in the gaps for the following paragraphs:

### Soap as a cleaning agent

A soap is often described as a s..... . Its function is to assist water to remove g..... , o..... , d..... and other water-i..... materials that adhere to surfaces.

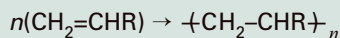
To understand the cleaning process, the nature of the surfactant needs to be examined. The surfactant is a large ion consisting of a n..... charged end and an uncharged, n.....-p..... end. Polar or charged particles tend to dissolve in p..... solvents, whereas non-polar substances tend to dissolve in n..... solvents. Water is a p..... solvent which can form h..... b..... with the c..... end of the surfactant. This c..... end is known as the h..... or 'water-loving' end of the surfactant. As a result, this end of the surfactant ion tends to d..... readily in water.

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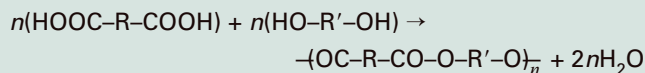


## MAJOR IDEAS

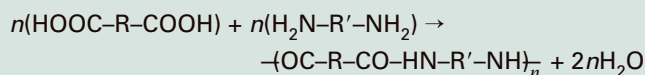
- Polymers are very large molecules often made up of a backbone or chain in which carbon atoms usually dominate.
- Polymers are formed from the reaction between small molecules known as monomers.
- Alkenes can join together to form polymers in a process called addition polymerisation.
- In this reaction each monomer molecule undergoes an addition reaction with adjacent molecules, in the presence of a catalyst, to form a long chain:



- The properties of the addition polymers can be changed by increasing the branched side chains on the polymer chain. The more branched side chains present, the weaker the dispersion forces between the molecules.
- Condensation polymers are formed between monomers that each have two reactive functional groups.
- During condensation polymerisation, the polymer is formed together with water.
- A reaction between a dicarboxylic acid and a diol can result in a condensation polymer. The monomers are 'joined' by ester groups:

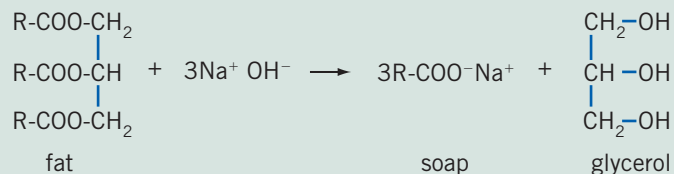


- A condensation polymer can also form in the reaction of a dicarboxylic acid with a diamine. The monomers are 'joined' by amide bonds:



- Proteins are natural polyamides, formed by the condensation polymerisation of amino acids.
- Each amino acid molecule has two functional groups, a carboxylic acid group and an amine group, that can react with the functional groups on other amino acids.
- The bonds between the amino acids are amide bonds, but they are also called peptide bonds.
- Hydrogen bonding (and ionic bonding) between parts of a protein chain cause it to fold in a particular way to give the secondary structure of the protein.
- Silicones are a group of polymers that are built on a backbone of silicon and oxygen atoms bonded into long chains.

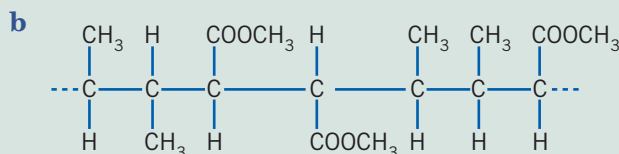
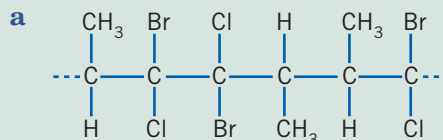
- Soap is made in a saponification reaction in which an oil or fat is boiled with NaOH or KOH solution:



- Soaps are the sodium or potassium salts of fatty acids.
- Detergents are the salts of alkylbenzenesulfonates.
- Soaps and detergents act as cleaning agents because the charged end of the surfactant ion dissolves in the polar solvent, water, while the non-polar hydrocarbon chain dissolves in the non-polar grease, oil or dirt.
- Soaps do not function effectively in hard water as the surfactant ion precipitates out with the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions. Detergents function effectively in all types of water.

## QUESTIONS

- Draw the structure of the monomer(s) used to make polymers having the following partial structures.



- Write the equation for the formation of Teflon from tetrafluoroethene.
  - RESEARCH** Recently there have been concerns expressed about the use of Teflon in cookware. List these concerns and debate whether the use of Teflon in cookware should be banned.
- Explain why the branched chain polymer of ethene is called low density polyethylene (LDPE).
  - Why is high density polyethylene (HDPE) less flexible than LDPE?

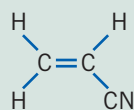
- c LDPE has a density of around  $0.92 \text{ g cm}^{-3}$  while HDPE has a density above  $0.94 \text{ g cm}^{-3}$ . How do the structures of the carbon skeletons of these two polymers account for these differences?
- d Predict the difference, if any, between the melting (or softening) points of LDPE and HDPE. Justify your answer.
- e Why is it preferable to make children's toys from polyethene rather than from metals?

4 The cling wrap plastics used in kitchens to wrap food were originally made from PVC (poly(vinyl chloride)). However there were concerns about the possible toxicity and leaching of the plasticisers added to the PVC to produce the thin flexible film. As a result, this material is now made predominantly from LDPE, even though in this form it is less 'clingy' than PVC.

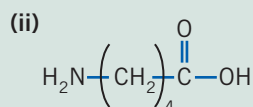
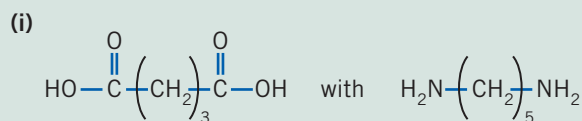
- a What properties of LDPE make it suitable for use as a plastic cling film?
- b Draw a partial structure for LDPE and PVC, showing at least six carbon atoms in the backbone.
- c Why would LDPE be 'less clingy' than PVC?

To deal with the problems associated with the LDPE film having inferior sticking properties, ethylene vinyl acetate (EVA) is incorporated into the cling film as it is made. EVA is a copolymer of ethene and vinyl acetate (ethenyl acetate,  $\text{CH}_2=\text{CHOCOCH}_3$ ).

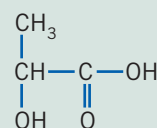
- d Assuming ethene and vinyl acetate are mixed in a 1:1 ratio during the polymerisation, draw an ideal representation of the repeating unit in the EVA polymer.
- e Why is this repeating unit unlikely to be the best representation for the structure of the polymer?
- f What properties of EVA would enhance the 'clinginess' of a plastic wrap made from a combination with LDPE?
- 5 Polyacrylonitrile is made from the monomer shown below. Draw the structure of the polymer, showing at least three repeating units.



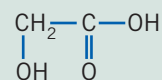
6 What are the similarities and differences in the structures of the polymers obtained from using the reactants in part (i) below compared with using the reactant in part (ii)?



7 Lactic acid is a molecule with both alcohol and carboxylic acid functional groups present in the same compound (see below). Lactic acid is produced during the metabolism of glucose to carbon dioxide and water.

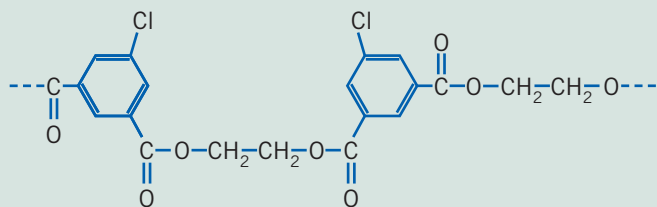


- a Draw at least three repeating units in the polymer obtained from lactic acid.
- b What is the general name given to polymers of this type?
- c What other biologically important monomer has a structure similar in type to lactic acid? What is this similarity?
- 8 The lactic acid in question 7 can also form a condensation polymer with glycolic acid, shown below:

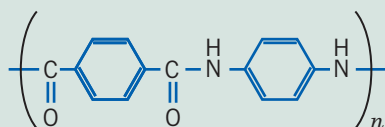


- a Draw the structure of the repeating unit for the polymer formed from the reaction between these two monomers (lactic acid and glycolic acid).
- b This polymer is used in medicine to make stitches that dissolve over a period of time in the body. Explain what is likely to happen to these stitches in the body over the 2 weeks that it takes for them to 'dissolve'.

- 9 Part of the structure of a polymer is shown in the diagram below:

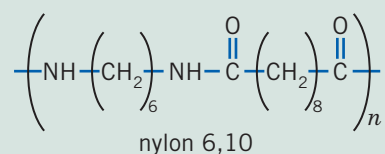
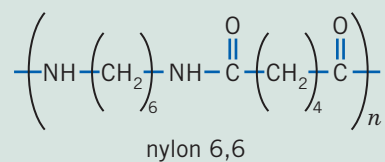
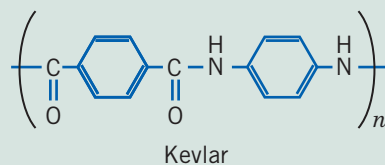


- a What type of polymer is this?  
 b What else is produced in the reaction between the monomers during the formation of this polymer?  
 c Draw the structure of the monomers that were used in the formation of this polymer.
- 10 The repeating unit in Kevlar is drawn below:



Draw the structures of the monomer(s) from which this polymer is made.

- 11 Consider the structures of Kevlar, nylon 6,6 and nylon 6,10:



- a What is common to each of these polymers?  
 b Which one of nylon 6,6 or nylon 6,10 would you expect to be more flexible? Explain your answer.  
 c Which one of nylon 6,6 or nylon 6,10 would you expect to be stronger when used as a rope or as a fibre?

- d Kevlar is used in bullet-proof vests. What properties does Kevlar possess, in comparison to the two forms of nylon, that make it suitable for this use?  
 e Nylon 6 is the name given to a form of nylon made by condensation polymerisation using only one monomer. Using the information above about the structure of nylon 6,6 and nylon 6,10, propose a structure for this monomer and draw the repeating unit in nylon 6.

- 12 In Figure 13.9 the structure of a tripeptide formed from alanine, glycine and leucine is drawn. When peptides such as this are drawn, it is convention to have the amino group on the left-hand side and the carboxylate group on the right. The short-hand representation of Ala-Gly-Leu then conveys not only the sequence of amino acids, but also the way that the peptide or amide link is formed between the monomers.

- a Are the tripeptides Ala-Gly-Leu and Leu-Gly-Ala the same molecule? Explain your answer.  
 b Represent all the possible sequences of these three amino acids that could exist using the three letter codes and the convention that the amine group is always on the left.

- 13 A particular polypeptide undergoes partial hydrolysis to produce several smaller peptides. Four of the hydrolysis products are found to be (the three-letter code represents a particular amino acid):

Glu-Trp-Met-Arg

Ser-Glu-Trp

Arg-Gly-Pro-Val

Met-Arg-His-Arg-Gly

Assuming all of the amino acids in the polypeptide are represented in these hydrolysis products, use this information to draw a representation (showing the correct order of amino acids) of the polypeptide.

- 14 What is the difference between the primary structure and the secondary structure of a protein in terms of the types of bond involved?







## Unit 3B Review Questions

## \*PART A: MULTIPLE-CHOICE QUESTIONS

- 1 Which of the following is a list of acidic salts?
- A NaCl, CH<sub>3</sub>COONa, NaHCO<sub>3</sub>  
 B NH<sub>4</sub>Cl, AlCl<sub>3</sub>, KHSO<sub>4</sub>  
 C CH<sub>3</sub>COOH, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, HF  
 D KBr, MgHPO<sub>4</sub>, NaHS
- 2 If 100 mL of water is added to 200 mL of 0.0100 mol L<sup>-1</sup> Ca(OH)<sub>2</sub> solution, the pH of the resulting solution would be approximately:
- A 1.9      B 11.8      C 12.1      D 12.3
- 3 The pH ranges at which some indicators change colour are as follows.
- i methyl violet    0.5–1.5  
 ii methyl orange    3.1–4.4  
 iii methyl red    4.2–6.3  
 iv phenolphthalein 8.0–9.6

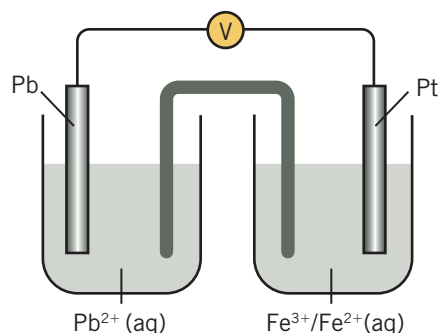
Which of the above indicators could be used to standardise a solution of ammonium nitrate against 0.1 mol L<sup>-1</sup> potassium hydroxide solution?

- A i only  
 B iv only  
 C ii and iii only  
 D iii only
- 4 Which one of the following aqueous solutions has the highest pH?
- A 0.01 mol L<sup>-1</sup> KOH  
 B 0.01 mol L<sup>-1</sup> Ba(OH)<sub>2</sub>  
 C 0.05 mol L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub>  
 D 0.1 mol L<sup>-1</sup> PO(OH)<sub>3</sub>
- 5 In a 1.0 mol L<sup>-1</sup> sodium phosphate solution, Na<sub>3</sub>PO<sub>4</sub>, which one of the following concentration relationships is correct?
- A [H<sup>+</sup>] = [OH<sup>-</sup>]  
 B [H<sup>+</sup>] > [OH<sup>-</sup>]  
 C 3[Na<sup>+</sup>] = [PO<sub>4</sub><sup>3-</sup>]  
 D [PO<sub>4</sub><sup>3-</sup>] > [HPO<sub>4</sub><sup>2-</sup>] > [H<sub>2</sub>PO<sub>4</sub><sup>-</sup>]
- 6 The addition of solid ammonium chloride to an aqueous solution of ammonia will cause:

- A the pH of the solution to decrease  
 B the concentration of the ammonia in the solution to decrease  
 C the concentration of hydroxide ions in the solution to increase  
 D a precipitate to form.

- 7 For water at 100°C, the self-ionisation constant of water ( $K_w$ ) is  $1 \times 10^{-12}$ . Which of the following statements concerning boiling water are correct?
- i The pH of boiling water is 7.  
 ii The pH of boiling water is 6.  
 iii The pH of boiling water is 12.  
 iv Boiling water is a neutral solution.  
 v Boiling water is an acidic solution.  
 vi Boiling water is a basic solution.
- A i and ii only  
 B ii and v only  
 C iii and vi only  
 D ii and iv only

- 8 The equation  $2\text{H}^+(\text{aq}) + \text{Mg}(\text{s}) \rightarrow \text{H}_2(\text{g}) + \text{Mg}^{2+}(\text{aq})$  represents a redox reaction. Which of the following statements about this reaction is false?
- A Electrons are transferred from the Mg to the H<sup>+</sup> ions.  
 B H<sup>+</sup> ions undergo reduction.  
 C Mg<sup>2+</sup> is a weaker oxidant than H<sup>+</sup>.  
 D H<sub>2</sub> is a stronger reductant than Mg.
- 9 This question refers to the diagram below.



For the system shown:

- A electrons will flow in the wire from Pt to Pb  
 B positive ions will flow in the salt bridge away from the Fe<sup>3+</sup>/Fe<sup>2+</sup> half-cell  
 C electrons will flow in the salt bridge from the Pb<sup>2+</sup> solution to the Fe<sup>3+</sup>/Fe<sup>2+</sup> solution  
 D if the solutions are 1 mol L<sup>-1</sup>, the potential of the cell will be approximately 0.9 V.

- 10** The steel hull of a ship will often have pieces of another metal fastened to it to reduce rusting of the hull. Which of the following can be deduced regarding the metal that should be used for this purpose?
- A** Copper would be effective since copper does not react with water.
  - B** Iron will not rust in the presence of nickel since nickel is a weaker reductant than iron.
  - C** Sodium would be suitable because it is a stronger reductant than iron.
  - D** Zinc will be effective because zinc loses electrons more readily than iron.
- 11** Two strips of clean metal are dipped in dilute sulfuric acid. Between which of the following pairs of metals would there be the greatest voltage output?
- A** Fe and Pb
  - B** Zn and Mg
  - C** Cu and Zn
  - D** Sn and Mg
- 12** In which of the following species is vanadium exhibiting the highest oxidation number?
- A**  $\text{VO}^{2+}$
  - B**  $\text{NH}_4\text{VO}_3$
  - C**  $\text{V}_2(\text{SO}_4)_3$
  - D**  $\text{VCl}_4$
- 13** At the equivalence point of a titration involving  $0.1 \text{ mol L}^{-1} \text{CH}_3\text{COOH}$  and  $0.1 \text{ mol L}^{-1} \text{NaOH}$  solutions, the species present in the aqueous solution in concentrations greater than  $0.01 \text{ mol L}^{-1}$  would be:
- A**  $\text{CH}_3\text{COOH}$ ,  $\text{Na}^+$  and  $\text{OH}^-$
  - B**  $\text{CH}_3\text{COOH}$ ,  $\text{H}^+$ ,  $\text{Na}^+$  and  $\text{OH}^-$
  - C**  $\text{CH}_3\text{COO}^-$ ,  $\text{H}^+$ ,  $\text{Na}^+$  and  $\text{OH}^-$
  - D**  $\text{CH}_3\text{COO}^-$  and  $\text{Na}^+$ .
- 14** Which of the following pairs of substances would you not expect to react?
- A** Chlorine gas and a solution of sodium bromide
  - B** A solution of iron(III) chloride and a solution of potassium iodide
  - C**  $1 \text{ mol L}^{-1}$  hydrochloric acid and manganese (Mn)
  - D** Hydrogen sulfide gas and a solution of zinc nitrate
- 15** Which of the following is *not* true about an electrochemical cell composed of a standard  $\text{Cl}_2/\text{Cl}^-$  half-cell and a standard  $\text{Ni}^{2+}/\text{Ni}$  half-cell?
- A** Electrons would flow in the external circuit towards the chlorine half-cell.
  - B** The nickel electrode would be the anode.
  - C** The  $\text{Cl}^-$  ions would undergo oxidation.
  - D** Negative ions would flow, in the internal circuit, towards the nickel half-cell.
- 16** One property of a buffer solution, prepared from a weak acid and its sodium salt, is that its pH is:
- A** 7
  - B** greater than the pH of the original acid
  - C** unaffected by the addition of any quantity of  $0.1 \text{ mol L}^{-1} \text{HCl}$
  - D** unaffected by the addition of any quantity of  $0.1 \text{ mol L}^{-1} \text{NaOH}$ .
- 17** If a reaction is endothermic, it means that:
- A** during the reaction, heat is transferred from the system to the surroundings
  - B** the heat content of the products is greater than that of the reactants
  - C** the temperature of the surroundings increases
  - D** the heat content of the reactants is greater than that of products.
- 18** The pH of a  $0.0642 \text{ mol L}^{-1}$  solution of a monoprotic acid is 3.86.
- This solution is an example of a:
- A** dilute solution of a strong acid
  - B** dilute solution of a weak acid
  - C** concentrated solution of a weak acid
  - D** concentrated solution of a strong acid.
- 19** What will be the effect of adding  $0.5 \text{ mL}$  of  $0.1 \text{ mol L}^{-1} \text{NaOH}$  to  $100 \text{ mL}$  of a solution in which  $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-] = 0.5 \text{ mol L}^{-1}$ ?
- A** The pH will increase slightly.
  - B** The pH will increase significantly.
  - C** The pH will decrease slightly.
  - D** The pH will decrease significantly.
- 20** Equal volumes of the following solutions are mixed. Which pair will produce a buffer solution?
- A**  $0.1 \text{ mol L}^{-1} \text{HCl}$  and  $0.05 \text{ mol L}^{-1} \text{NaOH}$
  - B**  $0.1 \text{ mol L}^{-1} \text{HCl}$  and  $0.15 \text{ mol L}^{-1} \text{NH}_3$
  - C**  $0.1 \text{ mol L}^{-1} \text{HCl}$  and  $0.20 \text{ mol L}^{-1} \text{CH}_3\text{COOH}$
  - D**  $0.1 \text{ mol L}^{-1} \text{HCl}$  and  $0.20 \text{ mol L}^{-1} \text{NaCl}$

## PART B: SHORT-ANSWER QUESTIONS

- 1 Oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , is found in the leaves of rhubarb. A student boiled down 100 g of chopped rhubarb leaves to extract the oxalic acid. She then drained off the liquid, which was found to measure 530 mL. She titrated 50.00 mL of this liquid with acidified  $0.0206 \text{ mol L}^{-1} \text{ KMnO}_4$  and obtained the following results.

Titration number	1 Rough titration	2	3	4
Final burette reading (mL)	13.50	26.34	39.40	13.23
Initial burette reading (mL)	0.23	13.62	26.78	0.65

- Write half-equations and hence the balanced overall equation for the reaction between oxalic acid and permanganate ions in the presence of acid.
  - Calculate the average volume of potassium permanganate solution used in the titration.
  - Find the percentage, by mass, of oxalic acid in the rhubarb leaves.
  - How could the student judge when she had reached the end point in each titration?
- 2 Choose your answers to the following questions from the compounds contained in the box.

Compound A: but-1-ene

Compound B:  $\text{C}_{10}\text{H}_{22}$

Compound C:  $\text{CH}_3\text{—CH=CH—CH}_2\text{—CH}_2\text{—CH}_3$

Compound D:  $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{H}_3\text{C—C—C—CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$

Compound E:  $\begin{array}{c} \text{CH}_2\text{—CH}_2 \\ | \quad | \\ \text{CH}_2\text{—CH}_2 \end{array}$

- Which are saturated compounds?
- Which compounds would rapidly decolourise bromine solution?
- Which compounds are soluble in water?
- Which compounds are alkenes?
- Which compounds exhibit geometrical isomerism?

- Which compounds would not undergo addition reactions?
- Which compound is a structural isomer of cyclohexane?

- 3 a Give the structural formulas and names of a primary alcohol, a secondary alcohol and a tertiary alcohol with the molecular formula of  $\text{C}_7\text{H}_{16}\text{O}$ . Clearly indicate which example is the primary alcohol, which is the secondary alcohol and which is the tertiary alcohol.
- b Compare the reaction of each of your alcohols with an acidified solution of sodium dichromate. Give balanced equations to support your answer.

- 4 Labels have fallen off four reagent bottles in a laboratory. One bottle contains hexane, one contains ethanamine, one contains cyclohexene and one contains ethanol. The fumes from several of these liquids are poisonous, so smelling the chemicals cannot be used to identify which bottle contains which chemical.

Using chemicals and equipment available in the school laboratory, outline how you could identify each of the liquids in the four bottles. Explain your answer in terms of the properties of the four liquids.

- 5 A dilute solution of calcium hydroxide has a pH of 12.6. In this solution, what are the concentrations, in  $\text{mol L}^{-1}$ , of:

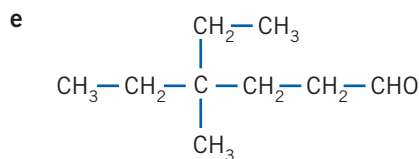
- hydrogen ions
- hydroxide ions
- calcium ions.

- 6 Give the structural formulas of the following compounds.

- 4-ethylhexanoic acid
- 3,3-dichlorobutanal
- ethyl methanoate
- 2-methyl-4-propyloctan-3-one

- 7 Give the systematic names of the following compounds.

- $(\text{CH}_3)_2\text{CHCH}_2\text{CO}(\text{CH}_2)_2\text{CH}_2\text{Cl}$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{Na}$
- $\text{HOOC—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH—CH}_2\text{—CH—CH}_3$   
 $\quad \quad \quad \quad \quad \quad | \quad \quad \quad |$   
 $\quad \quad \quad \quad \quad \quad \text{CH}_3 \quad \quad \quad \text{CH}_3$
- $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—C—O—CH}_3$   
 $\quad \quad \quad \quad \quad \quad ||$   
 $\quad \quad \quad \quad \quad \quad \text{O}$



- 8 Give balanced equations for the following reactions.
- Ethyl butanoate is heated with a solution of sodium hydroxide.
  - Propanoic acid is mixed with a solution of potassium hydroxide.
  - Acetic acid (ethanoic acid) and pentan-1-ol are heated with a small amount of concentrated sulfuric acid.
- 9 Describe a chemical test you could carry out to distinguish between butanal and butanone. Also include the expected observations and equations for any relevant reactions in your answer.
- 10 The concentration of a solution of ammonia was determined by titration against a standard solution of hydrochloric acid. The hydrochloric acid solution was placed in the burette and the ammonia was pipetted into the conical flask.
- With what would you rinse the following pieces of equipment just prior to use?
    - the burette
    - the pipette
    - the conical flask
  - Name a suitable indicator for this titration.
  - An indicator which is not suitable for this titration is cresol red. This indicator is a red colour in solutions with a pH greater than 8.8 and a yellow colour in solutions with a pH less than 7.2.  
If this indicator is used for the titration, will the calculated concentration of the ammonia solution be larger, smaller or the same as the correct concentration? Explain your reasoning.
- 11 Sodium nitrite,  $\text{NaNO}_2$ , has a wide variety of uses, including its controversial application as a preservative in processed meats such as bacon, ham and hot dogs. In a particular frankfurt-making factory, a careless worker accidentally contaminated their supply of sodium nitrite with sodium carbonate. The contaminated sodium nitrite was quantitatively analysed by the factory's chemist to determine its percentage purity.

Because nitrites are unstable in acid solution, the chemist decided to use a back titration method rather than direct titration. She used the following method for this titration.

Weigh accurately about 1 g of the contaminated nitrite and make it up, with distilled water, to 250 mL of solution. Pipette 25.00 mL of this solution into exactly 50.00 mL of standard cerium(IV) sulfate solution to which has been added about 20 mL of dilute sulfuric acid. Titrate the solution containing the excess cerium(IV) sulfate solution with a standard solution of ammonium iron(II) sulfate solution, using ferroin as an indicator.

The amounts, concentrations and titration results she used/obtained are given below:

$$\text{mass of contaminated sodium nitrite dissolved in 250 mL solution} = 1.026 \text{ g}$$

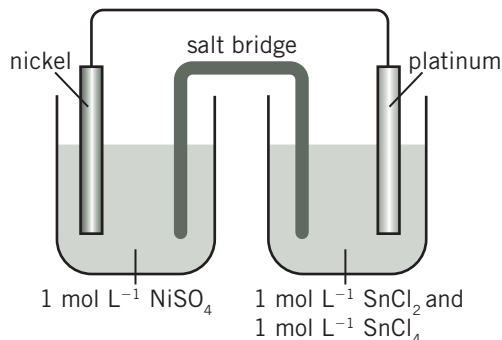
$$\text{concentration of standard } \text{Ce}(\text{SO}_4)_2 \text{ solution} = 0.146 \text{ mol L}^{-1}$$

$$\text{concentration of standard } (\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \text{ solution} = 0.202 \text{ mol L}^{-1}$$

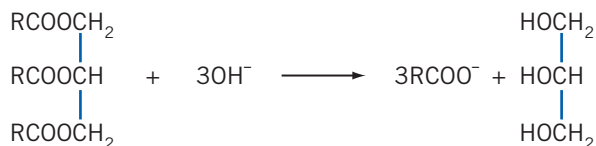
$$\text{average titre} = 25.87 \text{ mL}$$

- In the initial reaction involving nitrite ions and cerium(IV) ions, the nitrite ions are oxidised to nitrate ions and the cerium(IV) ions are reduced to form cerium(III) ions. By first writing the half-equations, give the overall balanced ionic equation for this initial reaction between nitrite ions and cerium(IV) ions.
  - In the titration reaction, a redox reaction occurs between the excess cerium(IV) ions and iron(II) ions, to form cerium(III) ions and iron(III) ions. Give the balanced ionic equation for this reaction.
  - Use the chemist's results to determine the percentage purity, by mass, of the contaminated sodium nitrite.
- 12 Write equations for any reactions that occur in the following procedures. If no reaction occurs write 'no reaction'. In each case, describe in full what you would observe.
- Dilute sulfuric acid is added to some solid iron(III) oxide.
  - Some small pieces of lead are placed in a  $1.0 \text{ mol L}^{-1}$  solution of silver nitrate.
  - An acidified solution of potassium dichromate is mixed with a solution of hydrogen peroxide.
- 13 Copy the diagram of the cell on the next page into your workbook.
- Show the direction of electron flow in the external circuit.
  - Give the half-equation for the reaction that occurs at each electrode.

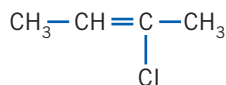
- c Label the anode and the cathode.  
 d Show the direction of flow of the positive and negative ions in the internal part of the cell.  
 e Estimate the potential of the cell.



- 14 Indicate, giving your reasons, whether you agree or disagree with the following assertions.
- Because molecular substances usually have lower melting points than ionic substances, covalent bonds must be weaker than ionic bonds.
  - A solution of  $0.1 \text{ mol L}^{-1} \text{ NH}_3$  has a higher concentration of  $\text{NH}_4^+$  ions than a solution of  $0.05 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$ .
  - An aqueous solution which is strongly acidic, for example  $1 \text{ mol L}^{-1} \text{ HCl}$ , will contain no  $\text{OH}^-$  ions.
  - Because ethane,  $\text{C}_2\text{H}_6$ , has a larger number of electrons than water, ethane will have a higher boiling point than water.
- 15 Fats consist of triglycerides with a general formula shown in the equation below. ( $\text{R}\text{O}\text{R}$  represents a long hydrocarbon chain.) The saponification number of a fat is defined as the mass in mg of  $\text{KOH}$  that reacts with 1 g of the fat, according to the equation given below. When a 2.209 g sample of olive oil was boiled with 50.00 mL of  $0.2582 \text{ mol L}^{-1} \text{ KOH}$ , a back titration of the excess base required 10.93 mL of  $0.5210 \text{ mol L}^{-1} \text{ HCl}$ .



- Calculate the saponification number of the sample of olive oil.
  - Assuming olive oil is a pure triglyceride, calculate the molecular weight of olive oil.
- 16 a Give the structural formula (showing at least three repeat units) of the polymer formed from the polymerisation of the following monomer:



- b What type of polymer, addition or condensation, have you drawn?

- 17 Potassium permanganate is an effective oxidising agent when mixed with sulfuric acid. It is able to oxidise iron(II) ions to iron(III) ions. Solutions containing  $\text{Fe}^{2+}(\text{aq})$  can be titrated against potassium permanganate. This titration forms the basis of an analytical technique for the estimation of iron in substances such as flour.

100 g of flour was vigorously shaken with dilute sulfuric acid and the volume of solution was made up to 100 mL in a volumetric flask. The iron in the flour reacts with the acid to form iron(II) ions. 10.00 mL portions of this acidified mixture were titrated with  $5.10 \times 10^{-6} \text{ mol L}^{-1}$  potassium permanganate. An average titre of 11.0 mL was recorded.

- Write a balanced equation for the reaction of permanganate ions and iron(II) ions in an acidified solution.
  - Calculate the concentration, in ppm, of iron in the flour.
  - If the 100 mL of acidified flour mixture is not titrated immediately after preparation, the calculated concentration of iron in the flour is often less than the true value. Explain why this is so.
- 18 An organic amine contains the elements carbon, hydrogen and nitrogen only. It was found to contain 54.7% carbon and 13.7% hydrogen by mass. A  $0.106 \text{ mol L}^{-1}$  solution of the amine was prepared. 20.00 mL of this solution was neutralised completely by 23.49 mL of  $0.181 \text{ mol L}^{-1} \text{ HCl}$  solution.
- Calculate the empirical formula of the amine.
  - Using the titration data, determine the number of amine groups in each molecule of the amine.
  - Determine the molecular formula of the amine.
  - Draw two possible structural formulas for the amine.

- 19 A student used the following procedure to prepare and standardise a hydrochloric acid solution, with a concentration of approximately  $0.1 \text{ mol L}^{-1}$ .

**Step 1.** Prepare 250 mL of a solution of hydrochloric acid with concentration approximately  $0.1 \text{ mol L}^{-1}$  from concentrated (approximately  $12 \text{ mol L}^{-1}$ ) hydrochloric acid.

**Step 2.** Prepare 250 mL of a solution of sodium carbonate with concentration of approximately  $0.05 \text{ mol L}^{-1}$ , using anhydrous sodium carbonate.

**Step 3.** Standardise the diluted hydrochloric acid (from step 1) by titration against the sodium carbonate solution. The hydrochloric acid is placed in the burette and the sodium carbonate in the conical flask.

The experimental data from step 2 are:

mass of empty weighing bottle = 26.032 g

mass of weighing bottle +

anhydrous sodium carbonate = 27.377 g

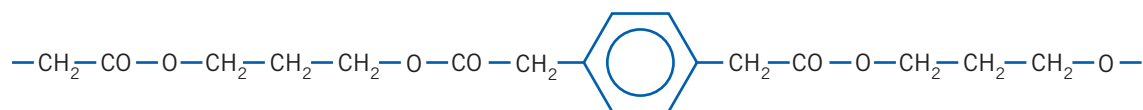
The experimental data from step 3 are:

volume of sodium carbonate solution used in each

titration = 20.00 mL

Burette readings				
Final reading (mL)	21.23	40.46	19.57	42.44
Initial reading (mL)	1.65	21.36	0.48	23.38

- Describe how the dilute hydrochloric acid solution could be prepared in step 1. Show any relevant calculations.
  - Explain why the hydrochloric acid was standardised using sodium carbonate instead of sodium hydroxide.
  - In step 3, which liquid would be used to rinse each of the following pieces of equipment prior to its use?
    - burette
    - 20.00 mL pipette
    - conical flask
  - Using the given experimental data, calculate the concentration, in  $\text{mol L}^{-1}$ , of the diluted solution of hydrochloric acid prepared in step 1.
- 20 a** Give the structural formula of the monomer used to prepare the following polymer:



- Is this polymer an addition or condensation polymer?



# 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)

( $1 \text{ cm}^3 = 1 \text{ mL}$ ,  $1 \text{ dm}^3 = 1 \text{ L} = 1000 \text{ mL}$ )

Temperature degrees Celsius ( $^\circ\text{C}$ ) or kelvin (K). ( $0.0^\circ\text{C} = 273.1 \text{ K}$ )

Energy change kilojoule (kJ)

Pressure kilopascal (kPa), atmospheres (atm), or in millimetres of mercury (mmHg)

( $1.000 \text{ atm} = 101.3 \text{ kPa} = 760.0 \text{ mmHg}$ )

### 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  $3.400 \times 10^3$  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

$$1.21 \times 10^3 \text{ g}$$

### 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 cm  $\times$  5.715 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
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.9
Lawrencium	Lr	103	(260)
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	175.0
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Mendelevium	Md	101	(258)

<b>Name</b>	<b>Symbol</b>	<b>Atomic Number</b>	<b>Relative atomic mass</b>
Mercury	Hg	80	200.6
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.2
Neon	Ne	10	20.18
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)
Tellurium	Te	52	127.6
Terbium	Tb	65	158.9
Thallium	Tl	81	204.4
Thorium	Th	90	232.0
Thulium	Tm	69	168.9
Tin	Sn	50	118.7
Titanium	Ti	22	47.88
Tungsten	W	74	183.8
Uranium	U	92	238.0
Vanadium	V	23	50.94
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.0
Yttrium	Y	39	88.91
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

## Appendix 4 Standard reduction potentials at 25°C

Half-reaction	$E^\circ$ (volts)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.78
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	+1.69
$2 HClO(aq) + 2H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O(l)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
$HClO(aq) + H^+(aq) + 2e^- \rightleftharpoons Cl^-(aq) + H_2O(l)$	+1.48
$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l)$	+1.46
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$NO_3^-(aq) + 2H^+(aq) + e^- \rightleftharpoons NO_2(g) + H_2O(l)$	+0.80
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.15
$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(aq)$	+0.14
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0 exactly
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	-0.13
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	-0.14
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	-0.26
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	-0.28
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$	-0.36
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	-0.40
$2 CO_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons HOCCOOH(aq)$	-0.43
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$Au(CN)_2^-(aq) + e^- \rightleftharpoons Au(s) + 2CN^-(aq)$	-0.60
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	-0.73
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.83
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	-1.18
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	-1.66
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.37
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	-2.76
$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	-2.89
$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	-2.91
$K^+(aq) + e^- \rightleftharpoons K(s)$	-2.93
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.04

# GLOSSARY

**Absolute temperature scale** See *kelvin temperature scale*.

**Absolute zero** The lowest possible temperature ( $-273^{\circ}\text{C}$  or  $0\text{ K}$ ).

**Accuracy** The closeness of a measurement to the true value.

**Acid** A substance that can act as a hydrogen ion (proton) donor (Brønsted–Lowry) (or a substance that produces  $\text{H}^+$  in solution – Arrhenius definition).

**Acid–base buffer** A solution that resists changes in pH when a small amount of either acid or base is added.

**Acid–base indicator** A species whose colour is different in acidic and in basic solutions, and is used to monitor the equivalence point in an acid–base titration.

**Acid–base titration curve** A plot of pH of a solution of acid (or base) versus the volume of base (or acid) added to the solution.

**Acid rain** Rain that has reacted with oxides, such as  $\text{SO}_2$  and  $\text{NO}_2$ , in the atmosphere and so has a pH lower than 5.

**Acidic oxide** An oxide that reacts with a base.

**Acidic salt** A salt that dissolves in water to give an acidic solution because one of its ions undergoes a hydrolysis reaction to form  $\text{H}_3\text{O}^+$  ions.

**Acidic solution** A solution in which the  $[\text{H}_3\text{O}^+]$  is greater than the  $[\text{OH}^-]$ .

**Acidity constant ( $K_a$ )** An equilibrium constant that provides a measure of the strength of an acid. It is the equilibrium constant for the hydrolysis of an acid HA, in water, to form the conjugate base,  $\text{A}^-$ ;  $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$ .

**Actinides** Period 7 metals from actinium (Ac) to lawrencium (Lr) in the periodic table.

**Activated complex** See *transition state*.

**Activation energy** The minimum energy with which particles must collide to react.

**Activity series** A listing of metals in decreasing order of their strength as a reductant ('desire' to lose electrons).

**Actual yield** The amount of product actually obtained in a chemical reaction.

**Addition polymerisation** The process in which monomers containing a carbon–carbon double bond join together to form a polymer by addition reactions.

**Addition reaction** A reaction in which two new atoms are added 'across the double bond' of an alkene, and the double bond becomes a single bond.

**Adsorption** When a substance adheres or 'sticks' to the surface of a solid.

**Alcohol** An organic compound containing the  $-\text{OH}$  functional group; its name ends in 'ol'.

**Aldehyde** An organic compound containing the  $-\text{CHO}$  functional group; its name ends in 'al'.

**Aliquot** The volume of a solution delivered by pipette.

**Alkali metal** A metal in group 1 of the periodic table.

**Alkaline earth metal** A metal in group 2 of the periodic table.

**Alkanes** A family of hydrocarbons that contain only carbon–carbon single bonds; general formula  $\text{C}_n\text{H}_{2n+2}$ .

**Alkenes** A family of hydrocarbons that contain one carbon–carbon double bond; general formula  $\text{C}_n\text{H}_{2n}$ .

**Alkyl group** A hydrocarbon group with one bond 'available' to attach to another atom, for example, methyl  $-\text{CH}_3$ , ethyl  $-\text{CH}_2\text{CH}_3$ .

**Alkynes** A family of hydrocarbons that contain one carbon–carbon triple bond; general formula  $\text{C}_n\text{H}_{2n-2}$ .

**Allotropes** Different structural forms of the same element; for example, diamond and graphite are allotropes of carbon.

**Alloy** A mixture with metallic properties, formed when a metal is combined with other elements, such as carbon or other metals.

**Alpha particle** A particle emitted in a radioactive process; identical to a helium nucleus,  ${}^4_2\text{He}$ .

**Amide** An organic compound that contains a  $-\text{CONH}-$  functional group.

**Amine (primary)** An organic compound that contains a  $-\text{NH}_2$  functional group.

**$\alpha$ -Amino acids** A group of organic compounds with molecules containing both an amine ( $-\text{NH}_2$ ) and a carboxylic acid ( $-\text{COOH}$ ) functional group; the monomer unit of a protein.

**Amorphous solid** A solid that lacks a regular crystalline structure.

**Amphoteric (amphiprotic) substance** A substance that is able to act as either an acid or a base.

**Amphoteric oxides** Oxides that are able to react with both acids and bases.

**Anion** A negatively charged ion.

**Anode** The electrode in electrochemical cells and electrolytic cells at which oxidation occurs. In an electrochemical cell, it is the negative electrode (in an electrolytic cell it is the positive electrode).

**Aqueous solution** A solution in which water is the solvent.

**Aromatic compound** An organic compound that contains a benzene ring.

**Arrhenius acid–base theory** An early theory that proposes acids produce  $\text{H}^+$  in aqueous solution and bases produce  $\text{OH}^-$  in aqueous solution.

**Atmosphere** A mixture of gases that surrounds the Earth's surface.

**Atom** The smallest possible particle of an element that retains the chemical nature of the element; composed of protons, neutrons and electrons.

**Atomic mass** See *relative atomic mass*.

**Atomic number (Z)** The number of protons in the nucleus of an atom.

**Avogadro constant ( $N_A$ )** The number of elementary particles in 1 mole of a substance; equal to approximately  $6.022 \times 10^{23}$ .

**Avogadro's law** Equal volumes of gases at the same temperature and pressure contain the same number of particles.

**Back titration** A procedure involving adding a measured excess of one reactant to another (the substance being analysed), and determining the amount that remains unreacted by titration.

**Base** A substance that can act as a hydrogen ion (proton) acceptor (Brønsted–Lowry), or produces  $\text{OH}^-$  ions in aqueous solution (Arrhenius definition).

**Basic oxide** An oxide that reacts with an acid.

**Basic salt** A salt that dissolves in water to form a basic solution because one of its ions undergoes a hydrolysis reaction to form  $\text{OH}^-$  ions.

**Basic solution** A solution in which  $[\text{OH}^-]$  is greater than  $[\text{H}_3\text{O}^+]$ .

**Battery** Several electrochemical cells connected in series. The term is also used for any commercial galvanic cell.

**Bent shape** See *V-shaped*.

**Beta particle** A particle emitted in a radioactive process; an electron.

**Biocell** A cell that contains materials from living things, such as glucose.

**Biodegradable** Able to degrade when exposed to living things for a reasonable period of time.

**Biodiesel** A fuel produced by the reaction of triglycerides, sodium hydroxide and an alcohol such as methanol.

**Biofuel** Renewable energy source made from organic matter; includes ethanol produced by fermentation and biogas produced by the decomposition of organic matter.

**Biosphere** The living systems that inhabit the Earth.

**Blast furnace** A large furnace in which heat and hot air blasts are used to convert iron ore with coke (C) to iron metal and carbon dioxide.

**Boiling point** The temperature at which a liquid boils. This occurs when its vapour pressure is equal to the atmospheric pressure.

**Boiling point elevation** The increase in boiling point of a solvent caused by the presence of a dissolved solute.

**Bond angle** The angle between two bonds 'joined to' a central atom (the angle formed by the nuclei of two surrounding atoms with the nucleus of the central atom at the vertex).

**Bond dissociation energy (or bond energy)** The amount of energy that must be supplied to separate atoms joined by a chemical bond.

**Bond length** The distance between a pair of nuclei held together by a chemical bond.

**Bonding electron pair (or bonding pair)** A pair of electrons shared by two nuclei.

**Boyle's law** At constant temperature and amount of gas, the volume occupied by the gas is inversely proportional to its pressure.

**Brønsted–Lowry acid–base theory** A theory that proposes that an acid is a substance that donates a hydrogen ion (proton) to a base.

**Buffer** See *acid–base buffer*.

**Buffer capacity** A measure of the ability of a buffer to resist a change in pH. It increases with an increase in concentrations and relative proportions of buffer components.

**Buffer range** The pH range over which a buffer acts effectively.

**Burette** A piece of analytical equipment with a graduated scale and a tap to allow delivery of a variable volume of solution.

**Calibration** The process of correcting for systematic error of a measuring device by comparing it to a known standard.

**Calorimeter** A device used to measure the thermal energy absorbed or released during a chemical reaction.

**Carbohydrate** A class of organic compounds having the general formula  $\text{C}_m(\text{H}_2\text{O})_n$ . Types of carbohydrates include monosaccharides, disaccharides and polysaccharides.

**Carboxylic acid** An organic compound containing the  $-\text{COOH}$  functional group; its name ends in 'oic acid'.

**Carcinogen** A cancer-causing agent.

**Catalyst** A substance that increases the rate of a chemical reaction without itself being consumed in the reaction. It provides an alternative pathway with a lower activation energy.

**Catalytic converters** Devices in cars that reduce toxic emissions in car exhausts.

**Cathode** The electrode at which reduction occurs in both electrochemical and electrolytic cells. In an electrochemical cell, it is the positive electrode and in an electrolytic cell it is the negative electrode.

**Cathodic protection** Protection of a metal from corrosion by connecting it to the negative terminal of a power source, or by connecting it to a more active metal. This makes the protected metal negatively charged and therefore unable to be oxidised.

**Cation** A positively charged ion.

**Cell potential (also emf or cell voltage)** The potential difference between the electrodes of an electrochemical cell; usually measured in volts; the driving force in an electrochemical cell that pulls electrons from the reductant in one half-cell to the oxidant in the other.

**Celsius scale** A temperature scale in which the freezing and boiling points of water are defined as 0°C and 100°C respectively.

**Change in enthalpy ( $\Delta H$ )** The heat lost or gained during a chemical reaction. Exothermic reactions have negative  $\Delta H$  values and heat is released to the surroundings. Endothermic reactions have positive  $\Delta H$  values and heat is absorbed from the surroundings.

**Charge density** The ratio of the charge of an ion to its volume.

**Charged cloud (or electrons)** Regions of space around atoms in which electrons are moving.

**Charles' law** At constant pressure and amount of gas, the volume of the gas is proportional to its kelvin temperature;  $V \propto T(K)$ .

**Chemical change** The change of substances into different substances through the reorganisation of atoms; a chemical reaction.

**Chemical equilibrium** A dynamic system in which the concentrations of all reactants and products remain constant over time.

**Chemical property** A characteristic of a substance that results in the substance changing into a different substance during a chemical change.

**Chemical reaction** A change in which at least one new substance is formed.

**Chlorination** The addition of chlorine.

**Chlorofluorocarbons (CFCs)** Ozone-destroying chemicals formerly used as solvents, refrigerants and aerosol propellants. These compounds contain carbon, chlorine and fluorine.

**Chlorophyll** Light-absorbing green pigment necessary for photosynthesis.

**cis-trans isomers** See *geometrical isomers*.

**Colligative property** A property of a solution that depends on the concentration, not identity, of solute particles.

**Collision theory** A model that explains reaction rate as a result of particles colliding with a certain minimum of energy.

**Combustion reaction** Rapid, flame-producing (exothermic) reaction in which oxygen reacts with a substance.

**Complex ion** An ion consisting of a central metal ion bonded by ion-dipole forces to ions of polar molecules.

**Compound** Two or more elements chemically combined in fixed proportions.

**Concentrated solution** A solution in which the ratio of amount of solute to amount of solvent is high.

**Concentration** A measure of how much solute is dissolved in a particular volume of solution.

**Concordant titres** Titres that fall within a specified range of each other, for example,  $\pm 0.02$  mL.

**Condensation** The process of a gas changing into a liquid.

**Condensation polymerisation** The process in which monomers containing at least two functional groups join together to form a polymer, with the loss of a small molecule (often water).

**Conductor (electrical)** A substance that conducts an electric current well.

**Conjugate acid-base pair** A pair of substances that differ by a hydrogen ion ( $H^+$ ). The acid has one more  $H^+$  than its conjugate base.

**Contact process** An industrial process for the manufacture of sulfuric acid based on the catalysed oxidation of  $SO_2$ .

**Controlled experiment** An experiment that measures the effect of one variable at a time by keeping the other variables constant.

**Core charge** The effective nuclear charge 'felt' by an outer-shell electron in an atom; equal to the nuclear charge minus the total number of inner shell electrons.

**Corrosion** The spontaneous reaction of a metal with oxygen or other substances in its environment.

**Covalent bond** The electrostatic attraction between one or more pairs of electrons that are shared between two nuclei, and the nuclei are shared between.

**Covalent molecular substance** A substance composed of molecules. The atoms in the molecules are bonded by covalent bonds.

**Covalent network substance** A substance whose atoms are arranged in a lattice with strong, covalent bonds between all the atoms.

**Cracking** A chemical process during which alkanes decompose by the breaking of carbon-carbon bonds to form smaller molecules and some unsaturated molecules.

**Cross links** Covalent links between adjacent polymer chains.

**Crystalline solid** A solid with particles arranged in a regular pattern.

**Dalton's law of partial pressure** For a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each gas would exert if it were alone in the container (partial pressures).

**Dehydrogenation reaction** A reaction in which two hydrogen atoms are removed from adjacent carbon atoms to form an unsaturated compound.

**Delocalised electrons** Electrons that are not confined to a particular location, but are able to move throughout a structure.



**Denaturation (of protein)** Destruction of the three-dimensional structure of a protein by agents such as chemicals and heat.

**Denitrification** Reduction, by bacteria, of nitrate ions,  $\text{NO}_3^-$ , to elemental nitrogen,  $\text{N}_2$ , in soil.

**Density** The mass per unit volume of a substance; usually measured in  $\text{g mL}^{-1}$  or  $\text{g cm}^{-3}$ .

**Deoxyribonucleic acid (DNA)** A naturally occurring polymer formed by the condensation polymerisation of three components—a sugar (deoxyribose), a phosphate and a nitrogenous base. DNA provides the genetic code that determines inherited characteristics.

**Detergent** A surfactant used as a cleaning agent.

**Diatomic molecule** A molecule consisting of two atoms covalently bonded together.

**Diffusion** The mixing of one substance with another due to the random movement of particles of both substances.

**Dilute solution** A solution in which the ratio of amount of solute to amount of solvent is low.

**Dilution** When more solvent is added to a solution, resulting in a decreased concentration.

**Dipeptide** A molecule formed by the condensation reaction of two amino acids. The amino acid residues are joined by a peptide link.

**Dipole** Has positively charged and negatively charged regions separated by a distance.

**Dipole–dipole forces** The electrostatic attraction that occurs between polar molecules.

**Dipole moment** A measure of the polarity of a molecule. Its size depends on the magnitude of the centres of partial positive and negative charges in the polar molecule and the distance between these centres of charges.

**Diprotic acid** An acid that is able to donate two hydrogen ions.

**Disaccharide** A sugar formed from two monosaccharides joined together, for example, sucrose.

**Dispersion forces** The weak attraction between molecules that occurs due to the instantaneous dipoles formed as a result of the random movement of electrons within the molecules.

**Displacement reaction** A reaction in which an element reacts with the dissolved ions of another element to produce the second element; often involves the reaction of a metal with the ions of another metal.

**Dissociation** The process by which ions separate when an ionic solid dissolves in a solvent.

**Distillation** A separation technique based on the different boiling points of the components of a solution.

**Double bond** A covalent bond in which four electrons (two pairs) are shared between two nuclei.

**Double helix** The two intertwining polynucleotide strands held together by hydrogen bonds that form the structure of DNA.

**Dry cell** A common electrochemical cell comprising Zn,  $\text{MnO}_2$ , C and  $\text{NH}_4^+$ , used in small objects such as radios, torches and toys.

**Dynamic equilibrium** A state of balance where the forward and reverse reactions continue at equal rates, so there is no net change in the amounts of reactants and products present in the mixture.

**Ecosystem** A community of organisms and their environment.

**Electrochemical cell** A cell in which chemical energy in the redox reaction is converted to electrical energy. It consists of two half-cells connected internally by a salt bridge and externally by wires.

**Electrode** A solid, conducting surface in an electrochemical or electrolytic cell.

**Electrolysis** The passage of electrical energy through a substance in order to force a non-spontaneous redox reaction to occur.

**Electrolyte** A substance that produces a liquid that can conduct an electric current; in particular, a substance that forms ions when it dissolves in water.

**Electrolytic cell** A cell through which a current is passed in order to force a non-spontaneous redox reaction to occur. Electrical energy is converted to chemical energy.

**Electron** Negatively charged particle that moves around the nucleus of an atom.

**Electron affinity** The energy change associated with the addition of an electron to a gaseous atom.

**Electron cloud** An imaginary representation of an electron's changing position over time around the nucleus.

**Electron configuration** The arrangement of electrons in the energy levels (shells) within an atom.

**Electron dot diagram** A diagram showing the outer-shell electrons, in the form of dots and/or crosses, in atoms, ions or molecules.

**Electron shell** A fixed energy level for an electron in the Bohr model of the atom.

**Electronegativity** A measure of the tendency of an atom to attract electrons to itself.

**Electrophoresis** A separation technique based on the different movement of charged particles of different mass and/or charge under the influence of an applied electric field.

**Electroplating** An electrolytic process in which a metal is coated with a thin layer of another metal.

**Electrorefining** An industrial electrolytic process in which a sample of an impure metal acts as an anode and a sample of the pure metal acts as the cathode.

**Electrostatic attraction** The attraction between a negatively charged species and a positively charged species.

**Electrovalency** The charge on an ion.

**Element** A substance that consists of only one type of atom, so it cannot be broken down into any simpler substance.

**Emf** See *cell potential*.

**Emission spectrum** A set of lines on the electromagnetic spectrum emitted when an excited atom returns to its ground state.

**Empirical formula** A formula that shows the simplest, whole-number ratio of atoms of each element present in a compound.

**End point** The point during a reaction where an indicator changes colour to show that the reaction is complete.

**Endothermic reaction** A reaction that absorbs energy from the surroundings, resulting in a decrease in temperature of the surroundings. The reaction has a positive  $\Delta H$  value.

**Entropy** A measure of the disorder or randomness of a system.

**Enzymes** Biological catalysts made of protein.

**Equilibrium** A state of balance. In chemical reactions, the state when the concentrations of reactants and products are constant and the rate of forward and backward reactions are equal.

**Equilibrium constant ( $K$ )** The value obtained when the equilibrium concentrations of the reactants and products are substituted in the equilibrium law expression. This value indicates the extent of the reaction at equilibrium.

**Equilibrium law** For a particular equation for a reaction, the value of the equilibrium law expression will be constant, at a constant temperature, despite how the equilibrium mixture was formed.

**Equilibrium law expression** The expression obtained by multiplying the product concentrations and dividing by the multiplied reactant concentrations, with each concentration raised to the power the same as the respective coefficient in the balanced equation.

**Equivalence point** The point during a reaction at which stoichiometric amounts of reactants have been reacted.

**Ester** An organic compound ( $\text{RCOOR}'$ ) containing the ester ( $-\text{COO}-$ ) functional group; formed by the condensation reaction of an alcohol ( $\text{R}'\text{OH}$ ) and a carboxylic acid ( $\text{RCOOH}$ ).

**Ether** An organic compound containing the ether ( $\text{R}-\text{O}-\text{R}'$ ) functional group.

**Eutrophication** A process involving the rapid growth of plant material in waterways, leading to oxygen depletion and death of aquatic animals.

**Excess reagent** The reactant that is not completely consumed in a reaction that is 100% complete.

**Excited state** Any electron configuration of an atom where the electrons are not in the shells of lowest possible energy.

**Exothermic reaction** A reaction that releases energy to the surroundings resulting in an increase in the temperature of the surroundings. The reaction has a negative  $\Delta H$  value.

**Extent of reaction** A measure of how complete a reaction is at equilibrium. The larger the amount of products compared to the reactants, the larger the value of the equilibrium constant and the greater the extent of the reaction.

**Fatty acid** A carboxylic acid with a long hydrocarbon chain.

**Filtration** A method for separating the components of a mixture containing a solid and a liquid or gas.

**Flash point** The minimum temperature at which a fuel produces enough vapour to form an explosive mixture.

**Flotation** A method used to separate mineral particles from unwanted ore material. Oil and detergents are used to produce bubbles, in a slurry of the ore, which carry the wanted mineral to the top of the mixture.

**Fluoridation** The addition of fluoride ions to drinking water to aid in the prevention of tooth decay.

**Formula unit** The chemical unit of a compound that contains the number and type of atoms shown in the empirical formula.

**Fossil fuel** Fuel formed by the decomposition of plant and animal material over millions of years; includes coal, oil and natural gas.

**Fractional distillation** A separation method based on the different boiling points of the components of a mixture. The fractionating tower contains a series of trays holding condensed liquid, through which vapour rising up the tower must bubble, to provide better separation.

**Free radicals** Reactive molecules with unpaired electrons.

**Freezing** The process of cooling a liquid until it solidifies.

**Freezing point depression** The lowering of the freezing point of a solvent caused by the presence of dissolved solute particles.

**Fuel cell** An electrochemical cell in which there is a continuous supply of gaseous reactants, one of which is oxygen. Electrical energy is produced from chemical energy.

**Functional group** An atom or group of atoms attached to a hydrocarbon stem that causes the molecule to exhibit certain properties.

**Fusion** See *melting*.

**Galvanic cell** See *electrochemical cell*.

**Galvanising** A process in which steel is coated with zinc to prevent corrosion.

**Genetic code** The set of three-base sequences, in a DNA molecule, that is translated into specific amino acids during the formation of a protein.

**Geometrical isomers** Isomers that have the same structural formula but their atoms are arranged differently in space. The *cis*-isomer has similar groups on the same side of the double bond; the *trans*-isomer has the groups on the opposite side.

**Global warming** The phenomenon caused by heat-trapping gases in the atmosphere, resulting in increased temperatures.

**Gravimetric analysis** Any procedure in which the masses of substances are measured in order to determine the composition of a sample.

**Green chemistry** The design of chemical products and processes that reduce the use and generation of hazardous substances.

**Greenhouse effect** The natural warming of the Earth due to gases in the atmosphere trapping heat.

**Greenhouse gases** Gases that absorb infrared radiation in the atmosphere.

**Ground state** The state of an atom where the electrons are in the lowest possible energy levels.

**Group** A vertical column of the periodic table, numbered 1 to 18. Elements in the same group have the same number of outer-shell electrons, and as a consequence exhibit similar chemical properties.

**Haber process** The industrial process used for the production of ammonia.

**Half-cell** An arrangement consisting of a conjugate redox pair, an electrode and an electrolyte. A reduction or oxidation reaction occurs in each half-cell when an electrochemical cell is operating to generate electricity.

**Half-equation** An ionic equation showing either an oxidation or a reduction reaction. Electrons donated or gained are shown in the half-equation as either a product or a reactant.

**Haloalkane** An organic compound containing either a fluoro- (-F), chloro- (-Cl), bromo- (-Br) or iodo- (-I) functional group.

**Hard water** Water containing a significant concentration of metal ions, such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . These ions cause soap to precipitate, thereby reducing its cleaning ability.

**Heat of combustion** The amount of energy produced by the combustion of a given amount of substance. Measured in units such as  $\text{kJ mol}^{-1}$  or  $\text{kJ g}^{-1}$ .

**Heat of fusion** The energy change that occurs when 1 mole of a substance melts.

**Heat of reaction ( $\Delta H$ )** The enthalpy change of a reaction; the heat released or absorbed when the molar amounts shown in a chemical equation react.

**Heat of solution** The heat released or absorbed when 1 mole of a solute dissolves in water.

**Heat of vaporisation** The energy change that occurs when 1 mole of a liquid vaporises.

**Heterogeneous catalyst** A catalyst that is in a different phase than the reactant; for example, a solid catalyst with gaseous reactants.

**Heterogeneous mixture** A mixture that has more than one phase, for example, oil mixed with water.

**High-density polymer** A polymer formed from closely packed, unbranched polymer chains.

**Homogeneous mixture** A mixture where all the components are in the one phase, for example, a solute dissolved in a solvent (a solution).

**Hydrate** A compound in which a specific number of water molecules are associated with each formula unit.

**Hydration shell** An oriented cluster of water molecules that surround an ion in aqueous solution. The polar water molecules are attracted by ion-dipole forces to the ions.

**Hydrocarbon** A compound composed of only hydrogen and carbon atoms.

**Hydrogen bonding** A type of strong, dipole-dipole bonding occurring between molecules that contain hydrogen bonded to fluorine, oxygen or nitrogen (H-FON).

**Hydrolysis** Reaction with water.

**Hydronium ion** A hydrogen ion covalently bonded to a water molecule,  $\text{H}_3\text{O}^+$ .

**Hydrophilic** 'Water-loving'; used to refer to a substance or part of a substance that dissolves in water.

**Hydrophobic** 'Water-fearing'; used to refer to a substance or part of a substance that repels (is not soluble in) water.

**Hydrosphere** The liquid part of the Earth's crust.

**Hypothesis** A testable proposal made to explain an observation. If inconsistent with experimental results, a hypothesis is revised or discarded.

**Ideal gas** A hypothetical gas whose volume, pressure, temperature and amount can be predicted using the gas laws; has no forces of attraction or repulsion between the particles.

**Ideal gas equation** The relationship between the pressure, temperature, volume and amount of a gas; formula  $PV = nRT$ .

**Ignition temperature** The temperature to which a fuel must be heated before it will spontaneously combust.

**Immiscible** Describes two liquids that do not mix to form a homogeneous solution.

**Incomplete combustion** Combustion that occurs in a limited supply of oxygen.

**Indicator (acid-base)** A weak acid and its conjugate base, at least one of which is highly coloured; used to indicate when the reaction in a titration is at the equivalence point.

**Infrared (IR) radiation** Electromagnetic radiation with wavelengths 750 nm to 1 mm.

**Inner electrons** Electrons in an atom that are not in the valence (outer) shell.

**Instantaneous rate** The reaction rate at a particular time, given by the slope of a tangent to a graph of amount of reactant or product versus time.

**Interface** The boundary between one substance and another.

**Intermolecular bond** Any form of bonding between molecules.

**Intramolecular bond** The bond within a molecule (covalent bond).

**Ion** A charged species due to an unequal number of protons and electrons.

**Ion exchange** A process involving the selective adsorption of ions onto the surface of a resin, and their selective desorption from the resin.

**Ion-dipole bond** The electrostatic attraction between an ion and a polar molecule.

**Ionic bond** The electrostatic attraction between oppositely charged ions.

**Ionic compound** A compound composed of positive and negative ions.

**Ionic equation** A chemical equation that only shows species undergoing chemical changes.

**Ionisation** The reaction of two or more uncharged molecular substances to form ions.

**Ionisation constant of water ( $K_w$ )** The product of the concentrations of hydronium ion and hydroxide ion in pure water at a specified temperature; equal to  $10^{-14}$  at  $25^\circ\text{C}$ .

**Ionisation energy (first)** The energy needed to remove 1 mole of electrons from 1 mole of gaseous atoms.

**Isoelectronic** Species containing the same number of electrons.

**Isomers (structural)** Molecules with the same molecular formula but different structural formulas.

**Isotopes** Species having the same number of protons (hence the same element), but different numbers of neutrons.

**Kelvin temperature scale** The scale that takes absolute zero ( $-273^\circ\text{C}$ ) as the lowest temperature.

**Ketone** An organic compound containing a  $-\text{CO}-$  functional group; named by adding the suffix ‘-one’ to the parent chain name.

**Kinetic energy** The energy due to the movement of an object; calculated using the formula  $E_k = \frac{1}{2}mv^2$ .

**Kinetic molecular theory** A model that describes the behaviour of the particles making up an ideal gas.

**Lanthanides** A group of 14 metallic elements, from La to Lu, shown at the bottom of the periodic table.

**Latent heat** The energy required to change a given amount of substance (usually 1 mole) from one state to another.

**Law of conservation of energy** Energy can be converted from one form of energy to another but it cannot be created or destroyed.

**Law of conservation of mass** Matter can neither be created nor destroyed during a chemical reaction.

**Le Châtelier’s principle** If a system is at equilibrium and any of the temperature, pressure or concentrations of the species are changed, the reaction will proceed in such a direction as to partially compensate for this change.

**Leaching** Washing out of ions out of an insoluble mixture by water.

**Lead-acid battery** A battery (used in vehicles) in which the anode is lead, the cathode is lead coated with lead(IV) oxide, and the electrolyte is sulfuric acid.

**Ligand** A neutral polar molecule or an ion attracted to a positive or negative ion, for example, water.

**Limestone** Naturally occurring impure form of calcium carbonate,  $\text{CaCO}_3$ .

**Limiting reagent** The reactant that is completely consumed in a reaction.

**Lone pair** See *non-bonding electron pair*.

**Low-density polymer** Polymer formed from loosely packed, branched polymer chains.

**Mass** The quantity of matter in an object.

**Mass number (A)** Number of protons plus neutrons in the nucleus of an atom.

**Matter** Anything that occupies space and has a mass.

**Maxwell Boltzmann distribution** A graph showing the distribution of particle velocities in a gas at a given temperature.

**Melting** To be changed from a solid to a liquid, especially on heating.

**Metallic bonding** The electrostatic attraction between positive ions and the delocalised electrons that move between them.

**Metallic substance** A substance composed of a lattice of positive ions surrounded by a sea of electrons.

**Metalloids** Elements along the ‘zig-zag’ line in the periodic table between metals and non-metals. They exhibit both metallic and non-metallic properties.

**Metallurgy** The process of separating a metal from its ore and purifying it for use.

**Micelles** Microscopic, spherical particles composed of surfactant molecules.

**Millimetres of mercury (mmHg)** A unit of pressure;  $760 \text{ mmHg} = 101.3 \text{ kPa}$ .

**Mineral** A naturally occurring compound of a metal.

**Miscible** Describes two substances that mix to form a homogeneous solution.

**Molar mass (M)** The mass of 1 mole of a substance measured in  $\text{g mol}^{-1}$ .

**Molar volume** The volume occupied by 1 mol of a gas. It is 22.41 L at STP.

**Molarity (M)** The concentration of a solution measured in the units of  $\text{mol L}^{-1}$ .

**Mole (mol) (n)** The amount of substance containing the same number of elementary particles as there are atoms in 12 g of carbon-12.

**Molecular equation** A chemical equation showing the reactants and products in their undissociated forms.

**Molecular formula** A formula that shows the actual number of atoms of each element present in one molecule of a compound.

**Molecular mass** The sum of the atomic masses of the atoms shown in a chemical formula.

**Molecular polarity** The overall distribution of charge in a molecule, determined by its shape and bond polarities.

**Molecular shape** The three-dimensional structure defined by the relative positions of the atomic nuclei in a molecule.

**Molecule** A discrete group of atoms, of known formula, covalently bonded together.

**Monatomic** Composed of only single atoms.

**Monatomic ion** An ion composed of only one atom.

**Monomers** Small molecules that are able to bond to each other, or other monomers, to form a large covalently bonded molecule (polymer).

**Monoprotic acid** An acid that is able to donate only one hydrogen ion (proton).

**Monosaccharide** A single sugar; examples include fructose and glucose.

**Nanotechnology** The creation of materials, devices and systems with a size in the range of 1–100 nanometres. Technology developed at the atomic and molecular level to create and use structures and devices that exhibit novel properties because of their small size.

**Nanotube** A graphite-like, cylindrically shaped carbon structure.

**Natural gas** Mixture of gaseous hydrocarbons, mainly methane, formed over millions of years in the Earth's crust.

**Neutralisation** An acid reacting with a base to form a salt and water.

**Neutron** Electrically neutral subatomic particle found in the nucleus of the atom. It has a mass slightly greater than that of a proton.

**Nitrogen fixation** The process of converting atmospheric, molecular nitrogen into soluble forms that can be taken up by plants.

**Noble gases** The extremely stable group 18 elements.

**Non-bonding electron pair** A pair of outer-shell electrons in a molecule that are not shared between nuclei; also known as a lone pair.

**Non-electrolyte** A substance that does not form ions when dissolved in water. Its solution will not conduct electricity.

**Non-metal** An element that does not exhibit metallic properties. They are positioned in the upper right-hand corner of the periodic table.

**Non-polar** Having an even distribution of charge.

**Non-polar covalent bond** A covalent bond between identical atoms in which the electrons are equally shared.

**Non-renewable energy source** An energy source for which there are finite reserves. The source is used at a faster rate than it can be replaced.

**Nuclear fission** When a nucleus splits apart to form smaller nuclei.

**Nuclear fusion** When two or more smaller nuclei combine to form a larger nucleus.

**Nucleotide** The monomer of DNA, consisting of a sugar, phosphate and a nitrogenous base.

**Nucleus** Positively charged central core of the atom; contains protons and neutrons and is responsible for most of the mass of the atom.

**Observation** A fact obtained with the senses, sometimes with the aid of an instrument such as a thermometer.

**Octet rule** Atoms will bond together in such a way as to obtain an outer shell containing eight electrons.

**Ore** A naturally occurring mixture of rock material and a mineral from which a metal may be economically extracted.

**Ostwald process** The industrial process used for the production of nitric acid by the oxidation of ammonia.

**Outer electrons (or outermost or outer-shell electrons)** Electrons in the outer or valence shell of an atom or ion.

**Overall equation** See *molecular equation*.

**Overall redox equation** The equation that can be obtained by adding the oxidation and the reduction half-equations together so that the electrons 'cancel out'.

**Oxidant** A substance that causes another substance to be oxidised by accepting electrons from it.

**Oxidation** A reaction in which a substance loses one or more electrons.

**Oxidation numbers** Numbers assigned to atoms, according to a set of rules, to help determine whether redox reactions are occurring.

**Oxidation–reduction (or redox) reaction** A reaction in which electrons are transferred from one reactant (the reductant) to another (the oxidant).

**Oxyacid** An acid in which the acidic hydrogen ion is bonded to an oxygen atom.

**Ozone layer** An area in the atmosphere of highest ozone concentration, at about 19–48 km altitude.

**Partial pressure** The pressure exerted by a gas, in a gaseous mixture, if it were alone in the container.

**Pascal (Pa)** The SI unit for pressure.

**Peptide link** The group –CONH– that joins two amino acid residues following the condensation reaction between two amino acids.

**Percentage yield** The actual yield of a reaction expressed as a percentage of the theoretical yield.

**Period** A horizontal row of the periodic table, numbered 1 to 7. Elements in the same period have their outer-shell electrons in the same shell.

**Periodic table** A chart showing all the known elements organised horizontally in increasing atomic number and vertically in groups of similar outer-shell configuration.

**Pesticide** Chemical used to kill or control pests.

**Petroleum** Crude oil; mainly a mixture of hydrocarbons.

**pH** A measure of the acidity of a solution; formula  $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$ .

**pH curve (titration graph)** A graph showing how the pH of a solution changes as a function of volume of solution (usually from a burette) added.

**Phase** A physically distinct portion of a system.

**Photochemical smog** Atmospheric pollution involving a range of compounds whose reactions are initiated by sunlight.

**Photosynthesis** The endothermic reaction (occurring in green plants) by which carbon dioxide and water react to produce glucose and oxygen.

**Physical change** A change in a substance that does not alter its composition; that is, no chemical bonds are broken and a new substance is not formed.

**Physical property** A characteristic of a substance itself, without interacting with or changing into other substances.

**Pipette** A piece of analytical equipment that allows delivery of an accurately known volume of solution.

**Polar** Has a permanent dipole.

**Polar covalent bond** A covalent bond in which the electrons are not equally shared between the two nuclei due to a difference in the electronegativities of the elements involved.

**Polar molecule** A molecule that acts as a permanent dipole. The molecule has an uneven distribution of charge.

**Polyatomic ion** An ion composed of more than one atom. The atoms are covalently bonded in the ion.

**Polymer** A large, covalently bonded molecule composed of small repeating units (monomers).

**Polypeptide** A polymer formed by the condensation polymerisation of many amino acids.

**Polyprotic acid** An acid that is able to donate more than one hydrogen ion (proton).

**Polysaccharide** A complex carbohydrate composed of simple sugars covalently linked; examples are starch, cellulose and glycogen.

**Potential energy** The energy possessed by an object due to position and forces existing on the object.

**ppm** A measure of concentration equivalent to  $\text{mg kg}^{-1}$ .

**Precipitate** An insoluble solid that forms when two or more solutions are mixed.

**Precision** The degree of agreement among several measurements of the same quantity; the reproducibility of a measurement.

**Pressure** The force exerted on a surface, per unit area of surface.

**Primary cell** A cell that cannot be recharged because the products of the discharge reaction migrate away from the electrodes and are consumed in side reactions.

**Primary standard** A substance that can be used directly to prepare a standard solution. The substance has a known formula, is obtainable in pure form and is stable over time.

**Products** The substances produced in a chemical reaction.

**Property** A characteristic that gives a substance its unique identity.

**Protein** A naturally occurring polymer formed by condensation polymerisation of amino acids.

**Proton** Positively charged subatomic particle found in the nucleus of an atom.

**Pure substance** A substance with constant composition. It has a chemical formula.

**Pyramidal shape** A molecular shape caused by the presence of a lone pair in a tetrahedral arrangement. The three atoms bonded to the central atom are positioned at the vertices of a triangular pyramid.

**Qualitative analysis** Analysis involving the identification of a substance or the components of a mixture.

**Quantitative analysis** Analysis involving the determination of the relative amounts of the components of a mixture.

**Radiation** The transmission of energy by electromagnetic waves.

**Radioactivity (or radioactive decay)** Disintegration of a nucleus, with the accompanying radiation released.

**Random error** Human error that occurs in all measurements and results in values both higher and lower than the actual value.

**Reactants** The substances initially present in a chemical reaction.

**Reaction mechanism** A series of elementary steps making up the overall reaction.

**Reaction rate** The change in amount of one of the reactants or products over time.

**Recrystallisation** A purification technique where an impure solid is dissolved in a small volume of hot solvent and then allowed to recrystallise.

**Redox reaction** A reaction that involves the transfer of electrons from a reductant to an oxidant.

**Reductant** A substance that causes another substance to be reduced by donating electrons to it.

**Reduction** A reaction in which a substance gains one or more electrons.

**Reference cell** A cell containing a reference, usually a pure solvent, used for comparison in an analytical instrument.

**Refluxing** Condensing of the compounds that evaporate during a reaction. The compounds are returned to the reaction mixture.

**Relative atomic mass ( $A_r$ )** The weighted mean of the masses of the naturally occurring isotopes on the scale where the mass of an atom of carbon-12 is taken to be 12 exactly.

**Relative formula mass** The sum of the relative atomic masses of the elements as given in the formula for any non-molecular compound.

**Relative molecular mass ( $M_r$ )** The sum of the relative atomic masses of the elements as given in the molecular formula of a compound.

**Renewable energy source** An energy source that can be continually replaced.

**Respiration** A biological process in which molecules are broken down to release energy; involves reaction of glucose with oxygen to produce carbon dioxide and water.

**Reversible reaction** A reaction in which both the forward and reverse reactions can occur.

**Roasting** A metallurgical process in which metal sulfides are converted to oxides by heating.

**Rounding off** The process of removing digits based on a series of rules to obtain an answer with the proper number of significant figures.

**Sacrificial anode** A reactive metal that provides cathodic protection for a less reactive metal to which it is connected. The sacrificial anode undergoes oxidation, providing electrons to prevent the protected metal from being oxidised.

**Salt** An ionic compound other than an oxide or hydroxide.

**Salt bridge** A device used to connect the two half-cells in an electrochemical cell. It provides ions to each half-cell to maintain their electrical neutrality.

**Saturated compound** An organic compound in which all the carbon-carbon bonds are single bonds.

**Saturated solution** A solution containing the maximum mass of solute that can be dissolved in a given volume of solvent at a particular temperature.

**Scanning tunnelling microscopy** An instrumental technique that uses electrons moving across a minute gap to 'observe' the surface of a material on the atomic scale.

**Secondary cell** An electrochemical cell that can be recharged by the passage of an electric current through the cell because the products of the discharge reaction remain in contact with the electrodes.

**Secondary structure of a protein** The three-dimensional structure of the protein chain.

**Self-ionisation** A process where a substance reacts with itself to form ions.

**Shells** Major energy levels within an atom in which electrons move.

**Shielding** The ability of complete shells of electrons to lessen the nuclear attraction on an outer-shell electron.

**Side chain** A group of atoms bonded to the parent hydrocarbon chain in an organic molecule.

**Side reaction** A different chemical reaction that consumes some of the reactant and reduces the overall yield of the desired product.

**Significant figures** The certain digits and the first uncertain digit of a measurement.

**Silicate** A type of compound, found throughout rocks and soil, consisting of Si-O bonds, and often metal positive ions.

**Silicone** A type of synthetic polymer containing Si-O chains with organic groups and cross-links.

**Single bond** A bond in which two electrons are shared by two atoms.

**Slag** A molten waste product formed from metal extraction processes, such as the blast furnace, formed by the reaction of acidic silicates with a basic metal oxide.

**Smelting** Heating a mineral with a reducing agent to obtain a metal.

**Smog** Hazy, polluted air.

**Soap** The salt of a fatty acid. Its negative ion consists of a long hydrocarbon chain with a negatively charged group bonded to one end.

**Solubility** The amount of a substance that will dissolve in a given amount of solvent, at a given temperature; usually measured as g per 100 g of solvent.

**Solubility curve** A graph of solubility of a substance in a given solvent versus temperature.

**Solute** The dissolved component of a solution.

**Solution** A homogeneous mixture, formed by a solute dissolving in a solution.

**Solvent** A substance, usually a liquid, that is able to dissolve another substance, the solute.

**Specific heat capacity** The energy required to raise the temperature of 1 g of a substance by 1°C.

**Spectator ion** An ion present in a reaction that does not undergo chemical change.

**Spectroscopy** The study of the radiation absorbed or emitted by matter.

**Spectrum (in spectroscopy)** A display of the wavelengths of light emitted or absorbed by a substance.

**Spontaneous reaction** A reaction that occurs immediately the reactants are mixed together.

**Standard hydrogen electrode** A platinum electrode in contact with

1 mol L<sup>-1</sup> H<sup>+</sup> ions and surrounded by hydrogen gas at a pressure of 101.3 kPa.

**Standard laboratory conditions (SLC)** Pressure of 101.3 kPa and temperature of 25°C (298 K).

**Standard reduction potential ( $E^\circ$ )** The potential of a half-reaction under standard conditions, as measured against the potential of the standard hydrogen electrode.

**Standard solution** A solution of accurately known concentration.

**Standard temperature and pressure (STP)** Pressure of 101.3 kPa and temperature of 0°C (273 K).

**Standardised solution** A solution of a non-primary standard of accurately known concentration. The concentration is determined by titration.

**States of matter** The three different forms in which matter can exist; solid, liquid and gas.

**Steel** An alloy of iron with small amounts of carbon and usually other metals.

**Stoichiometric amounts** When the reactants are present, in a reaction mixture, in the mole ratio given by the coefficients in the balanced chemical equation.

**Stoichiometry** Area of chemistry that deals with quantitative aspects of chemical reactions.

**Stratosphere** A layer of the atmosphere at approximately 16–50 km altitude.

**Strong acid** An acid that readily donates a hydrogen ion (proton) to water.

**Strong base** A base that readily accepts a hydrogen ion (proton) from water.

**Strong electrolyte** A substance that completely breaks up into ions when dissolved in water.

**Strong force (nuclear force)** An attractive force that exists between all protons and neutrons in a nucleus. It is about 100 times stronger than the electrostatic repulsive force between two protons.

**Structural formula** The representation of a molecule in which the relative positions of the atoms or groups of atoms are shown.

**Structural isomers** Compounds composed of the same number and type of atoms, but where the atoms are organised differently.

**Subatomic particles** Particles within atoms (protons, neutrons and electrons).

**Sublimation** When a substance changes directly from a solid to a gas.

**Subshells** Energy levels within an atom. A subshell is composed of a set of orbitals of equal energy.

**Substitution reaction** A typical reaction of alkanes (and benzene) where one or more hydrogen atoms are replaced by other atoms or groups of atoms such as a halogen.

**Supercooling** A process of cooling a liquid below its freezing point without it changing into a solid.

**Superoxide** A compound containing the O<sup>2-</sup> ion.

**Supersaturated solution** An unstable solution containing more than the maximum mass of solute that can be dissolved in a given volume of solvent at a particular temperature.

**Surfactant** Molecule that contains two sections, a hydrophobic or ionic 'tail' and a hydrophilic or non-polar (long hydrocarbon chain) 'head'. It can interact with fat/oil molecules to make them more miscible with water.

**Surroundings** Everything surrounding a chemical system (the chemicals involved in a chemical reaction).

**Systematic error** A type of consistent error producing values that are either higher or lower than the actual value; often caused by faulty equipment or a consistent fault in technique.

**Tempering** Heating a quenched metal then cooling it slowly, resulting in a strong, but malleable, metal.

**Tertiary structure of a protein** The overall shape of the protein, for example, globular.

**Tetrahedral arrangement** The geometrical arrangement when four groups of electron pairs maximise their separation around a central atom.

**Theoretical yield** The maximum amount of product that can be formed when the limiting reagent is completely consumed.

**Thermochemical equation** A chemical equation that includes the enthalpy change  $\Delta H$ .

**Thermoplastic polymer** A polymer that will soften and can be moulded when heated. It cools and hardens to retain the moulded shape.

**Thermosetting polymer** A polymer that does not soften when heated.

**Titration** The procedure where one solution is added to another solution until the reaction between them is complete. One solution has a known concentration.

**Titration curve** A graph of pH versus volume of solution to show the progress of a reaction during a titration.

**Titre** The volume of solution delivered by a burette during a titration.



**Transition metals** Elements in the d block, or middle block, of the periodic table.

**Transition state (activated complex)** An unstable species formed in an effective collision of reactants that exists momentarily when the system is highest in energy.

**Transpiration** Water loss by evaporation from plant leaves through their stomata.

**Trigonal planar arrangement** The geometrical arrangement formed when three groups of electrons maximise their separation around a central atom.

**Trigonal planar shape** A molecular shape formed when three atoms around a central atom lie at the corners of a triangle.

**Trigonal pyramidal shape** See *pyramidal shape*.

**Triple bond** A covalent bond in which six electrons (three pairs) are shared between two nuclei.

**Triprotic acid** An acid that is able to donate three hydrogen ions (protons).

**Ultraviolet (UV) radiation** Electromagnetic radiation with wavelengths 10 to 380 nm.

**Uncertainty (in measurements)** A characteristic of every measurement that results from the inexactness of the measuring device and the necessity of estimating when taking a reading.

**Universal gas constant** The constant,  $R$ , in the ideal gas law,  $PV = nRT$ . Its value depends on the units used for  $P$  and  $V$ . It is 8.315 when  $P$  is measured in kPa and  $V$  in L.

**Unsaturated compound** An organic compound containing at least one or more double or triple carbon-carbon bonds.

**Unsaturated solution** A solution containing less than the maximum mass of solute that can be dissolved in a given volume of solvent at a particular temperature.

**V-shaped** A molecular shape that arises when a central atom is bonded to two atoms and has one or two lone pairs.

**Valence electrons** The outer-shell electrons in an atom.

**Valence shell** The outermost occupied electron shell in an atom.

**Valence shell electron pair repulsion (VSEPR)** The electron pairs in a molecule (both bonding and nonbonding) will repel each other and take up positions as far from one another as possible in order to minimise these repulsions.

**Van der Waals forces** The weak bonds between molecules, comprising dispersion forces, dipole-dipole forces and hydrogen bonding.

**Vapour pressure** The pressure exerted by a gas at equilibrium with its liquid in a closed vessel.

**Vapour pressure lowering** The lowering of the vapour pressure of a solvent caused by the presence of dissolved solute particles.

**Volatility** The tendency of a substance to become a gas.

**Volumetric analysis** A form of quantitative analysis that involves measuring the volumes of solutions taking part in a chemical reaction.

**Water softening** The process of removing hard-water ions such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from washing water.

**Weak acid** An acid that does not readily donate a hydrogen ion (proton) to water.

**Weak base** A base that does not readily accept a hydrogen ion (proton) from water.

**Weak electrolyte** A substance that only partially breaks up into ions when dissolved in water.

**Work hardening** Repeated hammering or bending of a metal, resulting in a harder, more brittle metal.

**X-rays** Penetrating electromagnetic radiation; region of the electromagnetic spectrum with wavelength of approximately 1 to 0.01 nm.

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