### Atomic structure



### The structure of atoms

Our understanding of the structure of atoms evolved over centuries and continues to change in the light of new evidence. When the idea of atoms was first proposed, they were thought to be tiny solid spheres that could not be divided into smaller parts. This idea of solid indivisible atoms could not explain some experiments involving electricity, nuclear energy and chemical reactions, so chemists began to explore theories on the subatomic structure of atoms.

Chemists use **models** to represent atomic structure. These models change and develop as new discoveries are made. Current understanding of the atom is based on a model consisting of a **nucleus** and a surrounding region containing **electrons**. The nucleus is actually quite small compared to the size of the atom. Figure 1.1 shows an aerial view of a football ground. If an atom was the size of this football ground, its nucleus would be the size of a marble.  $\bigcirc$ 

Atoms are too small to be seen, even with the assistance of the world's most powerful microscopes.



Electrons are negatively charged particles that move around the nucleus of an atom.

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figure 1.1 If the nucleus of an atom were about 1 cm in diameter, the electrons would have a region the size of this football ground to move around in.

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Protons have a positive charge, electrons have a negative charge and neutrons have no charge.

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In the nucleus of an atom there are positively charged particles called **protons** and particles with no charge called **neutrons**. Protons are similar in size and mass to neutrons. Electrons are negatively charged and their mass is much smaller than that of protons and neutrons. The relative masses of protons, neutrons and electrons are shown in table 1.1. Atoms generally have diameters in the order of  $10^{-9}$  m while the nucleus has a diameter in the order of about  $10^{-13}$  m. This reveals that most of an atom is actually empty space.

table 1.1	Subatomic particles, their charges and re	lative masses.
Subatomic particle	Mass relative to a proton	Charge
proton (p)	1	+1
neutron (n)	1	0
electron (e)	<u>1</u> 1836	-1

The nucleus of an atom makes up most of the mass of an atom but occupies only a small portion of its volume. Electrons account for only a small fraction of the mass of an atom but as they move rapidly around the nucleus they occupy most of the atom's volume.

Protons are positively charged and therefore repel each other; electrons are negatively charged and also repel each other. As protons and electrons are oppositely charged they attract each other. These forces of attraction and repulsion within an atom are carefully balanced to maintain a stable structure.

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Different types of atoms contain different numbers of protons, neutrons and electrons but a neutral atom will always have the same number of protons and electrons. Figure 1.2 is a diagram showing the arrangement and number of subatomic particles of a lithium atom. The relative sizes of the particles and the nucleus are not to scale.



**figure 1.2** The arrangement of the protons, neutrons and electrons within a lithium atom.

This diagram shows a lithium atom with four neutrons and three protons in the nucleus. The three electrons surrounding the nucleus cancel out the positive charge of the three protons resulting in a neutral atom.

The smallest and simplest atom is that of hydrogen. The nucleus of a hydrogen atom has only one proton and no neutrons. All other types of atoms contain neutrons. Since the hydrogen atom contains one proton it must also have one electron to balance the charges and make it a neutral atom.



figure 1.3 A hydrogen atom consists of one proton and one electron.

A single gold atom has 79 protons, 118 neutrons and 79 electrons. Its mass is much greater than that of hydrogen and it is a more complex atom. The different nuclear structure and corresponding different electronic structure of various atoms determines their individual chemical properties.

### Questions

- 1 How are protons, electrons and neutrons arranged in an atom?
- 2 Compare the mass and charge of protons, electrons and neutrons.
- **3** Explain why the number of electrons in an atom equals the number of protons.
- **1.2 Elements and isotopes**

### Elements

All hydrogen atoms contain one proton. All lithium atoms contain three protons. All gold atoms contain seventy-nine protons. All atoms of the same type contain the same number of protons and it follows that they will also have the same number of electrons. Substances consisting of atoms with the same number of protons are called **elements**. Hydrogen, lithium and gold are all elements.



The nucleus of an atom is

made up of protons and neutrons, which make up

volume of the atom but most of its mass.

In a neutral atom the

electrons is the same. The positive and negative charges cancel out.

The chemical properties

of a substance are those observed during chemical changes which result in

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All the atoms of an element have the same number of protons. This number is called the **atomic number**.

The **mass number** is the total number of protons and neutrons in the nucleus of an atom.

Isotopes of an element have the same atomic number but different The number of protons in the atoms of an element is known as the **atomic number**. Every carbon atom has 6 protons in the nucleus so the atomic number of carbon is 6. The atomic number of lithium is 3.

Most of the mass of an atom is made up of protons and neutrons, which have very similar masses. The total number of protons and neutrons is called the **mass number**. Figure 1.2, a diagram of a lithium atom, shows an atom with 3 protons and 4 neutrons and so it has a mass number of 7.

### Isotopes

All atoms of the same element have the same number of protons but the number of neutrons can vary. All oxygen atoms have 8 protons and 99.76% of oxygen atoms have 8 neutrons. The oxygen atoms with an atomic number of 8 and a mass number of 16 can be represented as:

 $\begin{array}{l} \text{mass number} \to 16 \\ \text{atomic number} \to 8 \\ \end{array} O \ \leftarrow \text{symbol of element} \end{array}$ 

0.04% of oxygen atoms have a mass number of 17 and 0.20% of oxygen atoms have a mass number of 18. They can be represented as:

 $^{17}_{8}O$   $^{18}_{8}O$ 

Oxygen atoms must all have 8 protons but they may have 8, 9 or 10 neutrons. These different types of oxygen atoms are called **isotopes**. Isotopes of an element have the same number of protons but different numbers of neutrons.



figure 1.4

The oxygen reacting during combustion is made up of different isotopes yet all the atoms react identically. They are still the same element.

### Names and symbols

So far in this chapter we have looked at the structure of atoms, elements and isotopes. The use of symbols as a shorthand way of representing these will become increasingly important.

The origin of symbols of some elements is obvious since they are simply the first letter of the name. For example the symbol for oxygen is O, hydrogen is H and carbon is C.

For some it became necessary to use the first two letters when the first letter was already used and so calcium is represented as Ca and helium as He. Sometimes the first letter and a second letter from somewhere else in the name are used, for example magnesium has the symbol Mg (although M and Ma are not used for any other element).

The most recently created artificial elements have been given temporary names and symbols of three letters until their discovery is verified. The name represents the atomic number of the element. Unpentium (115), Uup, is an example of this.

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Sometimes the letters used do not have any obvious connection to the names because they are taken from their names in other languages, for example copper Cu (cuprum—Latin), mercury Hg (hydor argyros meaning 'liquid silver' —Greek) and tungsten W (wolfram—German).

Table 1.2 includes some elements and their symbols.

names. For ot	名 The sym hers it is les	bols of some elem s than obvious.	nents have ob	vious connections	to their
Element	Symbol	Element	Symbol	Element	Symbol
aluminium	Al	gold	Au	nobelium	No
americium	Am	helium	He	oxygen	0
argon	Ar	hydrogen	Н	phosphorus	Р
arsenic	As	iodine	I	platinum	Pt
bromine	Br	iron	Fe	plutonium	Pu
calcium	Ca	krypton	Kr	silicon	Si
carbon	С	lead	Pb	silver	Ag
chlorine	Cl	magnesium	Mg	sodium	Na
copper	Cu	neon	Ne	sulfur	S
europium	Eu	neptunium	Np	tin	Sn
einsteinium	Es	nickel	Ni	roentgenium	Rg
fluorine	F	nitrogen	Ν	zinc	Zn

### Questions

- 4 For the cadmium atom containing the nucleus <sup>112</sup><sub>48</sub>Cd, state:
  - **a** the number of protons
  - **b** the number of electrons
  - c the number of neutrons.
- 5 Use the convention for representing isotopes, e.g. <sup>112</sup><sub>48</sub>Cd, to describe the following atoms.
  - a a carbon atom that has 6 protons, 6 neutrons and 6 electrons
  - **b** a carbon atom that has 6 protons, 7 neutrons and 6 electrons
  - c a carbon atom that has 6 protons, 8 neutrons and 6 electrons

- d an aluminium atom that has 13 protons, 14 neutrons and 13 electrons
- 6 Represent each of the following atoms using the convention for representing isotopes, e.g. <sup>112</sup><sub>48</sub>Cd. (Refer to Appendix A to find the correct symbol for each element.)
  - a an atom which has 8 protons, 8 neutrons and 8 electrons
  - **b** an atom which has 16 protons, 18 neutrons and 16 electrons
  - an atom which has 56 protons, 74 neutrons and 56 electrons
  - d an atom which has 56 protons, 82 neutrons and 56 electrons

### 1.3 Atomic mass

If the masses of atoms were given in kilograms or grams, the amounts would be incredibly small and of little practical value. Chemists devised a standard for measuring the masses of individual atoms. The most common isotope of carbon,  ${}^{12}_{6}$ C, is given the value of 12 units. Each unit is one twelfth of the mass of a  ${}^{12}_{6}$ C isotope. Individual isotopes of each element are given a value known as the **relative isotopic mass**.



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Atomic structure

Table 1.3 shows the relative isotopic mass of the isotopes of some elements. It also shows the abundance of each isotope—a percentage used to indicate how much of one isotope is present in a sample of an element.

table	1.3 The iso	topes of so	me common elemer	ts and their isotopic masses.
Element	lsoto	ре	Relative isotopic mass	Abundance (%)
hydrogen	1 <sup>1</sup> H		1.008	99.986
	<sup>2</sup> H		2.014	0.014
	ЗН		3.016	0.0001
carbon	<sup>12</sup> C		12 exactly	98.888
	<sup>13</sup> C		13.003	1.112
	<sup>14</sup> C		14.003	approx. 10 <sup>-10</sup>
oxygen	<sup>16</sup> 0		15.995	99.76
	<sup>17</sup> 0		16.999	0.04
	<sup>18</sup> 0		17.999	0.20
copper	<sup>63</sup> Cu		62.931	69.10
	<sup>65</sup> Cu		64.931	30.90

The relative mass of individual isotopes is of limited use, so chemists calculate a weighted average to determine a value for each element known as the **relative atomic mass**.

Any sample of chlorine atoms is made up of two isotopes <sup>35</sup>Cl and <sup>37</sup>Cl. The relative isotopic mass and abundance of these isotopes are shown in table 1.4. The two isotopes of chlorine have the same number of protons and electrons but different numbers of neutrons giving them different masses.

table	ි ් අපි Relative isotopic mass and abundance	of chlorine isotopes.
lsotope	Relative isotopic mass	Relative abundance (%)
<sup>35</sup> Cl	34.969	75.80
<sup>37</sup> Cl	36.966	24.20

The relative atomic mass of chlorine is calculated using the relative isotopic mass and the relative abundance of each isotope. Since 75.80% of all chlorine atoms are <sup>35</sup>Cl then 0.7580 of all chlorine atoms have a relative isotopic mass of 34.969. Similarly, 0.2420 of all chlorine atoms are <sup>37</sup>Cl and have a relative isotopic mass of 36.966.

The average relative mass of a chlorine atom is:

 $0.7580 \times 34.969 + 0.2420 \times 36.966$ 

= 26.507 + 8.946

= 35.453

The relative atomic mass of chlorine is 35.45. The term relative atomic mass can be abbreviated  $A_{\rm r}$ .

For chlorine,  $A_r = 35.45$ 

The relative atomic mass of all the elements has been calculated in a similar way. A table of the relative atomic masses of elements can be found as Appendix A.

The relative isotopic mass is the mass of an individual isotope of an element

number of an atom is omitted as it can be determined from the

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About the elements

The relative atomic mass of an element is the weighted average of

masses of all the naturally occurring isotopes.

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### Questions

7 Consider the isotopic compositions of some common elements in table 1.3. Use the data in the table to calculate the relative atomic mass of:

- a oxygen
- **b** copper
- c hydrogen.

8 The element lithium has two isotopes: <sup>6</sup>Li has a relative isotopic mass of 6.02. <sup>7</sup>Li has a relative isotopic mass of 7.02.

The relative atomic mass of lithium is 6.94. Calculate the percentage abundance of the lighter isotope. (Hint: let the percentage abundance of the lighter isotope be *x*. What will the percentage abundance of the heavier isotope be?)

### 1.4 Electronic structure

Since the electrons of an atom repel each other, they tend to arrange in particular ways to minimise these forces of repulsion. An understanding of how electrons are arranged is important as it helps in understanding their physical properties as well as how atoms interact chemically.

There are several models used to describe the **electron configuration** of atoms. In this section, one of the simpler ones is explained. Electrons can be described as being located in different regions around the nucleus called **electron shells**. All of the electrons in a particular shell have similar energy and are approximately the same distance from the nucleus.

Electrons in the shells closest to the nucleus have the lowest energy. They also have the strongest attraction to the nucleus and take the most energy to remove from the atom. Electrons in shells further away from the nucleus have more energy and a weaker attraction to the nucleus. It takes less energy to remove these electrons from the atom.

Since the amount of energy of an electron is closely related with the shell it is in, electron shells are often called **energy levels**.



The physical properties of a substance are observed as the substance changes from one form into another without any chemical change.



The electron configuration is a description of the arrangement of electrons around the nucleus of an atom.



**figure 1.5** Electron shells closer to the nucleus are smaller and contain fewer electrons. These electrons are difficult to remove from the atom.



energy are found in the lowest energy levels or electron shells closest to the nucleus.





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Electron shells further from the nucleus are larger and can hold more electrons. Electrons in the outer shells take less energy to remove from the atom The electron shells closer to the nucleus are smaller and contain fewer electrons than the larger shells further away from the nucleus. The number of electrons in a shell is determined by the size of the shell. Table 1.5 shows the maximum number of electrons that can occupy each shell according to the formula  $2n^2$  where *n* is the shell number.

**table**  $\Im_n \boxtimes$  The maximum number of electrons in each shell is determined by  $2n^2$  where *n* is the shell number.

Shell number	Maximum number of electrons
1	2
2	8
3	18
4	32
п	2 <i>n</i> <sup>2</sup> (where <i>n</i> is the shell number)

The table shows that the third shell can contain a maximum of eighteen electrons. This can be calculated as shown below.

 $2n^2 = 2 \times 3^2$  $= 2 \times 9$ = 18

The third shell can hold more electrons than the first shell, which can only hold two electrons. The first shell is closer to the nucleus and therefore smaller.

For stable atoms the shells closest to the nucleus are occupied before the outer shells. Table 1.6 shows that hydrogen's single electron occupies the first shell.

Beryllium has four electrons. Two of these electrons occupy the first shell, which is then full. The other two occupy the second shell.

Sodium has eleven electrons. Two occupy the first shell, eight occupy the second shell and the last electron occupies the third shell.

For any element, the outermost shell can contain a maximum of 8 electrons. For example, potassium and calcium have only 8 electrons in the third shell. Even though this shell is not full (using the  $2n^2$  rule it can hold up to eighteen electrons), their remaining electrons occupy the fourth shell.

As atoms increase in size and have more electrons, they use more electron shells and the rules for filling the available shells become more complex. Other more complex models better describe electron configurations for atoms with many electrons.



**figure 1.6** Representations of electron configurations of lithium, sodium and potassium. Notice that each of these has only one valence electron.

(table 1.6	The electron c	onfigurations of sor	ne elements.			
Flomont	Cumhal	Number of		Electronic co	onfiguration	
Element	Symbol	Electrons	First shell	Second shell	Third shell	Fourth shell
hydrogen	Н	1	1			
helium	He	2	2			
lithium	Li	3	2	1		
beryllium	Be	4	2	2		
boron	В	5	2	3		
carbon	С	6	2	4		
nitrogen	Ν	7	2	5		
oxygen	0	8	2	6		
fluorine	F	9	2	7		
neon	Ne	10	2	8		
sodium	Na	11	2	8	1	
magnesium	Mg	12	2	8	2	
aluminium	Al	13	2	8	3	
silicon	Si	14	2	8	4	
phosphorus	Р	15	2	8	5	
sulfur	S	16	2	8	6	
chlorine	Cl	17	2	8	7	
argon	Ar	18	2	8	8	
potassium	K	19	2	8	8	1
calcium	Ca	20	2	8	8	2
scandium	Sc	21	2	8	9	2
titanium	Ti	22	2	8	10	2
iron	Fe	26	2	8	14	2
zinc	Zn	30	2	8	18	2
bromine	Br	35	2	8	18	7
krypton	Kr	36	2	8	18	8

In figure 1.6 the atoms of lithium, sodium and potassium are drawn to include only electron shells that actually contain electrons. The electrons in the outermost shell of an atom are known as the **valence electrons**. The valence electrons of an element are the ones most easily removed from an atom and determine how it will chemically react with other elements. Elements with the same number of valence electrons tend to have similar chemical properties. Lithium, sodium and potassium each have one valence electron and you would expect them to have similar properties—and they do.

Valence electrons are the ones in the outermost shell. The chemical properties of an element are due to the valence electrons.

Questions	<del>-</del> -	
<ul> <li>9 Consider table 1.6, where electron configuration the table, give the nuin atoms of each of the amagnesium</li> <li>c K</li> <li>e Be</li> </ul>	hich gives the symbols and as of some elements. Using mber of valence electrons e following elements. b boron d carbon f Ar	<ul> <li>10 Consider table 1.6, which gives the symbols and electron configurations of some elements. Using the table, name the element(s) that has (have):</li> <li>a the same number of valence electrons as chlorine</li> <li>b the same number of valence electrons as C</li> <li>c one more valence electron than P</li> <li>d two fewer valence electrons than nitrogen.</li> </ul>

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#### **11** Write the electron configuration of each element.

- **a** Be
- **b** sulfur
- **c** Ar
- d magnesium
- e Ne

- Write the name and symbol of the elements with the following electron configurations.a 2
  - **b** 2,7
  - **c** 2,8,3
  - **d** 2,5
  - **e** 2,8,7

Orbitals are the regions of space around the nucleus of an atom in which electrons move.

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### figure 1.7

The electron of a hydrogen atom is described as a cloud of negative charge around the nucleus.

### 1.5 Electronic structure in more detail

The description of electronic structure of atoms according to electron shells is a simple one. Scientists found that electrons could not only be described as particles but that they could also be thought of as waves around the nucleus. This complex mathematical description of electrons is known as quantum mechanics.

Instead of thinking of electrons as particles in fixed shells around the nucleus, quantum mechanics describes regions of space around the nucleus known as **orbitals** in which electrons act as a cloud of negative charge. The term shells is still used to describe the major energy levels of the electrons of an atom.

There are several key features of the quantum mechanical model. The shells (or energy levels) are numbered 1, 2, 3, 4 and so on. Electrons in the lower energy levels have less energy and occupy regions closer to the nucleus.

Within each shell, there are subshells named s, p, d, f and g. They are of similar energy, increasing slightly from the s subshell, with the lowest energy, to the g subshell, the highest energy subshell.



**figure 1.8** The order of energy levels of atoms with more than one electron.

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Shell

2p 2s

15

2

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5d

5p

5s

5

4f

4d

4p

4s

4

Зd

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Energy

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table 1.7	Energy levels within an at		
Shell number	Number of subshells in shell	Subshell in shell	Number of orbitals in subshell
1	1	15	1
2	2	25	1
		2р	3
3	3	35	1
		3р	3
		3q	5
4	4	4S	1
		4p	3
		4d	5
		4f	7
5	5	55	1
		5p	3
		5d	5
		5f	7
		58	9

Each subshell is made up of orbitals. Within a particular energy subshell there can be 1 orbital in the s subshell, 3 orbitals in the p subshell, 5 orbitals in the d subshell and so on. Electrons within a particular type of subshell (1s, 2s, 2p, etc.) will all have the same energy. Table 1.7 shows the electron shells, subshells and orbitals within an atom.

Electrons of lower energy occupy regions closer to the nucleus of an atom. Electrons of higher energy occupy regions further out from the nucleus. There are fewer subshells with fewer orbitals for the lower energy levels (see table 1.7). For electrons of higher energy there are more subshells containing more orbitals, which are further out from the nucleus.

Each orbital can contain a maximum of 2 electrons, with the orbitals of lowest energy filling first. The order of energies of the subshells is: 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s and so on.

This order is also shown in figure 1.8 and can be remembered according to the pattern shown in figure 1.10.

In the last section the electron configurations of lithium, sodium and potassium were given as:

Li 2,1

Na 2,8,1

K 2,8,8,1

Using the quantum mechanical model, these electron configurations are written as follows.

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

Each of these elements have one valence electron in the outer shell. The electron configurations of magnesium and chlorine are:

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

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

This shows that magnesium has two valence electrons and chlorine has seven valence electrons.





Quantum mechanics is a mathematical description of electrons according to their wave properties and was developed in 1926 by the German scientist Erwin Schrödinger.



**figure 1.10** The geometric pattern shown here is a useful way of remembering the order of energy levels in atoms.

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Atomic structure

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filling the lowest energy subshells first, the electron configuration for copper can be written as:

 $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$ 

The 3d subshell can hold 10 electrons and only needs to be partially filled for copper. This shows the order of filling but an electron configuration is normally written with the subshells of each energy level grouped together so that of copper would be written as:

Copper atoms have 29 electrons. By giving two electrons to each orbital and

 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$ 

### Questions

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Electronic structure

- 13 Write the electron configuration for each of the following.
  - a helium
  - b Cl
  - c potassium **d** iron

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e Ag

- 14 Which elements have atoms of the following electron configurations? **a**  $15^2 25^2$ 
  - **b**  $15^2 25^2 2p^6$
  - $15^{2} 25^{2} 2p^{6} 35^{2} 3p^{2}$

  - **d** 15<sup>2</sup> 25<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>4</sup> 4s<sup>2</sup> **e** 15<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>6</sup> 5s<sup>2</sup>



Horizontal rows of the periodic table are known

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### 1.6 Organising information—the periodic table

Most of the information presented so far in this chapter can be found in tables of chemical data. Possibly the most useful summary of this data is presented in the periodic table (figure 1.12).

Each column of the periodic table is called a group. The periodic table shown gives two ways of numbering the groups. The old method of numbering used Roman numerals but the latest method simply numbers each group from 1 to 18 working from left to right. Some sets of groups are given special names such as transition elements, lanthanides and actinides.

Each horizontal row of elements is called a period. The periods are numbered from top to bottom down the periodic table.

The elements are arranged in order of increasing atomic number.

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Each element is presented in its own box. In this simplified version of the periodic table the information provided for each element includes name, symbol, atomic number and relative atomic mass.



figure 1.11 Each box of the periodic table contains information about an individual element.

										Grou	р								
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	د	1 H 1.00797- Hydrogen	At Cl Ri N	tomic nun hemical sy elative atc ame of ele	nber ymbol omic mas ement	6S													<b>2</b> <b>He</b> 4.0026 Helium
	N	3 Li 6.939 Lithium	<b>4</b> <b>Be</b> 9.0122 Beryllium											5 B 10.811 Boron	6 C 12.01115 Carbon	7 N 14.0067 Nitrogen	<b>8</b> <b>0</b> 15.9994 <b>0</b> xygen	<b>9</b> <b>F</b> 18.9984 Fluorine	<b>10</b> <b>Ne</b> 20.183 Neon
	ω	11 Na 22.9898 Sodium	12 Mg 24.312 Magnesium				Trans	sition ele	ments					<b>13</b> <b>AI</b> 26.9815 Aluminium	14 Si 28.086 Silicon	<b>15</b> <b>P</b> 30.9738 Phosphorus	16 S 32.064	<b>17</b> <b>CI</b> 35.453 (blorine	<b>18</b> <b>Ar</b> 39.948 Armon
Period	4	<b>19</b> <b>K</b> 39.102 Potassium	20 Ca 40.08 (glcium	<b>21</b> <b>Sc</b> 44.956 Scapdium	<b>22</b> <b>Ti</b> 47.90 Titanium	<b>23</b> <b>V</b> 50.942 Vanadium	24 <b>Cr</b> 51.996 (hromium	<b>25</b> <b>Mn</b> 54.938	26 Fe 55.847	27 Co 58.933 Cohalt	<b>28</b> <b>Ni</b> 58.71 Nickel	<b>29</b> <b>Cu</b> 63.54 Copper	<b>30</b> <b>Zn</b> 65.37 Zinr	31 Ga 69.72 Gollium	32 Ge 72.59 Germanium	33 As 74.922 Arsenic	<b>34</b> <b>Se</b> 78.96 Selenium	35 Br 79.909 Bromine	36 Kr 83.80 Krynton
	បា	<b>37</b> <b>Rb</b> 85.47 Rubidium	<b>38</b> <b>Sr</b> 87.62 Strontium	<b>39</b> <b>Y</b> 88.905 Yttrium	<b>40</b> <b>Zr</b> 91.22 Zirconium	<b>41</b> <b>Nb</b> 92.906 Niobium	42 Mo 95.94 Molybdenum	43 Tc [98] Technetium	<b>44</b> <b>Ru</b> 101.07 Ruthenium	<b>45</b> <b>Rh</b> 102.905 Rhodium	<b>46</b> <b>Pd</b> 106.4 Palladium	47 Ag 107.870 Silver	<b>48</b> <b>Cd</b> 112.40 Cadmium	<b>49</b> <b>In</b> 114.82 Indium	<b>50</b> <b>Sn</b> 118.69 Tin	51 Sb 121.75 Antimony	<b>52</b> <b>Te</b> 127.60 Tellurium	<b>53</b> <b>1</b> 126.904 Iodine	<b>54</b> <b>Xe</b> 131.30 Xenon
	ດ	55 Cs 132.905 Caesium	56 Ba 137.34 Barium	57-71 Lanthanoids	72 Hf 178.49 Hafnium	73 <b>Ta</b> 180.948 Tantalum	74 W 183.85 Tunasten	75 <b>Re</b> 186.2 Rhenium	<b>76</b> <b>OS</b> 190.2 Osmium	77 <b>Ir</b> 192.2 Iridium	78 Pt 195.09 Platinum	79 Au 196.967 Gold	80 Hg 200.59 Mercury	<b>81</b> <b>TI</b> 204.37 Thallium	82 Pb 207.19 Lead	83 Bi 208.980 Bismuth	<b>84</b> <b>Po</b> (210) Polonium	85 At (210) Astatine	86 <b>Rn</b> (222) Radon
	7	87 Fr (223) Francium	88 <b>Ra</b> (226) Radium	89-103	104 Rf (261) Rutherfordium	<b>105</b> <b>Db</b> (262)	106 <b>Sg</b> (263)	107 Bh (262) Bohrium	<b>108</b> <b>Hs</b> (265) Hassium	109 Mt (266) Meitnerium	110 Ds (271)	111 Rg (272)	<b>112</b> <b>Uub</b> (277)	113 <b>Uut</b> (284)	114 Uuq (289)	115 Uup (288)	116 Uuh (289)		
		Truncion	Kuulom	Actinolus	Komerfordion	Dopinoni	Jeanordion		Trassion	Mennenon		Koenigenioni	UIUIDIUII	ononnion				1	1
				<b>57</b> <b>La</b> 138.91 Lanthanum	58 Ce 140.12 Cerium	59 Pr 140.907 Praseodymium	60 Nd 144.24 Neodymium	61 Pm [147] Promethium	62 Sm 150.35 Samarium	63 Eu 151.96 Europium	64 Gd 157.25 Gadolinium	<b>65</b> <b>Tb</b> 158.924 Terbium	66 Dy 162.50 Dysprosium	67 Ho 164.930 Holmium	68 Er 167.26 Erbium	<b>69</b> <b>Tm</b> 168.934 Thulium	<b>70</b> <b>Yb</b> 173.04 Ytterbium	<b>71</b> <b>Lu</b> 174.97 Lutetium	
				89 Ac (227) Actinium	<b>90</b> <b>Th</b> 232.038 Thorium	91 Pa (231) Protactinium	92 U 238.03 Uranium	93 Np (237) Neptunium	94 Pu (242) Plutonium	95 Am (243) Americium	<b>96</b> <b>Cm</b> (247) Curium	97 Bk (247) Berkelium	98 Cf (249) Californium	99 Es (254) Einsteinium	<b>100</b> <b>Fm</b> (253) Fermium	101 Md (256) Mendelevium	<b>102</b> <b>No</b> (254) Nobelium	103 Lr (257) Lawrencium	

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Atomic structure

Most periodic tables do not include details about isotopes as this information has only been used to derive the relative atomic mass.

You will notice that information has not been included about the electron structure of each element. Electronic configurations are actually implied by the rather strange shape of the table. Figure 1.13 shows the electronic configurations of the first thirty-six elements. You will notice that the elements of each group have the same number of valence electrons. For example, all elements in Group 1 have one valence electron and all elements in Group 18 have eight valence electrons. This also suggests that elements in each group have similar chemical and physical properties.

Any course in chemistry will continually refer to the periodic table. Many other features of the elements discussed in coming sections of this book will be related back to their position in the periodic table.

					1.												
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1		_															2
2,1	2,2											2,3	2,4	2,5	2,6	2,7	2,8
2,8,1	2,8,2											2,8,3	2,8,4	2,8,5	2,8,6	2,8,7	2,8,8
2,8,8,1	2,8,8,2	2,8,9,2	2,8,10,2	2,8,11,2	2,8,12,2	2,8,13,2	2,8,14,2	2,8,15,2	2,8,16,2	2,8,17,2	2,8,18,2	2,8,18,3	2,8,18,4	2,8,18,5	2,8,18,6	2,8,18,7	2,8,18,8

figure 1.13 The shape of the periodic table is a result of the electron configuration of each element.

### Questions

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Worksheet

Atomic structure

- **15** Use the periodic table and/or the electron configuration of elements to answer the following questions.
  - a In which group of the periodic table will you find:

Groun

- **i** B?
- ii Cl?
- iii Na?
- iv Ar?
- v Si?
- **b** In which period of the periodic table will you find:
  - i K? ii F?
  - iii He?
  - iv P?
  - **v** H?

MATTER IS COMPOSED OF ATOMS

- **c** What is the name, symbol and electronic configuration of:
  - i the second element in Group 14?
  - ii the second element in Period 2?
  - iii the element which is in Group 18 of Period 3?
- **16** Use the periodic table to predict the number of valence electrons for each of the following.
  - a Ba
  - **b** Br
  - c Cs
  - **d** Te
  - e Ge

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### Summary **DDDD**

- The current model of the atom describes it as a tiny concentrated nucleus containing positively charged protons and neutrons (which have no charge), surrounded by a region where negatively charged electrons move about. Most of an atom's mass is in the nucleus.
- Substances consisting of atoms with the same number of protons in the nucleus are known as elements.
- The atomic number is the number of protons in the atoms of an element. The total number of protons and neutrons in an atom is known as the mass number. Isotopes of an element have the same number of protons but different numbers of neutrons.
- The mass of individual isotopes is measured against a unit given as one twelfth of the mass of a <sup>12</sup><sub>6</sub>C isotope.
- The measured mass of an isotope is called the relative isotopic mass. A weighted average of the relative isotopic masses of an element gives the relative atomic mass of that element.

- The electron configuration is the way that electrons are arranged around the nucleus of an atom. Electrons are located in specific electron shells around the nucleus. Electron shells contain electrons of similar energy and are also called energy levels.
- The outermost electron shell of an atom contains the valence electrons of that atom, the ones that determine its chemical properties.
- Quantum mechanics is a mathematical description of electrons according to their wave properties, describing the regions around the nucleus of an atom where electrons can be found as **orbitals**.
- Information about the elements is presented in the periodic table. Vertical columns are called groups and horizontal rows are called periods. Elements in the same group have similar properties. The electron configuration of each element is implied by its position in the periodic table.

### Key terms

- atomic number electron electron configuration electron shell element
- energy levels group isotope mass number neutron
- nucleus orbital period periodic table proton
- quantum mechanics relative atomic mass relative isotopic mass valence electrons



### Chapter **Review**

### 1.1 The structure of atoms

- **17** According to the nuclear model of the atom, the volume between the nucleus and the electrons contains:
  - A air.
  - **B** empty space.
  - C photons.
  - D neutrons.
- 18 Which of the following has no charge?
  - A neutron
  - **B** proton
  - **C** electron
  - **D** ion
- **19** The nucleus of an atom has a radius of the order of  $10^{-13}$  cm. The radius of the atom itself is of the order of  $10^{-9}$  cm. If the nucleus could be scaled up to the size of an orange (radius 5 cm), what would be the radius of the atom on that same scale?

### 1.2 Elements and isotopes

- **20** Isotopes of an element have:
  - A the same atomic number and the same mass number.
  - **B** the same atomic number and a different mass number.
  - **C** a different atomic number and the same mass number.
  - **D** a different atomic number and a different mass number.
- **21** The number of neutrons in  $^{39}_{19}$ K is:
  - **A** 18

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- **B** 19
- **C** 20
- D 39
- **22** The following is a list of atoms:
  - <sup>27</sup><sub>13</sub>A, <sup>40</sup><sub>20</sub>B, <sup>32</sup><sub>16</sub>C, <sup>14</sup><sub>7</sub>D, <sup>8</sup><sub>3</sub>E, <sup>15</sup><sub>7</sub>F, <sup>19</sup><sub>9</sub>G, <sup>20</sup><sub>9</sub>H, <sup>4</sup><sub>2</sub>I
  - a Which pairs of atoms are isotopes?
  - **b** Which atoms have equal numbers of protons and neutrons in the nucleus?
  - c Which is an isotope of sulfur?
  - d Which has one more electron than a magnesium atom?
  - e How many different elements are shown?
- 23 What is the meaning of each of the following terms: atomic number, mass number, isotope?
- 24 An atom of uranium can be represented by the symbol  $^{235}_{92}$ U. Give its atomic number and mass number.
- 25 Make a sketch representing each of the following atoms.
  - <sup>4</sup><sub>2</sub>He, <sup>19</sup><sub>9</sub>F, <sup>23</sup><sub>11</sub>Na, <sup>40</sup><sub>20</sub>Ca

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- 26 Two atoms both have 20 neutrons in their nucleus. The first also has 19 protons and the other has 20 protons. Are they isotopes? Why or why not?
- 27 Using the element bromine as an example, explain why elements are best identified by their atomic number and not their mass number.

### 1.3 Atomic mass

28 When a sample of palladium is placed in a mass spectrometer the following peaks are recorded with corresponding percentages (see table 1.8). Calculate the relative atomic mass of palladium.

### table 1.8

Relative isotopic mass	Percentage abundance
101.9049	0.9600%
103.9036	10.97%
104.9046	22.23%
105.9032	27.33%
107.9039	26.71%
109.9044	11.80%

- 29 The standard on which all relative masses are based is the <sup>12</sup>C isotope, which is given a mass of 12 exactly. However, the relative atomic mass of carbon in tables of masses and on the periodic table is listed as 12.011. Explain why these two masses are different.
- **30** Calculate the relative atomic mass of each element in table 1.9 using the data given.

#### table 1.9

Element	Relative isotopic mass	Relative abundance (%)
lithium	6.02	7.4
	7.02	92.6
magnesium	23.99	78.8
	24.99	10.2
	25.99	11.0
copper	62.95	69.1
	64.95	30.9
silicon	27.98	92.2
	28.98	4.7
	29.98	3.1
gallium	68.95	60.5
	70.95	39.5

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**31** Table 1.10 gives isotopic composition data for argon and potassium.

table	1.10 \		
Element	Atomic number	Relative isotopic mass	Relative abundance (%)
argon	18	35.978	0.307
		37.974	0.060
		39.974	99.633
potassiu	m 19	38.975	93.3
		39.976	0.011
		40.974	6.69

- a Determine the relative atomic masses of argon and potassium.
- **b** Explain why the relative atomic mass of argon is greater than that of potassium, even though potassium has a larger atomic number.
- **32** The relative atomic mass of rubidium is 85.47. The relative isotopic masses of its two isotopes are 84.94 and 86.94. Calculate the relative abundances of the isotopes in naturally occurring rubidium.
- **33** Determine the percentage abundance of the lighter isotope of each of the following elements.
  - a silver: relative isotopic masses 106.9 and 108.9; *A*<sub>r</sub> = 107.87
  - **b** gallium: relative isotopic masses 68.95 and 70.95;  $A_r = 69.72$
  - **c** boron: relative isotopic masses 10.02 and 11.01; *A*<sub>r</sub> = 10.81
  - **d** chlorine: relative isotopic masses 34.98 and 36.98; *A*<sub>r</sub> = 35.45

### 1.4 Electronic structure

- 34 What is the maximum number of electrons in the second shell of an atom?
- **35 a** Write the electron configurations of the following elements.
   <sup>35</sup>/<sub>17</sub>X, <sup>27</sup>/<sub>13</sub>Y and <sup>39</sup>/<sub>19</sub>Z
  - **b** What is their position in the periodic table?

# 1.5 Electronic structure in more detail

- **36** Write electron arrangements for atoms of the following elements. The atomic number of each element is shown in brackets.
  - a helium (2)
  - **b** carbon (6)
  - **c** fluorine (9)
  - d aluminium (13)
  - e argon (18)

- f nickel (28)
- g bromine (35)
- **37** Using the fluorine atom as an example, explain the difference between the terms shell, subshell and orbital.
- **38** Draw your own concept map using the following terms: atom, proton, neutron, electron, charge, shell, nucleus.

### 1.6 Organising information the periodic table

- **39** An element belongs to Group 14 in the periodic table.
  - **a** How many electrons would be present in the outer shell of its atoms?
  - **b** This element is found in Period 3 of the periodic table.
    - i In each of its atoms, how many shells contain electrons?
    - ii What is the electron configuration of this element?
- **40** The following electron configurations represent atoms of four different elements.
  - **a** 2,1
  - **b** 2,8,4
  - **c** 2,8
  - **d** 2,8,8,1
  - For each element, give:
  - i the period and group to which it belongs ii its name and chemical symbol.
- 41 Which of the following elements belong to the
- same group of the periodic table as sodium? Cu, Be, K, Zn, Li, Ag, Au, Cs
- **42** In which period of the periodic table will you find:
  - a Na?
  - **b** F?
  - c He?
  - d Se?
  - e Cs?
- **43** Suppose you were familiar with the properties, reactions and compounds formed by the following elements: sodium, chlorine, magnesium, argon and sulfur. Which element would you use to predict the properties of:

225

Atomic structure

- a krypton?
- **b** selenium?
- c fluorine?
- d potassium?
- e barium?
- 44 How many valence electrons are there in:
  - a a Group 18 element?
  - **b** hydrogen?
  - c fluorine?
  - **d** P?
  - e Ca?

# Elements and compounds



a substance, for example cutting, breaking and melting. You have the same substance before and after a physical change but in a different form.



Chemical properties are observed as elements undergo chemical changes.

### Physical and chemical properties

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The characteristics of an element, its unique features, are known as the properties of an element. **Physical properties** include features such as appearance, hardness, melting temperature and the ability to conduct an electric current.

During a chemical change, an element may react with other elements to produce a new substance with completely different physical properties. For example, if you cut a piece of sodium with a knife you will expose the shiny metallic sodium to the air. The shiny metal revealed along the cut soon turns a dull grey colour as the sodium reacts with oxygen in the air. The sodium oxide that forms has a totally different appearance to sodium metal. The way sodium reacts with oxygen is known as a **chemical property**.

The properties of a substance are related to the way the atoms are held together or bond with each other. Physical properties are due to the way atoms of an element bond with other atoms of the same element; chemical properties are due to the way atomic bonds rearrange as they bond with atoms of other elements.

### Properties and the periodic table

It was mentioned in Chapter 1 that the shape of the periodic table reflects the electron configurations of the elements. It is the electron configuration that determines how atoms bond together and so the periodic table also groups elements according to their similar physical and chemical properties.

		group																	
			2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	1	1 <b>H</b>		_															2 <b>He</b>
	2	З Li	4 <b>Be</b>											5 <b>B</b>	6 <b>C</b>	7 N	8 <b>0</b>	9 F	10 <b>Ne</b>
-	3	11 <b>Na</b>	12 <b>Mg</b>	<b>↓</b>		1	RANS	SITION	ELEN	/IENTS	6		ł	13 <b>Al</b>	14 <b>Si</b>	15 <b>P</b>	16 <b>S</b>	17 CI	18 <b>Ar</b>
perio	4	19 <b>K</b>	20 <b>Ca</b>	21 Sc	22 <b>Ti</b>	23 V	24 <b>Cr</b>	25 <b>Mn</b>	26 <b>Fe</b>	27 <b>Co</b>	28 Ni	29 <b>Cu</b>	30 <b>Zn</b>	31 <b>Ga</b>	32 <b>Ge</b>	33 <b>As</b>	34 <b>Se</b>	35 <b>Br</b>	36 <b>Kr</b>
	5	37 <b>Rb</b>	38 <b>Sr</b>	39 <b>Y</b>	40 <b>Zr</b>	41 <b>Nb</b>	42 <b>Mo</b>	43 <b>Tc</b>	44 <b>Ru</b>	45 <b>Rh</b>	46 <b>Pd</b>	47 <b>Ag</b>	48 <b>Cd</b>	49 <b>In</b>	50 <b>Sn</b>	51 <b>Sb</b>	52 <b>Te</b>	53 	54 <b>Xe</b>
	6	55 <b>Cs</b>	56 <b>Ba</b>	57–71 Lanthanides	72 <b>Hf</b>	73 <b>Ta</b>	74 <b>W</b>	75 <b>Re</b>	76 <b>Os</b>	77 <b>Ir</b>	78 <b>Pt</b>	79 <b>Au</b>	80 <b>Hg</b>	81 <b>TI</b>	82 <b>Pb</b>	83 <b>Bi</b>	84 <b>Po</b>	85 <b>At</b>	86 <b>Rn</b>
	7	87 <b>Fr</b>	88 <b>Ra</b>	89–103 Actinides	104 <b>Rf</b>	105 <b>Db</b>	106 <b>Sg</b>	107 <b>Bh</b>	108 <b>Hs</b>	109 <b>Mt</b>	110 <b>Ds</b>	111 <b>Rg</b>	112 <b>Uub</b>	113 <b>Uut</b>	114 <b>Uuq</b>	115 <b>Uup</b>	116 <b>Uuh</b>		
	met	als		57 <b>La</b>	58 <b>Ce</b>	59 <b>Pr</b>	60 <b>Nd</b>	61 <b>Pm</b>	62 <b>Sm</b>	63 <b>Eu</b>	64 <b>Gd</b>	65 <b>Tb</b>	66 <b>Dy</b>	67 <b>Ho</b>	68 <b>Er</b>	69 <b>Tm</b>	70 <b>Yb</b>	71 <b>Lu</b>	
	met non-	alloids metals	5	89 <b>Ac</b>	90 <b>Th</b>	91 <b>Pa</b>	92 U	93 <b>Np</b>	94 <b>Pu</b>	95 <b>Am</b>	96 <b>Cm</b>	97 <b>Bk</b>	98 Cf	99 <b>Es</b>	100 <b>Fm</b>	101 <b>Md</b>	102 <b>No</b>	103 <b>Lr</b>	

figure 2.1 The shading in this periodic table shows that metals, non-metals and metalloids are grouped together in particular regions of the table.

The metallic elements can be found on the left side of the periodic table and non-metallic elements on the right side. Hydrogen is an exception to this. It is placed in Group 1 because it has one valence electron and has many properties similar to the metals in that group. At times hydrogen also behaves similarly to the gases of Group 17. Hydrogen's properties are so exceptional that at times it is simply placed on its own.

Between the metals and non-metals of the periodic table are the **metalloids**. Metalloids can demonstrate properties of either metals or non-metals depending on the conditions under which they are observed. The semiconductive properties of metalloids make them useful in electronic components such as computer chips.

The vertical columns or **groups** of the periodic table tend to have elements with similar physical and chemical properties. Table 2.1 is a summary of the properties of some of these groups.

Sometimes it is useful to refer to the **blocks** of elements of the periodic table. Groups 1, 2 and 13–18 are often referred to as the **main group** elements. The elements of groups 3–12 are referred to as the **transition metals**. The **lanthanides** are the elements of atomic numbers 58–71 and the **actinides** have atomic numbers 90–103. Elements are blocked like this because of their electron configurations but elements within each block can have a wide variety of physical and chemical properties.



Metalloids can demonstrate properties of both metals and nonmetals. They are also known as semi<u>-metals.</u>  $\cap$ 

table 2.	The general			
Group number	Group name	Elements	Physical properties	Chemical properties
1	alkali	Li, Na, K, Rb, Cs, Fr	bright, shiny, metallic	highly reactive with
	metals		relatively soft	water or oxygen
			good conductors of electricity	
2	alkaline earth metals	Be, Mg, Ca, Sr, Ba, Ra	metallic appearance harder and higher melting temperature than alkali metals good conductors of electricity	highly reactive (less reactive than alkali metals)
17	halogens	F, Cl, Br, I	exist as gases at reasonably	strong ability to remove
		(These exist as	low temperatures	electrons from other
		diatomic molecules	distinctive colours	elements
		$F_2$ , $Cl_2$ , $Br_2$ , $l_2$ )		
18	noble gases	He, Ne, Ar, Kr, Xe, Rn	exist as gases	extremely unreactive

### Why do atoms bond?

The noble gases-helium, neon, argon, krypton, xenon and radon-are known for being highly unreactive. They are extremely stable elements. Each one has a full outer shell of electrons, i.e. 2 electrons ( $s^2$ ) for helium and 8 electrons ( $s^2p^6$ ) for each of the others.

The noble gases are unreactive because their electron configurations are so stable. Atoms of other elements with less stable electron configurations attempt to attain a stable configuration by bonding with other atoms. The atoms of elements other than the noble gases attempt to do this in three ways:

- accepting electrons from other atoms or donating electrons to other atoms 1 to form charged particles which are attracted to each other
- 2 sharing electrons with other atoms in groups of two or more atoms
- 3 forming lattices of positive particles through which electrons can move.



figure 2.2 The noble gases have full outer shells of electrons-a very stable electron configuration.

These bonding types are known as ionic, covalent and metallic bonding. The next sections of this chapter will describe these methods in detail.

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STRUCTURE,

BONDING AND PROPERTIES OF MATERIALS

### Questions

- 1 Which of the following are physical changes and which are chemical changes? boiling water, cooking a cake, iron rusting, wax melting, a candle burning, nail polish remover evaporating, milk going sour, concrete setting, sugar dissolving in water
- 2 Group these elements into pairs with similar properties.
  - Li, S, He, Cu, Ar, K, Mg, Au, O, Sr

### 2.2 Ionic bonding

In ionic bonding the substances are comprised of **ions**. Ions are atoms or groups of atoms that have gained or lost electrons. If they gain electrons they have a negative charge and if they lose electrons they have a positive charge. Salt (sodium chloride) is one example of an **ionic compound**. It is composed of positive sodium ions and negative chloride ions.

Elements in the columns on the left side of the periodic table tend to lose electrons to become positive ions, for example lithium, sodium and potassium lose one electron to become the ions  $Li^+$ ,  $Na^+$  and  $K^+$ .

Elements in the columns on the right side of the periodic table tend to gain electrons to become negative ions, for example fluorine, chlorine and bromine tend to gain one electron each to become the ions  $F^-$ ,  $Cl^-$  and  $Br^-$ .

<b>table</b> $2.2$ An atom can gain or lose electrons in order to attain the more stable electron configuration of its closest noble gas.							
Element	Electron configuration of element	lon	Electron configuration of ion	Noble gas electron configuration the element attains			
lithium	2 1	Li <sup>+</sup>	2	helium			
sodium	281	$Na^+$	28	neon			
potassium	2881	$K^+$	288	argon			
fluorine	27	F <sup>−</sup>	28	neon			
chlorine	287	Cl⁻	288	argon			
bromine	2 8 18 7	Br <sup>-</sup>	28188	krypton			

These ions form as the atoms gain or lose electrons to have the same electron configuration as a noble gas. It is the outer electrons, called the **valence** electrons, which are lost or gained to form ions. When a sodium atom loses one of its 11 electrons, it has the stable electron configuration of neon which has 10 electrons (see table 2.2).

When chlorine atoms gain an electron they have 18 electrons and the same electron configuration as argon. When an atom has gained electrons we add -ide to its name. Cl is the symbol for a chlorine atom and Cl<sup>-</sup> is the symbol for a chloride ion.

Elements in Group 2 of the periodic table tend to lose 2 electrons. Magnesium atoms lose 2 electrons to become  $Mg^{2+}$  ions with an electron configuration the same as neon. Aluminium atoms (in Group 13) tend to lose 3 electrons to become  $Al^{3+}$ . Phosphorus and sulfur attain the electron

- 3 Which element in each group below would you expect to have different properties?
  - a krypton, helium, hydrogen, neon
  - b magnesium, potassium, lithium, sodium
  - c copper, silver, gold, platinum
  - d magnesium, beryllium, aluminium, calcium



In ionic bonding, atoms lose or gain electrons to form charged ions. Ions of opposite charge are attracted to each other and the forces of attraction create a bond.



The valence electrons of an atom are the electrons in the outermost electron shell.

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Positive ions are also known as cations and negative ions as anions. configuration of argon by gaining 3 and 2 electrons respectively to become  $P^{3\text{-}}$  and  $S^{2\text{-}}.$ 

Metallic elements on the left of the periodic table tend to lose electrons to become positive ions; non-metallic elements on the right side of the periodic table tend to gain electrons to become negative ions. Groups of atoms can also be charged. They are groups of non-metallic elements. Table 2.3 lists some of the common ions.

table 2.3	The names and formulae of some commor	n ions.
-----------	---------------------------------------	---------

			Positive ions (	cations)			
	+1			+2			+3
hydrogen	H⁺		magnesium	Mg <sup>2+</sup>		aluminium	Al <sup>3+</sup>
lithium	Li⁺		calcium	Ca <sup>2+</sup>		chromium(III)	Cr <sup>3+</sup>
sodium	Na⁺		barium	Ba <sup>2+</sup>		iron(III)	Fe <sup>3+</sup>
potassium	K <sup>+</sup>		zinc	Zn <sup>2+</sup>			
silver	$Ag^+$		copper(II)	Cu <sup>2+</sup>			
copper(l)	Cu <sup>+</sup>		mercury(II)	Hg <sup>2+</sup>			
ammonium	$NH_4^+$		iron(II)	Fe <sup>2+</sup>			
			nickel(II)	Ni <sup>2+</sup>			
			tin(II)	Sn <sup>2+</sup>			
			lead(II)	Pb <sup>2+</sup>			
			Negative ions	(anions)			
		-1			-2		-3
hydroxide		OH⁻	oxide		0 <sup>2-</sup>	nitride	N <sup>3-</sup>
hydrogen sul	fide	SH⁻	sulfide		S <sup>2-</sup>	phosphate	PO4 <sup>3-</sup>
hydrogen sul	fite	HSO <sub>3</sub> <sup>−</sup>	sulfite		S03 <sup>2-</sup>		
hydrogen sul	fate	$HSO_4^-$	sulfate		S04 <sup>2-</sup>		
hydrogen car	bonate	$HCO_3^-$	carbonate		CO3 <sup>2-</sup>		
dihydrogen p	hosphate	$H_2PO_4^-$	hydrogen ph	osphate	$HPO_4^{2-}$		
nitrite		$NO_2^{-}$	dichromate		$Cr_{2}O_{7}^{2-}$		
nitrate		$NO_3^-$					
acetate		$CH_3COO^-$					
fluoride		F <sup>−</sup>					
chloride		Cl⁻					
bromide Br <sup>-</sup>		Br <sup>-</sup>					
iodide		Ι-					
permanganat	e	MnO <sub>4</sub> <sup>-</sup>					

Positive and negative ions may be single atoms or groups of atoms that have lost or gained electrons. Note that the transition metals have Roman numerals to indicate their valency as it can vary.

### lonic substances

Since metals tend to lose electrons to become positive ions and non-metals tend to gain electrons to become negatively charged, most ionic substances are made up of metallic and non-metallic elements.

The burning of magnesium is a reaction between the metal magnesium and oxygen in the air.

magnesium + oxygen  $\rightarrow$  magnesium oxide

A substance which is made up of two or more different types of atoms is called a **compound**.

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Magnesium oxide is an ionic compound. It is formed from magnesium ions and oxide ions. Magnesium and oxygen ions are created during the reaction because an exchange of electrons occurs when magnesium ribbon burns. A magnesium atom loses two valence electrons to become an ion with a charge of +2 represented as  $Mg^{2+}$ . Magnesium ions are said to have a **valency** of +2.

An oxygen atom gains two valence electrons to become an ion with a charge of -2 represented as  $O^{2-}$ . Oxygen has a valency of -2.

The oppositely charged ions are attracted to each other and the +2 and -2 charges balance. The compound magnesium oxide is formed. The cation (positive ion) is named and written first and the anion (negative ion) second. As one oxygen anion is needed to balance each magnesium cation, MgO is the chemical formula of magnesium oxide. The formula for an ionic substance shows the ratio of atoms not a set number of atoms in a particular sample.

To write the chemical formula of an ionic compound follow the steps below.

- 1 Write the ions with their charges.
- 2 Swap each of the charges and make them subscripts.
- **3** If the subscripts are the same then they can be cancelled out. For example, MgO is the balanced formula for the compound. Check: (+2) + (-2) = 0.

Sodium ions have a charge of +1 and chloride ions have a charge of -1, so sodium chloride will form in the ratio 1 : 1.

Sometimes the ionic charges do not balance as easily. Consider magnesium chloride—a magnesium ion has a charge of +2 and a chloride ion has a charge of -1. Magnesium chloride will have the formula MgCl<sub>2</sub>. (Note that the 1 on the Mg can be omitted.)

Groups of atoms can also have a charge. The  $NO_3^-$  ion has one nitrogen atom and three oxygen atoms and overall the group has a charge of -1. (Note that when ions have a charge of -1 the 1 can be omitted.) Table 2.3 shows that some of the ions result from groups of atoms as well as single atoms.

When ions composed of groups of atoms are involved, the same steps are used. Sodium hydroxide is formed from the ions Na<sup>+</sup> and OH<sup>-</sup>, and is written as NaOH. If more than one of these ions is used to balance the compound, brackets are used, for example magnesium hydroxide is formed from the ions  $Mg^{2+}$  and  $OH^-$ . It is written as  $Mg(OH)_2$ .

### Properties of ionic compounds

In ionic compounds, the forces between the positive and negative ions are quite strong. They hold the ions in a tightly ordered arrangement.



figure 2.6 In sodium chloride the ions are held in structured lattices called crystals.



The valency of an ion is

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figure 2.7 Sodium chloride in solution will conduct an electric current because its ions are free to move.



Most ionic compounds melt at fairly high temperatures and so they are solids at room temperature. They have high melting and boiling points. They are crystalline because of the ordered way the ions are arranged. If you apply a force to an ionic crystal you are trying to push together ions of the same charge. As ions of the same charge repel each other, the crystal shatters. Most ionic compounds dissolve in water.



figure 2.8 The forces of repulsion between ions of the same charge cause the sodium chloride crystal to shatter.

For an object to conduct electricity, electrons or some other charged particles must be able to move. The electrons in ionic compounds are held tightly and are not free to move, so solid ionic compounds do not conduct electricity. If you melt an ionic compound or dissolve it in water, the ions are able to move freely. If you connect either a molten ionic compound or a solution containing a dissolved ionic compound to a power supply the ions will move through the solution carrying an electric current.

### Questions

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- 4 Would you expect barium (atomic number 56) to gain or lose electrons? How many?
- 5 lodine atoms tend to gain an electron. When this happens, to which noble gas does it have a similar electron arrangement?
- 6 Sulfur and oxygen are in the same column because of their similar chemical properties. Why are they similar?
- **7** Write the symbols for the ions that form from nitrogen and phosphorus atoms.
- 8 Explain how an atom becomes positively or negatively charged when it gains or loses electrons.
- 9 For each of the following describe the number of protons, number of electrons and overall charge of the ions formed. (You will find the periodic table useful.)
  - a A hydrogen atom loses one electron.
  - **b** A fluorine atom gains one electron.
  - c An oxygen atom gains two electrons.
  - **d** An aluminium atom loses three electrons.

- 10 How many electrons do each of the following ions have? (Make use of the periodic table.)

  - **b** Cl<sup>-</sup>
  - C Mg<sup>2+</sup>
  - **d** H<sup>+</sup>
  - e Al<sup>3+</sup>
    f O<sup>2-</sup>
- **11** Write a formula for each of the following ionic compounds.
  - a copper(I) nitrate
  - **b** silver oxide
  - c chromium(III) fluoride
  - **d** lithium nitride
  - e potassium carbonate
- **12** Name the ionic compounds with the following formulae.
  - **a** KF
  - b LiOH
  - c ZnCl<sub>2</sub>
  - d AlN
  - **e**  $(NH_4)_2CO_3$

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### 2.3 Covalent bonding

**Covalent bonding** takes place between atoms of non-metallic elements through the sharing of electrons. In contrast, ionic bonding takes place between atoms of metallic and non-metallic elements which gain or lose electrons.

The simplest example of covalent bonding is hydrogen gas. Elemental hydrogen exists as pairs of hydrogen atoms described by the formula H<sub>2</sub>.



**figure 2.9** The two atoms which make up a hydrogen molecule are held together by a covalent bond. This type of bond is the result of sharing valence electrons. Each hydrogen atom has two electrons (like the noble gas helium) making it a stable molecule. (a) The arrangement of the valence electrons and (b) the charge cloud diagram of hydrogen.

**Charge cloud diagrams** are more realistic 'pictures' of molecules. They attempt to show that the electrons within the molecules are continuously moving. This gives the appearance of 'negative-charge clouds' in the molecules.

### Forming covalent bonds

In covalent substances, the atoms do not gain or lose valence electrons; instead they share electrons with the other atoms to which they are bonded. This sharing of electrons gives each atom the same number of electrons as a noble gas making it more stable. Since most noble gases have 8 electrons in their outer shell (all except helium) we often talk about atoms bonding to achieve a stable outer shell of 8 electrons or a **stable octet**.

Figure 2.9 shows how hydrogen atoms share a pair of electrons in a hydrogen **molecule**. Each hydrogen atom contributes one electron and the pair of electrons is shared equally between both hydrogen nuclei. The sharing of a pair of electrons creates a **single covalent bond**.

Chlorine atoms also combine with a single covalent bond to form chlorine molecules,  $Cl_2$ . Each chlorine atom has an electron configuration of 2,8,7 and the valence shell only needs to gain one electron to obtain a stable octet. The chlorine atoms achieve this by sharing a pair of electrons.

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**figure 2.10** Chlorine molecules are formed when a pair of electrons are shared between two chlorine atoms in a single covalent bond. (a) Only the outer shell (valence) electrons are shown here. (b) This shows the charge cloud diagram.



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Covalent bonding is the sharing of electrons between atoms of non-metallic elements.

A molecule is a group of two or more atoms held together by covalent bonds

When an atom has 8 electrons in its outer shell it is described as having a **stable** octet. This is a highly stable configuration comprising a full s orbital (2 electrons) and 3 full p orbitals (6 electrons).

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Bonding pairs of electrons are those that are shared between atoms, forming a bond. Non-bonding pairs of electrons are not shared.

Elements and compounds

The pair of electrons that are shared between the two atoms is known as the **bonding pair**. Any pairs of electrons that are part of the outer shells but not shared between atoms are known as **non-bonding pairs**, or **lone pairs**.

Covalent bonds do not only form between atoms of the same element but also between atoms of different non-metallic elements. Figure 2.11 illustrates the covalent bonding between a chlorine and hydrogen atom to form a hydrogen chloride molecule. Each atom contributes an electron to a bonding pair to form a covalent bond.



As well as single covalent bonds, double and triple covalent bonds can be formed. A double covalent bond is the sharing of two pairs of electrons between two atoms. Oxygen molecules are two oxygen atoms held together by a **double** covalent bond. Nitrogen molecules are two nitrogen atoms bonded by the sharing of three pairs of electrons in a triple covalent bond.



figure 2.12 A representation of the double covalent bond in an oxygen molecule and the triple covalent bond in a nitrogen molecule.

The same bonding can also result in larger molecules. Water consists of two hydrogen atoms and an oxygen atom covalently bonded. Two single covalent bonds are formed as each hydrogen atom shares a pair of electrons with the oxygen atom. The oxygen has an electron configuration of 2,6 and by sharing a pair of electrons with each hydrogen atom the oxygen attains a stable outer shell of eight electrons. The hydrogen atoms also have two electrons in their outer shell, making the molecule very stable.





figure 2.11 A stable arrangement of outer shell electrons can also be attained by the covalent bonding of different elements. (a) A representation of a hydrogen chloride molecule showing outer shell electrons. (b) A charge cloud diagram of hydrogen chloride.

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Carbon atoms have four valence electrons and can form four covalent bonds. Methane consists of a carbon atom covalently bonded to four hydrogen atoms. It has the formula  $CH_4$ . The sharing of valence electrons between carbon and hydrogen is illustrated in figure 2.14.





There are many possible combinations of elements in covalent substances. Many others will be introduced in following sections and chapters.

### Molecules and molecular substances

All of the examples of covalent bonding used so far in this section are molecular substances. A molecule is a set number of atoms joined together. As discussed above, the elements hydrogen, oxygen, nitrogen and chlorine exist as **diatomic molecules**, that is molecules consisting of two atoms joined together. Some molecules are made up of one type of atom (homonuclear); other examples such as hydrogen chloride, water and methane consist of atoms of different elements covalently bonded together (heteronuclear). Some molecules are far more complex and consist of many atoms. Examples include plastics, proteins and the DNA (deoxyribonucleic acid) found in all living things.

There are a variety of ways that molecules can be represented. So far in this chapter bonding has been shown by using electron shells.

Figure 2.16 shows two other ways of representing bonding. The electron dot formula shows the valence electrons of the atoms but the actual shell has been omitted. The structural formula represents pairs of electrons by a simple line. When two atoms are joined by a single line it shows that a pair of electrons is shared between them as a covalent bond, two lines represents a double bond and three lines represents a triple bond. A line drawn from one atom but not joined to another atom represents a non-bonding pair.





The structural formula is one of the best ways of illustrating the different shapes that molecules can have. Pairs of electrons repel each other determining the overall shape of a molecule. Table 2.5 summarises the names and reasons for particular molecular shapes. Note the shape indicates the position of the atoms, not the pairs of electrons. Diatomic molecules consist of two atoms bonded together. They can be atoms of the same element (homonuclear) or different elements (heteronuclear).



figure 2.15 DNA is a very complex molecule made up of millions of atoms. DNA makes up the chromosomes in our cells.



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Elements and compounds

table 2.4 Some covalent molecular substances represented by an electron dot formula and a structural formula.

Compound	Electron dot formula	Structural formula
water	о н н	H H
oxygen		
hydrogen chloride		н — а

table 2.5 Molecular shapes.

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	Shape	Description	Example
Sauce	linear	The two atoms of a diatomic molecule must be in a straight line.	
2		The double bonds of triatomic molecules such as carbon dioxide repel each other—a straight line is as far apart as the electrons can get.	Carbon dioxide
)	V-shaped (also known as angular or bent)	In a triatomic molecule, non-bonding pairs repel the bonding pairs of electrons. As the bonding pairs also repel each other and try to achieve a linear shape, a V shape results.	$\begin{array}{c} & & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ $
	pyramidal	A molecule consisting of a central atom and three bonded atoms might be expected to form a flat triangular shape. As these central atoms will usually have a non-bonded pair that repels the three bonded pairs, the triangular shape is turned into a pyramid.	H H H Ammonia
	tetrahedral	A molecule consisting of a central atom and four bonded atoms has four sets of bonding pairs trying to get as far apart as possible. The resulting shape is described as tetrahedral.	H C H H H H H

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### Intermolecular forces

Many of the physical properties of ionic substances are determined by the strength of the ionic bonds. Most ionic substances exist as solids at room temperature due to the strong bonds holding the ions together. Conversely, covalent substances tend to exist as liquids and gases at room temperature. This does not indicate that covalent bonds are weaker than ionic bonds. When a covalent molecular substance melts it is not the covalent bonds that are broken but the forces between the molecules known as intermolecular forces. There are several types of intermolecular forces. To explain these types we need to understand electronegativity.

Two different atoms bonded together may not attract the shared electrons to the same degree—one of the atoms may have a stronger pull on the electrons. Electronegativity is a measure of the attraction of a bonded element for the electrons in the bond.

Table 2.6 shows the electronegativities of some elements. The electronegativity of elements tends to increase from left to right across the periodic table and decrease down a group.

When two elements are bonded together, the bonding electrons are more attracted to the element with the higher electronegativity. This means that the electrons spend more time around that atom and the region becomes slightly negatively charged. The other atom, with lower electronegativity, becomes slightly positively charged.



are the forces **between** molecules. They are not hold the atoms **within** the molecule together.



A measure of the of an element is known as its **electronegativity** 



In a polarised bond the electrons are not shared equally between the two

	tabi	<b>e</b> 2.6	I he electro	negatı	vities o	t some	e eleme	ents (ar	rangeo	accor	rding to	their	positior	ns in th	ne perio	odic tal	olej. 🔨
						ME	TALS							NON	I-META	LS	
	Li	Be							Н				В	С	Ν	0	F
	1.0	1.5							2.1				2.0	2.5	3.0	3.5	4.0
	Na	Mg											Al	Si	Р	S	Cl
	0.9	1.2											1.5	1.8	2.1	2.5	3.0
	К	Са	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br
	0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6	1.8	1.8	2.0	2.4	2.8
	Rb	Sr	Y	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	I
	0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5
	Cs	Ba	(lanthanides)	Hf	Та	W	Re	0s	lr	Pt	Au	Hg	Τl	Pb	Bi	Ро	At
	0.7	0.9	1.1-1.2	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.8	1.9	2.0	2.2
	Fr	Ra	(actinides)														
	0.7	0.9	1.1–1.7														/
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Notice that the

difference 2 <u>1 = 0</u>.9. ectronegativity difl HCl is 3.0 – 2.1 the electrons are not just unevenly shared—each loses an electron and each chlorine atom gains one forming ions of

The hydrogen atom of the hydrogen chloride molecule has an electronegativity of 2.1 and the chlorine atom has an electronegativity of 3.0. The chlorine atom will attract the electrons in the bonding pair more strongly and have a partial negative charge. The hydrogen atom will have a partial positive charge. This is shown in figure 2.17.

 $\delta$  + represents a small amount of positive charge.  $\delta$  – represents a small amount of negative charge.

figure 2.17 A hydrogen chloride molecule has a polarised bond due to the difference in electronegativities of hydrogen and chlorine atoms.

The hydrogen chloride molecule has a polarised bond. It can also be described as being a **polar molecule** or a **dipole**.

Since each hydrogen chloride molecule has regions of positive and negative charge, the positive area of one molecule can be attracted to the negative area of another. These intermolecular forces are much weaker than covalent or ionic bonding. This explains why hydrogen chloride exists as a gas at room temperature.

Formaldehyde has three bonds, two C-H bonds and a C=O bond. Carbon has a higher electronegativity than hydrogen and so a polar bond exists between these atoms. Oxygen has a higher electronegativity than carbon and so another polar bond exists in the formaldehyde molecule. These dipoles combine and overall the hydrogen end of the formaldehyde has a partial positive charge and the oxygen end has a partial negative charge. Formaldehyde is a polar molecule. It is not just the electronegativity of the atoms present that determines whether a molecule is polar.

Carbon dioxide has two polar bonds due to the different electronegativities of carbon and oxygen. However, unlike formaldehyde, carbon dioxide is symmetrical across the polar bonds and the polarity cancels out. The carbon dioxide molecule is not a dipole.

Tetrafluoromethane (CF<sub>4</sub>) is also a symmetrical molecule and is tetrahedral in shape (figure 2.19). The bonds between carbon and fluorine are polarised due to the electronegativity difference of the atoms but the symmetry of the atom means that the molecule is not a dipole. It does not have a negative and positive end.

With an understanding of electronegativity and polar molecules the types of intermolecular forces can be explained. There are three types of intermolecular forces: dipole-dipole attractions, hydrogen bonding and dispersion forces. Their features are summarised in table 2.7.



Carbon dioxide

figure 2.18 Formaldehyde is an asymmetrical molecule across its polar bonds while carbon dioxide is symmetrical and not a dipole.



figure 2.19 Tetrafluoromethane has polarised bonds but is not a dipole.

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table 2.1	7 The types of	f intermolecular forces.
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	e types of intermolecular forces.		
Type of intermolecular force	Explanation	Examples	L
dispersion forces (also called van der Waal's forces)	The weakest type of intermolecular forces Due to a brief and temporary electrostati charge on an atom as electrons move abo an atom or molecule causing a momenta imbalance of charge. The more electrons in an atom or molecul the stronger the dispersion forces. Dispersion forces become insignificant w molecules are influenced by stronger intermolecular forces. They are only considered when stronger forces do not o	s.       Hydrogen and chlorine molecules.         c       CI—CI         but       H—H         ry       Dispersion forces result as the electrons         le       momentarily spend more time around one atom         than the other. Symmetrical molecules such as         hydrogen, chlorine and tetrafluoromethane are         non-polar. The forces of attraction between such         molecules are due to dispersion forces.         Noble gases rarely combine with other elements.         They can be liquefied and solidified (at low         exist.	
dipole–dipole attraction	Stronger than dispersion forces (but wea than hydrogen bonding). The partial positive charge of one molecu is attracted to the partial negative charge of another. This type of force only exists when the molecules are dipoles.	ker $ \begin{array}{ccccccccccccccccccccccccccccccccccc$	
hydrogen bonding (a special form of dipole– dipole attraction)	The strongest type of intermolecular forces.(a)Hydrogen bonds only occur when a molecule contains a hydrogen atom bonded to one of the highly electronegative atoms—nitrogen, oxygen or fluorine. $\delta +$ The hydrogen atom has a relatively high partial positive charge due to a large difference in electronegativity.(c)The hydrogen atom is strongly attracted to a non-bonding pair of electronegative atom of a nearby molecule. $\delta +$	$\begin{bmatrix} b \\ \vdots \\$	

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#### materials

- glass or cellulose acetate rod rubbed with silk (positively charged)
- polystyrene rod or a balloon rubbed with wool (negatively charged)
- $2 \times \text{burettes}$
- $2 \times 250$  mL beakers
- $2 \times$  stands, bossheads and clamps
- de-ionised water
- 50 mL hexane ( $C_6H_{14}$ )

safety

- Wear safety glasses and a laboratory coat for this experiment.
- Hexane is extremely flammable. The vapour is irritating to the skin, eyes and respiratory system. Ensure that the solvent does not remain open in the laboratory for extended periods.



figure 2.20

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Polar bonding within water molecules

A stream of water bends when charaed rods are brought near it. A stream of hexane is almost unaffected by the presence of the rods.

#### Purpose

To demonstrate the dipolar nature of water molecules.

Experiment 2.1

#### Method

- 1 Fill one burette with water and another with hexane. Place a beaker under each burette.
- 2 Open the burette taps so that fine continuous streams of liquid run from the burettes into beakers from a height of about 40 cm. (A tall gooseneck tap, such as is often found on a front bench, may be used as an alternative source of the water stream.)
- 3 Bring the positively charged glass rod close to, but not touching, each of the streams of liquid. The water stream should be attracted markedly towards the charged rod.
- 4 Repeat with a negatively charged rod.

#### Theory

Oxygen is more electronegative than hydrogen. As a result it attracts the shared bonding electrons in the water molecule more strongly than the hydrogen atom. The oxygen atom therefore behaves as if it has a small negative charge, and the hydrogen atom behaves as if it has a small positive charge. The molecule is described as dipolar.

When charged rods are placed near a fine stream of water, the charged ends of the molecule become attracted to the charged rod, causing the water to deviate from its normal flow.

The orientation of atoms in the hexane molecule, and the similar electronegatives of carbon and hydrogen, cause hexane to be non-polar. (Models may help make these ideas easier to understand.) As a result, hexane is attracted to a charged rod to a much lesser extent than water. However, the charged rod does induce dipoles in the liquid, and slight attraction does occur.

#### Discussion

- **1** Explain the principles behind charging one article by rubbing it with a piece of material.
- 2 Why is the stream of water attracted to both the positively and negatively charged rods?
- 3 Sketch a diagram of a water molecule.
- 4 Why is hexane less strongly attracted to the charged rods?

### Properties of molecular substances

Since the forces between molecules in molecular substances are weak, molecular substances tend to have low melting and boiling points, and many of them exist as gases or liquids at room temperature. Hydrogen, oxygen, chlorine, carbon dioxide and methane exist as gases at room temperature, and water, ethanol (CH<sub>3</sub>CH<sub>2</sub>OH), formaldehyde and tetrachloromethane (or carbontetra-

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chloride, CCl<sub>4</sub>) exist as liquids at room temperature. Notice that larger molecules tend to be liquids and involve the stronger types of intermolecular forces. Only quite large molecules, with stronger intermolecular forces, exist as solids. These solids are usually soft and pliable. The molecules in the solid can move around each other to some extent, allowing it to bend. Waxes and plastics are some examples of solid molecular substances.

The electrons in covalent bonds are held tightly and do not move to carry an electric current. Molecular substances do not contain ions either. This means that molecular substances are non-conductors of electricity.

Some molecules are attracted to water molecules and can be dissolved. Ethanol for example is soluble in water, while baby oil is insoluble.

# Names and formulae of molecular substances

Some molecular substances are elements. For example oxygen, nitrogen and chlorine gases are made up of molecules consisting of two atoms. This is shown by their formulae— $O_2$ ,  $N_2$ ,  $Cl_2$ . When we talk about oxygen gas we mean  $O_2$  molecules not atoms. Molecular elements are known by the name of the element.

Molecular compounds consist of more than one type of atom. Prefixes are used to indicate how many atoms of each type are in a molecule (see table 2.8). The first element in the formula is given its full name and the second element has its name shortened and -ide is added as a suffix. For example, the name carbon dioxide tells us that the molecule consists of one carbon atom and two oxygen atoms. Note the prefix mono is not used on the first element.

Some molecular compounds are given common (or trivial) names. Carbon tetrahydride (CH<sub>4</sub>) is more commonly known as methane (found in natural gas). Table 2.9 shows the name and formula for some common molecular substances.

table 2.9 The names of som molecular compounds and their	e common formulae.		
Name	Formula		
sulfur dioxide	S0 <sub>2</sub>		
carbon monoxide	CO		
carbon tetrachloride	CCl <sub>4</sub>		
dinitrogen dioxide	$N_2O_2$		

### **Covalent lattices**

Not all substances made up of covalently bonded atoms are molecules. A **covalent network lattice** is a vast lattice of non-metallic atoms covalently bonded together. In case you are tempted to consider covalent bonds to be weaker or inferior to ionic bonds you may find it interesting to learn that one example of a covalent network lattice is the hardest naturally occurring substance on earth—diamond.

Diamond consists of a lattice of carbon atoms. Each carbon atom is covalently bonded to four other carbon atoms. The four surrounding atoms are positioned at the corners of a tetrahedron. This three-dimensional structure, held together by strong covalent bonds, forms an extremely stable threedimensional lattice as illustrated by figure 2.21.

table 2.용 The prefixes used to name molecular compounds.			
mono	1		
di	2		
tri	3		
tetra	4		
penta	5		
hexa	6		
hepta	7		
octa	8		
nona	9		
deca	10		



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figure 2.21 The covalent network lattice of diamond. Each carbon atom is covalently bonded to four other carbon atoms.

The strength of the carbon lattice makes diamond extremely hard. It takes a lot of energy to break down the diamond lattice. At extremely high temperatures, the covalent bonds within the lattice break and, rather than forming a liquid, the carbon atoms form individual atoms of a gas. This process is called sublimation; diamond is said to sublime.

The valence electrons of a diamond lattice are held tightly in covalent bonds. They are said to be **localised**. Without free electrons to carry an electric current, diamond does not conduct electricity.

Other covalent network lattice substances have similar properties to diamond. Some of these are described in table 2.10.

tadie 2.10	The properties of some co	valent network substar	ices.
Material	Formula	Melting temperature (°C)	Boiling temperature (°C)
diamond*	С	>3550	-
silicon	Si	1410	2680
silicon carbide	e* SiC	2200	-
silicon dioxide	e SiO <sub>2</sub>	1700	2230

\*Diamond and silicon carbide do not have boiling temperatures as they undergo sublimation at normal pressures.

Graphite is another covalent lattice of carbon (figure 2.22). In graphite, each carbon atom is attached to three other carbon atoms by strong covalent bonds in a flat layer structure called a covalent layer lattice. Graphite has only three of carbon's four valence electrons involved in covalent bonding. The fourth valence electron is delocalised. The delocalised electrons are free to move between the layers of the covalent lattice.

Graphite, like diamond, has a high melting temperature due to the large amount of energy required to break the strong covalent bonding of the lattice. Unlike diamond, graphite is able to conduct an electric current as the delocalised electrons are free to move. While bonding within the layers of graphite is strong, the forces between layers are weak and they readily slide over each other. This gives graphite a soft greasy texture and makes it useful as a lubricant. Lead pencils actually contain graphite and during writing layers are left behind on the paper as the pencil slides over it.

A substance is said to sublime if it changes from a solid to a gas

Localised electrons belong atoms. Delocalised electrons are able to move around and be

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orksheet 3 Terms and definitions



BONDING AND PROPERTIES OF MATERIALS

STRUCTURE,

### Questions

- **13** Draw electron dot and structural formulae for the following molecules.
  - a fluorine  $(F_2)$
  - **b** hydrogen fluoride (HF)
  - c methane (CH<sub>4</sub>)
  - **d** tetrachloromethane (CCl<sub>4</sub>)
  - e ethane  $(C_2H_6)$
  - f ammonia (NH<sub>3</sub>)
  - g carbon dioxide (CO<sub>2</sub>).
- 14 How many lone pairs would you expect atoms of the following elements to have when they form covalent bonds with other non-metal atoms?
  - a H
  - **b** F
  - c C
  - d N
  - e Ar
- **15** Draw electron dot formulae for the following molecules and identify the number of bonding and non-bonding electrons in each molecule.
  - a NCl<sub>3</sub>
  - **b** CH<sub>4</sub>
  - C H₂S
- 16 Consider the table of electronegativities (table 2.6). Covalent bonds can form between the following pairs of elements in a variety of compounds. Use the electronegativity values given in the table to identify the atom in each pair that would have the larger share of bonding electrons.
  - a S and O
  - **b** C and H
  - c C and N
  - d N and H
  - e F and O
  - f P and F
- 17 Are the following molecules polar or non-polar? (Draw structural formulae or make models to help you to answer this question.)
  - a CS<sub>2</sub>
  - **b** Cl<sub>2</sub>O
  - c SiH<sub>4</sub>
- **18** Between which of the following molecules are there
  - i dipole-dipole interactions?ii hydrogen bonds?
  - a NH<sub>3</sub>
  - **b** CHCl<sub>3</sub>
  - C CH<sub>3</sub>CÍ

**d**  $F_20$ 

e HBr f H<sub>2</sub>S

g HF

h H₂O

i H<sub>2</sub>

**19** The melting temperatures of four of the halogens are given in table 2.11 below. Describe and explain the trend in melting temperatures of these elements. (Refer to the periodic table to establish where the halogens occur in the table.)

### table 2.11

Halogen	Melting temperature (°C)
fluorine (F2)	-220
chlorine (Cl <sub>2</sub> )	-101
bromine (Br <sub>2</sub> )	-7
iodine (I <sub>2</sub> )	114

- **20 a** Write chemical formulae for these molecular substances.
  - i hydrogen gas
  - ii dinitrogen monoxide
  - iii phosphorus trihydride
  - iv carbon tetrachloride
  - v dihydrogen sulfide
  - **b** Name the following molecular substances.
    - i F<sub>2</sub> ii NO<sub>2</sub>
    - ii CH<sub>4</sub>
    - iv NF<sub>3</sub>
    - $V N_2H_4$
- 21 Explain the following properties of
  - a diamond and
  - **b** graphite
  - in terms of their respective structures.
    - i high melting temperature
    - ii hardness or softness
  - iii ability or inability to conduct electricity
- 22 Explain the following uses in terms of the
  - structures of graphite and diamond.
  - **a** Graphite is used as a lubricant.
  - **b** Diamond is often used as an edge on saws and a tip on drills.

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### 2.4 Metallic bonding

The properties of metals are a result of the way metal atoms bond together. This characteristic form of bonding is called metallic bonding.

Metals consist of positive ions in a regular, three-dimensional lattice with delocalised valence electrons, which are free to move throughout the lattice. Compare this to ionic substances in which electrons belong to particular ions or molecular substances in which electrons are shared between particular atoms. However, metallic bonding achieves a similar result to the other forms of bonding. By setting free the valence electrons into a common pool or sea of electrons, the metal ions achieve a stable electron configuration similar to the noble gases.



figure 2.23 The structure of a metal. The positive ions are arranged in a fixed, threedimensional lattice. The valence electrons are free to move and can be thought of as a sea of negative charge.

metallic structure and bonding are unchanged.

The metallic bonds are the attraction between positive ions and the freemoving electrons. The strength of these bonds can be seen in the fact that metals (except mercury) are solids at room temperature.

Metals can be hammered into shape or drawn into wires because the atoms can be forced to move without breaking up the lattice. The positive ions and electrons just move around to take up the new shape.



figure 2.24 As a force is applied to a metal, the positive ions move and the electrons adjust to the new shape.

If a piece of metal is connected into an electric circuit it will conduct electricity. The delocalised electrons are free to move within the metal, allowing an electric current to flow.

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Metallic bonding is the between positive metal ions in a fixed lattice and their delocalised electrons.

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When the circuit is complete, electrons will flow through the metal



Flow of electrons

This end of the circuit is connected to the positive terminal of the battery.

**figure 2.25** Metals conduct electricity because the electrons are able to move freely through the lattice.

# Growing metal crystals

#### Purpose

To grow crystals of a range of metals and to observe their shapes.

#### Method

- 1 Add 0.5 g of agar to 40 mL of de-ionised water in a beaker and warm gently, stirring until the agar is dissolved. Remove from the heat.
- **2** Add 0.3 g of one of the available solids to the agar solution, stirring until it dissolves.
- **3** Pour the agar solution into a Petri dish and place the strip of zinc in the centre. Do not move the Petri dish until the agar has set.
- **4** Once the agar has set, place a lid on the Petri dish to prevent the agar from drying out.
- 5 Observe the formation of metal crystals over the next 1–2 days.
- 6 Repeat the above procedure using each of the metal salts listed.
- 7 Sketch the appearance of the different metal crystals that have been grown in your class.

#### Theory

Zinc is a more reactive metal than silver, lead, copper or tin. When a piece of zinc is placed in solutions that contain the positive ions of these other metals, the zinc metal reacts to form ions and the ion of the less reactive metal reacts to form its metal. This process can be summarised by the word equation:

zinc + silver nitrate  $\rightarrow$  zinc nitrate + silver

Each of the other compounds react in a similar way. These reactions are known as **displacement reactions**.

When a metal is formed quickly, as would be the case if the displacement reaction occurred in aqueous solution, the metal crystals tend to be small. It is difficult to see the details of their shape. If, however, the formation of the metal is slowed down, as when the reaction occurs in agar, larger crystals form and it is easier to examine their shape.

If your crystals have a regular, uniform shape, you can conclude that the particles in the metal are arranged in a regular manner in a crystal lattice.

## 0.5 g agar 40 mL de-ionised water approximately 0.3 g of one of the following solids: AgNO<sub>3</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, CuSO<sub>4</sub>, SnCl<sub>2</sub> 1 cm × 4 cm strip of clean zinc sheet 250 mL beaker Petri dish hotplate *or* Bunsen burner, tripod and gauze mat

glass stirring rod

materials

#### safety

- Wear gloves, safety glasses and a laboratory coat for this experiment.
- AgNO<sub>3</sub> causes burns and stains skin and clothing.
- Pb(NO<sub>3</sub>)<sub>2</sub> is poisonous.
  CuSO<sub>4</sub> irritates the skin
- and eyes.
- SnCl<sub>2</sub> can irritate the skin and eyes.

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Elements and compounds



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Malleable substances are able to be beaten into



## The properties of metals

Metals tend to have a shiny appearance (lustre), and high melting and boiling points. Mercury is a liquid but all other metals are solids at room temperature.

Metals are good conductors of electricity. Some metals conduct an electric current better than others. They are also good conductors of heat.

The ability of a metal to be bent or hammered into shape is called its malleability. Some metals can be drawn into a wire. They are said to be ductile.

table 2.12 The physical properties of metals and what they indicate about metallic structure

Property	What this tells us about structure
Metals conduct electricity in the solid state.	Metals have charged particles that are free to move.
Metals are lustrous or reflective.	Metals can reflect light.
Metals are malleable and ductile.	The forces between the particles must be able to adjust when the particles are moved.
Metals tend to have high melting and boiling temperatures.	The forces between particles in a metal are strong.
Metals generally have high densities.	The particles are closely packed in a metal.

### Questions

- 23 Which properties listed in table 2.12 could be used to tell the difference between a piece of nickel and a piece of tin?
- 24 What is the difference between malleability and ductility?
- 25 If two metals have similar melting points, electrical conductivity and lustre, what other feature could be used to separate the two metals?
- **26** Explain why mercury is a liquid at room temperature while iron is a solid.
- 27 The bonds in an ionic solid can be described as directional while those in a metal are nondirectional. Why are these terms used?

# Hydrocarbons consist only

BONDING AND PROPERTIES OF MATERIALS

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## 2.5 Organic compounds

Carbon atoms have four valence electrons and can form four covalent bonds. Hydrocarbons are molecules consisting only of hydrogen and carbon atoms. The smallest hydrocarbon is methane consisting of one carbon and four hydrogen atoms but there are an infinite number of possible combinations of hydrogen and carbon, some of which are quite large. Figure 2.26 shows some examples of fairly simple hydrocarbon molecules.



figure 2.26 The covalent bonding of methane, ethane and propane.

Some hydrocarbon molecules consist of very long chains called polymers. Figure 2.27 shows one example—polyethene. Polyethene is the substance used to make items such as plastic milk containers and cling wrap. It is manufactured from ethene a hydrocarbon with two carbons held together by a double covalent bond.





**figure 2.27** (a) A portion of a polyethene molecule which can contain tens of thousand of atoms linked in a long chain. (b) Ethene, the starting material of polyethene, contains a double covalent bond.

## Alkanes

Methane, ethane and propane are the first compounds in a series of molecules that have similar properties and vary in structure from each other by one  $-CH_{2}$ -section of a molecular chain. They are said to belong to a **homologous series**. This particular homologous series is known as the **alkanes**. Other molecules in this series are listed in table 2.13.

table $2.13$ The first ten molecules of the alkane series.			
Formula	Name	Formula	Name
CH <sub>4</sub>	methane	$C_6H_{14}$	hexane
$C_2H_6$	ethane	$C_7H_{16}$	heptane
C <sub>3</sub> H <sub>8</sub>	propane	$C_8H_{18}$	octane
$C_4H_{10}$	butane	C <sub>9</sub> H <sub>20</sub>	nonane
$C_5H_{12}$	pentane	$C_{10}H_{22}$	decane

Alkanes are described by the general formula  $C_nH_{2n+2}$ . For hexane, n = 6 so  $2n + 2 = 2 \times 6 + 2 = 14$ . The molecular formula for hexane is  $C_6H_{14}$ .

Alkanes are hydrocarbon molecules that only have single bonds, i.e. the bonds between carbon atoms share only one pair of electrons. 0

The structural formulae of methane, ethane and propane are shown in figure 2.28. Recall from Section 2.3 Covalent bonding that compounds like methane have a tetrahedral shape due to the four bonds around the carbon atom. Similarly, the forces of repulsion influence the shape of the alkane molecules causing the chain of carbon atoms to zig zag.



figure 2.28 The structural formulae of methane, ethane and propane.

### Alkenes

In alkanes, carbon atoms form only single bonds with adjacent atoms. **Alkenes** contain one carbon to carbon double bond. The alkenes are another homologous series. Again, molecules with the homologous series have similar properties and differ from the next molecule in the series by a  $-CH_2$ - group. The general formula for alkenes is  $C_nH_{2n}$ .

The simplest alkene is ethene (figure 2.29). Propene (figure 2.30) is the second alkene of the series. Notice that these molecules have fewer hydrogen atoms than their corresponding alkanes due to the double bond. Alkenes are said to be **unsaturated** because they contain fewer than the maximum possible number of hydrogen atoms. Alkanes are said to be **saturated**.



Note that each molecule of the alkene series contains only one double bond. The -ene part of the name indicates the presence of a double bond just as the -ane part of the alkane names indicate the molecules contain only single bonds. When naming alkenes, the same prefixes are used to indicate the number of carbon atoms in the molecule.

table $2.14$ The first nine molecules of the alkene series.			
Formula	Name	Formula	Name
C <sub>2</sub> H <sub>4</sub>	ethene	C <sub>7</sub> H <sub>14</sub>	heptene
$C_3H_6$	propene	C <sub>8</sub> H <sub>16</sub>	octene
$C_4H_8$	butene	C <sub>9</sub> H <sub>18</sub>	nonene
$C_5H_{10}$	pentene	$C_{10}H_{20}$	decene
$C_6H_{12}$	hexene		

Alkenes are hydrocarbon molecules that include a double bond.

Saturated hydrocarbons only contain single covalent bonds between carbon atoms while unsaturated hydrocarbons include at least one multiple bond

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It is possible for longer molecules to have more than one double bond. Molecules with two double bonds are known as **dienes** and those with three double bonds are **trienes**.

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### Purpose

To investigate the properties of hydrocarbons.

#### Method

Carry out the following tests in a fume cupboard.

#### A. Solubility of hydrocarbons in water

Mix ten drops of each hydrocarbon to be tested with ten drops of coloured water in a small test tube. Record your observations about the solubility of each hydrocarbon.

#### B. Combustion of hydrocarbons

Light a Bunsen burner. The major hydrocarbon present in natural gas is methane ( $CH_4$ ). Keep the Bunsen flame yellow by closing the air hole of the burner. Using a test tube holder or a pair of tongs, hold an empty test tube in the flame for 10 seconds. Describe what happens to the bottom of the test tube. After a few minutes, open the air hole of the Bunsen burner and continue heating the test tube in the blue flame. Describe what now happens to the outside of the test tube.

#### C. Saturation and unsaturation in hydrocarbons

Place ten drops of each of the hydrocarbons to be tested into separate test tubes. Add bromine solution dropwise to each test tube. Note whether the distinctive colour of the bromine solution remains or disappears.

#### Theory

Hydrocarbons are non-polar molecules and therefore are insoluble in polar solvents.

When they undergo complete combustion, they react with oxygen to form carbon dioxide and water. If the combustion is incomplete, carbon (or carbon monoxide) and water form.

If bromine solution reacts with a hydrocarbon, the hydrocarbon must be unsaturated. The distinctive colour of the bromine disappears as the double or triple bond in the hydrocarbon breaks and a bromine atom is added to each of the carbon atoms that were originally involved in the double or triple bond.

#### Discussion

1 With the air hole of the Bunsen burner closed, methane is said to undergo incomplete combustion which can be described by the equation:

 $CH_4(g) + O_2(g) \rightarrow C(s) + 2H_2O(g)$ 

With the air hole of the Bunsen burner open, ethane is said to undergo complete combustion which can be described by the equation:

 $CH_4(g) + 2O_2(g) \rightarrow CO_2(s) + 2H_2O(g)$ 

What evidence of these different reactions did you observe?

- **2** Why is bromine solution used to test whether a hydrocarbon is saturated or unsaturated?
- **3** The equation for the reaction between an unsaturated hydrocarbon and bromine can be represented by the equation:  $-CH_2=CH_2-+Br_2(aq) \rightarrow -CH_2Br-CH_2Br-$

How does this reaction relate to your observations?

#### materials

- dropper bottle of bromine solution
- dropper bottles containing different hydrocarbons, for example, cyclohexane, cyclohexene
- small test tube for each hydrocarbon
- coloured waterBunsen burner
- Bunsen burn
   banah mat
- bench matmatches
- matche
   tongs

#### safety

- Wear safety glasses and a laboratory coat for this experiment.
- Keep hydrocarbons well away from the Bunsen burner flame.
- Do not pour hydrocarbons down the sink. Place all organic waste in a waste bottle in a fume cupboard.
- Carefully follow the instructions given relating to the treatment of the hydrocarbons used in this experiment.
- Use bromine solution
- in the fume cupboard.HCl and NaOH are both corrosive.

Elements and compounds

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**figure 2.31** The structural formula for propyne (C<sub>3</sub>H<sub>4</sub>).



Alkynes are hydrocarbon molecules that have a triple bond—a bond between carbon atoms that involves the sharing of three pairs of electrons.

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## Alkynes

Alkynes are another type of unsaturated hydrocarbon. The -yne part of the name is used to indicate the presence of a triple bond. Alkynes have the general formula  $C_nH_{2n-2}$ .

## Naming saturated hydrocarbons

The molecular formula of a compound does not always indicate the full extent of the structure of the molecule. It is possible to have molecules that are different in structure but the same molecular formula. This is particularly true for larger molecules. Systematic naming allows us to distinguish between molecules with the same formula but different structure.

Figure 2.32 shows the different structures of two molecules that both have the same formula  $C_4H_{10}$ . The first molecule is the straight-chain molecule known as butane; the second molecule is a branched-chain molecule which consists of three carbon atoms joined in a row with another carbon branching off. This molecule is named methyl propane. The propane part describes the three carbons in a row and the branch containing only one carbon is a methyl group.



figure 2.32 The straight-chain and branched-chain isomers of C<sub>4</sub>H<sub>10</sub>.

In naming hydrocarbon molecules, the same prefixes are repeatedly used to indicate the number of carbon atoms. The -yl part of a name indicates that it is a branch.

table 2.15 The prefixes used in the systematic naming of hydrocarbons.			
No. of carbon atoms	Prefix	No. of carbon atoms	Prefix
1	meth-	6	hex-
2	eth-	7	hept-
3	prop-	8	oct-
4	but-	9	non-
5	pent-	10	dec-



Butane and methyl propane are said to be **structural isomers**. Structural isomers are molecules with the same molecular formula but a different physical structure. Structural isomers tend to have similar chemical properties but may have slightly different physical properties; for example, the different shapes of the molecules may result in different melting and boiling temperatures.

Four isomers with the molecular formula  $C_6H_{14}$  are shown in figure 2.33 (others are possible). Hexane is a member of the alkane series; 2-methylpentane and 3-methylpentane are both branched-chain molecules. In order to name the second two molecules, the carbon atoms of the longest straight chain (pentane) are numbered and used to indicate which carbon the methyl group is attached to. The longest chain is numbered from the end closest to any branching groups so that the smallest possible numbers are used in the name. For example, 2-methylpentane could be incorrectly named 4-methylpentane if the chain was numbered from the wrong end.



The name 2,2-dimethylbutane indicates that the structure of the molecule consists of a butane chain of four carbon atoms. The dimethyl prefix indicates that there are two methyl branches and the 2,2 indicates that both methyl branches are on the second carbon of the butane chain.

## Naming unsaturated hydrocarbons

The first alkenes ethene and propene are simple to name. In ethene, there are only two carbon atoms for the double bond to lie between (see figure 2.29). In propene, there are two possible positions for the double bond but they are mirror images of each other and are essentially the same molecular structure (see figure 2.30).

Butene has two possible (truly) different positions for the double bond. The isomer illustrated in figure 2.34(a) is named by numbering the carbons from the end closest to the double bond. It is called but-1-ene, indicating that the double bond falls between the first and second carbons atoms. The isomer of figure 2.34(b) is called but-2-ene, indicating that the double bond falls between the second and third carbon atoms. This name is the same whether the carbon atoms are numbered right to left, or left to right. This method applies to carbon chains of all lengths and for both alkenes and alkynes.









Elements and compounds

## Intermolecular forces of hydrocarbons

Hydrocarbon molecules are all non-polar as the tetrahedral orientation of the atoms attached to each carbon atom cancels any polar bonds. Therefore any intermolecular forces between hydrocarbon molecules are due to dispersion forces. These dispersion forces tend to be larger for molecules with greater numbers of atoms.

Shorter alkanes tend to have lower melting and boiling temperatures than longer alkanes-methane exists as a gas at room temperature while hexane is a liquid. Smaller molecules are said to be more volatile (as liquids they evaporate more easily) due to their weaker intermolecular forces. Longer molecules such as oils tend to have a higher viscosity or thickness than shorter molecules, which flow more easily.

Unsaturated hydrocarbons have fewer atoms and therefore weaker dispersion forces than their corresponding saturated hydrocarbons. Table 2.16 shows that ethene has a lower boiling temperature than ethane and hexene has a lower boiling temperatures than hexane.

<b>table</b> 2.16 Boiling temperatures of some alkanes compared with the corresponding alkenes.		
Hydrocarbon	Boiling temperature (°C)	
ethene ( $C_2H_4$ )	-103.7	
ethane $(C_2H_6)$	-88.6	
hexene ( $C_6H_{12}$ )	63.5	
hexane ( $C_6H_{14}$ )	68.7	

Branched-chain isomers tend to have weaker intermolecular forces than their straight-chain counterparts. In branched-chain molecules some atoms are buried within the molecule and their electrons are not available to contribute to the dispersion forces of the molecule. Most atoms of straightchain molecules are very much exposed and dispersion forces are greater. The melting and boiling temperatures of hexane can be expected to be higher than 2,2-dimethyl butane although they have the same molecular formula.

### **Ring molecules**

It is possible for the carbons at either end of an alkane chain to bond together to form a ring or cycloalkane. Cycloalkanes are described by the general formula  $C_nH_{2n}$ . Table 2.17 shows some examples of these molecules and their structural formulae.

There are also ring molecules that are unsaturated. Cyclohexene and cyclohexa-1,3-diene are examples of these (figure 2.35).





Cycloalkanes are saturated hydrocarbon molecules that form

The more volatile a liquid

ring structures.

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Benzene is a special type of ring molecule. It has the chemical formula  $C_6H_6$ . Sometimes its structure is thought of as alternating quickly between the two structures shown in figure 2.36. This is not an accurate representation as the electrons that would form the double bonds are actually delocalised and shared equally with all six carbon atoms. Benzene is better represented by figure 2.37.



figure 2.36 There are two possible ways of drawing structures for a molecule with the formula  $C_6H_6.$ 





The hydrogen atoms of benzene can be substituted for different alkyl groups forming substances such as methylbenzene and 1-ethyl-4-methylbenzene (figure 2.38).

In some cases it is the benzene ring which is thought of as the substituted group. In this situation it is known as a phenyl group. In phenylethene (figure 2.39) one of the hydrogen atoms from an ethene molecule has been substituted with a benzene ring.

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**figure 2.38** The hydrogens of benzene can be substituted for different alkyl groups.

**figure 2.39** The benzene ring is considered to have replaced one of the hydrogen atoms of ethene in phenylethene.

## Alcohols

The organic molecules mentioned so far have all been hydrocarbons, consisting only of atoms of hydrogen and carbon. When other elements are introduced, the properties of the new compounds are very different. Alcohols have their particular properties because they contain a hydroxyl (–OH) group, often described as a **functional group**. Alcohols are also known as **alkanols**. One of the more familiar alcohols is ethanol (figure 2.40), the alcohol found in alcoholic drinks such as wine and beer. Note that ethanol is similar to ethane (two carbon atoms joined together) but the –OH group replaces one of the hydrogen atoms. The molecular formula of ethanol is  $CH_3CH_2OH$ . The addition of a hydroxyl group alters the properties of the original ethane molecule.

figure 2.40 The structural formula of ethanol.

The presence of the hydroxyl functional group makes alcohols quite polar the smaller the molecule, the greater the effect of the –OH group on the polarity of the molecule. This polarity also makes hydrogen bonding possible. As a result of stronger intermolecular forces, an alcohol is likely to have a higher boiling temperature than the corresponding alkane. The comparison between boiling temperatures of alkanes and alcohols is shown in table 2.18.

table 2.18	The boiling temperatures of these alcohols are higher than those	
of their corresp	oonding alkanes.	

Alkane	Boiling temperature (°C)	Alcohol	Boiling temperature (°C)
methane (CH <sub>4</sub> )	-161.5	methanol (CH <sub>3</sub> OH)	64.5
ethane ( $C_2H_6$ )	-88.6	ethanol (C <sub>2</sub> H <sub>5</sub> OH)	78.3
hexane ( $C_6H_{14}$ )	68.7	hexanol (C <sub>6</sub> H <sub>13</sub> OH)	157.1
octane ( $C_8H_{18}$ )	125.7	octanol ( $C_8H_{17}OH$ )	195.2

## **Carboxylic acids**

The characteristic properties of **carboxylic acids** (also known as **alkanoic** acids) are due to the carboxyl (–COOH) functional group. One of the smallest carboxylic acids, ethanoic acid (figure 2.41), is found in vinegar.



A functional group is

an atom or group of atoms that influence

the properties of compounds forming a homologous series.

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Carboxylic acids are organic molecules with particular properties due to their carboxyl (-COOH) functional groups.

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**figure 2.41** The structural formula of (a) the carboxyl group and (b) ethanoic acid.

Carboxylic acids are named according to the number of carbon atoms they contain; methanoic acid contains one carbon atom and propanoic acid (table 2.19) has three carbon atoms.



Like alcohols, carboxylic acids are polar allowing hydrogen bonding between molecules. Carboxylic acids have higher melting and boiling temperatures than corresponding alkanes.

## Questions

- **28** Methane (CH<sub>4</sub>) is the smallest hydrocarbon molecule.
  - a What is a hydrocarbon?
  - b Why does one carbon atom bond to four, rather than two, three, five or any other number of hydrogen atoms?
  - c Draw the structural formula of methane. Why does methane have this particular arrangement of hydrogen atoms around each carbon atom?
- **29** Ethene is an alkene.
  - **a** Draw the structural formula of ethene.
  - **b** Give the names and structural formulae of the next two alkenes.
- **30** Ethane and ethene are both hydrocarbons. Do these hydrocarbons belong to the same homologous series? Explain your answer to another student.
- **31** The following molecular formulae all represent hydrocarbons:
  - CH<sub>4</sub>, C<sub>5</sub>H<sub>12</sub>, C<sub>3</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>12</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>5</sub>H<sub>10</sub>, C<sub>25</sub>H<sub>52</sub>, C<sub>6</sub>H<sub>6</sub>. **a** Which of these hydrocarbons belong to the same homologous series as ethane?
  - **b** Which of these hydrocarbons belong to the same homologous series as ethene?

- **32 a** How do saturated hydrocarbons differ from unsaturated hydrocarbons?
  - **b** Draw structural formulae for the following hydrocarbons and indicate any that are saturated.

 $C_{2}H_{4}, C_{3}H_{8}, C_{3}H_{6}, C_{4}H_{8}.$ 

- **33** Draw structural formulae for each of the following hydrocarbons.
  - a propane
  - **b** propene
  - **c** methane
  - **d** but-1-ene
  - e 2-methylpropane
- **34** Explain why methane is a gas at room temperature whilst octane, one of the constituents of petrol, is a liquid.
- **35** Draw structural formulae for each of the following ring molecules.
  - a cyclopentane
  - **b** cycloheptane
  - c cyclopenta-1,3-diene
  - **d** 1,3-dimethylbenzene



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- **36 a** Describe any trend in the boiling temperatures of the corresponding alkanes, alcohols and carboxylic acids in table 2.20 below.
- **b** Explain the differences between boiling points of the alcohols and carboxylic acids.

table 2.2					
Alkane	Boiling temperature (°C)	Alcohol (°C)	Boiling temperature	Carboxylic acid (°C)	Boiling temperature
methane	-161.5	methanol	64.5	methanoic acid	100.7
ethane	-88.6	ethanol	78.3	ethanoic acid	117.9
hexane	68.7	hexanol	157.1	hexanoic acid	205.0
octane	125.7	octanol	195.2	octanoic acid	239.3

## 2.6 Patterns in properties

## Classifying matter by bonding—an overview

Matter can be divided into different groups according to its different properties. The classification key (figure 2.42) shows that all matter can be divided into two types: mixtures and pure substances. Pure substances are uniform all the way through. Mixtures often look uniform all the way through but they can be separated into their components. Every part of a salt crystal is pure salt, but salt water is a mixture—the water can be evaporated and separated from the salt.





Pure substances can be elements (such as iron or oxygen) or compounds (such as sodium chloride). The elements can be sorted into metals (such as aluminium) and non-metals (such as carbon or helium). Compounds are either formed when atoms have opposite charge (ionic compounds) or when they share electrons (molecular compounds and covalent lattice solids).

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Table 2.21 compares matter according to the way atoms are bonded together.

(table 泡泡 A summary of ionic, molecular and metallic substances. )			
	lonic substances	Molecular substances	Metallic substances
type of bonding	ionic bonding	covalent bonding	metallic bonding
the involvement of electrons	Atoms gain or lose electrons to become ions. lons of opposite charge are attracted to each other.	Atoms share electrons to gain a full outer-shell configuration.	Positive ions form a lattice. Electrons move throughout the lattice as a sea of negative charge.
types of atoms	Metallic and non-metallic elements are involved. Metallic elements lose electrons and become positively charged. Non- metallic elements gain electrons and become negatively charged.	Non-metallic elements are bonded together covalently.	The metallic elements from the left side of the periodic table are involved. Metals are elements of the one type bonded together.
states of matter	They tend to be crystalline solids. They have high melting and boiling points.	Most are gases and liquids at room temperature. Any solids tend to be soft and waxy. They have low melting and boiling points.	They are all solids at room temperature except mercury (a liquid). They have high melting and boiling points.
electrical conductivity	Solids are non-conductors of electricity. Solids dissolved in water will conduct electricity. Ionic substances will also conduct electricity in the molten state.	They are non-conductors of electricity in all states and when dissolved.	They are good conductors of electricity.

## Trends within the periodic table

As you move down a group of the periodic table, the number of electrons within each atom increases. These electrons are contained in higher electron shells or energy levels. The electrons are further away from the nucleus of the atoms and attracted to it less strongly. The gradual change in structure explains the trends in physical and chemical properties moving down a group. Some of these are outlined in figure 2.43. They are explained in table 2.22.



figure 2.43 Trends in properties of elements down a group of the periodic table.

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figure 2.44 The relative sizes of atoms of Group 1 elements.

table 2.22 Trends down a group.			
Pattern	Explanation		
Size of the atoms increases.	Electrons occupy most of the volume of an atom. Potassium with an electronic configuration of 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 4s <sup>1</sup> is much larger than lithium with 1s <sup>2</sup> 2s <sup>1</sup> , for instance.		
Elements become more metallic.	As elements lose outer-shell electrons more easily, they behave more like metals. The elements in some groups in the table change completely from non-metals to metals. For example, the non-metal carbon is located at the top of Group 14; metallic lead is at the bottom of the same group.		
First ionisation energy decreases.	As the atoms become larger, their outer electrons are further from the nucleus. The energy required to extract one electron from an atom (the first ionisation energy) decreases.		
Electronegativity decreases.	As the outer electrons become more distant, electrons are more weakly attracted to an atom.		

As you move across a period of the periodic table from left to right each element has more electrons in the same outer shell. At the same time, the size of the nucleus of each element is increasing due to increasing numbers of protons. This results in the electrons being more strongly attracted to the nucleus and the size of the atoms of each successive element decreases (figure 2.45).

Across a period each element has a different outer-shell electron arrangement and so properties across a period change a lot more than within a group (in which the elements have the same outer-shell electron arrangement).



figure 2.45 The relative sizes of atoms of elements in Period 3.

The trends in properties across periods are outlined in figure 2.46 and explained in table 2.23.



figure 2.46 Trends in properties of the elements across a period of the periodic table.

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table 2.23 Trends across a period.			
Pattern	Explanation		
The size of atoms decreases.	The increasing positive charge in the nucleus pulls the outer-shell electrons closer, causing the volume of an atom to reduce.		
Elements become non-metallic.	As the number of protons in the nucleus increases, electrons are bound more strongly within atoms. Atoms become less able to release electrons and form positive ions. For example, Period 3 begins with sodium metal which readily forms ionic compounds and ends with unreactive argon gas.		
First ionisation energy increases.	As the strength of attraction between the outer electrons and the nucleus increases, the energy required to extract one electron from an atom increases.		
Electronegativity increases.	As the outer electrons become closer to the nucleus, the electrons are more strongly attracted to the nucleus.		

## Questions

- **37** Name the following types of matter.
  - a metals and non-metals bonded together
  - **b** two or more non-metals bonded together
  - c atoms of one type of metallic element
- **38** Which type of matter is a non-conductor in the solid state but a good conductor in solution or in the molten state?
- **39** What features of a material are needed for it to conduct electricity?
- **40** Name the three types of bonding involving valence electrons. Order them according to which type involves sharing the valance electrons most to least.
- **41** Why do atoms form bonds by gaining or losing electrons to become ions, or by sharing electrons?

- **42** From each pair below, which element would you expect to have the larger atomic size?
  - a Li, F
  - b N, As
  - c Na, Rb
  - d S, Ca
- **43** From each pair below, which element would you expect to have the greater electronegativity?
  - a Li, F
  - b N, As
  - c Na, Rb
  - d S, Ca

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## Summary **DDDD**

- ▶ The periodic table is a useful tool for predicting the chemical properties and physical properties of the elements. It is divided into regions that allow the elements to be identified as metals, non-metals and metalloids. The groups of the periodic table contain elements with similar properties. This information enables chemists to predict how atoms of elements will bond together to form compounds.
- **Ionic bonding** involves atoms forming positive **ions** as they lose valence electrons or negative ions as they gain valence electrons. The charge on an ion is known as its **valency**. Positive and negative ions are attracted to each other forming crystalline solids.
- Covalent bonding involves atoms sharing electrons and forming groups of atoms called molecules. By bonding together atoms achieve a stable octet of electrons. The shared pairs of electrons are known as bonding pairs while electron pairs not involved in bonding are known as non-bonding or lone pairs. Single covalent bonds involve the sharing of one pair of electrons; double covalent bonds involve the sharing of two pairs of electrons between two atoms; and triple covalent bonds involve the sharing of three pairs of electrons between two atoms.
- The bonding and non-bonding pairs of electrons try to minimise forces of repulsion, resulting in different molecular shapes including linear, pyramidal, tetrahedral and V-shaped.
- The **electronegativity** of different elements and the individual shapes of molecules determine the type

of **intermolecular forces** that operate between molecules—**hydrogen bonding**, **dipole-dipole attraction** and **dispersion forces**.

- Covalent network lattices and covalent layer lattices are large arrays of atoms held together by covalent bonding.
- Metallic bonding involves positive metal ions surrounded by delocalised electrons. Conversely, electrons involved in ionic and covalent bonding are localised (fixed). The electron arrangement of metals allows them to be readily shaped. They are said to be malleable and ductile.
- Organic compounds are a special group of covalent molecular compounds. They include homologous series of hydrocarbon molecules such as alkanes (which have only single bonds), alkenes (which have one double bond) and alkynes (which have a triple covalent bond). Hydrocarbons which contain only single bonds are said to be saturated while those with multiple bonds are said to be unsaturated.
- Hydrocarbon ring molecules known as cycloalkanes can also be formed.
- Structural isomers are molecules with the same molecular formula but with different molecular structure.
- Some organic compounds include other groups of elements known as functional groups. These give the characteristic properties of substances, such as, alcohols and carboxylic acids.

## Key terms

alcohol alkane alkene alkyne bond bonding pair carboxylic acids chemical property compound covalent bonding covalent network lattices covalent layer lattices delocalised electrons dipole–dipole attraction dispersion forces double covalent bond ductile electronegativity group functional group homologous series hydrocarbon hydrogen bonding intermolecular forces ionic bonding

- ions localised electrons linear lone pair malleable metallic bonding metalloids metals molecule non-bonding pair non-metals organic compounds periodic table
- physical property pyramidal saturated single covalent bond stable octet structural isomers tetrahedral triple covalent bond unsaturated V-shaped valency

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## Chapter **Review**

# 2.1 Physical and chemical properties

- 44 In which groups of the periodic table would you not expect to find a metal?
  - A groups 14 and 15
  - B groups 14 and 18
  - C groups 13 and 17
  - D groups 17 and 18
- 45 Which one of the following elements is a metal?A the element of atomic number 5
  - **B** the element of atomic number 7
  - **C** the element of atomic number 9
  - **D** the element of atomic number 11
- **46** Select two elements from each group that you would expect to have similar properties.
  - a lithium, oxygen, potassium, vanadium
  - **b** nitrogen, neon, sodium, phosphorus
  - c manganese, magnesium, beryllium, sodium

## 2.2 Ionic bonding

- **47** Which of the following pairs of elements are most likely to form an ionic compound when reacted together?
  - A carbon and oxygen
  - **B** copper and nickel
  - **C** calcium and bromine
  - **D** phosphorus and chlorine
- **48** At room temperature, ionic compounds are usually:
  - A solids with a low melting temperature.
  - **B** solids with a high melting temperature.
  - **C** liquids with a low melting temperature.
  - D liquids with a high melting temperature.
- **49** In the molten state, an ionic compound conducts electricity because:
  - A the molecules are free to move.
  - **B** the electrons are free to move.
  - **C** the ions are free to move.
  - **D** the atoms are free to move.
- **50** Ionic compounds are often brittle, so that the crystal shatters when hit. This is because:
  - A forces between the ions are weak.
  - **B** layers of ions move and repulsion between ions of the same charge occurs.
  - **C** the positive and negative ions neutralise each other.
  - **D** the delocalised electrons are unable to hold the positive ions.

- **51** In an ionic compound formed between elements of atomic number 9 and atomic number 12, the ratio of positive ions to negative ions is:
  - A 1:1
  - **B** 1:2
  - C 2:1
  - **D** 2:3
- 52 An atom A has one electron in its outer shell and an atom B has six electrons in its outer shell. When they react, the most likely formula for the compound is:
  - A AB
  - **B**  $A_2B$
  - $C AB_2$
  - **D**  $AB_6$
- **53** The chemical formula for aluminium carbonate is: **A**  $Al_2(CO_3)_3$ 
  - **B**  $Al_2(CO_3)_2$
  - **C**  $Al_3(CO_3)_2$ **D**  $Al_3(CO_3)_3$
- 54 The chemical formula for calcium nitrate is:
  - A CaNO<sub>2</sub>
  - **B** CaNO<sub>3</sub>
  - C Ca( $NO_3$ )<sub>2</sub>
  - **D**  $Ca(NO_2)_2$
- **55** The charge on the cation in  $SrCr_2O_7$  is:
  - **A** +1
  - **B** +2
  - **C** -1
  - **D** -2
- **56** The nitrate ion has a formula NO<sub>3</sub><sup>-</sup>. This shows that:
  - A one oxygen atom has an extra negative charge.
  - **B** the three oxygen atoms each have an extra negative charge.
  - C the nitrogen atom has an extra negative charge.
  - **D** the group of atoms as a whole has an extra negative charge.
- **57** The element gallium, Ga, can have a charge of +3. The formula of gallium(III) oxide would be:
  - A Ga<sub>3</sub>O
  - **B**  $GaO_3$
  - $C Ga_2O_3$
  - **D**  $Ga_3O_2$
- **58** When an element reacts to form an ionic compound, electrons are gained or lost from the atoms. Write the symbol, the charge and the electron configuration of the ion formed from the following elements.
  - a beryllium c sodium
- b oxygend phosphorus
  - 261

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- 59 The elements X, Y and Z form ionic compounds when reacted with other elements. The following compounds are formed: Ca<sub>3</sub>X<sub>2</sub>, Y<sub>2</sub>CO<sub>3</sub> and Al<sub>2</sub>Z<sub>3</sub>.
  - a What is the valency (charge) of the ion formed by:
    - i element X?
    - ii element Y?
    - iii element Z?
  - **b** Use these charges on the ions to write correct chemical formulae for the following compounds.
    - i the sulfate compound of Y
    - ii the potassium compound of Z
    - iii the ionic compound formed between X and Y
    - iv the ionic compound formed between Y and Z
- **60** Explain why an ionic compound will not conduct electricity in the solid state even though it contains charged particles.
- **61** Write a chemical formula for each of the following ionic compounds.
  - **a** barium nitrite
  - **b** magnesium hydrogen carbonate
  - c potassium hydrogen phosphate
  - d iron(III) sulfite
  - e nickel(II) phosphate
- **62** Name the ionic compounds with the following chemical formulae.
  - a  $Cu(NO_3)_2$
  - **b** CrBr<sub>3</sub>

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- c BaHSO<sub>4</sub>
- d  $Pb_3(PO_4)_2$
- e  $Fe_3N_2$
- **63** The formula of sodium perchlorate is NaClO<sub>4</sub> and that of potassium ferrocyanide is K<sub>4</sub>[Fe(CN)<sub>6</sub>]. Using this information, write the formula of:
  - a calcium perchlorate
  - **b** aluminium ferrocyanide
  - **c** iron(III) perchlorate
  - d ammonium ferrocyanide.
- **64** Write the chemical formula for the ionic compound formed in the reaction between:
  - a potassium and bromine
  - b magnesium and iodine
  - c calcium and oxygen
  - **d** aluminium and fluorine
  - e calcium and nitrogen.

## 2.3 Covalent bonding

- **65** The number of bonding electrons in the nitrogen molecule is:
  - **A** 2
  - **B** 4 **C** 6
  - D 8

- 66 Each of the following substances is dissolved in water. Which will form a solution that will not conduct an electric current?
  - A hydrogen chloride
  - **B** sugar
  - C salt
  - **D** copper(II) sulfate
- **67** Pure water is a poor conductor of electricity because water:
  - **A** contains few charged particles.
  - **B** has a low melting temperature.
  - **C** is a neutral liquid.
  - D contains covalent bonds.
- 68 The bonding in graphite is best described as:
  - A covalent within the layers, ionic between the layers.
  - **B** ionic within the layers, dispersion forces between the layers.
  - **C** covalent within the layers, dispersion forces between the layers.
  - **D** ionic within the layers, covalent between the layers.
- 69 In dry ice (solid carbon dioxide), the carbon dioxide molecules are held together by:
  - A covalent bonds.
  - **B** hydrogen bonds.
  - **C** dipole-dipole attraction.
  - **D** dispersion forces.
- **70** Which one of the following groups of substances shows only covalent compounds?
  - A NaCl,  $CH_4$ ,  $CO_2$ ,  $N_2O$
  - **B** HCl, H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>SO<sub>4</sub>
  - C  $CO_2$ ,  $N_2$ ,  $O_2$ ,  $KNO_3$
  - **D**  $\operatorname{NH}_3$ ,  $\operatorname{H}_2$ O,  $\operatorname{Na}_2$ S,  $\operatorname{CO}_2$
- **71** Strong covalent bonding in three dimensions is shown by:
  - A the sublimation of dry ice from a solid to a gas.
  - **B** the electrical conducting properties of graphite.
  - **C** the hardness of diamond.
  - **D** the dipole nature of water.
- 72 Which type of solid has the lowest melting temperatures?
  - A a covalent network lattice solid
  - **B** a covalent layer lattice solid
  - C an atomic solid
  - **D** a molecular solid
- **73** Which one of the following pairs of elements reacts to form a compound containing covalent bonds?
  - A sodium and fluorine
  - **B** potassium and oxygen
  - C magnesium and fluorine
  - **D** carbon and chlorine

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74 What is the maximum number of covalent bonds an atom of each of the following elements can form?

- a F
- **b** 0
- **c** N
- **d** C
- e H
- f Ne
- **75** Draw electron dot diagrams for each of the following molecules.
  - a HBr
  - **b**  $H_2O_2$
  - c CF<sub>4</sub>
  - d  $C_2H_6$
  - e PF<sub>3</sub>
  - f Cl<sub>2</sub>0
- **76** Write the formulae for each of the following substances.
  - a hydrogen gas
  - **b** nitrogen monoxide
  - c carbon disulfide
  - **d** carbon dioxide
- 77 Identify the number of bonding and non-bonding pairs of electrons in the following molecules.
  - **a** N<sub>2</sub>
  - **b** CHCl<sub>3</sub>
  - $C 0_{2}$
- **78** When oxygen forms covalent molecular compounds with other non-metals, the structural formulae that represent the molecules of these compounds all show each oxygen atom with two lone or non-bonding electron pairs. Why are there always two lone pairs?
- **79** The following is a list of molecules: N<sub>2</sub>, Cl<sub>2</sub>, O<sub>2</sub>, NH<sub>3</sub>, HCl, CH<sub>4</sub>, H<sub>2</sub>O, CO<sub>2</sub>, CCl<sub>4</sub>, CHCl<sub>3</sub>.
  - a Draw a structural formula for each of the following from the list, showing bonding and non-bonding electron pairs.
    - i a molecule that contains one triple bond
    - ii a molecule that contains one double bond
  - iii a molecule that contains two double bondsb From the list:
    - i which molecules are overall polar?
    - ii which molecules are overall symmetrical?
    - iii which molecules show hydrogen bonding?
- **80** Consider the electronegativity values in table 2.6. Use the table to determine which of the following molecules contains the most polar bond.
  - $A CO_2$
  - **B** H<sub>2</sub>O
  - C H<sub>2</sub>
  - D H<sub>2</sub>S E NH<sub>3</sub>
- 81 For each of the structures in figure 2.47, state whether the molecule is polar or non-polar.

# Are the strongest intermolecular forces of attraction between molecules of each type dispersion forces, hydrogen bonding or dipole–dipole interactions?



### figure 2.47

- 82 Consider samples of the following compounds: tetrachloromethane  $CCl_4(s)$ ; sulfur dioxide  $SO_2(s)$ ; carbon dioxide  $CO_2(s)$ ; hydrogen sulfide  $H_2S(s)$ . In which cases will the only forces between molecules in the samples be dispersion forces? (You should first decide whether molecules of these compounds are polar or non-polar. You can do this by drawing an accurate structural formula for each one.)
- 83 The mass of a hydrogen fluoride molecule is similar to the mass of a neon atom. However the boiling temperatures of these substances are very different; hydrogen fluoride boils at 19.5°C and neon at −246°C. Explain the difference in this property of the two substances.
- **84** Predict the increasing order of melting temperatures for the following substances containing chlorine and explain the basis of your predictions: Cl<sub>2</sub>, NaCl, CCl<sub>4</sub>
- **85** At room temperature CCl<sub>4</sub> is a liquid whereas CH<sub>4</sub> is a gas.
  - a Which substance has the stronger intermolecular attractions?
  - **b** Explain the difference in the strengths of the intermolecular attractions.
- **86** What are the forces of attraction between the following molecules?
  - $a H_2$
  - **b** HCl
  - c NH<sub>3</sub>
  - d  $CH_4$
  - **e** H₂Ö
  - $f C_2 H_6$

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## 2.4 Metallic bonding

- **87** In which of the following pairs do both elements show mainly metallic bonding?
  - A H and He
  - **B** Li and Be
  - C Be and B
  - D Li and B
- **88** The bonding in metallic solids is best described as:
  - A electrostatic attraction between protons and neutrons.
  - **B** electrostatic attraction between metal cations and valence electrons.
  - **C** electrostatic attraction between metal cations and delocalised electrons.
  - **D** electrostatic attraction between protons and valence electrons.
- **89** Metals are malleable and ductile. This means that they:
  - A are hard and flexible.
  - **B** are hard and dense.
  - **C** can form sheets and wires.
  - **D** can form sheets and crystals.

- **90** Metals are malleable and ductile because when a metal is hit:
  - A some of the ions move but are held in a new position by the delocalised electrons.
  - **B** some of the delocalised electrons move but the positive ions stay in position.
  - **C** some of the protons move but are held in a new position by the neutrons.
  - **D** some of the atoms move but are held in a new position by the covalent bonds.
- 91 Metals conduct electricity:
  - A in the solid state only.
  - **B** in the liquid state only.
  - **C** in the solid state and the liquid state.
  - **D** only when reacted with a non-metal.
- **92** Consider the table of properties of some metals and non-metals below. Use the data in the table to answer the following questions.
  - a Which metal has the strongest forces of attraction between its metal ions and its delocalised electrons?
  - **b** Why is the metal in part a not used in place of aluminium in aircraft manufacture?
  - c Which metal has the lowest density?
  - d Why is the metal in part c not used in making light metal objects?

Element	Melting temperature (°C)	Boiling temperature (°C)	Electrical conductivity (MS m <sup>-1</sup> )*	Thermal conductivity (J s <sup>-1</sup> m <sup>-1</sup> K <sup>-1</sup> ) <sup>†</sup>	Density (g mL <sup>-1</sup> )
aluminium	660	2450	36.6	190	2.7
copper	1083	2600	57.9	390	8.96
gold	1063	2970	45	310	19.3
iron	1540	3000	9.6	78	7.86
lead	327	1740	4.8	37	11.4
mercury	-39	357	1	8.4	13.5
platinum	1770	3825	9.3	73	21.4
potassium	64	760	14	100	0.86
silver	961	2210	60	418	10.5
sodium	98	892	21	135	0.97
tungsten	3410	5930	19	180	19.3
carbon					
graphite	3730	4830	0.07	45	2.26
diamond	>3350	+	10 <sup>-17</sup>	—	3.51
iodine	114	183	10 <sup>-13</sup>	0.4	4.94
oxygen	-219	-183	_	0.026	1.15(1)
sulfur	119	445	10 <sup>-21</sup>	0.28	1.96

\* MS m<sup>-1</sup> = megasiemens per metre.

 $\dagger$  Thermal conductivity measures the conductance of heat (J s<sup>-1</sup> m<sup>-1</sup> K<sup>-1</sup>).

Diamond sublimes (changes straight from a solid to a gas) when it is heated.

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table 2.24 `

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**a** A piece of gold shines brightly in the sun. A  $CH_3CHCH_2$ ,  $(CH_3)_3CH$ ,  $C_2H_4$ B CH<sub>3</sub>CHCH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>, CH<sub>3</sub>CHCHCH<sub>3</sub> c A metal spoon used to stir a boiling mixture  $C C_3H_6, C_2H_4, C_4H_{10}$ **D**  $C_2H_4$ ,  $C_4H_8$ ,  $C_6H_{12}$ **d** Iron has a high melting temperature, 1520°C. **101** Which one of the following is an alcohol? e Lead has a density of 11.4 g mL<sup>-1</sup>, which is A CH<sub>3</sub>COCH<sub>2</sub>CH<sub>3</sub> much higher than a non-metal like sulfur. B CH<sub>3</sub>CH<sub>2</sub>COOH **f** Copper can be drawn out in the form of a wire. C CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH **D**  $CH_3CHCH_2$ **102** What is a correct name for the compound  $C_5H_{11}COOH?$ A pentanol **B** hexanol C pentanoic acid D hexanoic acid **103** The boiling temperature of alkanes increases as the number of carbon atoms increases because: A the dispersion forces get stronger with the extra atoms present. B the hydrogen bonding increases with the extra hydrogen atoms present. C the mass of the alkanes increases with the extra atoms present. **D** the forces within the molecules get stronger. **104** Write the names of the following compounds. a  $CH_2 = CH_2$ **b**  $C_8H_{18}$ c CH<sub>3</sub>CH<sub>2</sub>OH d  $CH_2 = CHCH_3$ e CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> g

> **105** Draw a structural formula for each of the following compounds.

**100** Which one of the following groups shows only

unsaturated hydrocarbons?

- a propene
- **b** 2-methylpentane
- **c** hex-2-ene
- **d** 2,2-dimethylbutane

- 94 Which of the following carbon compounds is most likely to show hydrogen bonding? **95** Which one of the following groups shows formulae of a homologous series? A CH<sub>4</sub>, CH<sub>2</sub>CH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
  - **B** CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CHCH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>CHCH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH<sub>2</sub>

93 Use the metallic bonding model to explain each

of the following observations.

becomes too hot to hold.

2.5 Organic compounds

**b** Copper wire transmits electricity.

- C CHCH, CH<sub>2</sub>CHCH, CH<sub>3</sub>CH<sub>2</sub>CHCH, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH
- **D**  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_2H_8$
- **96** Which one of the following correctly shows an alkene?
  - A  $C_2H_2$

A ethanol

**B** ethane

**C** ethene

**D** propane

- **B**  $C_3H_6$
- $C C_{4}H_{10}$
- **D**  $C_6H_6$
- 97 Which one of the following groups shows only alkanes?

A  $CH_4$ ,  $(CH_3)_3CH$ ,  $CH_3CH_3$ 

- B CH<sub>3</sub>CH<sub>3</sub>, CH<sub>3</sub>CHCH<sub>2</sub>, (CH<sub>3</sub>)<sub>3</sub>CH
- C (CH<sub>3</sub>)<sub>3</sub>CH, CH<sub>2</sub>CH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>

**D** 
$$C_2H_6$$
,  $C_3H_8$ ,  $C_7H_{12}$ 

- 98 Which one of the following is an alkene? A  $CH_3(CH_2)_3CCH$ 

  - B CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CHCH<sub>2</sub>
  - C CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>
  - **D**  $CH_3(CH_2)_3CH_3CH_3$
- 99 Ethanol has a much higher boiling temperature than ethane because:
  - A ethanol has a higher mass than ethane.
  - **B** ethanol contains stronger covalent bonds within the molecule than ethane.
  - C ethanol forms hydrogen bonds between molecules and ethane does not.
  - **D** ethanol has dispersion forces between molecules and ethane does not.



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**106** The names for the following carbon compounds are wrong. Give the correct names. a methylethane **b** 1,2-dimethylethene c trimethylmethane **d** 2,2-diethylpropane **107** Silicon, the element below carbon in the periodic table, forms a small number of compounds called silanes. The smallest of these silane molecules has the molecular formula SiH<sub>4</sub>. a Draw a structural formula for SiH<sub>4</sub>. **b** Predict the molecular formula and structural formula of the next member in the series of silanes. 108 Which of the following formulae represents an isomer of  $CH_3CH=CHCH_3$ ?  $C_3H_6$ ,  $C_4H_{10}$ ,  $CH_2=CH-CH_2CH_3$ 109 Draw and name all of the isomers of pentene ( $C_5H_{10}$ ). **110** Name each of the following ring structures. С

- Which of the following formulae represents an isomer of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH?
   HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, CH<sub>2</sub>CH(OH)CH<sub>2</sub>
- **112** Explain whether you agree or disagree with the following statements.
  - a If one structural isomer of a compound of carbon and hydrogen is saturated then all of the other structural isomers of that compound must be saturated.
  - **b** A compound that contains three carbon atoms can only have one structural isomer.
- **113** The table gives the boiling temperatures of the linear isomers of the first ten alkanes.
  - a What happens to the boiling temperatures of these alkanes as molecular size increases?
  - **b** Which alkanes would you expect to be gases at 25°C?
  - c Explain to another student why there is a change in boiling temperature with molecular size.
  - d Suggest a method you could use to separate a mixture of these ten alkanes into two different groups, based on their boiling temperatures.
  - e Investigate the method that is used in industry to separate crude oil into fractions of similar molecular size.

#### table 2.25

d

Alkane	Boiling temperature (°C)		
methane	-161.5		
ethane	-88.6		
propane	-42.1		
butane	-0.5		
pentane	36.1		
hexane	68.7		
heptane	98.4		
octane	125.7		
nonane	150.8		
decane	174.1		

STRUCTURE, BONDING AND PROPERTIES OF MATERIALS

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- **114** Which pair in each of the following sets of compounds would you expect to have the most similar properties?
  - a  $C_3H_6$ ,  $C_3H_5OH$ ,  $C_3H_8$ ,  $C_4H_9OH$
  - **b** CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CH<sub>3</sub>OH, CH<sub>3</sub>COOH
- **115** Ethane and ethene are gases at room temperature but ethanol and ethanoic acid are liquids. Explain these differences.

## 2.6 Patterns in properties

**116** Copy the table below and insert the statements in the best place.

mostly gases and liquids, all solids except one, crystalline solids, malleable and ductile, soft and waxy, hard and brittle, always nonconductors, always conductors, nonconducting solids but conducting when molten or dissolved

#### (table 2.26)

Pr	operty	Molecular compounds	lonic compounds	Metals			
sta nc te	ate at ormal mperature	S					
hardness							
el co	ectrical nductivity						
117	<ul> <li>117 Which of the following elements would be expected to show greatest similarity in chemical properties to the element that has 14 electrons in its neutral atoms?</li> <li>A Al</li> <li>B P</li> <li>C Ga</li> <li>D Ge</li> </ul>						
118	Which of atoms w A Li B Na C F	f the following e ith the largest a	elements would atomic radius?	have			

- DCL
- 119 Which of the following properties increases going down Group 1, from lithium to caesium?I atomic radius
  - II melting temperature
  - III electronegativity
  - A I and II.
  - B I only.
  - **C** II and III.
  - D III only.
- **120** As you move across a period, the number of subatomic particles in an atom increases but the size of an atom decreases. Why?

- **121** Account for the fact that it takes more energy to remove an electron from the outer shell of atoms of:
  - a phosphorus than magnesium
  - **b** fluorine than iodine.
- 122 The graphs below show trends in some of the properties of elements as you go from top to bottom down Group 17 of the periodic table. Which graph best represents the trend for:
  - a electronegativities?b first ionisation energies?
  - c number of outer-shell electrons?
  - d atomic radii?

- **123** The electron configurations of some elements are given below:
  - $Q 1s^2 2s^2 2p^6 3s^2$
  - R 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>5</sup> X 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>5</sup>4s<sup>2</sup>
  - X 15 25 2p 35 3p 3d 45 Y 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>10</sup>4s<sup>2</sup>4p<sup>5</sup>
  - a i Give the letters corresponding to the elements that would be found in the same
    - group of the periodic table. ii Explain briefly how you made your decision.
  - **b i** Which elements would be found in the transition metals of the periodic table?
    - ii What characteristic allows you to identify transition metal elements?
  - **c** How do we know that elements Q and R both belong to Period 3?
    - i What type of bonding would you expect to find in a compound of elements Q and R?
      - ii Explain this in terms of the trends in electronegativity to be found across a period.
    - iii Use the letters Q and R to write the expected formula of this compound.
- 124 a Give explanations for the variation that can be observed in the electronegativity of:
  i the elements of Period 3 from Na to Cl
  ii the elements of Group 1 from Li to Cs.
  - b Solid samples of elements from the left side of the periodic table, such as sodium, are very good conductors of electricity, while those on the right side, such as sulfur, are poor conductors. Account for this in terms of atomic structure and bonding.



Elements and compounds

# Stoichiometry



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## The mole

As atoms are very small, we deal with very large numbers of atoms in chemistry. The **mole** (**mol**), given the symbol *n*, is the SI unit for the amount of a substance. The actual number of particles in a mole has been experimentally determined to be  $6.02 \times 10^{23}$ , and is given the symbol  $N_A$ . For every one mole of any substance there are  $6.02 \times 10^{23}$  representative particles. A **representative particle** is the type of particle in which a substance normally exists (atom, molecule, ion or formula unit). For example, a mole of copper has  $6.02 \times 10^{23}$  atoms, a mole of water has  $6.02 \times 10^{23}$  molecules and a mole of sodium chloride has  $6.02 \times 10^{23}$  formula units.



**figure 3.1** This should give you an idea of how large a number a mole is—if there was one mole of soft drink cans, they would cover the Earth's surface to a depth of over 320 km.



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figure 3.2 Amedeo Avogadro (1776–1856).

Amedeo Avogadro was an Italian scientist who suggested that equal volumes of gases at identical temperature and pressure contained the same number of particles. This is now known as Avogadro's principle and in later years it led to the determination of the number of particles in a mole. The number of particles in a mole is referred to as Avogadro's number, although he had no knowledge of the mole or the number of particles in a mole.

The **molar mass** (*M*) of a substance is the mass, in grams, of one mole of that substance. The molar mass of any substance is equal to its relative atomic mass in grams. For example, the molar mass of copper is 63.5 g mol<sup>-1</sup>, which is equal to its relative atomic mass. For every one mole of copper there is 63.5 g. The molar mass of chlorine is 35.5 g mol<sup>-1</sup>, again equal to its atomic mass in grams. When copper is bonded with chlorine to form copper(I) chloride, CuCl, the molar mass of copper is 63.5 g + 35.5 g = 99.0 g. One mole of copper(I) chloride has a mass of 99.00 g.



**figure 3.3** The mass of one mole of a substance is equal to its relative formula mass. For a molecule or compound, relative formula mass is the sum of the relative atomic masses of the elements.

Some more complex examples are shown below.

# sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>)

 $M(Na_2CO_3) = (2 \times 23.0 \text{ g mol}^{-1}) + 12.0 \text{ g mol}^{-1} + (3 \times 16.0 \text{ g mol}^{-1})$ = 106.0 g mol^{-1}

## Worked example 3.1B

```
sulfuric acid (H_2SO_4)

M(H_2SO_4) = (2 \times 1.0 \text{ g mol}^{-1}) + 32.1 \text{ g mol}^{-1} + (4 \times 16.0 \text{ g mol}^{-1})

= 98.1 \text{ g mol}^{-1}
```



The **molar mass** of a substance, is the mass of one mole of that substance, and is equal to its relative atomic mass in grams.

# •

Une mole of carbon-12 atoms has a mass of 12.0 g, which makes it equal to its relative atomic mass. Section 1.3 Atomic mass describes relative atomic mass.



The molar mass of a substance is the sum of the molar mass of each atom present. Make sure you take into account the number of each type of atom, represented by a subscript.

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## Calculating the number of moles

As molar mass is defined as the mass, in grams, of one mole of substance, this relationship can be represented by the formula:

moles =  $\frac{\text{mass}}{\text{molar mass}}$  or  $n = \frac{m}{M}$ Number of particles =  $n \times N_A$ 

# Worked example 3.1C

How many moles are in 60.2 g of iron?  $M(Fe) = 55.8 \text{ g mol}^{-1}$ 

 $n = \frac{m}{M}$   $n(Fe) = \frac{60.2 \text{ g}}{55.8 \text{ g mol}^{-1}}$ = 1.08 mol

# / Worked example 3.1D

How many moles are in 124.5 g of calcium carbonate?  $M(CaCO_3) = 40.1 + 12.0 + (3 \times 16.0) = 100.1 \text{ g mol}^{-1}$  $n = \frac{m}{2}$ 

$$n(CaCO_3) = \frac{124.5 \text{ g}}{100.1 \text{ g mol}^{-1}}$$
  
= 1.24 mol

# Calculating the number of representative particles

Once you are able to calculate the number of moles of a substance, you can then use this information to calculate the number of representative particles in a sample using the equation:

Number of particles =  $n \times N_A$ 

worked example

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2.0 mol of water (H<sub>2</sub>O) number of H<sub>2</sub>O molecules =  $n \times N_A$ = 2.0 × 6.02 × 10<sup>23</sup> = 1.20 × 10<sup>24</sup>

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Number of particles = *n* × *N*<sub>A</sub>

the number of moles, m represents mass in grams and M represents



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## Worked example 3.1F

1.70 mol of aluminium chloride (AlCl<sub>3</sub>) number of AlCl<sub>3</sub> formula units =  $n \times N_A$ = 1.70 × 6.02 × 10<sup>23</sup> = 1.02 × 10<sup>24</sup>

# Determination of Avogadro's number

### Purpose

To determine experimentally the number of atoms in one mole.

#### Method

- **1** Record the mass of one of the metal samples as precisely as possible.
- 2 Half fill a 100 mL measuring cylinder with water. Record the volume.
- 3 Carefully slide the metal sample into the water. Record the new volume.
- **4** Record the volume of water displaced. This volume is equal to the volume of the metal sample.

#### Discussion

- 1 Calculate the amount, in moles, of metal used.
- 2 Calculate the volume occupied by each metal atom in the sample. Use the value of the atom's atomic radius from a data table and the formula  $V = \frac{4}{3}\pi r^3$ .
- **3** Assume that the metal atoms are packed on top of one another with no spaces in between. Use the volume of the metal sample, as measured by the displaced water and the volume of each metal atom, to calculate the number of metal atoms in the sample.
- 4 Calculate the number of metal atoms that would be present in one mole of the metal atoms. This is equal to Avogadro's number  $(N_A)$ .
- 5 How does the value you calculated compare with the accepted value of Avogadro's number?
- 6 In your calculations you assumed that the metal atoms are packed with no spaces between them. How does this assumption affect your result?
- 7 Assume that the metal atoms actually occupy 66% of the volume of the metal. Recalculate your value for Avogadro's number. Comment on this new value.
- 8 What are the largest sources of error in this experiment?

#### **Extension** activities

Repeat this experiment using as many different samples of metal as possible. In which case is the experimentally determined value of  $N_A$  closest to the accepted value?

#### materials

#### • metal samples

- 100 mL measuring cylinder
- electronic balance data tables listing
- data tables listing atomic weights and atomic radii

#### safety

• Wear safety glasses and a laboratory coat for this experiment.

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## Questions

- 1 Calculate the molar mass of:
  - a nitrogen (N<sub>2</sub>)
  - **b** ammonia (NH<sub>3</sub>)
  - c sulfuric acid  $(H_2SO_4)$
  - **d** iron(III) nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>)
  - e acetic acid (CH<sub>3</sub>COOH) f sulfur atoms (S)
  - f sulfur atoms (S)
  - g sulfur molecules (S<sub>8</sub>)
  - **h** hydrated copper(II) sulfate (CuSO<sub>4</sub>.5H<sub>2</sub>O).
- 2 Calculate the mass of:
  - a 1.0 mol of sodium atoms (Na)
  - **b** 2.0 mol of oxygen molecules  $(O_2)$
  - **c** 0.10 mol of methane molecules  $(CH_4)$
  - **d** 0.25 mol of aluminium oxide  $(Al_2O_3)$ .
- 3 Calculate the amount (in mol) of:
  - **a** H atoms in 5.0 g of hydrogen
  - **b** H<sub>2</sub> molecules in 5.0 g of hydrogen
  - c Al atoms in 2.7 g of aluminium
  - **d** CH<sub>4</sub> molecules in 0.4 g of methane
  - e O atoms in 0.10 g of oxygen
  - **f**  $O_2$  molecules in 0.10 g of oxygen
  - g P atoms in  $1.2 \times 10^{-3}$  g of phosphorus
  - **h**  $P_4$  molecules in  $1.2 \times 10^{-3}$  g of phosphorus.
- 4 What is the amount (in mol) of each of the following?
  - a carbon atoms in 1.201 g carbon

- **b** gold atoms in 39.39 g gold
- **c** sulfur molecules  $(S_8)$  in 10.0 g sulfur
- **d** phosphorus molecules (P<sub>4</sub>) in 10.0 g white phosphorus
- e methane molecules ( $CH_4$ ) in 20.0 g methane
- f aspirin molecules (C<sub>6</sub>H<sub>4</sub>(OCOCH<sub>3</sub>)COOH) in 300 mg aspirin
- **g** aluminium oxide  $(Al_2O_3)$  in 3.5 tonnes of aluminium oxide (1 tonne = 1000 kg).
- 5 Calculate the molar mass of a substance if:
  - **a** 2 mol of the substance has a mass of 80 g
  - **b** 0.1 mol of the substance has a mass of 9.8 g
  - c 1.7 mol of the substance has a mass of 74.8 g
  - **d** 3.5 mol of the substance has a mass of 371 g.
- 6 Calculate:
  - a the number of atoms of lead (Pb) in 1.50 kg lead
  - **b** the number of atoms of silver (Ag) in 20.0 g silver
  - **c** the number of molecules of glucose  $(C_6H_{12}O_6)$  in one tablespoon (20 g) of glucose.
  - **a** If 0.50 mol of a substance has a mass of 72 g, what is the mass of 1 mol of the substance?
  - **b** If  $6.0 \times 10^{22}$  molecules of a substance have a mass of 10 g, what is the molar mass of the substance?

# 3.2 Chemical reactions

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In any chemical reaction, the atoms involved are rearranged and new substances are produced. For this to occur, the bonds between atoms are broken and new bonds are formed.

## **Chemical equations**

The rearrangement of atoms during a chemical reaction can be represented by a **chemical equation**. A chemical equation shows the number and types of atoms of the reacting substances, called **reactants**, which are rearranged to form new substances called **products**. A plus (+) sign is used where there is more than one reactant or product. Reactants and products are separated by an arrow ( $\rightarrow$ ).

#### $REACTANTS \rightarrow PRODUCTS$

There are many symbols used when writing chemical equations.

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- (s) indicates the substance is in the solid state.
- (l) indicates the substance is in the liquid state.
- (g) indicates the substance is in the gaseous state.
- (aq) indicates the substance is in an aqueous solution (dissolved in water).
- $\Delta$  indicates heat has been added to the reaction.
- MnO2 indicates a catalyst (in this case MnO2) has been added to the reaction.

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CHEMICAL

right side

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A chemical equation

represents what happens

during a chemical reaction. The **reactants** are found on the left side

products are found on the

## **Balancing chemical equations**

In any chemical reaction mass is always conserved. The **Law of Conservation of Mass** states that in any chemical reaction the mass of the reactants is equal to the mass of the products. This means mass is neither created nor destroyed during a reaction. To satisfy this law, the number and types of atoms on the reactant side must be exactly the same on the product side of the equation only rearranged.

Worked example 3.2A

Consider the reaction between hydrogen gas and oxygen gas to form liquid water.

Step 1: Write a word equation for the reaction.

hydrogen + oxygen  $\rightarrow$  water

Step 2: Write formulae for the reactants and products.

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



**figure 3.5** The reaction between hydrogen and oxygen. Notice that the number of atoms on each side of the reaction equation is unbalanced.

Step 3: Identify any unbalanced atoms. The number of each type of atom must be the same on both the reactant and product side of the equation. This equation is unbalanced as there are two oxygen atoms on the reactant side, but only one oxygen atom on the product side. Placing a 2 in front of water balances the number of oxygen atoms on each side of the reaction equation. The number written in front of a reactant or product is called the coefficient.

 $\mathrm{H_2}(g) + \mathrm{O_2}(g) \rightarrow 2\mathrm{H_2O}(l)$ 

By balancing oxygen, the number of hydrogen atoms is now unbalanced. There are two hydrogen atoms on the reactant side, but now there are four hydrogen atoms on the product side. Placing a 2 in front of hydrogen gas balances the number of hydrogen atoms on each side of the reaction equation.

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





The equation is now balanced for this reaction. The equation tells us that two molecules of hydrogen gas react with one molecule of oxygen gas to produce two molecules of water. The coefficients can also be used to describe the number of moles of reactants and products. This makes it much more manageable to deal with the enormous numbers of particles involved in a chemical reaction. Therefore, the reaction also shows that two moles of hydrogen gas react with one mole of oxygen gas to produce two moles of water.

Lastly, always double check that the reaction equation is balanced.



Chemical equations are important as they show the nature and number of atoms in the reactants and products. Chemical equations do not tell us how fast the reaction occurs or whether all the reactant react to form products.



figure 3.4 The energy used to power a rocket comes from the reaction between hydrogen and oxygen to form water. Each reactant must be present in the correct ratio.





When balancing chemical equations only coefficients can be used. Subscripts cannot be added or changed



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#### materials

- magnesium
- hydrochloric acid (HCl)lead(II) nitrate solution
- (Pb(NO<sub>3</sub>)<sub>2</sub>) • potassium iodide
- solution (KI)copper(II) sulfate
- solution (CuSO<sub>4</sub>)
  sodium hydrogen
- carbonate (NaHCO<sub>3</sub>)
- marble chips (calcium carbonate) (CaCO<sub>3</sub>)
- hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)
- manganese dioxide (MnO<sub>2</sub>)
- aluminium foil
- test tubes
- test-tube rack
- Bunsen burner
- heatproof mat
- test-tube holder
- metal tongsspatula
- toothpicks/paddle-pop sticks
- matches

#### safety

- Wear safety glasses and a laboratory coat for this experiment.
- Compounds of lead are poisonous.
- Hydrochloric acid is corrosive.
- When heating solids in a flame, wave the test tube through the flame.
   Ensure the mouth of the test tube is pointing away from everyone.
- Do not look directly at burning magnesium.

Worksheet 1 Chemical reactions

LCHEMICAL QUANTITIES

- Purpose
- **1** To observe a variety of chemical reactions and predict possible products.

Observing chemical reactions

Experiment 3.2

2 To write balanced chemical equations for each of the reactions.

#### Method

- 1 Add a piece of magnesium to 2 mL of hydrochloric acid in a small test tube. Place an inverted test tube above this test tube to trap the gas produced. After a reasonable amount of gas has been generated, light a match, move the upper test tube to one side and immediately place the match into its mouth. Record your observations and suggest possible products.
- 2 Add 2 mL of lead(II) nitrate to 2 mL of potassium iodide in a small test tube. Let it stand for 5 minutes. Record your observations and suggest possible products.
- **3** Add a piece of magnesium to 2 mL of copper(II) sulfate in a small test tube. Let it stand for 5 minutes. Record your observations and suggest possible products.
- 4 Add a couple of marble chips to 2 mL of hydrochloric acid in a small test tube. Place an inverted test tube above this test tube to trap the gas produced. After a reasonable amount of gas has been generated, light a match, move the upper test tube to one side and immediately place the match into its mouth. Record your observations and suggest possible products.
- 5 Add a small amount of manganese dioxide to 2 mL of hydrogen peroxide in a large test tube. Place a piece of aluminium foil over the test tube to trap the gas produced. Remove the foil and immediately place a glowing splint in the mouth of the test tube. Record your observations and suggest possible products.
- 6 Add approximately 1 g of sodium hydrogen carbonate to a large test tube. Heat gently over a flame. Place a lit match in the mouth of the test tube. Record your observations and suggest possible products.
- 7 Using tongs, hold a long magnesium strip into a flame. Once the magnesium ignites, remove it from the flame. Record your observations and suggest possible products.

#### Discussion

- **1** From your observations make a list of factors that indicate a chemical reaction has occurred.
- 2 Describe the purpose of each of the gas tests you performed.

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- **3** Write word equations for each of the reactions.
- 4 Write balanced chemical equations for each of the reactions. Include the states of reactants and products.



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### Questions

- 8 What is the significance of the symbols (s), (l), (g) and (aq) in a chemical equation?
- **9** Balance the following equations.
  - **a**  $CO(g) + O_2(g) \rightarrow CO_2(g)$
  - **b**  $N_2(g) + H_2(g) \rightarrow NH_3(g)$
  - **c**  $Na(s) + Cl_2(g) \rightarrow NaCl(s)$
  - **d**  $SO_2(g) + O_2(g) \rightarrow SO_3(g)$
  - e  $CH_4(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$
  - $\mathbf{f} \quad \mathsf{C}_{5}\mathsf{H}_{10}(\mathsf{g}) + \mathsf{O}_{2}(\mathsf{g}) \to \mathsf{CO}_{2}(\mathsf{g}) + \mathsf{H}_{2}\mathsf{O}(\mathsf{g})$
- $\mathbf{g} \hspace{0.1cm} \mathsf{H_2S}(g) + \mathsf{O_2}(g) \rightarrow \mathsf{H_2O}(g) + \mathsf{SO_2}(g)$ 
  - **h**  $P_4(s) + Cl_2(g) \rightarrow PCl_5(s)$
  - i  $NH_3(g) + O_2(g) \rightarrow NO(g) + H_2O(g)$
  - $\mathbf{j} \quad \mathsf{P}_4 \check{\mathsf{O}}_{10}(\mathbf{s}) + \mathsf{H}_2 \mathsf{O}(\mathbf{l}) \rightarrow \mathsf{H}_3 \mathsf{PO}_4(\mathsf{aq})$

- **10** Write a balanced equation for each of the following reactions. Remember to include the states of the reactants and products.
  - a Gaseous methane and oxygen in the air react to form carbon dioxide gas and water vapour.
  - **b** Gaseous ethane and oxygen react to produce carbon dioxide gas and water vapour.
  - c Iron and oxygen react to produce solid iron(III) oxide.
  - d Solid sulfur and oxygen react to form sulfur dioxide gas.
  - e Solid magnesium and oxygen react to form solid magnesium oxide.
  - f Solid aluminium and oxygen react to form solid aluminium oxide.

# 3.3 Stoichiometry of chemical reactions

**Stoichiometry** examines the quantitative relationships between reactants and products in chemical reactions. It allows us to answer questions such as: 'If we know the quantity of a reactant or reactants, what quantity of products can be produced?' This is a very important question for a chemist. Similarly, if we know how much product we want to produce, the required quantity of reactants can be determined.

Consider the production of ammonia (NH<sub>3</sub>) from the reaction between nitrogen and hydrogen.

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

The reaction equation shows that one mole of nitrogen reacts with three moles of hydrogen to produce two moles of ammonia. In knowing the number of moles of reactants and products, other quantities can also be determined. We can calculate mass, representative particles and the volume of gases. For this example, we can determine that:

- 28.0 g of nitrogen reacts with 6.0 g of hydrogen to produce 34.0 g of ammonia
- $6.02 \times 10^{23}$  molecules of nitrogen reacts with  $1.81 \times 10^{24}$  molecules of hydrogen to produce  $1.20 \times 10^{24}$  molecules of ammonia
- 22.4 L of nitrogen reacts with 67.2 L of hydrogen to produce 44.8 L of ammonia.

### Stoichiometric calculations

Stoichiometric calculations always take into account the reacting mole ratios between the reactants and/or products. For example, the reacting mole ratios for the production of ammonia from nitrogen and hydrogen are:

- $A \quad 1 \mod N_2 : 3 \mod H_2$
- $B \quad 1 \mod N_2 : 2 \mod NH_3$
- C 3 mol H<sub>2</sub>: 2 mol NH<sub>3</sub>



The word **stoichiometry** is derived from the Greek word *stoicheion* (meaning 'element') and *metron* (meaning 'measure'). Stoichiometry gives us the quantitative relationships between reactants and products in a chemical reaction.

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Stoichiometry

Reacting ratio A shows that for every one mole of nitrogen reacted, three moles of hydrogen is needed to react completely. Reacting ratio B shows that for every one mole of nitrogen reacted, two moles of ammonia can be produced. Reacting ratio C shows that for every three moles of hydrogen reacted, two moles of ammonia can be produced.

# / Worked example 3.3A

Copper will react with oxygen in the air to form copper(II) oxide. How many grams of copper(II) oxide would be produced if 5.60 g of copper reacted completely? Assume there is ample oxygen available to react.

Step 1: Write a balanced chemical equation.

$$2Cu(s) + O_2(g) \rightarrow 2CuO(s)$$

Step 2: Determine the relevant reacting mole ratio.

The balanced equation shows that two moles of copper produces two moles of copper(II) oxide.

$$\frac{n(CuO)}{n(Cu)} = \frac{2}{2} = \frac{1}{1}$$

Step 3: Calculate the number of moles from the given information.

$$n(Cu) = \frac{5.60 \text{ g}}{63.5 \text{ g mol}^{-1}}$$

 $= 8.82 \times 10^{-2}$  mol

Step 4: Determine the number of moles of the unknown, using the reacting mole ratio. From step 2 it is a 1 : 1 reacting ratio.

n(CuO) = n(Cu)

 $= 8.82 \times 10^{-2}$  mol

Step 5: Determine the unknown quantity.

The unknown quantity could be mass, volume (for a gas) or the number of representative particles, all of which can be calculated from the number of moles found in step 4.

$$m(CuO) = n \times M$$
  
= 8.82 × 10<sup>-2</sup> mol × 79.5 g mol<sup>-1</sup>  
= 7.01 g

Let's put it all the working together as you would do it.

 $2Cu(s) + O_2(g) \rightarrow 2CuO(s)$ 

$$\frac{n(\text{CuO})}{n(\text{Cu})} = \frac{2}{2} = \frac{1}{1}$$

$$n(\text{Cu}) = \frac{m}{M}$$

$$= \frac{5.60 \text{ g}}{63.5 \text{ g mol}^{-1}}$$

$$= 8.82 \times 10^{-2} \text{ mol}$$

$$n(\text{CuO}) = n(\text{Cu})$$

$$= 8.82 \times 10^{-2} \text{ mol}$$

$$m(\text{CuO}) = n \times M$$

$$= 8.82 \times 10^{-2} \times 79.5 \text{ g mol}^{-1}$$

$$= 7.01 \text{ g}$$
1 g of copper(II) oxide would be produced if 5.60 g of coppe

7.01 g of copper(II) oxide would be produced if 5.60 g of copper reacted with excess oxygen.

Naturally, steps would be omitted if the information given is already in moles.

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## Stoichiometric calculation summary

- 1 Make sure the reaction equation is balanced.
- 2 Always work in moles.
- 3 All calculations must involve a reacting mole ratio.



## Questions

- **11** Hydrogen burns in oxygen to produce water.
  - a Write a balanced equation for this reaction.
  - **b** Calculate the mass of oxygen required to react with 10 g of hydrogen.
- **12** Octane  $(C_8H_{18})$  is a component of petrol. It burns in oxygen to produce carbon dioxide and water. Energy is released during this reaction. The equation for this reaction is:

 $2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$ 

- a Calculate the mass of oxygen required to react with 228 g of octane.
- **b** Calculate the mass of carbon dioxide produced in part a.
- **13** Silver nitrate solution will react with sodium chloride solution to give a precipitate of silver chloride according to the equation:

 $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$ 

- 2.4 g of silver nitrate in aqueous solution was added to excess sodium chloride.
- a What mass of silver chloride would be produced?
- **b** What mass of sodium nitrate would also be produced?
- c What mass of sodium chloride would react?

- 14 Hydrogen sulfide is bubbled through a silver nitrate solution until no further silver sulfide precipitates. The mass of precipitate obtained was 1.932 g.
  - **a** Write a full equation for the reaction.
  - **b** Calculate the mass of silver nitrate reacted.
- 15 Carbon dioxide can be prepared in the laboratory by reacting magnesium carbonate with dilute hydrochloric acid according to the equation:

$$MgCO_3(s) + 2HCl(aq) \rightarrow$$

$$MgCl_2(aq) + H_2O(l) + CO_2(g)$$

If 10.0 g of  $CO_2$  is produced, calculate:

- a the mass of magnesium carbonate reacted
- **b** the mass of hydrochloric acid reacted.
- **16** The reaction for the extraction of aluminium from alumina (Al<sub>2</sub>O<sub>3</sub>) can be represented by the equation:

 $2Al_2O_3(l) + 3C(s) \rightarrow 3CO_2(g) + 4Al(s)$ For the production of 1000 kg of aluminium, calculate:

- a the mass of alumina required
- **b** the mass of carbon required
- c the mass of carbon dioxide released into the atmosphere.

# 3.4 Limiting and excess reagents

Often when a chemical reaction is carried out, the amount of reactants are not present according to the stoichiometry of the reaction. The reactant that is consumed first in a chemical reaction determines the amount of product that can form. This reactant is called the **limiting reagent**. The reactant that is present in greater than needed quantity is the **excess reagent**.

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## / Worked example 3.4A

Sodium metal reacts with chlorine gas to produce sodium chloride. What mass of sodium chloride forms when 143 g of sodium reacts with 191 g of chlorine? How many grams of the excess reagent remain?

Step 1: Write a balanced chemical reaction equation.

 $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$ 

Step 2: Determine the number of moles of reactants  $(n = \frac{m}{M})$ .

$$n(Na) = \frac{143 \text{ g}}{23.0 \text{ g mol}^{-1}}$$
  
= 6.22 mol  
$$n(Cl_2) = \frac{191 \text{ g}}{71.0 \text{ g mol}^{-1}}$$
  
= 2.69 mol

Step 3: Identify the limiting and excess reagents.

Using the reacting mole ratio and the amount (in moles) available of one of the reactants, calculate the amount (in moles) needed of the other reactant. The balanced chemical equation shows that 2 moles of sodium are needed for every one mole of chlorine.

$$\frac{n(Cl_2)}{n(Na)} = \frac{1}{2}$$
  
 $n(Cl_2) = 6.22 \text{ mol} \times \frac{1}{2} = 3.11 \text{ mol}$ 

There are only 2.69 moles of  $Cl_2$  available, therefore  $Cl_2$  is the limiting reagent and Na is the excess reagent.

Step 4: Determine the amount of product.

Using the reacting mole ratio and the available number of moles of the limiting reagent, determine the maximum amount of product that can form. The balanced chemical equation shows that 1 mole of chlorine produces 2 moles of sodium chloride.

$$\frac{n(\text{NaCl})}{n(\text{Cl}_2)} = \frac{2}{1}$$
  
n(NaCl) = 2.69 mol ×  $\frac{2}{1}$  = 5.38 mol

 $m(NaCl) = n \times M$ 

$$= 5.38 \text{ mol} \times 58.5 \text{ g mol}^{-1}$$

= 315 g

The maximum amount of sodium chloride that can form is 315 g.

Step 5: Calculate the amount of excess reagent.

Calculate how many grams of the excess reagent are needed to completely react with the limiting reagent. Subtract this from the initial amount. The difference is the amount of excess remaining.

$$n(Na) = 2.69 \text{ mol} \times \frac{2}{1} = 5.38 \text{ mol}$$
  
 $m(Na) = n \times M$   
 $= 5.38 \text{ mol} \times 23.0 \text{ g mol}^{-1} = 124 \text{ g}$   
143 g - 124 g = 19 g  
19 g of sodium is in excess.

It doesn't matter which

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For limiting and exces reagent problems, all

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reagent problems, all calculations must begin with the limiting reagent.

## Experiment 3.3 Stoichiometry of a chemical reaction

#### Purpose

- 1 To determine the limiting reagent in a set of chemical reactions.
- **2** To write a balanced chemical equation by experimentally determining the reacting mole ratio.

#### Method

#### Day 1

- **1** Label five test tubes 1–5.
- ${\bf 2}$  Using the graduated pipette, place 5.0 mL of 0.5 M FeCl\_ in each test tube.
- **3** Using another graduated pipette, place 1.0 mL of 1.0 M AgNO<sub>3</sub> in to test tube 1, 3.0 mL in test tube 2, 5.0 mL in test tube 3, 7.0 mL in test tube 4 and 9.0 mL in test tube 5.
- 4 Mix, and allow to stand for a few minutes.
- 5 Label a piece of filter paper with test tube 1 and record its mass to the nearest 0.001 g.
- **6** Fold the filter paper and place in a filter funnel. Place the filter funnel in a small beaker.
- 7 Tip all the contents of test tube 1 into the filter funnel. Rinse the test tube with distilled water if necessary to remove all the precipitate. DO NOT discard the filtrate, you will need it for step 12.
- 8 Wash the residue (AgCl(s)) with distilled water.
- 9 Place the filter paper and residue on to a watchglass.
- **10** Repeat steps 5–9 for the remaining test tubes.
- 11 Leave to dry overnight.
- **12** Using the dropping pipette, place a few drops of FeCl<sub>2</sub> in each of the filtrates. Record your observations.

#### Day 2

- **1** Record the mass of each of the dried AgCl and filter paper, to the nearest 0.001 g.
- 2 Record the mass of the AgCl.

#### Calculations

- 1 Calculate the number of moles of AgNO<sub>3</sub> and FeCl<sub>2</sub> available.
- 2 Determine the mass of AgCl in each reaction.
- 3 Calculate the number of moles of AgCl produced in each reaction.

#### Discussion

- **1** Based on your observations (refer to step 12), determine which reactant is the limiting reagent.
- 2 From your data, determine the reacting mole ratios between AgNO<sub>3</sub> and AgCl, and FeCl<sub>2</sub> and AgCl.
- **3** Using the reacting mole ratios, write a balanced reaction equation for the reaction between AgNO<sub>3</sub> and FeCl<sub>2</sub>.

## materials

- 0.5 M iron(II) chloride (FeCl<sub>2</sub>)
- 1.0 M silver nitrate (AgNO<sub>3</sub>)
- distilled water
- test tubestest-tube rack
- 10 mL graduated pipettes
  - 100 mL beakers
- electronic balance
- dropping pipette
- pipette filler bulb
- filter funnel
- filter paper
- watchglasslabels
- labels

#### safety

- Wear safety glasses and a laboratory coat for this experiment.
- AgNO3 will stain skin and clothing.
- FeCl<sub>2</sub> causes burns to the eyes and skin.



Stoichiometry

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## Questions

17 Lead(II) nitrate and magnesium sulfate solutions react together to form a precipitate of lead(II) sulfate according to the equation:

 $Pb(NO_3)_2(aq) + MgSO_4(aq) \rightarrow PbSO_4(aq)$ 

 $PbSO_4(s) + Mg(NO_3)_2(aq)$ 

Which reactant would be in excess, and by what amount (mol), if solutions containing the following quantities of lead(II) nitrate and magnesium sulfate were added together?

- a 1.0 mol of lead(II) nitrate and 2.0 mol of magnesium sulfate
- b 0.50 mol of lead(II) nitrate and 2.0 mol of magnesium sulfate
- **c** 3.0 mol of lead(II) nitrate and 0.20 mol of magnesium sulfate
- 18 Potassium iodide and lead(II) nitrate solutions react together to form a precipitate of lead(II) iodide according to the equation:

 $2KI(aq) + Pb(NO_3)_2(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$ Which reactant would be in excess, and by what amount (mol), if solutions containing the following quantities of potassium iodide and lead(II) nitrate were added together?

- a 1.0 mol of potassium iodide and 1.0 mol of lead(II) nitrate
- b 0.50 mol of potassium iodide and 2.0 mol of lead(II) nitrate
- c 3.0 mol of potassium iodide and 0.20 mol of lead(II) nitrate
- 19 Which reactant would be in excess, and by how many grams, if solutions containing the following masses of lead(II) nitrate and magnesium sulfate were added together? Pb(NO<sub>3</sub>)<sub>2</sub>(aq) + MgSO<sub>4</sub>(aq) →

 $PbSO_4(s) + Mg(NO_3)_2(aq)$ 

- a 1.0 g of lead(II) nitrate and 1.0 g of magnesium sulfate
- b 5.0 g of lead(II) nitrate and 0.50 g of magnesium sulfate
- c 2.0 g of lead(II) nitrate and 10.0 g of magnesium sulfate



**figure 3.7** Quantities used in industry are usually very large. An important task of an industrial chemist is to increase percent yield to not only increase the amount of product, but also to reduce production costs.

# 3.5 Percent yield

In a chemical reaction, often the reactants are not completely converted to products. From the stoichiometry of the reaction it is possible to calculate the amount of product that can form if the reaction is 100% complete. This amount represents the **theoretical vield**. and can be defined as the amount of product that can theoretically form. Chemical reactions are complex processes and the theoretical yield of a reaction is not always achieved. Reactions may not achieve 100% yield for a number of reasons, such as the reaction is reversible, ideal reaction conditions are not provided, or the products react further to form new products. The amount of product that is formed during a chemical reaction is termed the actual yield. Percent yield describes the relationship between actual and theoretical yield. It can be represented by the formula:

percent yield =  $\frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$ 

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Worked example :

 $2NH_3(g) + CO_2(g) \rightarrow (NH_2)_2CO(aq) + H_2O(l)$ 

Calculate the percent yield if 1.50 kg of ammonia reacts with an excess of carbon dioxide to produce 2.19 kg of urea.

Step 1: Find the number of moles of ammonia.

$$n(NH_3) = \frac{m}{M}$$
  
=  $\frac{1.50 \times 10^3 \text{ g}}{17.0 \text{ g mol}^{-1}}$   
=  $8.82 \times 10^1 \text{ mol}$ 

Step 2: Use the reacting mole ratio to determine the number of moles of urea that can be produced.

The balanced chemical equation shows that 2 moles of ammonia produce 1 mole of urea.

$$\frac{n((\text{NH}_2)_2\text{CO})}{n(\text{NH}_3)} = \frac{1}{2}$$
$$n((\text{NH}_2)_2\text{CO}) = 8.82 \times 10^1 \times \frac{1}{2}$$
$$= 4.41 \times 10^1 \text{ mol}$$

Step 3: Find the mass of urea that can be produced.

 $m((NH_2)_2CO) = n \times M$  $= 4.41 \times 10^{1} \text{ mol} \times 60.0 \text{ g mol}^{-1}$  $= 2.65 \times 10^3 \text{ g}$ 

The theoretical yield for urea is 2.65 kg.

Use the formula to calculate percent yield.

percent yield = 
$$\frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$
  
=  $\frac{2.19 \text{ kg}}{2.65 \text{ kg}} \times 100\%$   
= 82.6%  
e percent yield of urea is 82.6%.

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### Questions

20 One of the steps involved in the production of phosphoric acid is the combustion of phosphorus to produce  $P_4O_{10}$ . If 2.79 × 10<sup>2</sup> g of phosphorus combusted in an environment rich in oxygen and  $5.89 \times 10^2$  g of P<sub>4</sub>O<sub>10</sub> was produced, calculate the percent yield of the reaction:

 $P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$ 

- **21** What is the percent yield if 4.06 g of sulfur trioxide forms when 4.08 g of sulfur dioxide reacts with an excess of oxygen?
- 22 Nitrous acid (HNO<sub>2</sub>) forms from the reaction between dinitrogen trioxide  $(N_2O_3)$  and water. Calculate the percent yield when 67.4 g of  $N_2O_3$ reacted with an excess of water and 61.8 g of nitrous acid was produced.

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Worksheet 2 Stoichiometry

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### Summary **DDDD**

- The **mole** (mol) is a useful unit to measure the amount of a substance.
- A mole of any substance has been found to contain  $6.02 \times 10^{23}$  representative particles. This number is also referred to as Avogadro's number ( $N_A$ ).
- The mass of one mole of any substance is its molar mass, and is equivalent to its relative formula mass.
- A chemical equation is used to represent what happens during a chemical reaction. The substances that react in a chemical reaction are the reactants. The bonds of the reactants break and the atoms rearrange to form new substances called products. When dealing with chemical reactions the equation must always be balanced.
- To satisfy the Law of Conservation of Mass, the number and types of atoms on the reactant side of a reaction equation must be the same as on the product side.

- The numbers, called coefficients, that are used to balance chemical equations are used to represent the number of moles of reactants and products.
- Stoichiometry involves using reacting mole ratios of a balanced chemical equation to determine quantities of reactants and products. Most reactants however are not present according to the stoichiometry of the reaction.
- The reactant that is consumed first and determines the amount of product that can form is the **limiting reagent**. The reactant that is left over (i.e. there is more than is needed) is the **excess reagent**.
- The **percent yield** of a reaction represents the ratio of **actual yield** to **theoretical yield**, as many reactions do not go to 100% completion.

### Key terms

actual yield Avogadro's number chemical equation chemical reaction

#### coefficient excess reagent Law of Conservation of Mass limiting reagent

molar mass mole percent yield product reactant representative particle stoichiometry theoretical yield





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### Chapter Review

3.1 The mole

- 23 What is the molar mass (M) of each of the following?
  - a iron (Fe)
  - **b** sulfuric acid  $(H_2SO_4)$
  - **c** sodium oxide  $(Na_2O)$
  - **d** zinc nitrate  $(Zn(NO_3)_2)$
  - e glycine (H<sub>2</sub>NCH<sub>2</sub>COOH)
  - **f** aluminium sulfate  $(Al_2(SO_4)_2)$
- 24 Calculate the molar mass of:
  - **a** phosphoric acid  $(H_3PO_4)$
  - **b** sodium acetate (CH<sub>2</sub>COONa)
  - **c** iron(II) phosphate  $(Fe_3(PO_4)_2)$
  - **d** hydrated iron(III) chloride (FeCl<sub>3</sub>.6H<sub>2</sub>O)
- 25 What is the mass of 0.060 mol of:
  - **a** ethane  $(C_2H_6)$ ?
  - **b** glucose  $(C_6H_{12}O_6)$ ?
  - c urea  $((NH_2)_2CO)$ ?
  - **d** calcium carbonate (CaCO<sub>3</sub>)?
  - e alumina  $(Al_2O_2)$ ?
  - f copper atoms (Cu)?
- 26 Calculate the number of atoms in:
  - a 23 g of sodium (Na)
  - **b** 4.0 g of argon (Ar)
  - **c** 0.243 g of magnesium (Mg)
  - **d** 10.0 g of gold (Au)
- 27 Calculate the number of molecules in:
  - **a** 16 g of oxygen  $(0_2)$
  - **b** 2.8 g of nitrogen  $(N_2)$
  - **c** 3.2 g of sulfur dioxide  $(SO_2)$
  - d 288 g of chlorine (Cl<sub>2</sub>)
- 28 Consider the following metal samples: 100 g copper; 4.0 mol of iron atoms;  $1.2 \times 10^{24}$  atoms of silver. Which has the greatest mass?
- **29 a** If  $6.0 \times 10^{23}$  atoms of calcium have a mass of 40.1 g, what is the mass of one calcium atom?
  - **b** If 1 mol of water molecules has a mass of 18 g, what is the mass of one water molecule?
  - c What is the mass of one molecule of carbon dioxide?
- 30 What mass of iron (Fe) would contain as many iron atoms as there are molecules in 20.0 g water  $(H_2O)$ ?
- **31** For each of the following ionic substances calculate:
  - i the amount of substance, in moles
  - ii the amount of each ion, in moles.
  - a 5.85 g of NaCl
  - **b** 45.0 g of CaCl<sub>2</sub>
  - **c** 0.35 g of AlCl<sub>3</sub>
  - **d** 1.68 g of  $Fe_2(SO_4)_3$
  - e 365 g of  $K_3PO_4$

- 32 For each of the following numbers of molecules calculate:
  - i the amount of substance, in moles
  - ii the mass, in g, of substance.
  - a  $4.50 \times 10^{23}$  molecules of water H<sub>2</sub>O
  - **b**  $9.00 \times 10^{24}$  molecules of methane, CH<sub>4</sub>
  - **c**  $3.6 \times 10^{18}$  molecules of hydrogen sulfate, H<sub>2</sub>SO<sub>4</sub> **d**  $2.3 \times 10^{28}$  molecules of chlorine, Cl<sub>2</sub>

  - e 1 molecule of sucrose,  $C_{12}H_{22}O_{11}$
- **33** For each of the following molecular substances calculate:
  - i the amount of substance in moles
  - ii the number of molecules
  - iii the total number of atoms.
  - **a** 18 g of oxygen,  $O_2$
  - **b** 4.2 g of phosphorus,  $P_4$
  - **c** 75.0 g of sulfur,  $S_8$
  - d 0.32 g of hydrogen chloride, HCl
  - **e** 2.2 × 10<sup>-2</sup> g of glucose,  $C_6H_{12}O_6$
  - f  $8.4 \times 10^{-6}$  g of dinitrogen tetroxide, N<sub>2</sub>O<sub>4</sub>
- **34** Methane  $(CH_4)$  is the major component of natural gas.
  - a What is the mass of 0.50 mol methane?
  - **b** How many molecules are there in 0.100 g methane?
  - c What is the percentage by mass of carbon in methane?
  - d What mass of carbon would be present in 34 g methane?
- 35 A new antibiotic has been isolated and only 2.0 mg are available. The molar mass is found to be 12.5 kg mol<sup>-1</sup>.
  - a Express the molar mass in g mol<sup>-1</sup>.
  - **b** Calculate the amount of antibiotic (in mol).
  - c How many molecules of antibiotic have been isolated?

### 3.2 Chemical reactions

- **36** Balance the following equations.
  - a SiCl<sub>4</sub>(l) + H<sub>2</sub>O(l)  $\rightarrow$  SiO<sub>2</sub>(s) + HCl(aq)
  - **b**  $HCl(g) + O_2(g) \rightarrow H_2O(g) + Cl_2(g)$
  - c Fe<sub>2</sub>O<sub>3</sub>(s) + HCl(g)  $\rightarrow$  FeCl<sub>3</sub>(aq) + H<sub>2</sub>O(l)
  - d MgO(s) + SO<sub>2</sub>(g)  $\rightarrow$  MgSO<sub>4</sub>(s) + MgS(s)
  - e  $NH_3(g) + NO(g) \rightarrow H_2O(g) + N_2(g)$
- **37** Write a balanced chemical equation for each of the following reactions. Remember to include states of reactants and products.
  - a Oxygen gas and hydrogen gas react to produce liquid water.
  - b Solid carbon burns in oxygen gas to produce gaseous carbon dioxide.
  - c Liquid sodium burns in oxygen gas to produce sodium oxide.
    - Stoichiometry

- **d** Solid phosphorus reacts with oxygen to produce solid phosphorus pentoxide, P<sub>4</sub>O<sub>10</sub>.
- e Solid magnesium reacts with gaseous chlorine to produce solid magnesium chloride.
- f Gaseous octane  $(C_8H_{18})$  burns in gaseous oxygen to produce carbon dioxide and water, both in the gaseous state.
- **g** Hydrogen sulfide (H<sub>2</sub>S) gas reacts with gaseous oxygen to produce sulfur dioxide (SO<sub>2</sub>) and water, both as gases.
- **38** Write a balanced chemical equation for each of the following reactions. Use your knowledge of structure and bonding to identify the states of the reactants and products.
  - a Aluminium reacts with fluorine to produce aluminium fluoride.
  - **b** Sulfur reacts with oxygen to produce sulfur dioxide.
  - c Diamond reacts with oxygen to produce carbon dioxide.
  - d Hydrogen reacts with chlorine to produce hydrogen chloride.
- **39** Write a balanced chemical equation, including states, for each of the following reactions, at 10°C.
  - a Hydrogen and fluorine react violently to form hydrogen fluoride. (Hint: Hydrogen fluoride boils at 19.5°C.)
  - **b** Ethene (C<sub>2</sub>H<sub>4</sub>) reacts with oxygen to produce carbon dioxide and water.
  - c Zinc metal is dissolved in nitric acid (HNO<sub>3</sub>) solution, releasing hydrogen and forming a solution of zinc nitrate.
  - d Lead(IV) sulfide burns in oxygen to form lead(II) oxide and sulfur.

# 3.3 Stoichiometry of chemical reactions

**40** Copper metal can be recovered from a solution of copper(II) sulfate by the addition of scrap metal iron to the solution. The equation for the reaction is:

 $Fe(s) + CuSO_4(aq) \rightarrow Cu(s) + FeSO_4(aq)$ 

What mass of copper would be obtained if 1.0 kg of scrap iron were added to enough copper sulfate to react all the iron?

**41** Lead(II) chromate has been used as a bright yellow pigment in some paints. It can be produced by the reaction of potassium chromate with lead nitrate.

- a Write a full equation for this reaction.
- **b** What mass of potassium chromate is required to produce 6.0 g of lead chromate?

42 The common drug aspirin ( $C_6H_4(OCOCH_3)COOH$ ) is prepared from salicylic acid ( $C_6H_4(OH)COOH$ ):  $C_6H_4(OH)COOH(s) + CH_2COOH(l) \rightarrow$ 

 $C_6H_4(OCOCH_3)COOH(s) + H_2O(l)$ 

What mass of salicylic acid is needed to prepare 300 g of aspirin?

**43** Ethanol is produced during the fermentation of glucose according to the following equation:

$$C_6H_{12}O_6(aq) \xrightarrow{yeast} 2C_2H_5OH(aq) + 2CO_2(g)$$

What mass of ethanol would be produced by the fermentation of 80.0 g of glucose?

44 Propane will burn in oxygen according to the equation:

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$

- If 6.70 g of propane was burned in excess oxygen:
- a what mass of carbon dioxide would be produced?
- **b** what mass of oxygen would be consumed in the reaction?
- c what mass of water would be produced?
- **45** The fertiliser sulfate of ammonia  $((NH_4)_2SO_4)$  can be produced by the reaction between aqueous ammonia  $(NH_3)$  and dilute sulfuric acid:

 $2NH_3(aq) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$ 

What mass of the fertiliser could be produced from 20 kg ammonia, assuming the process was only 80% efficient?

**46** Iron is produced when carbon monoxide reacts with iron(III) oxide according to the equation:

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

If 85.0 tonnes of iron were produced in such a reaction:

- a what mass of carbon dioxide would also be produced?
- b what mass of iron(III) oxide must have reacted?
- c what mass of carbon monoxide must have reacted?
- **47** Lead(II) nitrate reacts with potassium iodide according to the following equation:

 $Pb(NO_3)_2(aq) + 2KI(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$ The lead iodide forms as a bright yellow

- precipitate.
  a Describe an experiment you could carry out to demonstrate that the amount of lead iodide precipitated equals the amount of lead nitrate used. (You could give a description of your experiment or use a flowchart to show the
- sequence of steps.)b There would be sources of experimental error in this exercise. Give three.

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- c What safety precautions would you need to take? (You may need to consult a reference on safe handling of chemicals to answer this question.)
- **d** When solid lead nitrate is mixed with solid potassium iodide (both solids are white) the solid mixture turns yellow.
  - i What causes the colour change?
  - ii Why is a reaction between solids less satisfactory than a reaction between solutions of those solids for measuring reacting quantities?

# 3.4 Limiting and excess reagents

**48** Lead(II) nitrate reacts with potassium iodide according to the equation:

 $2KI(aq) + Pb(NO_3)_2(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$ 

In each of the following cases calculate:

- i the amount (in mol) of excess reactant ii the mass of precipitate.
- a 1.0 g of lead(II) nitrate and 1.0 g of potassium iodide
- **b** 0.60 g of lead(II) nitrate and 2.6 g of potassium iodide
- c 2.6 g of lead(II) nitrate and 0.6 g of potassium iodide
- d 0.20 g of lead(II) nitrate and 5.0 g of potassium iodide

**49** Aluminium can be produced by the reaction:

 $2Al_2O_3(l) + 3C(s) \rightarrow 3CO_2(g) + 4Al(l)$ 

Which of the following would result in the production of o.8 mol Al?

```
A 0.4 mol Al_2O_3 and 0.6 mol C
```

- **B** o.8 mol  $Al_2O_3$  and o.8 mol C
- **C** 0.4 mol  $Al_2O_3$  and 0.2 mol C
- **D** 2.0 mol  $Al_2O_3$  and 3.0 mol C

**50** For each of the following types of problems, summarise the steps you would take to reach a solution.

For example, a question that asked you to convert an amount of water to a mass of water could be summarised as follows:

amount of H<sub>2</sub>O (mol)  $\xrightarrow{\times M (g \text{ mol}^{-1})}$  mass of H<sub>2</sub>O (g)

- a Given a mass of NaCl, calculate the amount of NaCl.
- **b** Given a mass of CaCl<sub>2</sub>, calculate the amount of Cl<sup>-</sup> ions present.
- **c** Given an amount of chloride ions, calculate the mass of aluminium chloride required to produce them.
- **d** Given a mass of ethane  $(C_2H_6)$ , calculate the number of ethane molecules present.

### 3.5 Percent yield

51 Copper can be recovered from the roasting of copper(I) sulfide according to the reaction:

$$Cu_2S(s) + O_2(g) \rightarrow 2Cu(s) + SO_2(g)$$

1.25 kg of copper(l) sulfide is roasted in an excess of oxygen, and  $6.41 \times 10^{-1}$  kg of copper is recovered. Calculate percent yield.

**52** One of the steps of the Ostwald process to produce nitric acid involves the reaction between nitrogen monoxide and oxygen gas. Nitrogen dioxide gas is formed.

 $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ 

What is the percent yield when  $3.98 \times 10^3$  g of NO reacts with  $2.36 \times 10^3$  g of O<sub>2</sub> to produce  $3.88 \times 10^3$  g of NO<sub>2</sub>?

**53** Chromium is a useful metal that can be recovered from its ore, chromite (FeCr<sub>2</sub>O<sub>4</sub>), when reacted with carbon.

 $FeCr_2O_4(s) + 4C(s) \rightarrow Fe(s) + 2Cr(s) + 4CO(g)$ 

 $1.56 \times 10^4$  g of chromite reacted with  $3.72 \times 10^3$  g of carbon. How much chromium is produced if the reaction has a yield of 57.6%?

# Chemical solutions





Water is important because of its ability to form solutions. Detergents, alcoholic beverages, soft drinks, fish tanks and contact lens solutions are all examples of the ability of water to dissolve other substances. In the laboratory, one of the most common ways of reacting substances is to first dissolve them in water and then combine their solutions.

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The dissolved substance is known as the **solute**. In the examples above water is the **solvent** (though other liquids can also act as solvents). The mixture that is formed is known as a **solution**.



figure 4.1 A solution is formed from the combination of a solute and a solvent.

During dissolving, solvent particles collide with solute particles. If the forces of attraction between the solute and solvent particles are greater than the forces of attraction between the solute particles, the solute particles will separate from the main solute crystals. The solute particles become surrounded by solvent particles and become spread evenly throughout the solvent forming a **homogeneous** mixture. The solute particles are too small to be seen or filtered from the solution. Solutions are transparent to visible light though some solutions are coloured.



Solvent - particles moving at random





Solution – particles moving at random

- The forces between solute particles have been overcome.
- The forces between some solvent molecules have been overcome.
- New forces operate between solute particles and some solvent particles.

figure 4.2 As a solute dissolves, the solute particles spread evenly throughout the solvent. Each solute particle is surrounded by solvent particles.

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Chemical solutions

Solute - particles in lattice

### The forces of dissolving

Water is a polar covalent substance. The substances that dissolve in water tend to have ionic or polar covalent bonding, giving them an attraction to water molecules. There are three ways in which water soluble substances are attracted to water molecules.

1 Hydrogen bonding between polar covalent molecules and water molecules

Hydrogen atoms bonded to oxygen in one molecule can hydrogen bond with a lone pair of electrons of oxygen in another molecule. Hydrogen bonds between water molecules and between ethanol molecules are broken.

 $C_2H_5OH(l) \xrightarrow{H_2O} C_2H_5OH(aq)$ 

If a molecule has a polar section and a non-polar section, the polar section allows the whole molecule to dissolve in water. The larger the non-polar part of the molecule, the less soluble the molecule is in water.



**figure 4.3** Hydrogen bonding between a polar covalent molecule and water molecule.

#### 2 The ionisation of polar covalent molecules

Some compounds with highly polarised covalent bonds have such strong electrostatic forces of attraction with water that the bond breaks.

The bond of the solute molecules breaks with bonding electrons going to the more electronegative atom. Hydrogen chloride for example becomes  $Cl^-$  (chloride ion) and  $H_3O^+$  (hydronium ion) when dissolved in water.

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

Each of these ions is surrounded by water molecules and is dissolved. The ions are said to be **hydrated**.



figure 4.4 The dipoledipole attraction between the molecules of water and hydrogen chloride leads to the breaking of the polar covalent bond between the hydrogen and chlorine atoms.

#### 3 The ionisation of ionic compounds

The positive ends of water molecules are attracted to the negative ions. The negative ends of water molecules are attracted to positive ions.

Ionic bonds within the solid crystal lattice are broken by the forces of attraction with water molecules. The ions are **dissociated**.

Hydrogen bonds between water molecules are broken. Ion–dipole attractions form between the ions and the polar water molecules. The ions are hydrated, for example, when sodium chloride is dissolved.

$$\operatorname{NaCl}(s) \xrightarrow{H_2O} \operatorname{Na}^+(aq) + \operatorname{Cl}^-(aq)$$



(a)

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--- represents ion-dipole interaction

**figure 4.5** (a) Electrostatic attraction between polar water molecules and the ions in the sodium chloride lattice, and (b) the ion–dipole attraction in hydrated sodium and chloride ions.

represents attraction between ions in lattice and water dipoles

### Solubility

When a substance is dissolved it requires energy to break the forces of attraction holding the substance particles together. When the substance particles are hydrated, energy is released. If the energy produced during hydration is greater than the energy required to separate the solute particles, the substance is **soluble**. If the energy required to break the bonds between solute particles is greater than the energy of hydration the substance is **insoluble**. Most substances dissolve to some degree. Insoluble substances may dissolve to a very small extent while soluble substances dissolve to various extents. Table 4.1 provides a guide to the solubility of many ionic compounds in water.

table 4.1 A solubility guide for common ionic compounds.

Soluble ion	ic compounds	Insoluble ionic compounds		
Most compounds of the following ions are soluble	Important exceptions	Most compounds of the following ions are insoluble	Important exceptions	
nitrate NO <sub>3</sub> <sup>-</sup>	none	sulfide (S <sup>2-</sup> )	$Na_2S$ , $K_2S$ , $Li_2S$ , $(NH_4)_2S$	
ethanoate (CH₃COO <sup>-</sup> ) [common name: acetate]	none	carbonate ( $CO_3^{2-}$ )	$Na_2CO_3$ , $K_2CO_3$ , $Li_2CO_3$	
sodium, potassium (Na <sup>+</sup> , K <sup>+</sup> )	none	phosphate (PO <sub>4</sub> <sup>3–</sup> )	Na <sub>3</sub> PO <sub>4</sub> , K <sub>3</sub> PO <sub>4</sub> , Li <sub>3</sub> PO <sub>4</sub>	
ammonium (NH₄⁺)	none	hydroxide (OH⁻)	NaOH, KOH, Ba(OH) <sub>2</sub> Ca(OH) <sub>2</sub> is slightly soluble	
chloride (Cl⁻)	AgCl, HgCl₂ PbCl₂ is slightly soluble	2		
bromide (Br⁻)	AgBr, HgBr2, PbBr2			
iodide (l⁻)	Agl, Hgl <sub>2</sub> , Pbl <sub>2</sub>		solubility rules are that all	
sulfate (SO <sub>4</sub> <sup>2-</sup> )	Ag₂SO₄, BaSO₄, PbSO₄, SrSO₄ CaSO₄ is slightly solub	le	nitrates, ammonium compounds and compounds of group 1 metals are soluble.	

### Experilment 4.1 Solubility of compounds in water

### Purpose

To investigate the solubility of a variety of compounds in water.

#### Method

In this exercise you will investigate the solubility of these compounds in water: copper(II) sulfate, calcium sulfate, glucose, naphthalene, hexane, ethanol and ethanoic acid.

- 1 Half fill a test tube with water. Next add one small spatula full of the first compound listed above and shake the test tube from side to side. Place the test tube in a test-tube rack and leave for 5 minutes while you proceed with the rest of the exercise. Shake the test tube occasionally and observe several times before you make a decision about the solubility of the compound.
- 2 Repeat step 1 for the other compounds in the list. If the compound is a liquid, add 15 drops to a clean test tube half full of water.
- **3** For the substances tested, list those which:
  - a dissolved completely
  - **b** did not dissolve.

#### Discussion

**1** For any of the compounds that dissolved in water, list the particles present in the solution. Write an equation to represent the dissolving process.

#### materials

- solid samples of copper(II) sulfate, calcium sulfate, glucose powder and naphthalene
- dropper bottles containing hexane, ethanol and ethanoic acid
- 7 × large test tubes
- test-tube rack
- spatula

#### safety

- Wear safety glasses and a laboratory coat for this experiment.
- Copper(II) sulfate irritates the skin and eyes.
- WARNING: Do not heat any of the samples in steps 1 or 2 of this experiment.

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### Solubility of solids

Substances cannot be simply described as soluble or insoluble. They dissolve to varying extents and the extent depends on conditions such as temperature and the type of solvent being used. Oil is described as insoluble in water but it will dissolve in various hydrocarbon solvents. The solubility of potassium nitrate increases dramatically in water if the temperature is increased.

Solubility is often measured as the maximum mass of solute that can be dissolved in 100 g of a solvent at a specific temperature. The solution being described is called a **saturated solution**, as no more solute can be dissolved at that temperature. A solution in which more solute can be dissolved is known as an **unsaturated solution**.

Tables of data are readily available to research the solubility of substances under specific conditions. Table 4.2 shows that solubility of some substances including sugar, salt and limestone.

<b>(table</b> $4.2$ The solubility of some solutes in wate	r at 20°C.
Solute	Solubility (g per 100 g)
sucrose, $C_{12}H_{22}O_{11}$ (sugar)	203.9
sodium chloride, NaCl (salt)	36.0
copper sulfate, CuSO <sub>4</sub>	20.7
iodine, I <sub>2</sub>	0.029
calcium carbonate, CaCO <sub>3</sub> (limestone)	0.013

Information such as this enables us to compare the solubility of substances. It can be seen that the solubility of sugar is approximately six times that of salt at 20°C. Limestone has a much lower solubility than sugar or salt and can be described as insoluble.

Solubility curves are a way of showing the solubility of a substance at



figure 4.6 The solubility curves of various substances.

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can dissolve more solute. Saturated solutions cannot dissolve more solute.

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LCHEMICAL QUANTITIES different temperatures (see figure 4.6). The points on each line represent a saturated solution and the area below the line represents an unsaturated solution. According to the solubility curve, at 30°C a saturated solution of potassium nitrate would contain 50 g per 100 g of water. If a solution of sodium nitrate at 50°C contained 40 g per 100 g it would be an unsaturated solution.

If a saturated solution is cooled, excess solute will solidify or crystallise out of solution. If this does not happen, an unstable solution called a **supersaturated solution** results. A supersaturated solution is any point above a solubility curve. If a supersaturated solution is bumped or its container scratched, some of the solute will crystallise until the solution is reduced to a saturated solution. Adding a small crystal of solute will have the same effect. The solute particles will move from the solution to become a part of the seed crystal. This process is often called seeding a solution.

### Experiment 4-2 Deriving a solubility curve

### Purpose

To plot the solubility curve of an ionic compound, potassium nitrate, on the basis of experimental data.

#### Method

- **1** Weigh accurately, in a large test tube, approximately 6.5 g of potassium nitrate. Record the exact mass.
- 2 Use a burette to add exactly 5 mL of water to the test tube.
- 3 Immerse the test tube in a beaker of boiling water and stir the contents carefully with a thermometer until all the crystals dissolve.
- **4** Remove the test tube from the boiling water and continue to stir gently until the first signs of crystallisation are detected. Record the temperature (°C) at which crystals begin to form.
- 5 Add a further 3 mL of water from the burette into the test tube and repeat steps 3 and 4.
- 6 Repeat step 5 as many times as necessary until a stage is reached where crystallisation on cooling fails to occur even when the tube is placed on ice.
- 7 The solubility of 6.5 g of potassium nitrate dissolved in 5.0 g of water is equivalent to a solubility of  $\frac{6.5}{5.0} \times 100$ , i.e. the solubility of 130 g of

potassium nitrate in 100 g of water. Draw up a table which shows the mass of water added to the potassium nitrate, the solubility of the potassium nitrate and the temperature recorded in step 4.

8 Draw a solubility graph with temperature on the horizontal axis and solubility on the vertical axis.

Note: Spreadsheets could be used to calculate solubility data and then plot graphs.

#### Theory

The solubility of a solute measures the amount of solute that can dissolve in a given amount of solvent at a given temperature. In this experiment, Supersaturated solutions contain more solute than they should for the conditions.

#### materials

6.5 g potassium nitratelarge test tube

- burette
- 500 mL beaker
- electronic balance
- Bunsen burner
- bench mat
- tripod
  - gauze mat 110°C thermometer

#### safety

• Wear safety glasses and a laboratory coat for this experiment.

• Do not heat the test tubes directly in the Bunsen flame.

Chemical solutions

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you will determine and graph the solubility of potassium nitrate (in g of potassium nitrate per 100 g water) at various temperatures.

In your calculations, you will need to assume that the density of water is equal to 1 g mL<sup>-1</sup> at all temperatures. Although the density of water does vary with temperature, this is a reasonable approximation to make in view of the other errors associated with this determination. Therefore, when 5.0 mL of water is added to the solute, it can be said to be equivalent to the addition of 5.0 g of water, and so on.

#### Discussion

- **1** From your graph, determine:
  - **a** the solubility of potassium nitrate at 50°C
  - **b** the temperature at which the solubility of potassium nitrate is 80 g per 100 g water
  - c the maximum amount of potassium nitrate that would dissolve in 100 g of water at 60°C
  - **d** the temperature to which 20 g of potassium nitrate in 25 g of water needs to be heated in order to completely dissolve.
- 2 Suggest reasons for possible errors in the above determinations.

#### Extension activity

Repeat this procedure using another ionic compound. Determine the solubility curve of this compound and compare your results with those of other students. (Note: A spreadsheet could be used to calculate solubility and then plot the graphs.)

#### materials

- Bunsen burner
- gauze mat
- tripod

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- large test tube
  250 mL beaker half filled with nearboiling water
- spatula
- tongs

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- 30 g sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O)
- crystal of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O



• Wear safety glasses and a laboratory coat for this experiment. A solid becomes liquid when heated. When cooled, the substance remains liquid until a crystal is added. The liquid then rapidly solidifies and becomes hot.

#### Purpose

1 To demonstrate the concept of supersaturation.

Experiment 4.3

2 To show how crystallisation occurs.

Supersaturation

#### Method

- 1 Two-thirds fill a test tube with solid sodium thiosulfate. Place the test tube in a beaker of near-boiling water until the crystals dissolve in their water of crystallisation.
- 2 Cool the tube under running water for 3–5 minutes, avoiding undue agitation. When it is cold, ask a student to touch the test tube to check its temperature.
- **3** Drop in a small crystal of sodium thiosulfate. Observe what happens, and again check the temperature of the test tube.

#### Theory

Sodium thiosulfate readily forms a supersaturated solution, i.e. a solution that contains more of the solute than is necessary to saturate the solution

at that temperature. The addition of one crystal of the solute causes rapid deposition of the excess solute. Vigorous shaking has the same effect. When the liquid changes back to the crystalline hydrate, considerable heat (heat of hydration) is released.

 $Na_2S_2O_3(aq)$   $Na_2S_2O_3.5H_2O(s)$  (exothermic)

#### Discussion

- 1 What is a supersaturated solution?
- 2 Is this crystallisation process endothermic (absorbs energy) or exothermic (releases energy)?

#### Alternative activities

- An overhead projector allows the crystallisation to be observed by a class more easily. Pour the warm (not hot) solution into a Petri dish on the projector stage, allow it to cool and induce crystallisation as described earlier. The growth of quite large crystals may be observed.
- Crystallisation of the cold supersaturated solution may be induced by scratching the bottom of the container with a glass rod, or by stoppering the tube and shaking it vigorously.
- Divide the supersaturated solution into two halves and seed one half with a sodium thiosulfate crystal and the other with an NaCl crystal. Crystallisation occurs more slowly if the solution contains an NaCl crystal as the sodium thiosulfate fits imperfectly into the crystal lattice.

### Solubility of gases

Many gases consist of atoms or molecules that are non-polar. Their intermolecular forces are very weak. That is why they tend to exist as gases rather than liquids or solids. The attraction of gas particles for solvent particles is also weak and most gases are fairly insoluble.

When heated, solvents have more energy to break bonds between ions and molecules of solid solutes. Solubility of most solid solutes increases by heating. Heating a solution containing dissolved gases gives the gas particles the energy needed to escape the solvent. Increasing the temperature decreases the solubility of gases.

Table 4.3 shows the low solubility of some gases. Note that in this table the amounts are grams per kg of water compared to grams per 100 grams in table 4.2. Ammonia has a higher solubility than the other gases because hydrogen bonding can occur between ammonia molecules and water molecules.



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table 4.3 The solubility	y of common gas	ies.		
Gas Solubility (g of gas per kg of water)				
	o°C	20°C	60°C	
oxygen	0.069	0.043	0.023	
carbon dioxide	3.4	1.7	0.058	
nitrogen	0.029	0.019	0.011	
methane	0.040	0.023	0.011	
ammonia	897	529	168	

#### **Chemical solutions**

One way the solubility of a gas can be increased is to increase the pressure of the gas above the liquid. This forces the gas to dissolve into the liquid. This can be seen when opening a bottle of soft drink. In the factory, carbon dioxide is forced under pressure into the soft drink and the bottle sealed. When the bottle is opened the pressure is released and the carbon dioxide can escape creating bubbles in the drink.



**figure 4.8** The ability of gases to dissolve in liquids is vital for the survival of aquatic life. These fish depend on the oxygen dissolved in the water.

### Questions

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Norksheet Dissolving

- 1 Methanol (CH<sub>3</sub>OH) and glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) are compounds which can form hydrogen bonds with water. They will dissolve in water without ionising. Write equations to represent the dissolving process for each of these compounds.
- 2 Nitric acid (HNO<sub>3</sub>), and hydrogen fluoride (HF), will both ionise when they dissolve in water. The ionisation reaction is similar to that of HCl (see table 4.1). Write equations to represent the dissolving process for each of these compounds.
- 3 Sodium nitrate (NaNO<sub>3</sub>) and calcium hydroxide (Ca(OH)<sub>2</sub>) will both dissociate when they dissolve in water. Write equations to represent the dissolving process for each of these compounds.
- 4 Which of the following substances would you expect to be soluble in water?
  - a sodium carbonate
  - **b** lead(II) nitrate

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- **c** magnesium carbonate
- d ammonium sulfate
- 5 Which of the following compounds would you expect to be insoluble in water?

- a iron(II) sulfate
- **b** magnesium phosphate
- c zinc carbonate
- d sodium sulfide
- 6 Write the formulae of the ions produced when these compounds dissolve in water:
  - a magnesium hydrogen carbonate
  - **b** calcium nitrate
  - c potassium hydrogen sulfate
  - **d** iron(III) sulfate
  - e copper(II) chloride
- 7 With which of the following ions would an Fe<sup>2+</sup> ion combine to give a precipitate?
  - **a**  $SO_4^2$
  - **b** PO<sub>4</sub>
  - **c**  $Br^{2}$ **d**  $S^{2}$
- 8 Non-polar substances such as oil are attracted by the weakest of intermolecular forces, dispersion forces, and yet they are insoluble in polar substances such as water. Why is this?



- potassium nitrate:
  - **a** 50 g per 100 g?
  - **b** 100 g per 100 g?
  - **c** 150 g per 100 g?
- **10** What is the solubility of the following solids at 20°C?
  - a sodium nitrate
  - **b** potassium nitrate
  - c sodium chloride
- 11 What mass of the following compounds will dissolve in 100 g of water at 40°C?
  - a  $CuSO_4.5H_2O$
  - **b** KNO<sub>3</sub>
  - c NaNÓ<sub>3</sub>
- 12 What mass of the following compounds will dissolve in 200 g of water at 30°C?
  - a  $CuSO_4.5H_2O$
  - **b** KNO<sub>3</sub>
  - c NaNO<sub>3</sub>

- 13 What mass of copper sulfate needs to be dissolved in 50 g of water to make a saturated solution at 40°C?
- 14 25 g of potassium nitrate is dissolved in 100 g of water at 30°C. Is this solution saturated?
- **15** If 100 g of KNO<sub>3</sub> is added to 100 g of  $H_2O$  at 40°C, how much of it will remain undissolved?
- **16** A 40 g sample of NaNO<sub>3</sub> is added to 100 g of  $H_2O$ at 20°C. How much more NaNO<sub>3</sub> needs to be added to make a saturated solution at this temperature?
- **17** If 1 kg of water has a volume of 1 L, how much oxygen will dissolve in a 30 L fish tank at 20°C?
- 18 How much less nitrogen will a 6 000 000 L lake hold in summer at 20°C than in winter at 0°C? (Assume the water in the lake is still liquid at o°C.)



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# 4.2 Concentration

### Molarity

The contents of consumer products are described by a variety of units, but chemists use the term **molarity**. Molarity is a measure of concentration as the number of moles of solute per litre of solution. If a solution has one mole of solute in one litre of solution it would be described as 1 mole per litre,  $1 \text{ mol } \text{L}^{-1}$ , 1 molar or 1 M.

The number of moles (n), the volume of the solution (V) and the concentration of the solution (c) can be linked according to the formula:

 $c = \frac{n}{V}$ 



A solution consists of 0.56 mol of potassium nitrate in 4.0 L of solution. What is the concentration of the solution?

n = 0.56 mol V = 4.0 L  $c = \frac{n}{V}$   $= \frac{0.56}{4.0}$   $= 0.14 \text{ mol } \text{L}^{-1} \text{ or } 0.14 \text{ M}$ 



2.6 g of  $\text{NiCl}_{\text{2}}$  is dissolved in water, making 200 mL of solution. What is the concentration?

m = 2.6 g  $M = 58.7 + 2 \times 35.5 = 129.7 \text{ g mol}^{-1}$   $n = \frac{m}{M}$   $= \frac{2.6}{129.7}$  = 0.020 mol V = 200 mL = 0.20 L  $c = \frac{n}{V}$   $= \frac{0.020}{0.20}$ = 0.10 M

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figure 4.10 Preparing solutions of accurate concentration requires the use of precise glassware such as a volumetric flask, a pipette and a burette.

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Molarity is a measure of concentration in The formula for calculating molarity can also be used to derive a formula for calculating the number of moles of a substance in a solution.

amount of solute = concentration × volume of solution

 $mol = mol L^{-1} \times L$  $n = c \times V$ 

V Worked example 4.2C

How many moles of ammonia are in 50 mL of 0.10 M ammonia solution?

c = 0.10 M V = 50 mL = 0.050 L  $n = c \times V$   $= 0.10 \times 0.050$ = 0.0050 mol

 $= 5.0 \times 10^{-3} \text{ mol}$ 

Worked example 4.2D

Calculate the mass of glucose ( $C_6H_{12}O_6$ ) dissolved in 2.5 L of 1.0 M glucose solution.

c = 1.0 M V = 2.5 L  $n = c \times V$   $= 1.0 \times 2.5$  = 2.5 mol n = 2.5 mol  $M = 6 \times 12.0 + 12 \times 1.0 + 6 \times 16.0$   $= 180.0 \text{ g mol}^{-1}$   $m = n \times M$   $= 2.5 \times 180.0$ = 450 g glucose

### Dilutions

When a solution is **diluted**, an amount of the initial solution is taken and more solvent added. The final solution contains the same substance but it has a lower concentration. If the starting solution has a concentration of  $c_1$  in a volume of solution  $V_1$ , then the number of moles  $(n_1)$  is given as:

 $n_1 = c_1 V_1$ 

After the solvent has been added, the diluted solution of volume  $V_2$ , the new concentration  $c_2$  and the number of moles of solute  $n_2$  is related by:

 $n_2 = c_2 V_2$ 

However the number of moles of solute is the same for both solutions as water has simply been added to dilute the solution.

 $n_1 = n_2$ Therefore:

 $c_1V_1 = c_2V_2$ 

A solution of a certain concentration can be made dilute by adding more solvent  $\cap$ 



**figure 4.11** This is a common way of expressing the dilution formula.



### / Worked example 4.25

If 10 mL of 0.1 M hydrochloric acid solution is taken and 190 mL of water added to make the total volume 200 mL, what is the new concentration?

Notice that  $V_2$  is the final volume and not the amount of water added.

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 $c_{1} = 0.1 \text{ M}$   $V_{1} = 10 \text{ mL}$   $V_{2} = 200 \text{ mL}$   $c_{1}V_{1} = c_{2}V_{2}$   $c_{2} = \frac{c_{1}V_{1}}{V_{2}}$   $= 0.1 \times \frac{10}{200}$  = 0.005

Worksheet 2 Concentration

= 0.005 $= 5 \times 10^{-3} \text{ M}$ 

Worksheet 3 Dissolving and concentration

### Questions

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- **19** Calculate the concentration (mol L<sup>-1</sup>) of the following solutions.
  - a 0.50 L of solution, which contains 0.24 mol of glucose molecules
  - **b** 0.20 L of solution, which contains 0.010 mol of sodium chloride
  - **c** 25.0 mL of solution, which contains  $2 \times 10^{-3}$  mol of solute
  - d 4.1 L of solution, which contains 1.23 mol of solute
- **20** Calculate the concentration (in mol L<sup>-1</sup>) of the following solutions.
  - **a** 1.0 mL of a solution which contains  $1.0 \times 10^{-3}$  mol of solute
  - **b**  $2.6 \times 10^{-2}$  mL of solution which contains  $4.1 \times 10^{-5}$  mol of solute
  - **c**  $1.5 \times 10^2$  L of solution which contains 7.5 mol of solute
  - d 9.3  $\times$  10  $^5$  L of solution which contains 1.8  $\times$  10  $^3$  mol of solute
- **21** Calculate the concentration (in mol L<sup>-1</sup>) of the following solutions.
  - a 2.0 L solution which contains 74.6 g of potassium chloride
  - b 0.5 L solution which contains 30.0 g of sodium iodide
  - **c** 800 mL solution which contains 160.6 g of sodium chloride
  - d 4.5 L solution which contains 12.9 g of sodium hydroxide

- 22 Calculate the amount of glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) in:
   a 1.0 L of a 2.0 M glucose solution
  - **b** 2.0 L of a 2.0 M glucose solution
  - **c** 0.10 L of a 2.0 M glucose solution
  - d  $1.0 \times 10^2$  L of a 2.0 M glucose solution
  - e  $3.7 \times 10^3$  L of a 2.0 M glucose solution.
- **23** Calculate the mass of solute in each of the solutions in Question 22.
- 24 Calculate the amount of sodium chloride in:
  - a 2.0 L of a 1.0 M NaCl solution
  - **b** 1.0 L of a 0.5 M NaCl solution
  - **c** 0.5 L of a 2.0 M NaCl solution
  - **d**  $1.5 \times 10^2$  L of a 2.0 M NaCl solution
  - e  $2.6 \times 10^3$  L of a 3.0 M NaCl solution.
- **25** Calculate the amount of solute in each of the following solutions.
  - a 0.10 L of a 0.22 M solution
  - **b** 10 mL of a 0.22 M solution
  - c 1.0 mL of a 0.41 M solution

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- d 15.6 mL of a 0.015 M solution
- e 24.8 mL of a 0.056 M solution
- f  $1.5 \times 10^{-1}$  mL of a 5.2 M solution
- **26** Calculate the concentration of each of the following diluted solutions.
  - a 10 mL of water is added to 5 mL of 1.2 M HCl
  - **b** 10 mL of water is added to 3.0 L of 0.10 M HCl
  - c 2 L of water is added to 4 L of 3 M  $H_2SO_4$
  - d 5.0 mL of 0.50 M HCl is added to 95 mL of water

### Summary **DDDD**

- As solute dissolves in a solvent, each solute particle is surrounded by solvent particles and a homogenous mixture called a solution forms.
- Ionic compounds, polar covalent compounds and covalent molecules with the ability to hydrogen bond tend to be **soluble** in water due to the polar nature of water molecules.
- Ionic compounds undergo **dissociation** when dissolving. The ions separate in solution.
- The process of ions or molecules being surrounded by water molecules during dissolving is known as hydration.
- Saturated solutions have the maximum amount of solute dissolved for that temperature.
- Unsaturated solutions contain less than the maximum amount of solute for that temperature.

- Supersaturated solutions are unstable systems containing more than the maximum amount of solute for that temperature.
- The solubility of a substance can be shown at various temperatures on a **solubility curve**.
- Increasing the temperature increases the solubility of most solids but decreases the solubility of gases.
- A substance that only dissolves to a very small extent in a solute is said to be **insoluble**.
- The concentration of a dissolved substance is measured in moles per litre and called the molarity (M).
- Adding more solvent **dilutes** a solution.

### Key terms

concentration dilute dissociation homogenous hydration insoluble molarity saturated solution

solubility curve soluble solute solution solvent supersaturated solution unsaturated solution





### Chapter **Review**

### 4.1 Dissolving

- 27 One of the components of petrol is octane,  $C_8H_{18}$ . When water is added to octane, two separate layers form. The main reason for this is that:
  - A water molecules cannot form hydrogen bonds with octane molecules.
  - **B** covalent bonding exists in water molecules but not in octane molecules.
  - **C** water molecules are smaller than octane molecules so water will float on octane.
  - D octane molecules have more hydrogen atoms than water molecules so hydrogen bonds form between octane molecules and not water molecules.
- **28** Which of the following alternatives lists only compounds that have a very low solubility in water?
  - A NH<sub>3</sub>, CuCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>COOH
  - **B** CO<sub>2</sub>, N<sub>2</sub>, NH<sub>3</sub>, BaSO<sub>4</sub>
  - C Na<sub>2</sub>CO<sub>3</sub>, AgCl, CH<sub>3</sub>COOH, CO<sub>2</sub>
  - D AgCl, N<sub>2</sub>, BaSO<sub>4</sub>, CuCO<sub>3</sub>
- **29** Glucose has the formula C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> and is a white solid which is highly soluble in water. From this information we can deduce that glucose is:
  - A an ionic compound which ionises in water.
  - **B** an ionic compound which dissociates in water.
  - **C** a molecular compound which contains polar covalent bonds.
  - **D** a molecular compound which is attracted to water molecules by strong covalent bonds.
- **30** Hydrogen chloride gas is highly soluble in water. The solution consists of:
  - A hydrated hydrogen and chloride ions.
  - **B** dissolved hydrogen and chlorine gases.
  - C hydrogen chloride molecules attracted to water molecules by hydrogen bonds.
  - D hydrogen chloride molecules attracted to water molecules by ion-dipole attraction.
- **31** Under which of the following conditions are gases generally most soluble?
  - A high pressure and low temperature
  - **B** high pressure and high temperature
  - **C** low pressure and low temperature
  - **D** low pressure and high temperature
- **32** The solubilities of various salts were determined at a number of temperatures.

#### table 4.4

Substance	Solubility (g solute per 100 g wate		
	o°C	25°C	80°C
sodium chloride	34	36	38
potassium bromide	53	67	95
potassium dichromate	5	15	70
potassium chromate	4	67	95

Which solid shows the greatest increase in solubility with increasing temperature over the range shown?

- A sodium chloride
- **B** potassium bromide
- C potassium dichromate
- **D** potassium chromate
- **33** The solubility of potassium chromate was determined at a number of temperatures.

#### table 4.5

Temperature (°C)	Solubility (g per 100 g water)
0	4
25	67
80	95

6.0 g potassium chromate was dissolved in 20 g water at 80°C. The solution was cooled to 0°C. What mass of solute would crystallise, assuming a supersaturated solution was not formed?

- A 0.8 g
- **B** 1.0 g
- C 2.0 g
- **D** 5.2 g
- **34** Predict which of the following substances are likely to be soluble in water.
  - a ammonium sulfate, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>
  - **b** zinc nitrate,  $Zn(NO_3)_2$
  - **c** silicon dioxide, SiO<sub>2</sub>
  - **d** octane,  $C_8H_{18}$
  - e silver chloride, AgCl
  - **f** ethylene glycol, HOCH<sub>2</sub>CH<sub>2</sub>OH
- **35** Write down the formulae of three sulfate compounds that are:
  - **a** soluble in water

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b insoluble in water.

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- 36 Write down the formulae of three carbonate compounds that are:
  - a soluble in water **b** insoluble in water.
- 37 State whether the following compounds are soluble or insoluble in water.
  - a sodium chromate
  - **b** dysprosium carbonate
  - **c** silver sulfate
  - d ammonium permanganate
  - e mercury hydroxide
  - **f** hafnium nitrate
- 38 Examine figures 4.12 and 4.13 showing electrostatic attraction between NaCl and water molecules, and the arrangement of water molecules around ions. Describe in your own words the solution process for sodium chloride. Your description should include a discussion of the relevant forces involved.



represents attraction between ions in lattice and water dipoles

#### figure 4.12





39 The following ionic substances are all soluble in water. Write equations to represent their dissociation in water. Calcium nitrate  $(Ca(NO_3)_2)$ is done for you as an example:

$$Ca(NO_3)_2(s) \xrightarrow{H_2O(l)} Ca^{2+}(aq) + 2NO_3^{-}(aq)$$

- a sodium phosphate, Na<sub>3</sub>PO<sub>4</sub>
- **b** aluminium chloride, AlCl<sub>3</sub>
- c copper(II) sulfate, CuSO
- d potassium hydroxide, KOH
- calcium acetate, (CH<sub>2</sub>COO)<sub>2</sub>Ca ρ
- f ammonium sulfate,  $(NH_4)_2SO_4$
- g sodium hydrogen carbonate, NaHCO<sub>2</sub>
- **40** The table shows the solubility of a group of related carbon compounds.

#### table 4.6

Formula	Solubility (g per 100 g water)
CH₃OH	infinite (miscible in all proportions)
CH <sub>3</sub> CH₂OH	infinite (miscible in all proportions)
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	infinite (miscible in all proportions)
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	8.0
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	2.7
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	0.6

- a The compounds all belong to the same series of carbon compounds. What name is given to that series of compounds?
- **b** Explain why the solubility of these compounds decreases as the size of the molecule increases.
- **c** CH<sub>2</sub>CH<sub>2</sub>OH, like water, will dissolve ionic compounds such as NaOH. Unlike water, however, CH<sub>3</sub>CH<sub>2</sub>OH will also dissolve nonpolar compounds such as hexane,  $C_6H_{14}$ . By comparing the structure of CH<sub>2</sub>CH<sub>2</sub>OH and that of water, explain this difference in solvent properties.
- **41** Potassium chloride, KCl. is soluble in water.
  - a Give the electronic configuration of the elements:
    - i potassium
    - ii chlorine.
  - **b** Describe the structure of and bonding in: i solid potassium
    - ii gaseous chlorine
    - iii solid potassium chloride.
  - c When KCl dissolves in water, it is said to dissociate.
    - i What is meant by the term dissociate?
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- ii Write an equation for this dissociation reaction.
- d What bonds must be broken when KCl dissolves in water?
- e Sketch the arrangement of water molecules around potassium ions and chloride ions when these are dissolved in water. Name the bond that forms between the ions and the water molecule.
- **f** At 25°C, a maximum of 45.5 g of KCl will dissolve in 130 g of water to form a saturated solution.
  - i Calculate the solubility of KCl in water, in g per 100 g water, at 25°C.
  - ii Assuming that the density of the solution at 25°C is 1.0 g mL<sup>-1</sup>, calculate the concentration of a saturated solution of KCl in g L<sup>-1</sup>.
- g Would you expect KCl to be more or less soluble in oil than in water? Explain your answer.
- **42** Give concise explanations for the following observations.
  - a Ammonia (NH<sub>3</sub>) and methane (CH<sub>4</sub>) are both covalent molecular substances. Ammonia is highly soluble in water, but methane is insoluble.
  - b Glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) and common salt (NaCl) are very different compounds. Glucose is a covalent molecular substance, whereas common salt is ionic, yet both of these substances are highly soluble in water.
  - **c** When a saturated solution of potassium nitrate at 70°C is cooled to 20°C, crystals appear in the bottom of the solution.
  - **d** A glass of lemonade kept cold in the refrigerator tastes more fizzy than one kept at room temperature.
  - e The addition of heat to natural waterways sometimes leads to a reduction of animal life or a change in the type of organisms found there.
- **43** Figure 4.14 shows the solubilities of four different substances in water over a range of temperatures.
  - a What is the solubility of potassium nitrate at 40°C?
  - **b** Which of the four substances is most soluble at:
    - i 10°C?
    - ii 50°C?
  - c What mass of ammonium chloride is needed to make a saturated solution in 750 g water at 20°C?
  - d What mass of water must be added to 76 g NaCl at 80°C to make a saturated solution?

e In each of the following cases, decide whether the solution produced is unsaturated, saturated or supersaturated.



- i 25 g lead nitrate is added to 50 g water at 20°C.
- ii 90 g potassium nitrate is dissolved in 120 g water at 40°C.
- iii 39 g ammonium chloride is dissolved in 75 g water at 60°C.
- iv 50 g sodium chloride is dissolved in 150 g water at 70°C.
- f 10 g of potassium nitrate was dissolved in 50 g water at 20°C. What mass of potassium nitrate must be added to this solution in order to saturate it at that temperature?
- **g** A solution, at 100°C, contains 60 g ammonium chloride in 100 g water. Describe what you would expect to happen as the solution cools gradually to 25°C.
- h A saturated solution of potassium nitrate is made in 50 g water at 50°C.
  - i What mass of potassium nitrate would remain in solution if it were cooled to 20°C?
  - ii What mass of potassium nitrate would crystallise out?
- i At what temperature would each of the following solutions be saturated?
  - i 45 g of potassium nitrate in 50 g water
  - ii 1.7 g of potassium nitrate in 10 g water
- **44** The data in table 4.7 shows the solubility, in g per 100 g of water, of three different compounds over a range of temperatures.
  - a Plot the data shown. Label the lines and axes. Use the data and your graph to calculate the following information.

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table 4.7					
Substance	Temperature				
	o°C	20°C	40°C	60°C	80°C
CuSO <sub>4</sub> .5H₂O	14.3	20.8	29.0	39.1	53.6
NaCl	35.7	35.9	36.4	37.1	38.1
CsNO <sub>3</sub>	9.3	23.0	47.2	83.8	-

- b What mass of sodium chloride must be added to 200 g water to give a saturated solution at 50°C?
- i 200 g CuSO<sub>4</sub>.5H<sub>2</sub>O is dissolved in 1.0 L water at 25°C. Is the solution saturated, unsaturated or supersaturated? Assume 1 mL water at 25°C has a mass of 1 g.
  - ii This solution is now cooled to o°C. What mass of copper sulfate would you expect to crystallise out?
- **d** A white powder is known to be a mixture of NaCl and CsNO<sub>3</sub>. The percentage by mass of CsNO<sub>3</sub> in the mixture is 65% (w/w). The rest is NaCl.
  - i What mass of CsNO<sub>3</sub> would be present in 85 g of the mixture?
  - ii What mass of NaCl would be present in 85 g of the mixture?
  - iii 85 g of the mixture is added to 100 g of water. What is the minimum temperature to which the water must be heated so that both compounds are fully dissolved?
  - iv If the solution is now cooled to 20°C, what mass of CsNO<sub>3</sub> and NaCl remains in solution?
  - Using your answers to parts iii and iv as a guide, explain how you could obtain a pure dry sample of CsNO<sub>3</sub> from the above mixture of CsNO<sub>3</sub> and NaCl.
- **45** A group of students was set the task of deriving a solubility curve for potassium dichromate, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. They were given the following method outline.
  - Accurately weigh approximately 4.7 g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in a large test tube.
  - Using a burette, add exactly 6 mL of water to the tube.
  - Immerse the tube in boiling water and carefully stir the contents until all the crystals dissolve.
  - Remove the tube from the boiling water and stir continuously until crystals start appearing. Record the temperature.
  - Add an additional 6 mL of water in the tube and repeat steps 2 and 3.

- Repeat step 4 until a total of eight results has been obtained.
- In your calculations, assume the density of water to be 1 g mL<sup>-1</sup>. The results they obtained are given in table 4.8. Mass of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> used = 4.76 g.

/	table 4.8								
	Volume of water used (mL)	6.0	12	18	24	30	36	42	48
	Temperature at which crystallisation occurred (°C)	88	60	47	34	26	21	18	16

- a Calculate the solubility of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, in g per 100 g water, at each of the temperatures recorded in the results table and plot a graph of the variation of solubility with temperature.
- **b** From your graph, determine the solubility of  $K_2Cr_2O_7$  at 80°C.
- c State two safety precautions that the students must take when performing this experiment.
- **d** Why is it necessary to stir the solution continuously as it cools?
- e What effect would the formation of a supersaturated solution have on the results and how is this prevented?
- **f** One group of students had not completed their last reading by the end of the lesson. They left their test tube with the  $K_2Cr_2O_7$  solution sitting in the hot water bath until after school when they returned to complete their experiment. To their surprise, the temperature at which crystallisation occurred for this last reading was higher than the previous one. Suggest a possible reason.
- **46** Provide concise explanations for each of the following observations.
  - a Pure liquid nitric acid, HNO<sub>3</sub>, does not conduct electricity yet a solution of nitric acid in water will conduct electricity.
  - **b** Butanol is soluble in both water and kerosene.
  - **c** The arrangement of water molecules around dissolved magnesium ions is different from that around dissolved chloride ions.
  - d Covalent bonds are considered to be as strong as ionic bonds yet water, which is a covalent molecular compound, is a liquid at room temperature, whereas sodium chloride, an ionic compound, is solid with a high melting temperature.

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Chemical solutions



### 4.2 Concentration

47 A copper(II) sulfate solution was prepared and 20 mL samples of it of it were placed in two beakers, labelled A and B (figure 4.15). To beaker B, 20 mL of water was also added.





Beaker A

Beaker B

20 mL copper(II) sulfate solution

20 mL copper(II) sulfate solution and 20 mL water

#### figure 4.15

In comparison with the solution in beaker A, the solution in beaker B has:

- A the same concentration but a larger amount of copper(II) sulfate.
- **B** a lower concentration but a larger amount of copper(II) sulfate.
- C the same concentration and the same amount of copper(II) sulfate.
- **D** a lower concentration but the same amount of copper(II) sulfate.
- **48** The mass of anhydrous copper sulfate needed to make 500 mL of 0.200 M solution is:
  - A 4.00 g
  - **B** 16.0 g
  - **C** 40.0 g
  - **D** 1600 g

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- **49** Calculate the molar concentration of the following solutions.
  - a 3.5 L solution containing 2.2 mol potassium nitrate (KNO<sub>3</sub>)
  - **b** 250 mL solution containing 0.32 mol glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>)
  - c a mixture made by mixing 500 mL of a solution containing 0.24 mol sodium chloride (NaCl) and 300 mL of a solution containing 0.15 mol sodium chloride (NaCl)
  - **d** 100 mL solution containing  $3.0 \times 10^{20}$  ammonia molecules (NH<sub>3</sub>)
  - e 200 mL water is added to 40 mL of 0.25 M KCl

- **50** Calculate the amount of solute in each of the following solutions.
  - a 1.00 L of 2.00 M NaCl solution
  - **b** 2 L of 0.5 M HCl solution
  - c 500 mL of 1.00 M glucose solution
  - d 20 mL of 0.1 M NaOH solution
  - **e** 17 mL of 0.25 M HNO<sub>3</sub> solution
- **51 a** Calculate the mass of NaCl needed to make 2.00 L of an aqueous solution with a concentration of 0.600 M.
  - **b** Calculate the mass of sodium ions contained in 1 drop (0.0500 mL) of the solution in part a.
- 52 For each of the following solutions of aluminium chloride (AlCl<sub>3</sub>)
  - a 25.0 mL of 0.050 M
  - **b** 32.6 mL of 0.015 M
    - calculate:
      - i the amount (in mol) of aluminium chloride
    - ii the amount (in mol) of aluminium ions
    - iii the amount (in mol) of chloride ions
    - iv the number of ions present altogether.
- **53** For each of the following, state which solution is the more concentrated.
  - a 300 mL of 0.20 M NaCl or 500 mL of 0.20 M NaCl
  - b 25.0 mL solution containing 0.010 mol KCl or 1.20 L solution containing 0.813 mol KCl
  - c 2.7 L solution containing 3.0 mol HCl or 120 mL solution made by dissolving  $3.0 \times 10^{22}$  molecules HCl
- 54 What volume of 10 M hydrochloric acid would be required to prepare 250 mL of 0.30 M HCl?
- 55 Phosphoric acid is used in jams and jellies. If 50.0 mL of 3.0 M H<sub>3</sub>PO<sub>4</sub> is diluted to 800 mL, what amount of H<sub>3</sub>PO<sub>4</sub> (mol) is present in 40.0 mL of diluted solution?
- **56** Calculate the final molar concentrations when the following are mixed.
  - a 50.0 mL of 0.20 M NaOH and 50.0 mL of 0.20 M NaOH
  - b 100 mL of 0.20 M NaOH and 50.0 mL of 0.20 M NaOH
  - c 100 mL of 0.50 M NaOH and 20.0 mL of 0.14 M NaOH
  - d 200 mL of 0.50 M NaOH and 20.0 mL of 0.05 M NaOH
- **57** Construct a flow diagram or concept map which would help you to explain the connections between the following terms: mole, molarity, amount, concentration, dilution, number of particles.

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Gases

Gases are important to life on Earth in so many ways. Some gases act as raw materials for reactions which drive the basic processes of living things; for example, oxygen and carbon dioxide are necessary for the basic reactions of plant and animal cells. Without these, life on Earth could not exist. Other gases contribute to our lifestyle, from basics such as the cooking of foods to the luxuries such as the perfumed aerosol sprays with which many of us indulge ourselves.

Many of the attributes of gases which we find so useful can be explained by their unique physical properties.

It is known that gases are made up of particles which move rapidly and randomly to occupy as much space as possible. Compared to solids and liquids, gases have a low density, meaning their particles must be widely spread. This explains why gases can be easily compressed. Table 5.1 compares some properties of gases to those of liquids and solids.

table 5.1 A comparison of some properties of solids, liquids and gases.					
Gases	Liquids	Solids			
low density	high density	high density			
spread to fill the space available	fixed volume adopt shape of container	fixed volume generally rigid shape			
easily compressed	almost incompressible	almost incompressible			
mix together rapidly	mix slowly	do not mix unless finely divided			

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A gas takes up the shape and volume of a container.

of a container, but its volume remains constant.

figure **5.1** Liquids have a fixed volume. The volume occupied by a gas is dependent on the amount of space available.

# 5.2 Kinetic molecular theory

The explanation used by scientists for the behaviour of gases is called the **kinetic molecular theory**. The basic assumptions of this theory are as follows.

- Gases are made up of tiny, individual particles. The volume of the particles themselves is insignificant compared to the volume occupied by the gas, therefore gases are mostly empty space.
- Gas particles move rapidly and randomly in straight line motion. Particles collide with one another and with the walls of the container in elastic collisions (no overall loss or gain of energy).
- Individual particles are far apart and have very little attraction for each other. Particles are considered to move independently of each other.
- The average kinetic energies of particles of different gases are equal at a given temperature.
- The average kinetic energies of gas particles increase as the temperature increases.



**figure 5.2** The air bag in a car makes use of the rapid movement of gas particles produced by a chemical reaction to fill the space of their container.

### Diffusion

**Diffusion** is a term used to describe the movement of matter from one place to another due to the random movements of its particles. Applied to gases, it describes how particles of a gas will spread out to occupy as much space as possible.

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Kinetic molecular theory explains certain properties of gases in terms of the behaviour of their particles.

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The rate at which a gas diffuses depends on the average velocity of the gas particles. From the kinetic molecular theory, we know that at a particular temperature all gases have equal kinetic energy. Average kinetic energy =  $1/2 mv^2$ where *m* is the mass of the particle and *v* is the average velocity of the particle. If the average kinetic energy of individual particles is equal, particles with a smaller mass will have a greater velocity than heavier particles. Lighter particles with greater velocity will diffuse more rapidly than slower, heavier particles. This means that at the same temperature, the rate of diffusion of different gases is dependent on their molar mass.

Diffusion rate is also related to temperature. As the temperature increases, the average kinetic energy of the particles increases. Since their mass stays the same, this means that their velocity increases. If the particles are travelling faster, they will spread out at a greater rate.

#### Pressure

From the kinetic molecular theory, we know that gases collide with the walls of their container. The force per unit of area exerted by the gas particles as they collide with the walls of their container is called gas pressure. Pressure is determined by the number and force of collisions. The number of collisions is determined by the number of gas particles present and the volume of the container.

Increasing the number of gas particles will increase the collision rate and increase the pressure. Decreasing the number of particles will have the reverse effect and the pressure of the system will decrease. The effect of changing volume will be discussed later in the chapter.

Increasing the temperature of the system increases the average velocity of the particles and therefore the force and number of collisions. Increasing the temperature also leads to an increase in pressure.

### Partial pressure

Kinetic molecular theory also gives us the idea that gas particles move independently of each other. In a mixture of gases, each gas acts as if it were alone in the container, exerting its own pressure independently of the other gases. In a mixture of gases, the pressure exerted by each individual gas is called a partial pressure. The total pressure for a mixture of gases is equal to the sum of the individual partial pressures from each gas in the mixture. This is called Dalton's Law of Partial Pressures.

### Dalton's Law of Partial total pressure exerted by a mixture of gases is the sum of the pressure of



figure 5.3 The total pressure of a mixture of gases is the sum of the individual pressures (partial pressures) of each of the gases in the mixture.



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Diffusion describes the

movement of particles from one place to another.

movements of its atoms or molecules caus<u>e it to</u>

exerted per unit of area The SI unit for pressure



<Pa is a unit of</pre>

pressure.



### Questions

- 1 Explain the following properties of gases using the kinetic molecular theory.
  - a Liquid water cannot be easily compressed, but a sample of steam can.
  - **b** Solids will show very little mixing compared to gases, which mix easily.
  - c The smell of an aerosol sprayed in one corner of a room will quickly spread throughout the room.
- 2 Explain why a sample of ammonia gas (NH<sub>3</sub>) will diffuse more rapidly than a sample of hydrogen sulfide gas (H<sub>2</sub>S) at the same temperature.
- **3** Dry ice (frozen CO<sub>2</sub>) is placed inside a deflated balloon. The end of the balloon is tied off and it is left on a bench at room temperature. After several minutes, the balloon is checked and its

volume has increased. Use the kinetic molecular theory to explain why this happened.

- 4 According to the kinetic molecular theory, explain what would happen to the pressure on a container of gas if:
  - a some gas was removed from the container
  - **b** the container was put into a freezer
  - c the container was placed in the sun on a very hot day.
- 5 At sea level, a mixture of atmospheric gases contains mostly nitrogen and oxygen. Its total pressure was found to be 1 atm. The nitrogen gas was found to have contributed 0.78 atm. Other trace gases contributed 0.01 atm. What was the partial pressure of the oxygen gas?

### 5.3 Measuring pressure and volume

A method of measuring air pressure was invented in 1643 by Italian scientist Evangelista Torricelli. Figure 5.4 shows a diagram of Torricelli's device, which later came to be called a barometer. The mercury column rises or falls according to the pressure of the air on the mercury in the dish. The pressure was measured by the height of the mercury in the tube above the surface of the mercury in the dish. Torricelli found that at sea level this measurement was 760 millimetres.



A lesser known device used to measure pressure is the manometer. This device is often used in closed systems of gases, as shown in figure 5.5(a). With this instrument, the pressure is measured by calculating the difference in height between the two columns of liquid.

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**figure 5.5** (a) A closed tube manometer. Pressure is equal to the difference between the heights of the liquids (usually mercury) in the two tubes. (b) A modern barometer.

### Units of pressure

Pressure is determined by calculating force exerted per unit of area. The accepted SI unit for force is the newton and for area is the square metre, therefore the standard unit for pressure is the newton per square metre (N m<sup>-2</sup>). A more commonly known unit derived from this is the pascal (Pa). One newton per square metre is equivalent to 1 pascal. In 1982 a new pressure unit called the bar was introduced. One bar is equivalent to 100 000 pascals or 100 kilopascals (kPa). As many early pressure measuring devices used columns of mercury, millimetres of mercury (mmHg) is a commonly used unit which has been around since early times of pressure measurement. This unit is also known as the Torr, honouring Torricelli for his work in this field. The atmosphere (atm) is another commonly used unit. One atmosphere is the average atmospheric pressure at sea level. The unit called the hectopascal (hPa) is usually used on weather maps. One hectopascal is equal to 100 pascals. Table 5.2 summarises the value of some pressure units for atmospheric pressure at sea level at 25°C.

table	5.2 Standard	pressures at l	25°C at sea	level.		
atm	mmHg	bars	kPa	Pa	$N m^{-2}$	
1	760	1.01	101	101 × 10 <sup>3</sup>	$101 \times 10^3$	

When the standard atmospheric pressures are known, you can easily convert between the units of pressure.

Atmospheric pressure in an elevated region is measured at 650 mmHg. Convert this pressure into: a kilopascals b atmospheres.

Gases

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Working: **a** Use the known standard units: 760 mmHg = 101 kPa By proportion:  $\frac{650}{760} = \frac{x}{101}$   $x = \frac{650}{760} \times 101$  = 86.4 kPa **b** Use the standard units: 760 mmHg = 1 atm By proportion:  $\frac{650}{760} = \frac{x}{1}$   $x = \frac{650}{760} \times 1$ = 0.855 atm

### Units of volume

Volume can be expressed in many different units. Some common units include millilitres (mL), litres (L), cubic centimetres (cm<sup>3</sup>), cubic decimetres (dm<sup>3</sup>) and cubic metres (m<sup>3</sup>). The SI unit for volume is the cubic metre (m<sup>3</sup>).

Some conversion factors between these units are listed below.

- 1 L = 1000 mL
- $1 \text{ mL} = 1 \text{ cm}^3$
- $1 L = 1 dm^3$
- $1 \text{ m}^3 = 1000 \text{ L}$

### **Questions**

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- 6 Convert the given pressures to the units stated in each case.
  - a 2.5 atm to mmHg and kPa
  - **b** 0.73 bars to Pa and atm
  - c 145 kPa to mmHg and bars
  - d 68 ooo Pa to atm and kPa

- **7** Convert the given volumes to the unit stated in each case.
  - **a** 1.2 L to mL
  - **b** 65 mL to  $cm^3$
  - **c** 2.7 dm<sup>3</sup> to mL
  - **d** 550 mL to  $m^3$
  - **e** 5.4 dm<sup>3</sup> to m<sup>3</sup>
  - $\mathbf{f}$  0.65 L to cm<sup>3</sup>

# 5.4 The gas laws

Much of the early work in chemistry was centred on the study of gases, leading to the development of the gas laws. In general, the gas laws demonstrate the relationships between pressure, volume, temperature and number of moles (amount) of gas.

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### **Boyle's Law**

In 1662, the Irish chemist Robert Boyle described experimental results that showed a definite mathematical relationship between the pressure and volume of a sample of gas at a constant temperature. A Jesuit scientist who disagreed with his ideas had attacked a previous publication of Boyle's ideas about the nature of air. In response, Boyle designed an experiment to show how the pressure and volume of air change when air is compressed or expanded. As with many early scientists, Boyle developed his own apparatus for the experiment. His experiments showed that increasing the pressure on a sample of gas (keeping it at the same temperature) would lead to a decrease in its volume. His experiments showed that the reverse was also true—decreasing the pressure on a fixed sample of a gas at a constant temperature would lead to an increase in the volume the gas occupied. **Boyle's Law** derives to the mathematical relationship:

 $P_1V_1 = P_2V_2$  (at a constant temperature)

This relationship is supported by our knowledge of the behaviour of gases. For example, if the volume of a sample of gas is increased, the gas particles will move to occupy as much space as possible. As the gas particles spread out, the pressure of the system decreases.



Volume is increased. Particles are more widely spaced. Pressure decreases.

**figure 5.7** The smaller the volume, the greater the pressure on a fixed sample of gas at a particular temperature.



**figure 5.6** Robert Boyle was the fourteenth of fifteen children in a wealthy and influential family. He became well known for his commitment to proper experimental procedure and reporting of results.

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Boyle's Law describes the relationship between pressure and volume of a fixed mass of gas at a constant temperature. I derives to  $P_1V_1 = P_2V_2$ .



The relationship between the pressure and volume of a gas is also referred to as Mariotte's Law. Frenchman Edme Mariotte made the same discovery independently but his work was published later than Boyle's.

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**figure 5.8** A typical graph of experimental results showing that the volume of a fixed amount of gas varies inversely with pressure at a constant temperature.

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# Volume-pressure relationship

for gases (quantitative)

### Purpose

To develop a quantitative relationship between gas pressure and volume for a fixed amount of gas at a constant temperature.

### Method

It is advisable to do this experiment on a tray so that if a weight falls it does not damage the bench. The floor is a suitable surface, if clean, as it reduces the risk associated with falling weights.

- 1 Clamp the syringe on to the retort stand with the nozzle downwards and the plunger set at full capacity. Fit the rubber stopper to the nozzle and record the volume of air in the syringe at full capacity.
- 2 Place a 1 kg weight or half brick on top of the plunger and record the new volume of air in the syringe. Check your result by repeating this step twice. Record each reading and calculate the average volume.
- **3** Place a second weight or half brick on top of the first and record the volume. Check and average your results as in step 2.
- 4 Repeat this procedure until a total of five or six weights have been used. Clearly record your results in table form.
- **5** Calculate the reciprocal of each average volume and add these figures to your table.
- 6 Draw up a graph of your results plotting *volume* on the vertical axis against *pressure* (represented by the number of weights or bricks) on the horizontal axis. Label this 'Graph A'.
- 7 Draw up another graph plotting *reciprocal of volume* on the vertical axis against *pressure* on the horizontal axis. Label this 'Graph B'. To allow for the pressure that is caused by the atmosphere and by the weight of the plunger, raise the horizontal axis of Graph B until the straight line passes through the origin.

#### Theory

The quantitative relationship between volume and pressure is known as **Boyle's Law**.

#### Discussion

- 1 What type of relationship between the volume of a gas and its pressure does Graph B suggest?
- 2 Express the mathematical relationship between pressure (*P*) and the reciprocal of volume  $\begin{pmatrix} 1 \\ V \end{pmatrix}$  as shown in Graph B.

#### materials

- retort stand, clamp and bosshead
- 50 mL disposable plastic syringe
- rubber stopper with holes bored part way through it
- 5 or 6 weights of equal mass (e.g. 500 g weights or half bricks weighing approx. 1 kg)

#### safety

• Wear safety glasses and a laboratory coat for this experiment.

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Gases





Charles' Law states that for a fixed amount of gas at a constant pressure, there is a direct relationship between the volume of a gas and its temperature.

#### materials

- conical flask
- balloon
- container of hot water
- container of ice water

safety

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• Wear safety glasses for this experiment.

### **Charles' Law**

Frenchman Jacques Charles studied the relationship between the temperature and volume occupied by a gas. Charles theorised that various gases such as nitrogen, hydrogen and oxygen expanded in proportion to the temperature to which they were exposed. His results showed that changing the temperature of a gas directly changed the volume it occupied. In simple terms, increasing the temperature of a fixed amount of gas will increase its volume when the pressure stays constant. Decreasing the temperature of a fixed amount of gas will decrease its volume when the pressure stays constant. This relationship became known as **Charles' Law** and derives to the mathematical relationship:

 $\frac{V_1}{T_1} = \frac{V_2}{T_2}$  (for a fixed mass of gas at a constant temperature)

# Volume-temperature relationship for gases (qualitative)

#### Purpose

To examine qualitatively the relationship between the volume and temperature of a fixed amount of gas at constant pressure.

#### Method

- 1 Stretch the neck of the balloon over the opening of a conical flask.
- **2** Place the conical flask in a container of hot water and observe what happens to the balloon.
- **3** Place the conical flask in a container of ice water and observe what happens.

#### Theory

The quantitative relationship between volume and temperature of a gas is known as **Charles' Law**.

#### Discussion

- 1 How does the volume of air in the balloon change when the temperature is:
  - a increased?
  - b decreased?
- 2 What assumptions can you make about the amount of gas used in this experiment and its pressure?
- 3 Explain your results in terms of the kinetic theory of gases.

### The kelvin scale

A different temperature scale is used in gas calculations. This scale is the **kelvin** or **absolute temperature** scale.

Many substances are gases at temperatures below 0°C. It is inconvenient to measure negative values of Celsius temperature. Lord Kelvin suggested using **absolute zero** as the zero temperature for a new scale, kelvin (K). Absolute zero is the theoretical temperature at which molecules have zero kinetic energy (all molecular motion ceases). This scale eliminates the problem of negative measurements for gas temperatures. At 0 K, the gas phase would not exist.

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To convert between °C and K we can use the equation: K = °C + 273 (i.e. 0 K = -273°C).

Note that a degree symbol is not used for kelvin temperatures.







 $V_1 = 21.5 \text{ L}, T_1 = 20.0^{\circ}\text{C}$ (convert to kelvin) K = °C + 273 = 20.0 + 273 = 293 K  $V_2 = ?, T_2 = 35.0^{\circ}\text{C}$ (convert to kelvin) K = °C + 273 = 35.0 + 273 = 308 K

Step 2: State the rule.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Step 3: Put in the values.

 $\frac{21.5}{293} = \frac{V_2}{308}$ 

Step 4: Solve for the missing variable.

$$V_2 = \frac{21.5}{293} \times 308$$
  
 $V_2 = 22.6 \text{ L}$ 

The kelvin scale of temperature is used in calculations involving temperatures of gases.



Absolute zero is the theoretical temperature at which molecules have zero kinetic energy (all molecular motion ceases)



figure 5.10 The thermometer shows a comparison of the Celsius and kelvin scales of temperature. The scales differ only by their zero point; one degree increase or decrease is equal on either scale.

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# The relationship between pressure and temperature

Experimental procedures found that there was a relationship between pressure and temperature that was similar to the relationship between volume and temperature. It was found that increasing the temperature of a fixed amount and volume of gas caused an increase in its pressure. Decreasing the temperature on the same system would cause a decrease in pressure. This **pressure-temperature relationship** is described by the equation:

 $\frac{P_1}{T_1} = \frac{P_2}{T_2}$  (at a constant volume for a fixed mass of gas)

## Worked example 5.4D

A fixed volume of gas has a pressure of 0.85 atm at 20°C. The gas is heated to  $85^{\circ}$ C. What is the new pressure?

Step 1: List the quantities. (Temperatures must be changed to kelvin.)

$$\begin{array}{ll} P_1 = 0.85 \text{ atm } P_2 = ? \\ T_1 = 20^{\circ}\text{C} & T_2 = 85^{\circ} \\ = 20 + 273 & = 85 + 273 \\ = 293 \text{ K} & = 358 \text{ K} \end{array}$$

Step 2: State the rule.

 $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ 

Step 3: Put in the values.

 $\frac{0.85}{293} = \frac{P_2}{358}$ 

Step 4: Solve for the missing variable.

$$P_2 = \frac{0.85}{293} \times 358$$
  
 $P_2 = 1.0$  atm

### Amount of gas

In a system where the temperature and pressure of a gas are kept constant, the volume the gas will occupy depends directly on the amount of gas present. Changing the amount of gas (the number of moles) will change the volume the gas occupies. With temperature and pressure constant, an increase in the number of moles will increase the volume. Decreasing the number of moles will cause a decrease in volume. For a situation where the number of moles of gas are varied at constant temperature and pressure; the **volume–number of moles relationship** can be expressed as:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

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For a fixed amount of gas

pressure and temperature of a gas can be expressed


## The combined gas equation

When dealing with gases experimentally it is not always convenient to keep conditions such as pressure and temperature constant. To allow for many variables changing, the gas laws can be combined to give the **combined gas** equation:

 $\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$ 

There is a direct relationship between volume and number of moles of a gas at a fixed temperature and pressure. It can be expressed as the formula  $\frac{V_1}{n_1} = \frac{V_2}{n_2}$ .

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The combined gas equation is a combination of the relationships between pressure, volume temperature and number of moles. As the number of moles often remains constant, the relationship is often expressed as  $P_1V_1 - P_2V_2$  This equation is more commonly expressed in a form where the number of moles remains constant:

 $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ 

/ Worked example 5.4F

A gas cylinder of volume 20.0 L has a pressure of 1.80 atm at 25.0 $^{\circ}$ C. The gas is transferred into a new container where its pressure is 3.20 atm at 40.0 $^{\circ}$ C. What is the volume of the new container?

Step 1: List the quantities.  $P_1 = 1.80 \text{ atm}$   $P_2 = 3.20 \text{ atm}$   $V_1 = 20.0 \text{ L}$   $V_2 = ?$   $T_1 = 25.0 + 273 = 298 \text{ K}$   $T_2 = 40.0 + 273 = 313 \text{ K}$ Step 2: State the rule.  $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ Step 3: Put in the values.  $1.80 \times \frac{20.0}{298} = 3.20 \times \frac{V_2}{313}$ Step 4: Solve for the missing variable.  $V_2 = 1.80 \times 20.0 \times \frac{313}{298} \div 3.20$  $V_2 = 11.8 \text{ L}$ 

## Questions

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- 8 A sample of gas has a volume of 4.50 L at a pressure of 800 mmHg. The volume of the gas is increased to 8.00 L (the temperature remains constant). What is the pressure of the gas now?
- **9** A sample of hydrogen gas occupies a volume of 50.0 cm<sup>3</sup> at a pressure of 0.85 atm. Assuming the temperature remains constant, what pressure would be needed to reduce the volume of the gas to 20.0 cm<sup>3</sup>?
- **10** A sample of air at room temperature has a volume of 90.0 mL at 95.0 kPa pressure. If the air remains at room temperature, what volume will it occupy if the pressure is changed to 40.0 kPa?
- 11 The volume of a gas sample is increased from 2.70 L to 6.30 L at constant temperature. If the original pressure of the gas was 700 mmHg, calculate the new pressure of the sample in atmospheres.
- **12** A gas at a pressure of 850 mmHg has its volume decreased from 12.5 L to 9.00 L with the temperature remaining constant. Calculate the new pressure of the gas in kPa.

- **13** Convert the following Celsius temperatures to kelvin.
  - **a** -35
  - **b** 27
  - **C** 100
  - **d** o
- 14 Change the following kelvin temperatures to °C.
  - **a** 373 **b** 10
  - **C** 100
  - **d** 0
- **15** At 1 atm pressure and  $25^{\circ}$ C a gas filled balloon has a volume of 20.0 L. The balloon is cooled down to  $-5^{\circ}$ C. What would the volume of the balloon be now, assuming pressure remains constant?
- 16 A sample of gas occupies a volume of 1.5 L at 20°C and 1 atm pressure. Assuming pressure remains constant, what volume would the gas occupy at the following temperatures?
  - **a** 50°C
  - **b** -20°C

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- 17 A gas-filled balloon has a volume of 7.50 L conditions of temperature with the pressure remaining constant. Calculate the temperature (in °C) of the gas in the balloon when the conditions of temperature balloon when the conditions of temperature balloon when the conditions of temperature (in °C) of the gas in the balloon when the conditions of temperature balloon when the conditions of the gas in the balloon when the conditions of temperature balloon when the conditions of temperat
  - volume changes to: a 9.00 L
  - **b** 1.50 L
- 18 At 25.0°C, a sample of gas occupies a container of constant volume at a pressure of 820 mmHg. The gas is heated and the pressure increases to 1200 mmHg. What is the new temperature (in °C)?
- **19** A sample of gas at a pressure of 105 kPa and temperature of 28°C maintains a constant volume when its temperature is changed. What is the pressure of the gas when the temperature is changed to:
  - a 20°C
  - **b** 100°C
  - **c** –10°C
- **20** A balloon of volume 10.0 L contains 3.50 mol of gas. Gas is added to the balloon to increase the amount to 5.00 mol. What has the volume of the balloon increased to, assuming that temperature and pressure have remained constant?
- 21 A gas sample decreases in volume from 20.6 L to 17.4 L when some of the gas escapes from the

container. 5.26 mol are left in the sample. How many moles were in original sample?

- 22 A 6.50 L sample of hydrogen gas increases in volume to 9.00 L. The temperature and pressure have remained constant. The original sample contained 1.50 g of gas. How many grams of gas have been added to the sample to increase its volume?
- 23 A sample of gas has a volume of 2.40 L at 17°C and 40.0 kPa pressure. The gas is transferred to a 5.00 L container. What temperature, in Celsius, must the gas be warmed to so that the pressure increases to 60.0 kPa?
- 24 A balloon has a volume of 20.0 L at 760 mmHg pressure and 25°C. It is released and rises to an altitude where the pressure is 520 mmHg and temperature is 5.0°C. What would the volume of the balloon be now?
- 25 A sample of gas exerts a pressure of 0.950 atm at a temperature of 22.0°C. The volume of the gas is 27.5 L. What would be the new volume of the gas at 40°C and 180 kPa?
- 26 A sample of gas occupies a volume of 250 cm<sup>3</sup> at 100°C and a pressure of 760 mmHg. The pressure is increased to 1800 mmHg. To what temperature (in °C) would the gas need to be heated for it to now occupy a volume of 500 cm<sup>3</sup>?

## 5.5 The General Gas Equation

The individual gas laws can be combined into a single equation. This is called the **General Gas Equation**. It is also known as the **ideal gas equation**. The General Gas Equation is stated as:

PV = nRT

- where P = pressure
  - V= volume
  - n = number of moles
  - R = universal gas constant T = temperature in kelvin

The **universal gas constant** is also known as the **ideal gas constant**. The value of this constant varies depending on the units of volume and pressure. Table 5.3 shows some commonly used values of the universal gas constant.

<b>table</b> $5.3$ Values of the universal gas constant.					
Value of <i>R</i>	Volume	Pressure	Temperature		
62.4	litres	mmHg	К		
0.082	litres	atm	К		
8.31	litres	kPa	К		



The ideal gas equation shows the combined relationship between the temperature, pressure, volume and number of moles of an ideal gas. It includes the proportionality constant R and is expressed as PV = nRT.



The value of the universal or ideal gas constant that is used in the ideal gas equation is determined by the units of pressure and volume used for the gas measurements.

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An ideal gas obeys the ideas of the kinetic molecular theory, in particular that gas particles have no attraction for each other and that the volume occupied by an individual gas particle is insignificant compared to the volume of the gas. At high temperatures and low pressures these ideals are generally obeyed—the particles are moving rapidly and have less attraction to each other. However at high pressures and low temperatures, real gases do not behave according to the rules of an ideal gases. At high pressures, gases are compressed to the point where the volume of the atoms or molecules is significant compared to the total volume of the gas. At low temperatures, the velocity of gas particles is slower and particles do have some attraction for each other. This inhibits their movement.

Most gases under normal conditions obey the gas laws closely enough to successfully apply the ideal gas law.



27 0.500 mol of methane gas occupies a volume of 7.50 L at 12.0°C. What pressure (in kPa) is the gas exerting?

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- **28** A 22.0 g sample of carbon dioxide gas exerts a pressure of 810 mmHg at 35.0°C. What volume would this sample of gas occupy?
- **29** Calculate the temperature (in °C) of a 50.0 g sample of nitrogen gas which occupies a volume of 10.0 L at 112 kPa.
- **30** Calculate the mass of hydrogen gas in a balloon that occupies a volume of 5.00 L at 15.0°C and 0.97 atm.
- **31** Balloon A contains 4.75 L of helium gas at 120 kPa. Balloon B contains 5.00 L of hydrogen gas at 1.19 atm. Both balloons are at a temperature of 27°C. Which balloon contains the greater number of moles of gas?

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# 5.6 Molar volume

In 1811 Italian chemist Amedeo Avogadro stated that equal volumes of gas at the same temperature and pressure contain the same number of particles. This is often referred to as **Avogadro's hypothesis**.

This means that the volume of a one mole of a gas is dependent on temperature and pressure. This volume is defined as the **molar volume** of a gas.

A commonly used measurement of temperature and pressure is **STP** (standard temperature and pressure). STP conditions are 0°C and 1 atm (or 101.3 kPa). This is used internationally when measuring quantities that vary with temperature and pressure. At STP one mole of any gas occupies a volume of 22.4 L.

These conditions rarely apply to laboratory experiments (think about working in a lab at 0°C). Another commonly used value is **SLC** (standard laboratory conditions). This value uses the temperature at 25°C and pressure 1 atm or 101.3 kPa. At SLC, one mole of any gas occupies a volume of 24.5 L.



Molar volume is the volume of one mole of any gas at particular conditions of temperature and pressure. STP represents standard temperature (O°C) and pressure (1 atm). At STP, the molar volume of a gas is 22.4 L. SLC represents standard 25°C and 1 atm. At SLC, the molar volume of a gas is 24.5 L. 24.5 litres 32 g of O<sub>2</sub> (1 mole) 24.5 litres 2 g of H<sub>2</sub> (1 mole) 24.5 litres



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Gases

## / Worked example 5.68

What volume will 35.0 g of carbon dioxide gas occupy at SLC? Following from the previous example: volume at SLC = number of moles of gas  $\times$  molar volume  $V_{SLC} = n \times 24.5$  L

To find the number of moles of CO<sub>2</sub>:

 $n(\text{CO}_{2}) = \frac{m(\text{CO}_{2})}{M(\text{CO}_{2})}$  $n = \frac{35.0}{44.0}$ n = 0.795 mol $V_{\text{SLC}} = n \times 24.5$  $V_{\text{SLC}} = 0.795 \times 24.5$  $V_{\text{SLC}} = 19.5 \text{ L}$ 

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#### materials

- 20 mL of 2 M HCl
  8 cm length of magnesium ribbon
- 100 mL gas syringe
- 18 mm test tube

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- one-holed stopper to fit test tube
- retort stands, bossheads and clamps
- 4 cm length of glass tubing to fit stopper
- approx. 50 cm length of rubber tubing
- 100 mL measuring cylinder
- emery paper or steel wool

#### safety

- Wear safety glasses and a laboratory coat for this experiment.
- HCl is corrosive.

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#### **Purpose**

To measure the molar volume of hydrogen at standard laboratory conditions (SLC).

### Method

- 1 Clamp the stoppered test tube and gas syringe to their retort stands and connect the test tube and syringe using the rubber tubing. Check that the equipment is secure.
- 2 Remove the stopper from the test tube and carefully pour about 15 mL of 2 M hydrochloric acid into the test tube down one side, keeping the other side dry.
- **3** Clean and weigh the magnesium ribbon, making sure that it weighs no more than 0.08 g.
- 4 Tilt the test tube and carefully place the magnesium ribbon on the dry side of the test tube making sure that the magnesium does not contact the acid. Replace the stopper tightly.
- **5** Carefully withdraw the plunger of the syringe and then release it. If the system has no leaks, the plunger will return to its original position. Once any leaks have been fixed, record the initial volume shown on the syringe.
- 6 Tilt or shake the test tube so that the magnesium contacts the acid. As gas fills the syringe, rotate the plunger gently to prevent it from sticking.
- 7 Once the magnesium has been used up, allow the test tube to cool. Record the final volume of gas in the syringe when the plunger has completely stopped moving. Calculate and record the increase in the volume of gas in the syringe.
- 8 Record the room temperature and atmospheric pressure.
- 9 From data supplied by your teacher, record the water vapour pressure at room temperature. To allow for the pressure of water vapour in the syringe, subtract the water vapour pressure from atmospheric pressure.

## Theory

The molar volume of a gas is the volume occupied by 1 mole of the gas at a given temperature and pressure.

Standard laboratory conditions (SLC) are 1 atm or 101.3 kPa and 25°C

or 298 K.

To convert your results to SLC, use  $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ .

### Discussion

- **1** Write a balanced chemical equation for the reaction between magnesium and hydrochloric acid.
- **2** Convert the volume of hydrogen collected to SLC. You will need to allow for the water vapour pressure in this calculation.
- **3** From your equation, you will see that 1 mole or 24.3 g of magnesium produces 1 mole of hydrogen. Use this information, together with your results from Question 2 and the mass of magnesium used in the reaction, to calculate, by direct proportion, the molar volume of hydrogen at SLC.

Questions

- **32** Calculate the volume occupied by each of the following gases at SLC.
  - a 0.55 mol of nitrogen
  - **b** 8.00 g of oxygen
- **33** Calculate the volume occupied by each of the following gases at STP.
  - a 0.85 mol of hydrogen
  - **b** 14.0 g of argon

- 34 Calculate the mass of each of the following samples of gas under the conditions stated.a 47.5 L of carbon dioxide at STP
  - **b** 150 mL of helium at SLC
- **35** A sample of gas occupies a volume of 280 mL at a pressure of 380 mm Hg at 175°C. What volume would the gas occupy at SLC?

# 5.7 Stoichiometric calculations involving gases

Gases are often reactants, products or both in a chemical reaction. When this is the case, we can use the ideal gas equation or molar volume to determine masses and volumes of gases which are produced by or consumed in a chemical reaction.

# / Worked example 5.7A

. Methane gas (CH<sub>4</sub>) burns in oxygen gas to produce carbon dioxide and water vapour according to the equation:

 $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ 

What volume of carbon dioxide gas could be produced by the reaction of 25.0 L of methane with an excess of oxygen at SLC?
 Step 1: Calculate the number of moles of methane gas used.

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 $V_{SIC} = n \times 24.5$  $25.0 = n \times 24.5$ 25.0 24.5 n = 1.02 mol of methane gas Step 2: Use the balanced equation to calculate the number of moles of  $CO_2$  produced from 1.02 mol of  $CH_4$ . From the equation,  $n(CO_2) = n(CH_4)$ Therefore, 1.02 mol  $CH_4$  will produce 1.02 mol  $CO_2$ . Step 3: Calculate the volume of CO<sub>2</sub> produced. At SLC,  $V_{\rm SLC} = n \times 24.5$  $V = 1.02 \times 24.5$ V = 25.0 LThe volume of  $CO_2$  is 25.0 L. **b** What mass of water vapour could be produced by the reaction of 10.0 g of methane at STP? Step 1: Calculate the number of moles of methane used.  $n = \frac{m}{m}$ М  $n = \frac{10.0}{10.0}$ 16.0  $n = 0.625 \text{ mol of } CH_4$ Step 2: Use the balanced equation to determine the number of moles of water vapour produced. From the equation, 1 mole of  $CH_4$  produces 2 moles of  $H_2O$ . Therefore  $n(H_2O) = 2 \times n(CH_4)$  $= 2 \times 0.625$ = 1.25 The amount of water vapour produced is 1.25 mol. Step 3: Calculate the mass of water vapour produced. Use the formula  $n = \frac{m}{m}$ т 1.25 = -18.0  $m = 1.25 \times 18.0$ *m* = 22.5 g The mass of H2O(g) produced is 22.5 g. Questions **36** Carbon monoxide reacts with water to produce 4.40 L of H<sub>2</sub>S if the system is at a pressure of carbon dioxide according to the equation: 1 atm and a temperature of 300°C?  $CO(g) + H_2O(g) \rightarrow H_2(g) + CO_2(g)$ **38** Ammonia can be prepared from hydrogen and nitrogen according to the equation: At STP, how many litres of carbon dioxide could be produced from 750 g of carbon monoxide?  $N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$ **37** For the reaction: What mass of nitrogen would be needed to

 $2H_2S(g) + O_2(g) \rightarrow 2S(g) + 2H_2O(g)$ what mass of sulfur could be produced from

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produce 65.0 L of ammonia at SLC?

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## Summary **DDDD**

- Gases have a low density, are easily compressed and mix rapidly. The kinetic molecular theory of gases explains gas behaviour. Gas particles move from one place to another by the process of diffusion. Diffusion rate is dependent on the temperature and molar mass of the gas.
- Pressure is the force per unit of area exerted by the particles of a gas. Pressure is commonly measured in units of mmHg, atmospheres and pascals.
- In a mixture of gases, each gas will exert its individual partial pressure as if it were alone in the container. Dalton's Law of Partial Pressures states that the total pressure of a mixture of gases is equal to the sum of the individual partial pressures.
- Volume is the space occupied by the particles of a gas. Volume is commonly measured in units of litres (L), millilitres (mL) and cubic centimetres (cm<sup>3</sup>).
- Temperature of gases for use in gas calculations is measured using the kelvin scale. Zero kelvin is also known as absolute zero. Celsius temperatures are converted to kelvin by K = °C + 273.
- **Boyle's Law** derives to the formula  $P_1V_1 = P_2V_2$ .
- Charles' Law derives to the formula  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ .

- The pressure-temperature relationship at a fixed amount and volume of gas can be expressed as  $\frac{P_1}{T_1} = \frac{P_2}{T_2}.$
- The volume-number of moles relationship at a constant temperature and pressure can be expressed as  $\frac{V_1}{n_1} = \frac{V_2}{n_2}$ .
- The combined gas equation derives to the formula  $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ .
- The ideal gas equation (General Gas Equation) states that PV = nRT where R is the universal or ideal gas constant, whose value is dependent on the pressure measurement of the system.
- Avogadro's hypothesis states that equal volumes of gas at the same temperature and pressure contain the same number of particles. Molar volume is the volume occupied by one mole of a gas under particular conditions of temperature and pressure. At STP (0°C and 1 atm), molar volume equals 22.4 L. Under SLC (25°C and 1 atm) molar volume equals 24.5 L.

## Key terms

absolute zero Avogadro's hypothesis Boyle's Law Charles' Law combined gas equation Dalton's Law of Partial Pressures diffusion ideal gas equation (General Gas Equation) kelvin scale kinetic molecular theory molar volume partial pressure pressure pressure–temperature relationship SLC STP universal (or ideal) gas constant volume–number of moles relationship



## **Chapter Review**

# 5.1 Physical properties of gases

**39** Describe the main physical properties of gases.

## 5.2 Kinetic molecular theory

- **40** Describe the main points of the kinetic molecular theory of gases.
- **41** Explain Dalton's Law of Partial Pressures.
- **42** A flask containing a mixture of methane gas (CH<sub>4</sub>) and argon gas has its stopper removed. Explain which gas you would expect to diffuse more rapidly from the unsealed flask.
- 43 A sealed flask contains a mixture of three gases. The oxygen gas is exerting a pressure of 0.35 atm. The nitrogen gas is exerting a pressure of 71.0 kPa. The carbon dioxide gas is exerting a pressure of 125 mmHg. What is the total pressure (in atm) being exerted by the gases in the flask?

## 5.3 Measuring pressure and volume

- 44 Perform the following pressure unit conversions.a the atmospheric pressure on Venus (75 atm) to kilopascals
  - **b** 680 mmHg to kilopascals
- **45** Perform the following volume unit conversions.
  - a 23 mL to L
  - **b**  $85 \text{ cm}^3 \text{ to L}$
  - **c** 725 cm<sup>3</sup> to m<sup>3</sup>
- **46** Perform the following temperature unit conversions.
  - a 5°C to K
  - **b** 395 K to °C
  - **c** 10 K to °C
  - d  $-95^{\circ}$ C to K

## 5.4 The gas laws

- **47** A sample of gas occupies a volume of 500 mL at a pressure of 95.0 kPa. Calculate the pressure of the gas assuming the temperature remains constant, when the volume is changed to:
  - **a** 100 mL
  - **b** 3.50 L

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**48** A gas sample occupies a volume of 5.50 L at a temperature of 15°C. Calculate the volume of the gas when the temperature is changed to 25°C.

- **49** A sample of air at a pressure of 60.0 kPa at 10°C is heated to 80°C. Calculate the new pressure if the gas, assuming the volume remains constant.
- **50** A 5.00 L sample of gas at 25°C and 0.90 atm pressure expands to a volume of 9.50 L. The new pressure of the gas is 0.35 atm. Calculate the change in temperature, in °C, the gas has experienced.
- **51** A gas occupies a volume of 23.5 L at a temperature of 20.0°C. The gas has its temperature changed to 35.0°C. At this temperature the gas occupies a volume of 28.5 L and exerts a pressure of 135 kPa. What was the original pressure of the gas?
- **52** A 3.00 L sample of gas contains 0.85 mol of gas. What will its volume expand to if the number of moles is doubled?
- **53 a** A sample of 2.20 moles of gas occupying a volume of 2.50 L is kept at a constant temperature and pressure. How many moles of gas must be added to the sample to increase its volume to 4.00 L?
  - **b** If the gas involved was carbon dioxide, how many grams of gas would need to be added to increase the volume to 4.00 L?

## 5.5 The General Gas Equation

- **54 a** Under what conditions do real gases behave most like ideal gases?
  - **b** Use the kinetic molecular theory to explain why real gases do not behave ideally at low temperatures.
- 55 A sample of 0.0500 moles of gas at 5°C occupies a volume of 500 mL. Calculate the pressure (in kPa) of the gas.
- **56** Calculate the volume of 25.0 g of nitrogen gas at 28°C and 110 kPa pressure.
- **57** At what temperature will 2.40 g of carbon dioxide gas exert a pressure of 75.06 kPa in a 5.00 L container?
- **58** A container of oxygen holds 15.0 L at a pressure of 0.850 atm and a temperature of 20°C. What mass of oxygen is in the container?

## 5.6 Molar volume

59 What is molar volume?

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- **60** Calculate the volume at SLC occupied by:
  - a 15.5 g of nitrogen gas
  - **b**  $1.50 \times 10^{22}$  atoms of neon gas.

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- **61** Calculate the mass of gas present in each of the following samples at STP.
  - a 30.0 L of carbon monoxide
  - **b** 5.50 L of hydrogen
- 62 a A 7.49 g sample of gas occupies a volume of 5.49 L at STP. What is the molar mass of the gas?
  - **b** Explain which of the following gases the sample is most likely to be: carbon dioxide, methane, ammonia or oxygen.

# 5.7 Stoichiometric calculations involving gases

**63** Sodium metal reacts vigorously (sometimes explosively) with water to give off hydrogen gas. The equation for this reaction is:

 $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$ 

If 3.50 g of sodium reacts with an excess of water, how many litres of hydrogen gas would be produced at STP?

64 A sample of oxygen gas with a volume of 16.7 L at 19.0°C and 98 kPa reacts with an excess of hydrogen gas to form water. What mass of hydrogen gas is required to react with all of the oxygen? **65** Chlorine gas can be produced from the electrolysis of aqueous sodium chloride according to the equation:

 $2NaCl(aq) + 2H_2O(l)$ 

 $\rightarrow$  2NaOH(aq) + H<sub>2</sub>(g) + Cl<sub>2</sub>(g)

The chlorine gas is collected in a container. What is the minimum volume needed for the container if the gas is collected at 95.0 kPa and 23°C from a sample of NaCl of mass 1.25 kg which reacts completely?

**66** Lithium metal reacts with nitrogen gas according to the equation:

 $6Li(s) + N_2(g) \rightarrow 2Li_3N(s)$ 

A sample of lithium at a temperature of 20°C was placed into a 2.00 L container of nitrogen gas at a pressure of 2.15 atm. A later measurement showed that the pressure in the container had changed to 1.88 atm.

- a Calculate the mass of nitrogen gas which reacted with the lithium.
- **b** If the entire lithium sample reacted, what mass of lithium was originally placed into the container?



# Precipitation reactions

## **6.1 Types of chemical reactions**

There are many ways chemical reactions can be classified. One common method places reactions into one of four categories:

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- **1** combination reactions
- 2 decomposition reactions
- 3 single replacement reactions
- 4 double replacement reactions.

This method of classification covers a large number of chemical reactions, but by no means all reactions.

## **Combination reactions**

A **combination reaction** is a reaction in which two or more reactants combine to form a single product (which must be a compound). For example, magnesium metal burns in oxygen to produce magnesium oxide.

 $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$ 

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**Combination reactions** form a single product from two or more\_\_\_\_\_

Calcium oxide combines with carbon dioxide to produce calcium carbonate.

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



**figure 6.1** The vigorous combination reaction between sodium metal and chlorine gas forms sodium chloride (commonly known as salt).

## **Decomposition reactions**

Decomposition reactions are often called the opposite of combination reactions. In a **decomposition reaction** a single reactant breaks down into two or more products. For example, water can be decomposed to hydrogen gas and oxygen gas.

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

The heating of potassium chlorate gives off oxygen gas leaving solid potassium chloride.

 $2\text{KClO}_3(s) \rightarrow 2\text{KCl}(s) + 3\text{O}_2(g)$ 



**figure 6.2** The Hofmann voltammeter uses electric current to cause the decomposition reaction of water into hydrogen and oxygen gases.

## Single replacement reactions

In a **single replacement reaction** one element in a compound is replaced by another element. For example, a copper wire when placed into a solution of silver nitrate will grow crystals of silver.

 $Cu(s) + 2AgNO_3(aq) \rightarrow 2Ag(s) + Cu(NO_3)_2(aq)$ 

Magnesium metal when placed in hydrochloric acid produces hydrogen gas and magnesium chloride.

 $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$ 

Two or more products are formed from a single reactant in **decomposition reactions**. 6

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In a single replacement reaction, an element reacts with a compound to form a different element and a new compound.



**figure 6.3** Bubbles of hydrogen gas are produced in the single replacement reaction between magnesium ribbon and hydrochloric acid.

**Double replacement reactions** 

In a **double replacement reaction**, cations and anions swap partners to form new compounds. For example, sodium chloride reacts with silver nitrate to form sodium nitrate and silver chloride.

 $NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$ 

Hydrochloric acid reacts with a solution of sodium hydroxide to produce water and sodium chloride solution. This type of reaction in which an acid reacts with a base to form a salt and water is also known as a neutralisation reaction.

 $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$ 



**figure 6.4** The double replacement reaction between aqueous solutions of barium chloride and sodium sulfate produces a visible change in the reacting mixture.

Table 6.1 gives a simplified general description for each of the four types of reactions.

table 6.1 Types of chemical reactions.			
Reaction type	General statement		
combination	$A + B \rightarrow C$		
decomposition	$A \rightarrow B + C$		
single replacement	$A + BC \rightarrow AC + B$		
double replacement	$AB + CD \rightarrow AD + CB$		

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Double replacement reactions occur when two compounds in solution react by replacing one of their ions with an ion from the other compound.

## Questions

precipitation reaction.

- 1 Classify each of the following reactions as one of the four reaction types described in section 6.1.
  - **a**  $2K(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2(g)$
  - **b**  $P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(l)$
  - **c**  $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
  - **d**  $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$
  - e  $H_2SO_4(aq) + 2LiOH(aq) \rightarrow Li_2SO_4(aq) + 2H_2O(l)$
  - $\mathbf{f} \quad \mathsf{Zn}(s) + \mathsf{Cu}(\mathsf{NO}_3)_2(\mathsf{aq}) \to \mathsf{Cu}(s) + \mathsf{Zn}(\mathsf{NO}_3)_2(\mathsf{aq})$
  - $\textbf{g} \quad Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$

6.2 Precipitation reactions

In some double replacement reactions one of the new combinations forms an insoluble compound which separates from the solution. This solid which forms from the reaction of two solutions is called a **precipitate**. This type of

double replacement reaction in which a precipitate forms is called a

**h**  $2HgO(s) \rightarrow 2Hg(l) + O_2(g)$ 

- **2** Predict the formula of the missing substance in each of the following equations.
  - **a**  $2\text{KClO}_3(g) \rightarrow 2\text{KCl}(s) + 3$  (g)
  - **b**  $Fe(s) + 2HBr(aq) \rightarrow (aq) + H_2(g)$
  - **c**  $Ca(OH)_2(aq) + 2HBr(aq) \rightarrow (aq) + 2H_2O(l)$
  - **d**  $BaCO_3(s) \rightarrow \_\_(s) + CO_2(g)$
  - **e** 4 (s) +  $30_2(g) \rightarrow 2Al_2O_3(s)$
  - **f**  $Zn(s) + 2HBr(aq) \rightarrow ZnBr_2(aq) + (g)$



A **precipitation reaction** occurs when one of the new combinations in a double replacement reaction forms a compound which is insoluble in the reacting solution.

table 6.2 A solubility guide for	common ionic compounds	. )		
Soluble ioni	ic compounds	Insoluble ionic compounds		
Most compounds of the following ions are soluble	Important exceptions	Most compounds of the following ions are insoluble	Important exceptions	
nitrate NO <sub>3</sub> <sup>-</sup>	none	sulfide (S <sup>2-</sup> )	Na <sub>2</sub> S, K <sub>2</sub> S, Li <sub>2</sub> S, (NH <sub>4</sub> ) <sub>2</sub> S	
ethanoate (CH₃COO <sup>-</sup> ) [common name: acetate]	none	carbonate ( $CO_3^{2-}$ )	Na <sub>2</sub> CO <sub>3</sub> , K <sub>2</sub> CO <sub>3</sub> , Li <sub>2</sub> CO <sub>3</sub>	
sodium, potassium (Na <sup>+</sup> , K <sup>+</sup> )	none	phosphate (PO <sub>4</sub> <sup>3–</sup> )	Na <sub>3</sub> PO <sub>4</sub> , K <sub>3</sub> PO <sub>4</sub> , Li <sub>3</sub> PO <sub>4</sub>	
ammonium (NH₄⁺)	none	hydroxide (OH <sup>−</sup> )	NaOH, KOH, Ba(OH) <sub>2</sub> Ca(OH) <sub>2</sub> is slightly soluble	
chloride (Cl⁻)	AgCl, HgCl₂, PbCl₂ is slightly soluble			
bromide (Br <sup>-</sup> )	AgBr, HgBr2, PbBr2			
iodide (I⁻)	Agl, Hgl <sub>2</sub> , Pbl <sub>2</sub>			
sulfate (SO <sub>4</sub> <sup>2-</sup> )	$Ag_2SO_4$ , $BaSO_4$ , PbSO <sub>4</sub> , SrSO <sub>4</sub> CaSO <sub>4</sub> is slightly solubl	e	$\overline{\bigcirc}$	
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The **precipitate** is the insoluble substance which separates out from the solution in a double replacement reaction.

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Precipitation reactions

## / Worked example 6.2A

When solutions of lead(II) nitrate and potassium iodide are mixed, a precipitate forms. Write a balanced chemical equation for this reaction. Step 1: Write a word equation for the reaction.

The products of the reaction come from swapping the partners of the ion pairs.

lead(II) nitrate + potassium iodide  $\rightarrow$  lead(II) iodide + potassium nitrate Step 2: Rewrite the equation using the formulae for reactants and products.

 $Pb(NO_3)_2 + KI \rightarrow PbI_2 + KNO_3$ 

Step 3: Balance the equation.

 $Pb(NO_3)_2 + 2KI \rightarrow PbI_2 + 2KNO_3$ 

Step 4: Determine which of the new combinations is the precipitate and label the state of each substance accordingly.

From table 6.2, we see that nitrates are soluble with all common cations, so the precipitate could not be the KNO3. This leaves the lead iodide and the table confirms that this combination is insoluble.

 $Pb(NO_3)_2(aq) + 2KI(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$ 



Worksheet 1 Types of chemical reactions

## Questions

LCHEMICAL REACTIONS

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- **3** Write the chemical formula for the precipitate formed (if any) from the following combinations of solutions.
  - a silver nitrate and sodium sulfide
  - **b** zinc nitrate and sodium carbonate
  - c iron(III) nitrate and sodium hydroxide
  - **d** potassium nitrate and lithium hydroxide
  - e lithium carbonate and magnesium nitrate
- **4** Complete the following precipitation reactions then balance the equations.
  - **a** AgNO<sub>3</sub>(aq) + H<sub>2</sub>SO<sub>4</sub>(aq)  $\rightarrow$
  - **b**  $Pb(NO_3)_2(aq) + Nal(aq) \rightarrow$

- **c** AgNO<sub>3</sub>(aq) + Na<sub>2</sub>S(aq)  $\rightarrow$
- **d** BaCl<sub>2</sub>(aq) + Na<sub>2</sub>SO<sub>4</sub>(aq)  $\rightarrow$  \_
- e  $Pb(NO_3)_2(aq) + KOH(aq) \rightarrow$
- 5 Write a balanced equation for the precipitation reactions from the mixing of the following solutions.
  - a ammonium sulfate and barium chloride
  - **b** potassium sulfide and lead(II) nitrate
  - c copper(II) sulfate and sodium carbonate
  - **d** sodium phosphate and calcium nitrate

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# 6.3 Ionic equations

The balanced equation for a precipitation reaction discussed in section 6.2 does not give a completely accurate description of the nature of the solutions involved. In an aqueous solution, an ionic substance exists as separate ions in solution, not as a compound. For example in the formation of a precipitate of lead(II) iodide, the original solutions from the equation would be more accurately written as follows:

 $Pb(NO_3)_2(aq) \rightarrow Pb^{2+}(aq) + 2NO_3^{-}(aq)$ 

 $2KI(aq) \rightarrow 2K^{+}(aq) + 2I^{-}(aq)$ 

Rewriting the whole balanced equation in this manner would produce the equation:

 $Pb^{2+}(aq) + 2NO_3^{-}(aq) + 2K^{+}(aq) + 2I^{-}(aq) \rightarrow PbI_2(s) + 2K^{+}(aq) + 2NO_3^{-}(aq)$ 



figure 6.6 Possible exchange of ions in solution.

This is called an **overall ionic equation** for the reaction. The precipitate is not soluble and therefore does not dissociate into ions to a significant degree, so it is written with a solid phase notation.

Closer examination of an overall ionic equation shows that there are some ions which appear as both reactants and products, having remained unchanged throughout the reaction. These ions are called **spectator ions** as they do not participate in the reaction. In the case of the equation for the precipitation of PbI<sub>2</sub>, the K<sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions act as spectator ions in the reaction. For convenience, these ions can be left out of the chemical equation. In the case of the precipitation of PbI<sub>2</sub> this would leave the equation:

 $Pb^{2+}(aq) + 2I^{-}(aq) \rightarrow PbI_{2}(s)$ 

This is called a **net ionic equation** as it shows only the substances involved in the formation of the precipitate.



#### Introduction

The mixing of two aqueous solutions may result in a double replacement reaction in which one of the new ion pairs forms an insoluble compound. This insoluble compound appears in the solution as a precipitate. The ions remaining in the solution which are not involved in the formation of the precipitate are called spectator ions.

### Purpose

To mix aqueous solutions and observe the formation of a precipitate from the reaction.

# orksheet lonic equations An overall ionic equation shows all of the ion involved in a double Spectator ions are the ions which remain unchanged in a double A net ionic equation describes only the substances involved in the reaction which forms a materials small dropping bottles containing 0.1 M aqueous solutions of the compounds: sodium carbonate sodium iodide lead(II) nitrate copper(II) sulfate barium chloride silver nitrate small test tubes test-tube rack

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Precipitation reactions

#### safety

- Wear safety glasses and a laboratory coat for this experiment.
- Some compounds in this experiment may cause irritation to eyes, skin and respiratory system. They may be harmful if inhaled or swallowed.
- Compounds of barium and lead are toxic.
   Silver nitrate causes
- brown staining to skin and clothing. It is corrosive.
- Dispose of the resulting solutions by flushing down the sink with plenty of water.

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#### Method

- 1 Place a clean, dry test tube into the test-tube rack.
- 2 Drop 10 drops of lead nitrate into the test tube, then 10 drops of sodium iodide.
- 3 Repeat steps 1 and 2 for the following combinations of solutions: lead(II) nitrate + sodium carbonate lead(II) nitrate + barium chloride lead(II) nitrate + copper(II) sulfate silver nitrate + sodium iodide silver nitrate + barium chloride silver nitrate + sodium carbonate copper(II) sulfate + barium chloride copper(II) sulfate + sodium carbonate
  - barium chloride + sodium carbonate

#### Results

Design a table for your results. The table should include the aqueous solutions mixed as well as your observations of the results of the reaction.

#### Discussion

- 1 Write a net ionic equation for each of the reactions in which you observed a precipitate.
- 2 State which ions acted as spectator ions for each reaction in which a precipitate occurred.
- **3** Using substances from this experiment, write two different combinations of ions which would not be expected to form a precipitate.
- 4 Describe a simple method you could use to obtain a solution of sodium nitrate from aqueous solutions of sodium iodide and silver nitrate.

## 一 医xperilmenでもの。 Identifying unknowns using precipitation

#### Introduction

One method that can be used to determine the identity of certain ions in solutions is using precipitation. When aqueous solutions are mixed and a precipitate forms, information such as table 6.2 can be used to determine what the precipitate is likely to be.

#### Purpose

To determine the identity of an unknown solution using a knowledge of precipitation reactions.

#### Method

- 1 Collect dropping bottles of the solutions supplied.
- 2 Add a small amount of the solution (up to 10 drops) from a dropping bottle to a small amount of your unknown solution in a test tube or the spot tray.
- **3** Repeat this procedure until you have enough results to identify your unknown substance.

#### materials

- unknown solution labelled A, B, C or D, which could be potassium nitrate, sodium chloride, sodium sulfate or sodium hydroxide
- small dropping bottles containing 0.1 M solutions of the nitrates of:
  - lead silver zinc barium copper calcium magnesium ammonium

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potassium spot tray or small test tubes and test-tube rack

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### Results

Design a suitable table to present the results of mixing your unknown with the known solutions supplied. The table should include observations of the results of mixing the known solutions with your unknown substance.

#### Discussion

- 1 Write a net ionic equation for each reaction which formed a precipitate when the known solutions were mixed with the unknown solution.
- 2 State the name and chemical formula of the unknown solution.
- **3** Use experimental evidence and information from table 6.2 to give reasons justifying your choice for the unknown solution.
- 4 The labels have fallen off of the dropping bottles of lead(II) nitrate and magnesium nitrate. Design a simple method using precipitation reactions that could be used to identify the solutions so that the bottles could be re-labelled.

#### safety

- Wear safety glasses and a laboratory coat for this experiment.
- Some compounds in this experiment may cause irritation to eyes, skin and respiratory system. They may be harmful if inhaled or swallowed.
- Compounds of lead are highly toxic by all means of exposure.
- Silver nitrate causes dark brown staining to skin and clothing.
- Dispose of the resulting solutions by flushing down the sink with plenty of water.

## Questions

- 6 Write balanced equations to show the dissociation into ions when each of the following solids is dissolved into water.
  - **a** copper(II) nitrate
  - **b** sodium phosphate
  - c potassium carbonate
  - d lithium sulfate
  - e silver nitrate
  - **f** iron(II) chloride
- 7 Write an overall ionic equation for each of the following precipitation reactions between the given solutions.
  - a silver nitrate + sodium chloride
  - **b** potassium carbonate + calcium nitrate
  - c potassium phosphate + lead(II) nitrate
  - **d** magnesium chloride + silver nitrate
  - e copper(II) chloride + lithium hydroxide
  - **f** ammonium phosphate + zinc sulfate

- 8 Write an overall ionic equation then the corresponding net ionic equation for each of the following.
  - a silver nitrate + sodium bromide
  - **b** mercury(II) nitrate + potassium iodide
  - c strontium chloride + ammonium sulfate
  - **d** barium hydroxide + sodium carbonate
  - e magnesium chloride + lithium phosphate
  - **f** sodium hydroxide + iron(II) nitrate
- 9 Write a net ionic equation for each of the following precipitation reactions.
  - a lead(II) nitrate + copper(II) chloride
  - **b** sodium sulfate + barium chloride
  - **c** barium nitrate + potassium sulfate
  - **d** silver nitrate + lithium sulfate
  - e mercury(II) nitrate + magnesium sulfate
  - **f** ammonium carbonate + calcium chloride



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## Summary **DDDD**

- Many chemical reactions can be classified as one of four types.
- Combination reactions involve two or more reactants forming a single product.
- Decomposition reactions involve a single reactant forming two or more products.
- One element in a compound is relaced by another in a single replacement reaction.
- In a double replacement reaction two ionic substances swap partners to form new substances.
- A double replacement reaction in which one of products forms an insoluble compound is called a precipitation reaction. The insoluble compound formed in the reaction is called a precipitate.
- An overall ionic equation represents the ions as they exist in aqueous solution. Ions which do not take part in the precipitation process are called **spectator ions**. A **net ionic equation** eliminates the spectator ions and shows only the substances involved in the precipitation process.

## Key terms

combination reaction decomposition reaction double replacement reaction net ionic equation overall ionic equation

precipitate precipitation reaction

single replacement reaction spectator ions



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## Chapter **Review**

# 6.1 Types of chemical reactions

- **10** Classify each of the following reactions as one of the four types of reactions described in section 6.1.
  - a  $N_2O_5(s) + H_2O(l) \rightarrow 2HNO_3(aq)$
  - **b**  $BaCO_3(s) \rightarrow BaO(s) + CO_2(g)$
  - c AgNO<sub>3</sub>(aq) + HCl(aq)  $\rightarrow$  AgCl(s) + HNO<sub>3</sub>(aq)
  - **d**  $Cu(s) + 2AgNO_3(aq) \rightarrow 2Ag(s) + Cu(NO_3)_2(aq)$
  - e Pb(s) + 2HBr(aq)  $\rightarrow$  PbBr<sub>2</sub>(s) + H<sub>2</sub>(g)
  - f RbOH(aq) + HNO<sub>3</sub>(aq)  $\rightarrow$  RbNO<sub>3</sub>(aq) + H<sub>2</sub>O(l)
- **11** Complete the following equations. Include balancing coefficients and giving states where necessary.
  - a \_\_\_\_\_ +  $2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$
  - **b**  $Ba(NO_3)_2(aq) + K_2SO_4(aq) \rightarrow BaSO_4(s) + \_$
  - **c**  $C(s) + \_\_ \rightarrow CO_2(g)$
  - **d**  $_{2}HgO(s) \rightarrow \_\__ + O_2(g)$

## 6.2 Precipitation reactions

- **12** State the formula for the expected precipitate from the following combinations of solutions.
  - **a** barium nitrate + lithium sulfate
  - **b** silver nitrate + sodium sulfate
  - c sodium hydroxide + zinc nitrate
  - **d** potassium sulfide + aluminium nitrate
  - e copper(II) chloride + ammonium sulfide
- **13** For each substance listed, state two aqueous solutions that could be mixed to form a precipitate of the substance.
  - a Agl
  - **b** PbS
  - **c**  $Mg_3(PO_4)_2$
  - d NiCO<sub>3</sub>
  - e Al(OH)<sub>3</sub>

- 14 Predict the precipitate formed in the reactions below and write a balanced equation for each.a silver nitrate + ammonium bromide
  - **b** sodium hydroxide + nickel(II) chloride
  - c magnesium bromide + potassium carbonate
  - **d** sodium sulfate + silver fluoride
  - e calcium chloride + sodium carbonate

## 6.3 Ionic equations

- **15** Write a balanced equation to show the dissociation in water for the following ionic compounds.
  - a copper(II) chloride
  - **b** potassium hydroxide
  - c barium sulfide
  - d ammonium carbonate
  - e magnesium bromide
- **16** Write overall ionic equations for the following reactions.
  - a silver nitrate + potassium chloride
  - **b** nickel(II) chloride + magnesium sulfide
  - c lithium hydroxide + magnesium chloride
  - **d** sodium chloride + mercury(II) nitrate
  - e calcium chloride + potassium carbonate
- **17** Write net ionic equations for the following reactions.
  - **a** potassium carbonate + silver nitrate
  - **b** magnesium nitrate + sodium hydroxide
  - c strontium chloride + potassium sulfate
  - **d** calcium nitrate + lithium carbonate
  - e sodium bromide + lead(II) nitrate
- **18** State the spectator ions in the following reactions.
  - a silver nitrate + potassium iodide
  - **b** lithium sulfate + barium chloride
  - **c** strontium chloride + sodium carbonate
  - **d** aluminium chloride + sodium hydroxide
  - e potassium sulfate + barium nitrate

# Redox reactions

## 😰 Oxidation and reduction

The word 'redox' is a short form of two words, reduction and oxidation, once used to describe two different chemical processes. Like all reactions, redox reactions form new substances or products, and some or all of the reactants disappear. They include many reactions that are familiar everyday processes, such as combustion, the extraction and corrosion of metals, discolouration of fruit, and essential life reactions such as photosynthesis and respiration.

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figure 7.1 Extraction of iron in a blast furnace is a redox reaction.

The combustion reactions of carbon, C, and of methane,  $CH_4$ , are shown in the equations below.

$$\begin{split} &C(s)+O_2(g)\rightarrow CO_2(g)\\ &CH_4(g)+2O_2(g)\rightarrow CO_2(g)+2H_2O(g) \end{split}$$

Many metals are also readily oxidised, as in the example below.

 $2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$ 

The term reduction originally described the extraction of a metal from an ore. The resulting metal has a smaller mass than the mineral from which it was extracted. So this type of reaction became known as reduction.

For example, lead sulfide (or galena) is reduced to lead.

 $PbS(s) + O_2(g) \rightarrow Pb(s) + SO_2(g)$ 

In a blast furnace, coke is used to reduce iron(III) oxide to iron. Coke is an almost pure form of solid carbon, made from coal. The coke is first converted to carbon monoxide.

 $2C(s) + O_2(g) \rightarrow 2CO(g)$ 

Then the carbon monoxide reduces the iron oxide, in reactions like the one below.

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

Notice that oxygen is present in both reactions. In the second reaction, oxygen has been removed from the iron. This is reduction. Oxygen is combining with carbon monoxide, much like during a combustion reaction. This is oxidation. Reduction processes always occur at the same time as oxidation processes, and often involve the removal of oxygen.

In the extraction of iron, iron(III) oxide is reduced to pure iron. The carbon of carbon monoxide has been oxidised to form carbon dioxide.



2 Write a formula for each of the coatings.

**Redox reactions** 

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#### materials

- steel wool or sand paper
- magnesium strips
  wood, e.g. icy-pole stick
- wood, e.g. icy-pole si
  Bunsen burner
- matches
- matches
- evaporating dishcrucible and lid
- cruciple a
- tripod

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- clay triangle
- electronic balance
- metal tongs

#### safety

- Wear safety glasses and a laboratory coat for this experiment.
- Do not look directly at burning magnesium.

#### Purpose

To determine the nature of the products of two oxidation processes, and relate this to the mass change.

Experiment 7.2

Investigating combustion

#### Method

- 1 Heat the crucible and lid for 10 minutes, to remove moisture and volatile contaminants. Cool. Handle with tongs only.
- 2 Weigh the clean, dry evaporating dish, and the crucible with its lid. Record the masses.
- **3** Weigh a cleaned, coiled magnesium strip in the crucible with its lid. Weigh the icy-pole stick in the clean, dry evaporating dish. Record these masses.
- 4 Using tongs, hold the icy-pole stick in the Bunsen burner flame, until it catches alight. Place in the evaporating dish to catch any solid residue and burn completely.
- 5 Note the appearance of visible products and reweigh.
- 6 Heat the magnesium in the crucible with the lid slightly ajar. Continue heating until all the magnesium has reacted. Allow to cool.
- 7 Note the appearance of visible products and reweigh.

#### Results

All masses should be recorded. Also record the appearance of the substances before and after combustion.

#### Discussion

- 1 Calculate the mass of the unburnt icy-pole stick and the magnesium strip.
- 2 Calculate the masses of the different combustion products.
- **3** Compare the mass of the original substances with their combustion products. Explain.
- 4 How can reactions with oxygen explain these results?

## Questions

- 1 Write balanced equations for the combustion of: a ethane,  $C_2H_6$ 
  - **b** magnesium, Mg
  - **c** sodium, Na

LCHEMICAL REACTIONS

- **d** 1-propanol, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH.
- 2 Explain why the oxidation of a metal results in a product of greater mass than the original pure metal.
- **3** If lead(II) oxide is combined with carbon and heated, tiny drops of lead metal appear. The reaction for this process is

#### $PbO(s) + C(s) \rightarrow Pb(s) + CO(g)$

Which substance is being oxidised and which is being reduced in this process? Explain your answer.

4 Write a balanced equation for the roasting of copper sulfide, CuS, using oxygen from air, to form copper metal.

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# 7.2 Redox reactions

## **Electron transfer**

All of the reactions above have one aspect in common. They all involve the complete or partial transfer of electrons from one reactant to another.

To understand this, we will first of all look at reactions involving complete transfer of electrons. Recall the reaction in Experiment 7.2 in which magnesium reacted with oxygen to form magnesium oxide. Magnesium and oxygen are both pure elements. They have no overall charge and thus atoms of magnesium and atoms of oxygen are neutral. But magnesium oxide is a solid ionic compound. It is composed of a lattice of  $Mg^{2+}$  ions and  $O^{2-}$  ions. When the magnesium was oxidised, each magnesium atom lost two electrons. At the same time, each oxygen atom gained two electrons. The process of oxidation is associated with the loss of electrons. The process of reduction is associated with the gain of electrons. These processes always occur together and are called oxidation-reduction reactions or redox reactions.

A redox reaction can be expressed as two half equations, as shown below.

 $Mg \rightarrow Mg^{2+} + 2e^{-}$ 

This half equation shows the oxidation reaction during which each magnesium atom loses electrons. The two electrons are shown on the right, as they are released, to be gained by the oxygen atom.

 $O_2 + 4e^- \rightarrow 2O^{2-}$ 

This half equation shows the reduction reaction during which each oxygen atom gains two electrons to form an oxide ion. The electrons are shown on the left, as they are being accepted by oxygen.

We can add the two half equations to make a complete redox equation. To balance it, we must first ensure the total number of electrons gained and the total number of electrons lost is equal. We do this by multiplying the oxidation half equation by 2.

 $[Mg \rightarrow Mg^{2+} + 2e^{-}] \times 2$  $O_2 + 4e^{-} \rightarrow 2O^{2-}$ 

The two half equations become:

 $2Mg \rightarrow 2Mg^{2+} + 4e^ O_2 + 4e^- \rightarrow 2O^{2-}$ 

The 4e<sup>-</sup> on each side cancel, and the equations add to give:

 $2Mg + O_2 \rightarrow 2Mg^{2+} + 2O^{2-}$ or  $2Mg + O_2 \rightarrow 2MgO$ 

In the example above, magnesium was oxidised and caused oxygen to be reduced. Magnesium is called a reductant, or reducing agent. The reductant is a substance that causes another substance to be reduced, but is itself oxidised.

The oxidant or oxidising agent is a substance that causes another to be oxidised, but is itself reduced. In this example, the oxidant is oxygen.

Not all redox reactions involve oxygen, as we shall see in the next experiment.







Oxidation is the loss or partial loss of one or more electrons by a reactant. **Reduction** is the gain or partial gain of one or more electrons by a



The mnemonic **OIL RIG** can be used to remember these processes. The letters stand for **o**xidation is loss, reduction is gain.

A half equation shows either oxidation or reduction. Two half



equations by whole number factors to make



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#### Purpose

To determine the reactants and products in a redox reaction not involving oxygen.

#### Method

- 1 Form the copper wire into a coil, by wrapping it around a pencil.
- 2 Place it in the test tube and cover it with silver nitrate solution.
- **3** Observe for at least half an hour, noting any gradual changes. Leave overnight if you wish. Record all observations.

#### Discussion

- 1 What evidence for new products did you observe?
- 2 From this evidence, what new products have been formed?
- 3 Write half equations and an overall equation for the redox process.
- 4 Describe what is occurring at an atomic level in terms of atoms, ions and electron exchange.

## Partial electron transfer

Many redox reactions do not involve the complete transfer of electrons, but can still be identified as redox processes. These are usually reactions involving nonmetals, the elements on the right-hand side of the periodic table. Some examples of these reactions are the combustion of carbon and its compounds.

Look closely at the incomplete combustion of carbon to form carbon monoxide. The equation is shown below.

#### $2C(s) + O_2(g) \rightarrow 2CO(g)$

Pure elemental carbon is not ionic. Atoms in a covalent network lattice share electrons equally in covalent bonds. In oxygen molecules, the electrons are also shared equally in covalent bonds.

In the product, carbon monoxide, each oxygen atom is bonded covalently to a carbon atom. As oxygen has a higher electronegativity than carbon, it attracts the electrons in the covalent bond more strongly. The bonds in CO are polar covalent, rather than ionic. The electrons are partly transferred to oxygen, and carbon experiences a partial loss of electrons. Oxygen has been reduced and carbon has been oxidised.





#### materials

- 20 cm copper wire0.1 M silver nitrate
- solution (AgNO<sub>3</sub>) test tube
- test-tube rack
- copper(II) nitrate solution (for reference)

#### safety

- Wear safety glasses and a laboratory coat for this experiment.
- Reactants and products are toxic. Dispose of in container provided.
- Wash hands thoroughly.
   Silver nitrate can stain skin, clothing and benches.

the charge transfer is

LCHEMICAL REACTIONS

partial. The transferred

. charge is not as large as the charge on one electron

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## Questions

- 5 Identify each of the following processes as oxidation or reduction.
  - **a**  $K(s) \rightarrow K^{+}(aq) + e^{-}$
  - **b**  $0_2(g) + 4e^- \rightarrow 20^{2-}(aq)$
  - c  $Cu^+(aq) \rightarrow Cu^{2+}(aq) + e^-$
  - **d**  $F_2(g) + 2e^- \rightarrow 2F^-(aq)$
- 6 Magnesium metal reacts with copper sulfate solution according to the following ionic equation. (Sulfate ions are not included in the equation as they are spectator ions.)

 $Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$ 

- a What has been oxidised in this reaction? What is formed?
- **b** What has been reduced? To form what?
- c What is the oxidant?
- **d** What is the reductant?
- e Write separate half equations for the oxidation and reduction processes.
- 7 A student carried out the reaction in Question 6. Using your knowledge of copper metal and copper ions from Experiment 7.3, what observations would be expected?

- **8 a** Write an equation for the formation of sulfur dioxide from its elements.
  - **b** Oxygen has a higher electronegativity than sulfur. Explain why the reaction in part a is a redox reaction.
  - c Explain which element is oxidised.
  - **d** Explain which element is reduced.
  - e What is the oxidant?
  - f What is the reductant?
- **9** Hydrogen burns cleanly in oxygen and is a potential fuel for the future. Oxygen has a higher electronegativity than hydrogen.
  - a Write an equation for the combustion of hydrogen to form water vapour.
  - **b** Explain why this is a redox reaction, including a diagram to show the partial transfer of electrons in water. (The water molecule has a bent shape.)
  - c Identify what is oxidised, and what is reduced.
  - d Identify the oxidant and the reductant.

# 7.3 Oxidation numbers and half equations

## Assigning oxidation numbers

In reactions involving monatomic ions, it is easy to determine what has been oxidised and what has been reduced. It is more difficult to recognise what has been oxidised when there are polyatomic ions or molecules involved. To assist with this, a set of rules has been devised to assign **oxidation numbers**.

Oxidation numbers are assigned to each atom of the elements involved in a reaction. They are assigned using rules that take into account the unequal sharing of electrons between two atoms. However they have no physical meaning.

The rules for assigning oxidation numbers are as follows.

- 1 The oxidation number of a neutral element is zero. For example, metallic zinc, Zn, pure carbon, C, and oxygen atoms in an oxygen molecule, O<sub>2</sub>, all have an oxidation number of zero.
- 2 In monatomic ions, the oxidation number of the ion is equal to its charge. For example,  $Mg^{2+}$ , either free or in the ionic compound, MgO, has an oxidation number of +2. The oxide ion,  $O^{2-}$ , has an oxidation number of -2.
- **3** Hydrogen is assigned an oxidation number of +1 when combined, unless it is in a metal hydride. A metal hydride is a compound containing a metal and hydrogen, such as LiH. Hydrogen has an oxidation number of -1 in this case. Oxygen is assigned an oxidation number of -2 when combined, unless the compound is a peroxide. In hydrogen peroxide,  $H_2O_2$ , and barium peroxide,  $BaO_2$ , oxygen has an oxidation number of -1.

Oxidation numbers are also known as oxidation

Note the conventions here. The charge of the magnesium ion is written as 2+ but the oxidation

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4 In neutral compounds, the sum of the oxidation numbers is 0. In polyatomic ions, the sum of the oxidation numbers is equal to the charge on the ion.

# Worked example 7.3A

In NH<sub>3</sub>, the sum of the oxidation numbers is zero, as ammonia is a neutral molecule. H is fixed as +1, therefore N must be -3. 1 × (oxidation number of N) + 3 × (oxidation number of H) = 0

 $1 \times (-3) + 3 \times (+1) = 0$ 

The oxidation numbers are  $N H_3^{-3 +1}$ 

## Worked example 7.33

In NO<sub>3</sub><sup>-</sup>, the sum of the oxidation numbers is -1, the charge of the ion. O is fixed as -2 and there are three oxygen atoms, therefore N must be +5. 1 × (oxidation number of N) + 3 × (oxidation number of O) = -1

 $1 \times (+5) + 3 \times (-2) = -1$ 

The respective oxidation numbers are  $\stackrel{\sim}{N} O_3^{-1}$ 

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## / Worked example 7.3C

In the compound KMnO<sub>4</sub>, the sum of the oxidation numbers is zero. However, as this is an ionic compound, it is helpful to treat it as consisting of  $K^+$  ions and  $MnO_4^-$  ions.

K has an oxidation number of +1. The oxidation numbers of Mn and O can be found by applying the above rules. Oxygen must have an oxidation number of -2 and so Mn must have an oxidation number of +7.

 $1 \times$  (oxidation number of Mn) + 4 × (oxidation number of O) = -1  $1 \times$  (+7) + 4 × (-2) = -1

The oxidation numbers are  $\begin{array}{c} +1 & +7 & -2 \\ K & Mn & O_4 \end{array}$ 

## Using oxidation numbers

Oxidation numbers can be used for several purposes. First, if an element can have several oxidation numbers, then a relatively high number for that element often indicates that it may be a good oxidant in that form. For example, the permanganate ion,  $MnO_4^-$ , is recognised as a strong oxidant. The Mn has an oxidation number of +7. Pool chlorine is not  $Cl_2$  but hypochlorous acid, HOCl, in which chlorine has an oxidation number of +1. Chlorine has a strong tendency to form a  $Cl^-$  ion with an oxidation number of +1 that enables it to kill bacteria in the pool.

Oxidation numbers can also be used to identify which species has been oxidised and reduced in a reaction. Once oxidation numbers have been



Note that the oxidation number of each hydrogen atom is written as +1. It is not +3 for three H atoms.



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As you become familiar with the process of assigning oxidation numbers, there will be no need to show extensive explanations and calculations.

LCHEMICAL REACTIONS assigned to all elements in the equation, then inspection will show if the oxidation number of an element has increased. An increase in oxidation number indicates that the element has been oxidised. If the oxidation number of an element has decreased, that element has been reduced. This method is particularly useful for covalently bonded substances.

Oxidation numbers are used in naming compounds containing ions whose oxidation number can vary. For example, copper oxide can contain either  $Cu^+$  or  $Cu^{2+}$ . So  $Cu_2O$  is named copper(I) oxide and CuO is named copper(II) oxide. The Roman numerals indicate the oxidation number.

**Worked exemple 7.30** Show that the combustion of methane is a redox reaction. Write the equation for the reaction with all oxidation numbers shown.  $\begin{array}{c} -4 + 1 & 0 & +4 - 2 & +1 - 2 \\ C H_4 + 2O_2 \rightarrow C O_2 + 2H_2O \end{array}$ The oxidation number of carbon has increased from -4 to +4, so C has been oxidised. The oxidation number of oxygen has been reduced from o to -2, so O has been reduced. This is a redox reaction. **Weakeed exemple 7.38 Weakeed exemple 7.38** Is the formation of the precipitate lead iodide from solutions of lead nitrate and potassium iodide a redox reaction? Write the equation for the reaction with all the oxidation numbers shown.  $\begin{array}{c} +1 & +2 & +5 - 2 & +1 + 5 - 2 & +2 - 1 \\ 2K & 1 + Pb & (N O_3)_2 & \rightarrow 2K & N O_3 + Pb & I_2 \\ No elements have changed oxidation numbers. This is not a redox reaction.$ 

# Using oxidation numbers to balance redox equations

Oxidation numbers can be used to balance redox equations. To balance a redox reaction, the number of electrons transferred must be balanced. We will use this method to balance the oxidation of iron(II) ions to iron(III) ions by the permanganate ion. (Permanganate ions are reduced to  $Mn^{2+}$  ions.)

Step 1: Write the main reactants and products, and assign oxidation numbers to all elements.

 $\overset{^{+2}}{\mathrm{Fe}}{}^{^{2+}}+\overset{^{+7}}{\mathrm{Mn}}\overset{^{-2}}{\mathrm{O}_4^-}\to \overset{^{+3}}{\mathrm{Fe}}{}^{^{3+}}+\overset{^{+2}}{\mathrm{Mn}}{}^{^{2+}}$ 

Step 2: Identify the elements whose oxidation numbers have increased and decreased, and mark this on the equation. The oxidation number of iron has increased by 1 from +2 to +3. The oxidation number of manganese has decreased by 5 from +7 to +2.



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An increase in oxidation number indicates the species has been oxidised. A decrease in oxidation number indicates the species has been reduced.

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Step 3: Multiply each reactant and product by factors so that the total increase in oxidation numbers equals the total decrease.

$$(\text{increase of }+1) \times 5$$

$$5Fe^{2+} + MnO_4^- \rightarrow 5Fe^{3+} + Mn^2$$

$$(\text{decrease of }5) \times 1$$

Step 4: Add water to balance oxygen and  $\mathrm{H}^{\scriptscriptstyle +}$  ions to balance hydrogen, if necessary.

 $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$ 

With more practice, you won't need to write each step separately—this has been done to help explain the steps involved.



# Using half equations to balance redox equations

Half equations can also be used to balance redox equations. We will use the oxidation of  $Cu^+$  ions to  $Cu^{2+}$  by the dichromate ion,  $Cr_2O_7^{2-}$ , as an example.

Step 1: Write skeleton half equations for both the oxidation and the reduction processes.

 $\begin{array}{c} Cu^{\scriptscriptstyle +} \rightarrow Cu^{2 \scriptscriptstyle +} \\ Cr_2 O_7{}^{2 \scriptscriptstyle -} \rightarrow Cr^{3 \scriptscriptstyle +} \end{array}$ 

Step 2: Balance the atoms involved (excluding hydrogen and oxygen—you will see why later). In this example, Cu is balanced but there are two Cr atoms on the left and only one on the right. Thus two  $Cr^{3+}$  are needed.

$$\begin{array}{c} \mathrm{Cu}^{+} \rightarrow \mathrm{Cu}^{2+} \\ \mathrm{Cr}_{2}\mathrm{O}_{7}^{2-} \rightarrow 2\mathrm{Cr}^{3+} \end{array}$$

Step 3: Use water to balance oxygen atoms. There are seven O atoms on the left, so seven  $H_2O$  are needed on the right of the chromium half equation.

$$\begin{array}{l} Cu^+ \rightarrow Cu^{2+} \\ Cr_2 O_7^{2-} \rightarrow 2 Cr^{3+} + 7 H_2 O \end{array}$$

Step 4: Use  $H^+$  ions to balance hydrogen atoms. There are fourteen H atoms on the right, so fourteen  $H^+$  ions are needed on the left of the chromium half equation.

 $\begin{array}{l} Cu^{+} \rightarrow Cu^{2+} \\ Cr_{2}O_{7}^{\ 2-} + 14H^{+} \rightarrow 2Cr^{3+} + 7H_{2}O \end{array}$ 

When working, each step can be added to the skeleton equations, without rewriting. The reaction has been rewritten at each step to help explain the steps involved.

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The first half equation shows oxidation, as electrons are being lost.

shows oxidation, as electrons are being lost. The second half equation shows reduction, as electrons are gained.

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Step 5: Use electrons (e<sup>-</sup>) to balance charge. In the first half equation, the charge is +1 on the left and +2 on the right. Adding one electron to the right will make the charge balance. In the second half equation, the charge on the left is (-2) + (+14) = +12. The charge on the right is  $2 \times (+3) = +6$ . To make these equal, six electrons need to be added to the left-hand side.

 $\begin{array}{l} Cu^{+} \rightarrow Cu^{2+} + 1e^{-} \\ Cr_{2}O_{7}^{-2-} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_{2}O \end{array}$ 

Step 6: Balance the number of electrons being lost and gained by multiplying the equations by whole numbers. The number of electrons lost by oxidation should be the same as the number of electrons gained by reduction. In this case, the oxidation half equation needs to be multiplied by 6.

 $\begin{array}{l} 6Cu^{+} \rightarrow 6Cu^{2+} + 6e^{-} \\ Cr_{2}O_{7}^{\ 2-} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_{2}O \end{array}$ 

Step 7: Add the half equations. As the electrons cancel out, they are not shown in the final equation.

 $6Cu^{\scriptscriptstyle +} + Cr_2 {O_7}^{2-} + 14H^{\scriptscriptstyle +} \rightarrow 6Cu^{2+} + 2Cr^{3+} + 7H_2O$ 

These steps are summarised in figure 7.5.



- **13** Balance the following equations using the oxidation number method.
  - **a**  $Na(s) + Cl_2(g) \rightarrow NaCl(s)$
  - **b**  $Cu(s) + NO_3^{-}(aq) \rightarrow Cu^{2+}(aq) + NO_2(g)$
  - c  $NO_3^{-}(aq) + H_2S(g) \rightarrow S(s) + NO(g)$
  - **d**  $Cr_2O_7^{2-}(aq) + Pb^{2+}(aq) \rightarrow Cr^{3+}(aq) + Pb^{4+}(aq)$
- **14** Using the half equation method, write balanced equations for the reaction between:
- a Cu<sup>2+</sup>(aq) and Fe(s). The products are Cu(s) and Fe<sup>3+</sup>(aq).
- b NO<sub>3</sub><sup>-</sup>(aq) and Cu(s), in an acidic environment. The main products are NO<sub>2</sub>(g) and Cu<sup>2+</sup>(aq).
- ClO<sub>3</sub><sup>-</sup>(aq) and Br<sup>-</sup>(aq), in an acidic environment. The main products are Cl<sup>-</sup>(aq) and Br<sub>2</sub>(aq).
- **d**  $MnO_4^{-}(aq)$  and  $SO_2(aq)$ , in acid. The main products are  $Mn^{2+}(aq)$  and  $SO_4^{2-}(aq)$ .

## 7.4 Ease of oxidation

You will have noticed that some substances can be oxidised more readily than others. Sodium is so reactive in oxygen and water that it must be stored under kerosene. A freshly cut piece of this soft metal rapidly develops a dull oxide surface. Gold, platinum and to some extent silver are prized for their high lustre and lack of reactivity. All three of these metals are found naturally in their unreacted state. Substances other than metals also vary in their ease of oxidation.

#### materials

- .,
- silverzinc

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- lead
- copper
- iron
- 1 M hydrochloric acid0.1 M iron(III) nitrate
- (Fe(NO<sub>3</sub>)<sub>3</sub>) • O.1 M silver nitrate
- (AgNO<sub>3</sub>) • 0.1 M zinc nitrate
- $(Zn(NO_3)_2)$
- O.1 M lead(II) nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>)
- O.1 M copper(II) nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>)
- 25 small test tubes in racks
- steel wool

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#### safety



- Silver nitrate stains skin and surfaces.
- Wash hands thoroughly.

## Experimenで 7.4 Testing ease of oxidation

#### Purpose

To determine the relative ease of oxidation of various metals.

#### Procedure

- 1 Clean five small pieces of each metal with steel wool.
- 2 Place small volumes of each solution in the test tubes—four test tubes with each salt solution and five test tubes with hydrochloric acid.
- **3** For the zinc nitrate solution, place a piece of silver in one test tube, a piece of copper in another, a piece of lead in the third and a piece of iron in the fourth. (There is no need to test zinc in zinc nitrate.)
- 4 For each of the other salt solutions, set up the necessary combinations similarly. All five metals should be tested in acid.
- 5 Record detailed observations, including the rate of any reaction, in a table similar to the one below.

#### Results

table 7.1								
		Solutions						
Metals	$Zn(NO_3)_2$	$AgNO_3$	Cu(NO <sub>3</sub> ) <sub>2</sub>	$Pb(NO_3)_2$	$Fe(NO_3)_3$	HCl		
Zn	N/A							
Ag		N/A						
Cu			N/A					
Pb				N/A				
Fe					N/A			

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#### Discussion

- 1 Which metal seemed to be most readily oxidised by the solutions used? Justify your answer.
- 2 Which metal seemed to be least readily oxidised by the solutions used? Justify your answer.
- **3** Use your results to arrange the five metals in order, from the most difficult to oxidise to the easiest to oxidise. Explain your reasoning.
- 4 Write half equations and balanced redox equations for all the reactions which occurred.

You have already seen that copper metal is oxidised by the silver ions in silver nitrate solution. Which of these two metals is most easily oxidised? What do you think would happen if silver metal was placed in copper(II) nitrate solution? Would silver act as a reducing agent and be oxidised?

When reactions such as these and others are observed, you will notice that some metals are more reactive, and more easily oxidised than others. A list of metals, called the activity series (or reactivity series) can be constructed, as in figure 7.6.



figure 7.6 The activity series, showing the relative ease of oxidation of some metals.

## **Electrochemical cells**

Can we make use of the transfer of electrons between reactants? We can. This transfer can be very useful. If oxidation occurs in one place and reduction in another, the transfer of electrons can occur through a wire creating an electric current. This electric current can be harnessed in an **electrochemical cell** to power many devices.

An electrochemical cell uses a chemical reaction to produce electricity. Electrons are transferred from the electrode where oxidation occurs to the electrode where reduction occurs. An **electrode** is a solid electrical conductor in a cell. Oxidation or reduction can occur on the surface of an electrode.

Devices based on this principle are known as cells or batteries, and include the dry cells used in torches and other small appliances, the tiny button cells found in calculators and the large lead–acid batteries which power the starter motor and other electrical circuits in cars. Fuel cells are another type of cell which show great promise as a future energy source.



The term **battery** is used to describe two or more cells in series. It is commonly used incorrectly to describe a single cell.



Your teacher may suggest a list of other substances for you to test. Solutions of halogens and halide ions can be tested, as wel as oxidising agents such as acidified  $KMnO_4$ solution.

**Redox reactions** 





**figure 7.7** This watch is powered by a small button cell that provides a steady voltage. Button cells are also used in calculators and other electronic items.



figure **7.8** A lead-acid battery is used to start cars.

## ・ 三 次perilimenで 7.5 Making an electrochemical cell

### materials

- two small beakers
- copper electrode
- zinc electrode
- 1 M Cu(NO<sub>3</sub>)<sub>2</sub> solution
- 1 M Zn(NO<sub>3</sub>)<sub>2</sub> solution
- 1 M KNO<sub>3</sub> solution
   filter paper
- filter paper

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- light globe, 1 V or LEDinsulated connecting
- Insulated connecting leads
- voltmeter or multimeter



LCHEMICAL REACTIONS

### Purpose

To build and test an electrochemical cell.

#### Method

How can such an electrochemical cell be set up? Figure 7.9 below shows a simple laboratory design. Zinc and copper are used in this half cell. Since zinc is more easily oxidised than copper, zinc metal and copper ions must be present in separate beakers to avoid contact. A piece of copper metal is placed in the copper(II) nitrate solution, while the zinc metal is in zinc nitrate solution. The pieces of metal act as electrodes and are connected with a wire circuit, containing a light globe. A voltmeter could also be connected in parallel. Nothing will happen until the circuit is complete. The beakers of solutions are connected and the circuit completed using a salt bridge. In this case, use a strip of filter paper soaked in a solution of potassium nitrate or similar. The salt bridge allows a flow of ions between the two half cells, completing the circuit. The ions in the salt bridge are chosen so they do not react with ions in the beakers.



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### Results

Measure the voltage produced by the cell. Record observations of the light globe, and any changes to the solutions and the electrodes. You should observe the cell working for a period of time.

### Discussion

- 1 Explain what is happening in each part of the cell. Where is oxidation occurring? Where is reduction occurring?
- 2 Write half equations and a complete equation.
- 3 How are the electrons transferred? In which direction do they flow?
- **4** For electricity to flow in a circuit, the circuit must be complete. What happens if you remove the salt bridge? Why?
- 5 Electrons cannot flow in the solutions in the beakers or salt bridge. What is flowing?

Recall that positive and negative ions in solution can move. To understand how an electrochemical cell works, we need to be able to visualise the movement of the electrons and ions as well as how oxidation and reduction occur. Figure 7.10 below illustrates what is happening.



figure 7.10 A representation of the processes in an electrochemical cell.

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**Redox reactions** 

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A **half cell** is the part of a cell where a half equation, either oxidation or reduction, occurs. It consists of the electrode and solution, and its container



The anode is the electrode where oxidation occurs. The cathode is the electrode where reduction occurs. To help you remember this, use **AN OIL RIG CAT**. This stands for 'At the anode, oxidation is loss; reduction is gain at the cathode'.

laboratory, and compare their potentials.

LCHEMICAL REACTIONS On the left-hand side is the zinc **half cell**. Zinc is more easily oxidised than copper, so zinc atoms from the electrode are oxidised. You should have noticed that the appearance of the zinc electrode has changed due to oxidation. As the zinc is oxidised, zinc ions are formed. They leave this electrode, called the **anode**, and move into the surrounding solution. The electrons move through the wire towards the copper half cell. At the copper **cathode**, copper ions from the solution combine with the electrons and form a coating of copper on the surface of the cathode—you should have noticed this coating.

Within the solutions, electrons cannot be transported. Instead, both positive and negative ions move and carry the electric current. As positively charged zinc ions build up around the anode in this half cell, negatively charged nitrate ions ( $NO_3^-$ ) move from the salt bridge to balance the charge. Copper ions ( $Cu^{2+}$ ) move towards the cathode, attracted by the excess electrons there. As positive copper ions are depleted in this half cell, potassium ions ( $K^+$ ) from the salt bridge move into the half cell.

## Standard reduction potentials

A variety of different half cells can be constructed. Different voltages can be obtained from different pairings of half cells. By convention, the hydrogen half cell is used as a standard, set at 0.00 volts. Figure 7.11 shows a hydrogen half cell. The voltage, or cell potential, of other half cells can be determined using this hydrogen half cell.



#### figure 7.11 A hydrogen half cell.

When this is done under standard conditions (using 1.0 M solutions and 25°C and 101.3 kPa) the half cell **standard reduction potential** can be obtained. The list of standard half cell equations and their voltages is known as the **electrochemical series** (table 7.2). Strongest oxidants are on the top left of the table and the strongest reductants are on the bottom right of the table. The standard half cell potential is also known as the  $E^0$ , where *E* represents for electromotive force, emf, and the <sup>0</sup> indicates that it is measured under standard conditions.

The electrochemical series can be used to predict which way the current will flow in a cell. The half equation that is higher in the table will proceed as written, as a reduction process. The one lower in the table will proceed in the reverse direction as an oxidation process. Electrons will flow away from this half cell to the half cell where reduction is occurring. The electrochemical series can also be used to determine whether a redox reaction, such as those observed in Experiment 7.4, will be spontaneous. For example, copper and silver were not oxidised by the  $H^+$  ions in hydrochloric acid, as these metals are both too difficult to be oxidised by  $H^+$ .

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<b>table</b> $\mathbb{7}_2$ The electrochemical series.							
		Oxidants		Reductants			<i>E</i> <sup>o</sup> (V)
		$F_2(g) + 2e^-$	1	2F⁻(aq)			+2.87
	H <sub>2</sub>	$O_2(aq) + 2H^+(aq) + 2e^-$	$\neq$	2H <sub>2</sub> O(I)			+1.78
	2HC	$IO(aq) + 2H^{+}(aq) + 2e^{-}$	$\rightleftharpoons$	$Cl_2(g) + 2H_2O(I)$			+1.63
	MnC	$P_4^{-}(aq) + 8H^{+}(aq) + 5e^{-}$	$\neq$	$Mn^{2+}(aq) + 4H_2O(l)$			+1.51
		Au <sup>3+</sup> (aq) + 3e <sup>-</sup>	$\neq$	Au(s)			+1.50
		Cl <sub>2</sub> (g) + 2e <sup>-</sup>	$\neq$	2Cl⁻(aq)			+1.36
	$Cr_{2}O_{7}^{2}$	<sup>-</sup> (aq) + 14H <sup>+</sup> (aq) + 6e <sup>-</sup>	$\rightleftharpoons$	$2Cr^{3+}(aq) + 7H_2O(l)$			+1.36
		$O_2(g) + 4H^+(aq) + 4e^-$	$\downarrow$	2H <sub>2</sub> O(l)			+1.23
		Pt <sup>2+</sup> (aq) + 2e <sup>-</sup>	$\neq$	Pt(s)			+1.18
		$Br_2(aq) + 2e^-$	$\downarrow$	2Br <sup>-</sup> (aq)			+1.06
	NC	$P_3^{-}(aq) + 4H^{+}(aq) + 3e^{-}$	$\rightleftharpoons$	$NO(g) + H_2O(l)$			+0.96
		$Hg^{2+}(aq) + 2e^{-}$	$\rightleftharpoons$	Hg(l)			+0.85
	N	$0_3^{-}(aq) + 2H^{+}(aq) + e^{-}$	$\rightleftharpoons$	$NO_2(g) + H_2O(l)$			+0.80
		$Ag^{+}(aq) + e^{-}$	$\rightleftharpoons$	Ag(s)			+0.80
		Fe <sup>3+</sup> (aq) + e <sup>-</sup>	$\rightleftharpoons$	Fe <sup>2+</sup> (aq)			+0.77
		$O_2(g) + 2H^+(aq) + 2e^-$	$\neq$	$H_2O_2(aq)$			+0.68
		$I_2(s) + 2e^-$	$\neq$	2l⁻(aq)			+0.54
incre	asing	$0_2(g) + 2H_2O(I) + 4e^-$	$\neq$	4OH⁻(aq)	incr	easing	+0.40
oxid	lising	$Cu^{2+}(aq) + 2e^{-}$	$\neq$	Cu(s)	red	ucing	+0.34
stre	ngth	$Cu^{2+}(aq) + e^{-}$	$\rightleftharpoons$	Cu <sup>+</sup> (aq)	stre	ength	+0.16
		Sn <sup>4+</sup> (aq) + 2e <sup>-</sup>	$\neq$	Sn <sup>2+</sup> (aq)			+0.15
		$S(s) + 2H^{+}(aq) + 2e^{-}$	$\neq$	$H_2S(g)$			+0.14
		2H <sup>+</sup> (aq) + 2e <sup>-</sup>	$\rightleftharpoons$	$H_2(g)$			+0.00
		$Pb^{2+}(aq) + 2e^{-}$	$\neq$	Pb(s)			-0.13
		$Sn^{2+}(aq) + 2e^{-}$	$\neq$	Sn(s)			-0.14
		$Ni^{2+}(aq) + 2e^{-}$	$\neq$	Ni(s)			-0.23
		$Cd^{2+}(aq) + 2e^{-}$	$\Rightarrow$	Cd(s)			-0.40
		$Fe^{2+}(aq) + 2e^{-}$	$\neq$	Fe(s)			-0.41
		$[Au(CN)_2]^-(aq) + e^-$	$\neq$	Au(s) + 2CN⁻(aq)			-0.60
		Cr <sup>3+</sup> (aq) + 3e <sup>-</sup>	È	Cr(s)			-0.73
		$Zn^{2+}(aq) + 2e^{-}$	1	Zn(s)			-0.76
		$2H_2O(I) + 2e^{-1}$	=	$H_2(g) + 2OH^-(aq)$			-0.83
		$Mn^{2+}(aq) + 2e^{-}$	=	Mn(s)			-1.18
		Al <sup>3+</sup> (aq) + 3e <sup>-</sup>	Ę,	Al(s)			-1.71
		Mg <sup>2+</sup> (aq) + 2e <sup>-</sup>	1	Mg(s)			-2.37
		$Na^+(aq) + e^-$	,	Na(s)			-2.71
		Ca <sup>2+</sup> (aq) + 2e <sup>-</sup>	1	Ca(s)			-2.87
		Sr <sup>2+</sup> (aq) + 2e <sup>-</sup>	=	Sr(s)		1	-2.89
		Ba <sup>2+</sup> (aq) + 2e <sup>-</sup>	1	Ba(s)			-2.91
		K⁺(aq) + e <sup>-</sup>	)	K(s)			-2.93
		Li⁺(aq) + e <sup>-</sup>	$\neq$	Li(s)		V	-3.05

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Redox reactions

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A positive *E*<sup>0</sup> value indicates a reaction may proceed spontaneously.

A positive value for cell emf means that a redox reaction may occur. A

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The electrochemical series can be used to calculate the voltage produced by a cell. For example, to predict the results of a cell based on copper and lead, look at the half equations and their voltages in the table. Copper is higher in the table, so the copper half reaction will proceed as written and copper will be reduced. Lead will be oxidised, so its half equation is written in reverse and the sign of the  $E^0$  value is reversed. To write the complete redox reaction, electrons need to be balanced (if necessary) and the half equations and the  $E^0$  values are added. Note that even if a factor is used to balance the electrons in a half equation, the  $E^0$  value does not change.

$Cu^{2+}(aq) + 2e^{-}$	$\rightarrow$ Cu(s)	$0.34\mathrm{V}$
Pb(s)	$\rightarrow Pb^{2+}(aq) + 2e^{-}$	$0.13\mathrm{V}$
$\overline{Cu^{2+}(aq) + Pb(s)}$	$) \rightarrow Cu(s) + Pb^{2+}(aq)$	0.47 V

A cell made using these substances at standard concentrations should produce  $0.47 \, \text{V}$ .

### Cell emf and chemical reactions

Consider the zinc–copper electrochemical cell described in figure 7.10. In this cell the zinc anode dissolves in the  $Zn/Zn^{2+}$  half cell and copper deposits on the cathode in the Cu/Cu<sup>2+</sup> half cell. Electrons flow from the zinc half cell to the copper half cell through the external circuit and the cell has a positive value for its emf.

Anode:	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$	$E^0 = 0.76 \mathrm{V}$
Cathode:	$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$	$E^0 = 0.34  V$
Overall:	$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$	emf = 1.10 V

If we combine the two half cells and place a piece of zinc in a solution containing copper(II) ions, the same reaction will occur. That is, the zinc will dissolve and the copper will deposit on the zinc.

The reverse reaction (with a negative cell emf) does not occur. That is, if a piece of copper is placed in a solution of zinc ions there will be no reaction.

This principle can be generalised to all redox reactions whether or not the half reactions are separated in a cell.

To determine whether a redox reaction will occur or if a cell will produce a flow of electrons:

- Select the half equation and  $E^0$  from the table of standard reduction potentials (table 7.2).
- Reverse the appropriate half equation so that it represents an oxidation process. Change the sign of the  $E^0$  value.
- Combine the half equations so that the electrons gained and lost are equal. When multiplying an equation by an integral value to make the number of electrons gained and lost equal, do not change the value of the  $E^0$ ; the value of  $E^0$  does not depend on the number of times the reaction occurs.
- Add the  $E^0$  values to determine the cell emf.
- If the emf has a positive value, the reaction *may* occur.
- If the emf has a negative value, the reaction will not occur.

In general a cell emf of 0.2 V or larger is required if a redox reaction is going to proceed to any significant degree and only indicates that the reaction has the *potential* to occur. Other determining factors have a bearing on whether or not a redox reaction will occur. Remember also that the calculated values are for standard conditions. That is, concentrations of 1 mol L<sup>-1</sup>, gas pressure of 101.3 kPa and temperature of 25°C. Any change to these conditions changes the  $E^0$  values.

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Using the table of standard reduction potentials (table 7.2) determine whether iodide ions can be oxidised to iodine by permanganate ions in acidic solution. Write half equations and a balanced overall equation using the table of standard reduction potentials.  $2 \times (MnO_4^{-}(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+} + 4H_2O(l))$  $E^0 = +1.51 V$  $5 \times (2l^{-}(aq) \rightarrow l_2(aq) + 2e^-)$ The overall balanced equation is  $2MnO_4^{-}(aq) + 16H^+(aq) + 10l^{-}(aq) \rightarrow 2Mn^{2+} + 8H_2O(l) + 5l_2(aq) emf = +0.97 V$ The cell emf has a positive value, therefore the redox reaction will proceed as written.

### **Electrolytic cells**

Electrochemical cells rely on spontaneous redox reactions that have a natural tendency to go the way they are written. The most easily oxidised substance is being oxidised, and the other substance is reduced.

However, by using electricity, a redox reaction can be forced to occur, even if it is not spontaneous. This is achieved by forcing electrons to flow. An **electrolytic cell** is a cell in which electricity is used to cause a chemical change.

This process has many uses, for example copper is refined (purified) by this method at copper refineries (see figure 7.12). The power supply removes electrons from the anode of impure copper, oxidising the copper. Electrons are forced onto the cathode, where very pure copper is plated onto stainless steel.



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electrochemical cells this occurs at the anode. In electrolytic cells the power

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**Redox reactions** 

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Electrolysis can be used to deliberately plate metals with coatings, either to improve their appearance or to protect them. For example, silver plate is used on cutlery, chrome plate was used on the trims of many older cars, and zinc is used to coat iron to protect it from corrosion.

Some metal ions in minerals are so difficult to reduce that they cannot be extracted by electrolysis from a solution—molten ionic compounds must be used instead. The extraction of aluminium from the compound alumina is carried out in this way.

### Predicting the products of electrolysis

When considering the reactions that may occur in an electrolytic cell there are several variables that must be considered. Is the electrolyte molten or aqueous? Are the electrodes reactive or inert?

#### 1 Electrolysis of a molten salt electrolyte

The only reactions that need to be considered are the reduction of the metal cation at the cathode and the oxidation of the non-metal anion at the anode.

For example, the following half equations for the electrolysis of molten potassium chloride using inert electrodes are considered.

Cathode:	$K^+(l) + e^- \rightarrow K(l)$	$E^0 = -2.93 \mathrm{V}$
Anode:	$2Cl^{-}(l) \rightarrow Cl_{2}(g) + 2e^{-}$	$E^0 = -1.36 \mathrm{V}$
Overall:	$2\mathrm{K}^{\!\scriptscriptstyle +}(\mathrm{l}) + 2\mathrm{Cl}^{\!\scriptscriptstyle -}(\mathrm{l}) \to 2\mathrm{K}(\mathrm{l}) + \mathrm{Cl}_2(\mathrm{g})$	emf = -2.93 + -1.36 = -4.29 V

The products of the electrolysis are liquid potassium metal and chlorine gas. The negative value for the cell emf indicates that the reaction is not spontaneous (it must be induced using an electric current) and the minimum voltage required to make the reaction proceed is 4.29 V.

#### 2 Electrolysis of an aqueous electrolyte

When the electrolyte is dissolved in water and a current passed through the solution the cation and anion may be reduced and oxidised respectively, but so may water. The half equations for the oxidation and reduction of water are as follows.

Anode:	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	$E^0 = -1.23 \mathrm{V}$
Cathode:	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	$E^0 = -0.83 \mathrm{V}$

If we were electrolysing an aqueous solution of copper(II) chloride with inert electrodes, the possible anode and cathode reactions for the electrolysis of the electrolyte would be:

Anode: 
$$2\text{Cl}^{-}(l) \rightarrow \text{Cl}_{2}(g) + 2e^{-}$$
  $E^{0} = -1.36 \text{ V}$   
Cathode:  $\text{Cu}^{2+}(aq) + 2e^{-} \rightarrow \text{Cu}(s)$   $E^{0} = +0.34 \text{ V}$ 

When choosing the most likely reaction at either electrode, the reaction with the *most positive* value is selected. In this case, the more positive anode reaction is that for the oxidation of water and the more positive cathode reaction is that for the reduction of copper ions.

Anode:	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	$E^0 = -1.23 \mathrm{V}$
Cathode:	$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$	$E^0 = +0.34 \text{ V}$

The cathode reaction must be multiplied by a factor of two (to balance the number of electrons) and the half equations added together to give the overall reaction for the electrolysis as:

 $2Cu^{2+}(aq) + 2H_2O(l) \rightarrow 2Cu(s) + O_2(g) + 4H^+(aq) \text{ emf} = -1.23 + 0.34 = -0.89 \text{ V}$ 

A voltage of greater than 0.89 V must be applied for electrolysis to proceed.

#### 3 Electrolysis of an aqueous electrolyte using reactive electrodes

If we use the example above and replace the inert anode with copper, there is a further oxidation reaction that must be considered. The possible anode reactions are:

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	$E^0 = -1.23 \mathrm{V}$
$2\mathrm{Cl}^{-}(\mathrm{l}) \rightarrow \mathrm{Cl}_{2}(\mathrm{g}) + 2\mathrm{e}^{-}$	$E^0 = -1.36 \mathrm{V}$
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$	$E^0 = +0.34 \mathrm{V}$

The oxidation of the copper anode has the most positive reduction potential and is most likely to occur.

The possible cathode reactions don't change and are:

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	$E^0 = -0.83 \mathrm{V}$
$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$	$E^0 = +0.34 \text{ V}$



Under standard conditions the anode and cathode reactions with the most positive  $E^0$  values are most likely to occur.

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Always consider all possible anode and cathode reactions, including the electrolysis of water, electrolytes and reactive electrodes.

LCHEMICAL REACTIONS

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The reduction of copper ions has the most positive reduction potential and is most likely to occur.

The overall reaction for the electrolysis is:

 $Cu^{2+}(aq) + Cu(s) \rightarrow Cu(s) + Cu^{2+}(aq)$  $E^0 = 0.00 \,\mathrm{V}$ 

This may appear to be a futile process (dissolving and reforming a metal), but it is in fact a widely used process for the electrorefining of metals. In this type of process the impure metal is dissolved at the anode and the pure metal is deposited at the cathode.

It must be noted at this point that standard reduction potentials only provide us with a good theoretical method of predicting the outcome of an electrolytic process. In fact, most electrolytic processes are not performed under standard conditions, and factors such as concentration of electrolytes, current and temperature all affect the reduction potential of an oxidation or reduction process. This is most obvious if we examine the electrolytic reactions that occur in a pool filter.

Sodium chloride is dissolved in the pool water and electrolysed in the cell inside the filter.

The possible anode reactions are:

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	$E^0 = -1.23 \mathrm{V}$
$2Cl^{-}(l) \rightarrow Cl_{2}(g) + 2e^{-}$	$E^0 = -1.36 \mathrm{V}$
The possible cathode reactions are:	
$Na^+(aq) + e^- \rightarrow Na(aq)$	$E^0 = -2.71 \mathrm{V}$
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	$E^0 = -0.83 \text{ V}$

Even though the production of oxygen is favoured under standard conditions, at higher concentrations the reduction potentials change and the production of chlorine is favoured. The products of electrolysis in swimming pools are mainly chlorine and hydrogen.

#### Questions

- **15** Calculate the cell voltage predicted for a cell made from tin in a  $Sn^{2+}$  solution and aluminium in an  $Al^{3+}$  solution.
- **16** Draw and fully label the cell in Question 15. Specify all solutions used and the direction of electron and ion flow.
- **17 a** Compare the energy transformation occurring in an electrochemical cell with that occurring in an electrolytic cell.
  - **b** Explain why the negative electrode of an electrochemical cell is the site of oxidation, whereas the negative electrode of an electrolytic cell is the site of reduction.
- **18** Predict whether the following reactions (unbalanced) could proceed under standard conditions.

**a**  $Sn^{4+}(aq) + H_2O_2(aq) \rightarrow Sn^{2+}(aq) + H^+(aq) + O_2(g)$ **b**  $\operatorname{Cr}_2O_7^{2-}(\operatorname{aq}) + F^{-}(\operatorname{aq}) + H^{+}(\operatorname{aq}) \rightarrow$  $F_2(g) + H_2O(l)$ 

**c** 
$$Cu(s) + H^{+}(aq) \rightarrow Cu^{2+}(aq) + H_2(g)$$
  
**d**  $K(s) + H_2O(l) \rightarrow KOH(aq) + H_2(g)$ 

- **19** Using the table of standard reduction potentials find:
  - a a reducing agent that will convert Pb<sup>2+</sup> to Pb but not Cd<sup>2+</sup> to Cd
  - **b** an oxidising agent that will convert  $Cl^{-}$  to  $Cl_{2}$ but not  $F^-$  to  $F_2$
  - c a metal that will reduce water to hydrogen and a metal that will not.
- **20** In the electrolysis of the following 1.0 mol  $L^{-1}$ solutions, predict:
  - i the products formed at each electrode
  - ii the equations for the anode and cathode reactions

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- iii the overall reaction
- iv the minimum voltage that must be applied to produce the overall reaction.
- a  $Cul_2$
- **b** HBr

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- **c** AgNO<sub>3</sub> with a silver anode.
- **21 a** By referring to the electrochemical series, design an electrochemical cell that could act as the power source to electrolyse molten lead(II) iodide, PbI<sub>2</sub>, to produce lead metal and iodine.
- b Sketch a diagram to show how the cell that you designed in part a can drive the electrolytic cell containing molten lead(II) iodide. Label positive and negative electrodes of both cells.
- c The reaction  $2Li + I_2 \rightarrow 2LiI$ occurs in a cell as two half equations:  $Li \rightarrow Li^+ + e^ I_2 + 2e^- \rightarrow 2I^-$ Is it more likely to be an electrochemical cell or an electrolytic cell? Explain your reasoning.

## 7.5 Faraday's laws of electrolysis

Early in the nineteenth century scientists noted that when an electric current was passed through water, two gases hydrogen and oxygen were produced. It caused great controversy at the time and although many theories were proposed none stood up to scrutiny until Michael Faraday applied himself to the problem.

Faraday passed electric current through acidified water and in 1833 published his findings that were to set the foundations for the modern applications of electrolysis. He showed that electrolytic reactions follow all normal chemical stoichiometric principles in addition to certain stoichiometric rules related to electric charge. His findings are summarised in two laws known as **Faraday's laws of electrolysis**.

### Faraday's First Law

The mass of any substance (m) deposited, evolved or dissolved at an electrode during electrolysis is directly proportional to the quantity of electrical charge (Q) passed through the electrode and the time for which it flows.

The electrical charge is directly related to the number of electrons moving through the electrode. There are no instruments with which we can directly measure electrical charge, so we measure electrical current and time to determine it. The relationship between current flowing, the time it flows and electrical charge passed through an electrode is given by the following formula:

Q = It

where Q is the charge in coulombs (C)

*I* is the current measured in amperes (A)

*t* is the time in seconds (s).

The amount of charge flowing through an electrolytic cell can therefore be varied by varying the current and the time it flows.

- The charge on one electron is  $1.602 \times 10^{-19}$  C.
- The charge on one mole of electrons  $1.602 \times 10^{-19} \times 6.023 \times 10^{23} = 9.65 \times 10^4 \text{ C} = 96500 \text{ C}.$



For practical purposes Faraday's First Law can be restated to say 'the *number of moles of a substance* produced at an electrode is directly proportional to the *number of moles of electrons* transferred at the electrode'.

LCHEMICAL REACTIONS This is the quantity of charge carried by a mole of electrons and is known as the **faraday** (F). The number of moles of electrons that carry a certain charge can be determined using the following relationship:

$$n(e^{-}) = \frac{Q}{96\ 500}$$

where  $n(e^{-})$  is the number of moles of electrons (mol), and *Q* is the charge in coulombs (C).

This can be used with the appropriate oxidation and reduction half equations to calculate the quantities of products at the electrodes in an electrolytic cell.

Worked example 7.5A A molten sample of sodium chloride is electrolysed with a current of 15 A for 2 hours using inert electrodes. a What mass of sodium is produced at the cathode? What volume of chlorine will be collected at the anode at  $25^{\circ}$ C and b 100.0 kPa? **a** Calculate the charge passing through the electrodes and the number of moles of electrons. O = It $= 15 \times 2 \times 60 \times 60$ = 108 000 C Q  $n(e^{-}) = 1$ 96 500 96 500 = 1.12 mole Calculate the mass of sodium at the cathode.  $Na^{+}(l) + e^{-} \rightarrow Na(l)$ Number of moles of Na produced is equal to the number of moles of electrons that passed through the electrode. n(Na) = 1.12 mol $n = \frac{m}{2}$ М  $m = n \times M$  $m = 1.12 \times 23.0$ m(Na) = 25.7 g**b** Calculate the volume of chlorine produced at the anode.  $2Cl^{-}(l) + 2e^{-} \rightarrow Cl_{2}(g)$ 2 moles + 2 moles  $\rightarrow$  1 mole  $n(\operatorname{Cl}_2) = \frac{1}{2}n(e^-)$  $n(Cl_2) = \frac{1.12}{2}$  $n(Cl_2) = 0.56 \text{ mol}$ PV = nRT $V = -\frac{nRT}{2}$ Ρ  $V = 0.56 \times 8.31 \times \frac{298}{100.0}$ V = 13.9 L

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**Redox reactions** 

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If two or more cells are connected in series the same number of moles of electrons passes through each cell.

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### Faraday's Second Law

If the same amount of electrical charge (Q) is passed through several electrodes connected in series, the mass (m) of a substance discharged at the electrodes is proportional to the molar masses of the elements concerned and the number of moles of electrons passing through the circuit.

This law applies where two or more electrolytic cells are connected in series and the same current is passing through each cell. All anodes will accept the same number of electrons from their oxidations and all cathodes will liberate the same number of electrons from their reductions.

# / Worked example 7.5B

Platinum electrodes are placed in separate solutions of copper sulfate, silver nitrate and dilute sulfuric acid and connected in series (figure 7.13). A current was then passed through the circuit and 0.105 g of copper were deposited on the cathode of the first cell.



#### figure 7.13 Electrolytic cells in series.

- a Calculate the mass of silver deposited in the second cell.
- **b** Calculate the volume of hydrogen gas (measured at 96.4 kPa and 25°C) evolved from the third solution.
- **c** Determine the magnitude of the current that was used if the cells were operating for 5.00 minutes.
- a Determine the number of moles of copper deposited.

$$Cu2+(aq) + 2e- → Cu(s)$$
  
n(Cu) =  $\frac{m}{M}$   
=  $\frac{0.105}{63.5}$   
= 0.00165 mol

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Calculate the number of moles of electrons that passed through the circuit.

 $n(e^{-}) = 2 \times n(Cu)$ = 2 × 0.001 65

= 0.0033 mol

Calculate the number of mole and mass of Ag deposited.

 $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$   $n(Ag) = n(e^{-}) = 0.0033 \text{ mol}$   $m = n \times M$   $m(Ag) = 0.0033 \times 107.9$ = 0.357 g

**b** Determine the number of moles of hydrogen produced.  $2H^+(an) + 2e^- \rightarrow H_2(g)$ 

$$n(H_2) = \frac{n(e^-)}{2}$$

= 0.001 65 mol

Determine the volume of hydrogen at 96.4 kPa and 25°C. PV = nRT

 $96.4 \times V = 0.00165 \times 8.31 \times 298$ V = 0.0424 L

c Determine the total charge passing through the circuit.

$$n(e^{-}) = \frac{Q}{96\ 500}$$

 $0.0033 = \frac{Q}{96500}$ 

Q = 318.45 C Determine the current flowing in the circuit. Q = It $318.45 = I \times 5 \times 60$ I = 1.06 A

### Questions

- 22 How many coulombs per hour pass through an electroplating bath that uses a current of 5 amperes?
- **23** The Hall–Héroult cell is used to electrolytically extract Al from alumina  $(Al_2O_3)$ . In the process  $Al_2O_3$  is dissolved in molten cryolite and an electric current of 250 000 A is passed through the solution. The  $Al^{3+}$  is reduced to molten Al at the cathode and the carbon anode is oxidised to carbon dioxide. What would be the daily output of Al from the Hall–Héroult cell?
- 24 What volume of O<sub>2</sub>(g) at o°C and 101.3 kPa is produced when 5 A of current is passed through a dilute aqueous solution of KCl for 5 minutes?
- 25 Molar masses can be determined through electroplating. Determine the molar mass and identity of a metal X that exists as an ion X<sup>2+</sup>, given that 46.3 g of X is deposited by a current of 2 amperes in 6.75 hours.
- **26** How long will it take for 1.25 L of a 1.0 M CuSO<sub>4</sub> solution being electrolysed with a current of 3.40 A to reach a concentration of 0.25 M?
- 27 A given quantity of electricity flows through two electrolytic cells in series containing solutions of silver nitrate and tin(II) chloride respectively. If 2.0 g of silver is deposited on the cathode of the first cell, what mass of tin is deposited in the second cell in the same time?

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### Summary **DOD**

- A redox reaction occurs when one substance is oxidised and another substance is reduced.
- Oxidation is defined as the loss or partial loss of electrons. Reduction is defined as the gain or partial gain of electrons.
- The reductant is the substance which reduces another substance. It is itself oxidised. The oxidant is the substance which oxidises another substance. It is itself reduced.
- An oxidation number is a number assigned to each atom of the elements involved in a reaction. It can be used to determine if a reaction is a redox reaction, and to balance redox equations.
- A half equation shows either the process of oxidation or reduction, including the electrons. Half equations can also be used to balance redox equations.
- The activity series is a list of substances in order of ease of oxidation.
- An electrochemical cell uses a redox reaction to produce an electric current. An electrode is a surface in a cell at which oxidation or reduction can occur. The anode is the electrode at which oxidation occurs. The cathode is the electrode at which reduction occurs.

- A half cell consists of one electrode, the surrounding solution and the container. The salt bridge contains a solution of a salt, and is used to complete the circuit by connecting the two half cells electrically. Electrochemical cells are used to provide convenient sources of electricity.
- The standard reduction potential of a half cell is the voltage that the half cell produces when compared with a hydrogen half cell. The electrochemical series lists reduction half equations and their standard reduction potentials. The series can be used to calculate cell voltages and to predict if reactions occur spontaneously.
- An electrolytic cell uses an electric current to produce a chemical change. The redox reaction occurring is not spontaneous.
- Faraday's laws allow us to calculate the quantities of products at the anode and cathode of an electrolytic cell.
- A positive value for cell emf means that a redox reaction can occur. A negative value means that it can not.
- Standard reduction potentials can be used to determine which half reaction will occur at the anode and cathode. The reaction with the most positive  $E^0$  value may occur.

### Key terms

- activity series anode cathode electrochemical cell electrochemical series
- electrode electrolytic cell Faraday's laws half cell half equation
- oxidant oxidation oxidation number reduction redox reaction
- reductant salt bridge standard reduction potential

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### **Chapter Review**

### 7.1 Oxidation and reduction

28 Aluminium develops a surface layer of aluminium oxide, according to the equation  $4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$ 

For this reaction, identify what has been oxidised and what has been reduced.

### 7.2 Redox reactions

- 29 Iron reacts with sulfur to form iron(III) sulfide. For this reaction:
  - a write the half equations and the balanced equation for the reaction
  - **b** identify the oxidant and the reductant.

# 7.3 Oxidation numbers and half equations

- **30** Balance the following redox reactions, using a suitable method.
  - **a**  $Cu(s) + NO_3^{-}(aq) \rightarrow Cu^{2+}(aq) + NO_2(g)$
  - **b**  $Fe(s) + Pb^{2+}(aq) \rightarrow Fe^{2+}(aq) + Pb(s)$
  - **c**  $\operatorname{Cr}_2 \operatorname{O}_7^{2-}(\operatorname{aq}) + \operatorname{SO}_3^{2-}(\operatorname{aq}) \to \operatorname{Cr}^{3+}(\operatorname{aq}) + \operatorname{SO}_4^{2-}(\operatorname{aq})$
  - **d**  $Al(s) + Ag_2S(s) \rightarrow Ag(s) + Al_2S_3(s)$
- **31** What is the oxidation number of the following?
  - **a** N in the nitrate ion, NO<sub>3</sub>
  - **b** N in dinitrogen tetroxide,  $N_2O_4$
  - **c** N in the ammonium ion,  $NH_4^+$
  - d C in carbon monoxide, CO
  - e C in methanol, CH<sub>3</sub>OH
  - **f** C in the carbonate ion,  $CO_3^{2-}$
  - **g** S in sulfur dioxide, SO<sub>2</sub>
  - **h** S in the hydrogensulfate ion, HSO<sub>4</sub><sup>-</sup>
- **32** Sulfur dioxide is used as a preservative in fruit juice and dried fruits. Unfortunately, if the levels of this substance are too high, it can cause severe asthma in some people. The level of SO<sub>2</sub> in a solution derived from dried fruit can be determined by titrating with potassium permanganate, KMnO<sub>4</sub> solution.
  - **a** Write a balanced equation for the reaction occurring. The main products are  $SO_4^{2^-}$  and  $Mn^{2^+}$ .
  - **b** The permanganate ion is purple and the manganese ion is colourless. Explain why a separate indicator is not needed for this reaction.
  - **c** 20.00 mL of SO<sub>2</sub> solution requires 17.68 mL of 0.0050 M KMnO<sub>4</sub> solution to react completely. Calculate the concentration of SO<sub>2</sub> in the solution.

- **33** Predict whether reactions could occur in the following. Assume standard conditions.
  - a Chlorine gas is bubbled through a solution of potassium bromide.
  - **b** Fluorine gas is bubbled through a solution of sodium chloride.
  - c lodine is added to a solution of potassium fluoride.
- **34** Refer to your answer for Question 33 and make a generalisation about the displacement of halogens.
- **35** The following is a list of some metals from the activity series of metals (most reactive to least reactive). Note it does not correspond exactly to the standard reduction potentials:

K, Na, Ca, Mg, Al, Zn, Fe, Cu, Hg, Ag, Au

Using standard reduction potentials, determine the following:

- a Which metals have the potential to reduce water to hydrogen gas?
- b Which metals have the potential to reduce H<sup>+</sup> in HCl to hydrogen gas?
- c Which metals have the potential to reduce nitric acid to NO?

### 7.4 Ease of oxidation

- 36 Aluminium cans can be placed into dilute solutions of copper(II) ions, Cu<sup>2+</sup>, in order to extract the copper.
  - a Explain why this process will be spontaneous.
  - **b** Write a balanced equation for the reaction.
  - c Each can weighs approximately 16 g. Calculate the mass of copper that could be obtained using 100 cans.
- **37** Use the electrochemical series to help answer this question.



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Three beakers, labelled A, B and C, were set up containing solutions as shown in figure 7.14. A rod of nickel metal was placed in each beaker. Aqueous solutions of lead(II) nitrate and magnesium nitrate are colourless. Nickel nitrate solution is green.

- a In which, if any, of the three beakers would a reaction occur?
- b Write half equations for any reactions that occur, identifying the beaker in which the reactions take place.
- c Identify the reductant in any reaction that occurs.
- d Describe any colour change you would expect to see in any of the beakers and explain why this occurs.
- **38** Three beakers, labelled 1, 2 and 3, were set up containing aqueous solutions of B<sup>2+</sup>, C<sup>2+</sup> and C<sup>2+</sup> ions, respectively, as shown in figure 7.15.



#### figure 7.15

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Rods of metal A were placed in beakers 1 and 3, and a rod of metal B was placed in beaker 2. Reaction was observed to occur in beakers 2 and 3, but not in beaker 1.

- **a** Write half equations for the reactions that occur in beakers 2 and 3. (Note that element A forms ions with a double positive charge.)
- **b** From the substances in the three beakers name:
  - i the strongest reductant
  - ii the strongest oxidant.
- **c** Write an electrochemical series for the three elements in beakers 1–3.
- **39** Use the electrochemical series to help answer this question.

For the electrochemical cell shown in figure 7.16 state:

- a the direction of electron flow in the external circuit
- **b** a half equation for the reaction at each electrode

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c a full equation for the overall reaction in the electrochemical cell



#### figure 7.16

- **d** which electrode is the anode
- e which electrode is positive
- f which way negative ions flow in the salt bridge.
- **40** An electrochemical cell was set up by joining two half cells. One half cell consisted of a piece of nickel metal standing in a solution of aqueous nickel chloride solution. The other half cell was made up of a piece of copper metal in a solution of copper(II) sulfate.
  - a Draw a labelled diagram of the cell and show:
     i the direction of electron flow in the external circuit
    - ii which electrode is the anode
    - iii which electrode is positive
    - iv which way negative ions flow in the salt bridge.
  - **b** Write a half equation for the reaction at each electrode.
  - **c** Write a full equation for the overall reaction in the electrochemical cell.
- **41** The Hall–Héroult cell is used for the commercial production of aluminium metal. It is shown in figure 7.17. The redox reaction that occurs in this electrolytic cell is:

$$2Al_2O_3(l) + 3C(s) \rightarrow 4Al(l) + 3CO_2(g)$$



figure 7.17

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- In the Hall-Héroult cell, the reductant is:
- A carbon, in the anodes.
- **B** aluminium ions, from the alumina,  $Al_2O_3$ .
- **C** oxide ions, from the alumina,  $Al_2O_3$ .
- **D** cryolite, in the electrolyte.

### 7.5 Faraday's laws of electrolysis

- **42** Calculate the current required to deposit 5.0 g of gold per hour on the cathode from a solution containing a salt of gold in the +3 oxidation state.
- 43 Two electrolytic cells are connected in series. From one, containing sulfuric acid, 0.504 g of hydrogen gas is released in 2 hours. If the other cell, containing copper(II) sulfate, produced oxygen and copper at the anode and cathode respectively, what mass of each would be produced in the same time?

- **44** Lithium metal is prepared by electrolysis of a molten mixture of lithium chloride and potassium chloride.
  - **a** Write a half equation for the reaction occurring at the cathode in this cell.
  - **b** Write a half equation for the reaction occurring at the anode in the cell.
  - **c** Why is it not possible to produce lithium metal by the electrolysis of an aqueous solution of lithium chloride?
  - **d** Suggest why a mixture of lithium chloride and potassium chloride is used, rather than pure lithium chloride, in this electrolytic process.
  - e Assuming that lithium reacts in a similar way to sodium, describe two precautions that would need to be taken in this preparation.



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## Acid-basë reactions



Introducing acids and bases

**Acids** and **bases** are very common substances. They are widely used throughout industry and can be found in most households. Acids can be found in rain as a byproduct of air pollution and they can be used to clean concrete and flavour foods. They are even produced by our muscles when our muscles fatigue. Bases are used to make powerful cleaning products. They can also be found in cement and used to treat indigestion. Bases that are soluble in water are referred to as **alkalis**.

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There are many acids and bases that are commonly found in and around your home (see tables 8.1 and 8.2).

table 8.1 Common acids and some everyday uses.					
Name	Formula	Uses			
hydrochloric acid	HCl	present in stomach acid; used as a cleaning agent for brickwork			
sulfuric acid	$H_2SO_4$	one of the most common chemicals manufactured; used in car batteries, paints, fertilisers and detergents			
nitric acid	$HNO_3$	used in the manufacture of fertilisers, dyes and explosives			
ethanoic acid (acetic acid)	CH₃COOH	key ingredient in vinegar; used as a preservative			
carbonic acid	$H_2CO_3$	used in carbonated soft drinks and beer			
phosphoric acid	$H_3PO_4$	used in some soft drinks and the manufacture of fertilisers			
citric acid	$C_6H_8O_7$	occurs in citrus fruits			
lactic acid	$C_3H_6O_3$	occurs in milk products; produced in muscles during strenuous exercise			
ascorbic acid	$C_6H_8O_7$	vitamin C-found in citrus fruits			
formic acid (methanoic acid	) НСООН	gives the bite of the green ant its sting			

An alkalı ıs a base that dissolves in water to form an alkaline solution.

table 8.2 Common bases and some everyday uses.					
Name	Formula	Uses			
sodium hydroxide (caustic soda)	NaOH	used in drain and oven cleaners; soap making			
ammonia	NH <sub>3</sub>	used in household cleaners, fertilisers and explosives			
calcium hydroxide	Ca(OH) <sub>2</sub>	found in cement and mortar; in garden lime to adjust soil ph			
magnesium hydroxide	$Mg(OH)_2$	key ingredient in some antacids such as milk of magnesia— to overcome indigestion			
sodium carbonate	Na <sub>2</sub> CO <sub>3</sub>	used in manufacture of washing powder and glass			

### Properties of acids and bases

Acids and bases have characteristic properties, some of which are listed in table 8.3. Some properties are common to both acids and bases.

<b>table</b> $\mathbb{B}_{3}$ Properties of acids and bases.				
Properties of acids	Properties of bases			
sour tasting	bitter tasting			
cause indicators to change colour (e.g. turn litmus red)	cause indicators to change colour (e.g. turn litmus blue)			
react with bases to produce a salt and water	react with acids to produce a salt and water			
can be strong or weak	can be strong or weak			
can be dilute or concentrated	can be dilute or concentrated			
can be corrosive	can be corrosive			

### Neutralisation reactions

Acids and bases can be defined in many different ways. In simple terms, an acid is a substance that can neutralise a base, and a base is a substance that can neutralise an acid. When an acid and a base neutralise each other they always produce a salt and water.

For example:

HCl(aq)	+	NaOH(aq)	$\rightarrow$	NaCl(aq) +	$H_2O(l)$
hydrochloric		sodium		sodium	water
acid		hydroxide		chloride (a salt	z)

This is called a neutralisation reaction.

A neutralised solution is neither an acid nor a base and consists of a salt and water.

### Questions

- **1** Define an acid in simple terms.
- **2** Describe what the term neutralisation means when referring to acids and bases.
- **3** Give two examples of where you might find a base in your home.
- 4 Identify four properties acids and bases have in common.
- 5 From the neutralisation reaction described below, write a chemical equation. Calcium carbonate and water was produced when carbonic acid reacted with calcium hydroxide.



**salt** is the compound

can be summarised by the

word equation:

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Acid-base reactions

## 8.2 Reactions involving acids

Acids react with a number of elements and compounds in a highly predicable way. Some of the characteristic reactions of acids are described in this section.

### Acids and metals

The position of hydrogen in the electrochemical series (table 7.2) indicates that acids will react with the highly reactive alkali metals (such as lithium and sodium), and even some less reactive metals (such as tin and lead) will react with acids.

When a metal reacts with an acid it forms a salt and hydrogen gas.

metal + acid  $\rightarrow$  salt + hydrogen gas

For example:

Mg(s) magnesium metal	+	2HCl(aq) hydrochloric acid	$\rightarrow$	MgCl <sub>2</sub> (aq) magnesium chloride (a salt)	+	H <sub>2</sub> (g) hydrogen gas
2Al(s) aluminium	+	$3H_2SO_4(aq)$ sulfuric acid	$\rightarrow$	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (aq) aluminium sulfate (a salt)	+	3H <sub>2</sub> (g) hydrogen gas

### Metal hydroxides and acids

Metal hydroxides react with acids. A salt and water are also the products in this case.

metal hydroxide + acid  $\rightarrow$  salt + water

For example:

KOH(s)	+	HCl(aq)	$\rightarrow$	KCl(aq)	+	$H_2O(l)$
potassium		hydrochloric		potassium		water
hydroxide		acid		chloride (a salt)		

### Metal oxides and acids

When an oxidised form of some metals is placed in an acid it will react to produce a salt and water. The oxide behaves as a base.

### Metal carbonates and acids

Carbonated forms of metals also react to form a salt and water. Carbon dioxide gas is an additional product of this particular reaction.

metal carbonate + acid  $\rightarrow$  salt + water + carbon dioxide gas

For example:

MgCO <sub>3</sub> (s)	+	2HCl(aq)	$\rightarrow$	MgCl <sub>2</sub> (aq)	+	$H_2O(l)$	+	$CO_2(g)$
magnesium		hydrochloric		magnesium		water		carbon
carbonate		acid		chloride (a sa	lt)			dioxide



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some metals with dilute acid.

**figure 8.2** Effervescence in this antacid preparation is due to hydrogen ions and hydrogen carbonate ions reacting together to produce bubbles of carbon dioxide.

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### Metal hydrogen carbonates and acids

Metal hydrogen carbonates react with acids to form a salt, water and carbon dioxide.

metal hydrogen carbonate + acid  $\rightarrow$  salt + water + carbon dioxide For example:

NaHCO <sub>3</sub> (s)	+	HCl(aq)	$\rightarrow$	NaCl(s)	+	$H_2O(l)$	+	$CO_2(g)$
sodium		hydrochloric		sodium		water		carbon
hydrogen		acid		chloride				dioxide
carbonate				(a salt)				

### Metal sulfides and acids

Another characteristic reaction of acids is their response to metal sulfides. Most metal sulfides will react with acids to form a salt and hydrogen sulfide.

metal sulfide + acid  $\rightarrow$  salt + hydrogen sulfide

For example:

FeS(s)	+	2HCl(aq)	$\rightarrow$	FeCl <sub>2</sub> (aq)	+	$H_2S(g)$
iron(II)		hydrochloric		iron(II)		hydrogen
sulfide		acid		chloride (a salt)		sulfide

Metal sulfides that have very low solubilities will not react in this way.

# Reactions of hydrochloric acid

#### Purpose

To investigate some common reactions of hydrochloric acid.

#### Method

Note: A pH meter can be used as an alternative to universal indicator for this experiment. In this case, it may be necessary to replace test tubes with small beakers.

- 1 Add one drop of universal indicator to a test tube containing 20 drops of 0.1 M HCl. Add 0.1 M NaOH drop by drop and record any colour changes. Explain your observations and write an equation for the reaction that has occurred.
- 2 Carry out each of the following procedures and record your observations.
  - a Add about 1 mL of 1 M HCl to a test tube containing a small amount of solid CaCO<sub>3</sub>. Test the gas evolved with lime water.
  - **b** Add about 5 mL of 1 M HCl to a small amount of solid CuO in a test tube. Shake the test tube and allow it to stand for 5 minutes.
  - **c** Add about 10 mL of 0.1 M HCl to a test tube containing a 1 cm strip of magnesium. Use an inverted test tube to collect the gas evolved and test it with a lighted taper.
  - **d** Add 1 mL of 0.1 M HCl to a small amount of solid NaHCO<sub>3</sub> in a test tube. Test the gas evolved with lime water.
- **3** Summarise the reactions of hydrochloric acid observed in this experiment.

#### Discussion

- **1** Write a full balanced equation for each reaction.
- 2 Write a balanced ionic equation for each reaction. Indicate whether the reaction is an acid-base reaction.

materials

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- 1 M HCI
- O.1 M NaOH
- lime water
- universal indicator and pH chart or pH meter
- solid samples of CaCO<sub>3</sub>, CuO, NaHCO<sub>3</sub>, Mg
- test tubes/small beakers
- spatula
- teat pipette

#### safety

• Wear gloves, safety glasses and a laboratory

coat for this experiment.
HCl is very corrosive and HCl vapour irritates the respiratory system.





### Questions

- 6 Predict the products of the reactions involving acids below and balance the equations.
  - a  $CuO + H_2SO_4$
  - **b** CaS + HNO<sub>3</sub>
  - c Sn + HCl
  - d CaCO<sub>3</sub> +  $H_3PO_4$
  - e Mg(HCO<sub>3</sub>)<sub>2</sub> + HCl
- **7** For each of the following reactions write an overall equation.
  - a lead(II) hydrogen carbonate and sulfuric acid
  - **b** iron(III) hydroxide and hydrochloric acid
  - c calcium carbonate and nitric acid

- 8 One particular brand of indigestion tablet contains the following active ingredients:
   • calcium carbonate, 750 mg
  - magnesium carbonate, 750 mg
  - aluminium hydroxide, 120 mg.

It is claimed that this preparation relieves the discomfort caused by excess stomach acid.

- a Which acid is present in the human stomach?
- **b** Write a balanced equation for the reaction of each of the above active ingredients with stomach acid.
- c A short time after taking the tablets you burp. Why?

## 8.3 Defining acids and bases

### Arrhenius acids and bases

Over time chemists have defined acids and bases in different ways. In 1887 the Swedish chemist Svante Arrhenius released his ideas on acids and bases. Arrhenius defined an acid as a substance that contains hydrogen and produces  $H^+$  ions in aqueous solution and a base as a substance that contains one or more hydroxide groups and produces  $OH^-$  ions in aqueous solution.

For example, an acid such as hydrochloric acid will ionise in water to release hydrogen ions.

HCl(aq)	$\rightarrow$	H <sup>+</sup> (aq)	+	Cl <sup>-</sup> (aq)
hydrochloric acid		hydrogen ion		chloride ion

A base such as sodium hydroxide will ionise in water to release hydroxide ions.

NaOH(aq)	$\rightarrow$	Na <sup>+</sup> (aq)	+	OH <sup>-</sup> (aq)
sodium hydroxide		sodium ion		hydroxide ion:

**Monoprotic** acids only donate one proton per molecule. Hydrochloric acid is an example of a monoprotic acid. Some acids ionise to produce more than one hydrogen ion. These are known as **polyprotic** acids.

Sulfuric acid is referred to as a **diprotic** acid because it ionises to give two protons.

$H_2SO_4(aq)$	$\rightarrow$	2H <sup>+</sup> (aq)	+	SO4 <sup>2-</sup> (aq)
sulfuric acid		hydrogen ions		sulfate ion

Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) ionises to produce three protons and is known as a **triprotic** acid.

The Arrhenius theory did not allow for some compounds that were regarded as acids or bases but could not be described by the Arrhenius definitions. Ammonia (NH<sub>3</sub>) has all the properties of a base yet it does not contain hydroxide ions. The definition of acids and bases needed to be further developed.

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**figure 8.3** In this reaction hydrochloric acid acts as the proton donor and water as the proton acceptor.



figure 8.4 In this reaction the base ammonia acts as a proton acceptor and water as the proton donor.

### Brønsted-Lowry acids and bases

In 1923 Johannes Brønsted and Thomas Lowry developed a more inclusive definition of acids and bases. The Brønsted–Lowry theory defines acids and bases by the way they react with each other. When an acid and a base react, the the acid acts as a **proton donor** and the base as a **proton acceptor**. An acid donates a proton in the form of a  $H^+$  ion, and a base accepts the  $H^+$  ion.

 $\mathrm{H^{+}}$  ions react with water molecules to form the hydronium ions (H<sub>3</sub>O<sup>+</sup>) in aqueous solution.

According to the Brønsted–Lowry theory the base forms a **conjugate acid** when it receives a proton. Conversely an acid forms a **conjugate base** after donating a proton.

For example, in the reaction between nitric acid and water, water acts as a base and accepts a proton from nitric acid. It then forms a conjugate acid. The acid donates a proton and forms a conjugate base.

HNO <sub>3</sub> (aq)	+	$H_2O(l) \rightarrow$	$H_3O^+(aq)$	+	$NO_3^{-}(aq)$
acid		base	conjugate acid		conjugate base

Similarly, in the reactions between hydrochloric acid and ammonia, the acid donates a proton to form a conjugate base. Ammonia (a base) accepts a proton and forms a conjugate acid.

HCl(aq)	+	NH <sub>3</sub> (aq)	$\rightarrow$	$NH_4^+(aq)$	+	Cl <sup>-</sup> (aq)
acid		base		conjugate acid		conjugate base

Conjugate acids are paired with the base and conjugate bases are paired with the acid in a neutralisation reaction. In the reactions between nitric acid and water, nitric acid and the nitrate ion are a **conjugate acid–base pair**. Water and the hydronium ion are also a conjugate acid–base pair.

In the reaction between hydrochloric acid and ammonia, the hydrochloric acid and chloride ion are a conjugate acid–base pair, and ammonia and the ammonium ion are also a conjugate acid–base pair.

A **conjugate acid** is the species formed when a base accepts a proton. A **conjugate base** is the species formed when an acid donates a proton.

#### Acids ... donate a proton to form:



Bases ... accept a proton to form:







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### Amphiprotic substances

Amphiprotic substances can act as either an acid or a base according the Brønsted–Lowry theory.

For example water can act as a hydrogen ion donor (acid) in the reaction:

or as a hydrogen ion acceptor (base) in the reaction:

 $\begin{array}{rrrr} HCl(aq) & + & H_2O(l) & \rightarrow & Cl^-(aq) & & + \\ acid & & base & & conjugate \ base & \end{array}$ 

H<sub>3</sub>O<sup>+</sup>(aq) conjugate acid

Water is an example of an amphiprotic substance. Some others are listed below.



figure 8.6 Some amphiprotic substances.



### Purpose

To determine the relative acid and base strengths of some amphiprotic substances.

### Method

- 1 Place 20 drops of each solution into separate semi-micro test tubes. Add one drop of universal indicator to each solution. Record the colour of each solution. Alternatively, a pH meter can be used.
- 2 Use the indicator chart to determine the pH of each solution.

### Theory

Amphiprotic substances can act as both acids and bases. In aqueous solution, an amphiprotic substance will undergo two hydrolysis reactions, one as an acid and one as a base. In most cases, one of these reactions will predominate. If the acid reaction proceeds to a greater extent than the base reaction, the concentration of hydronium ions  $(H_3O^+)$  is greater than the concentration of hydroxide ions  $(OH^-)$  and the pH of the solution will be less than 7. If the base reaction proceeds further than the acid reaction, then the pH of the solution will be greater than 7.

In this experiment, the sodium salt of each amphiprotic anion is used. The Na<sup>+</sup>(aq) ion does not hydrolyse to any appreciable extent in water. Any change of pH can therefore be attributed to the acid-base reactions of the amphiprotic anion in each solution.

#### Discussion

1 Write equations for the acid and base hydrolysis undergone by each of the amphiprotic substances tested. In each case, deduce whether the substance is stronger as an acid or as a base.

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### Questions

- 9 Define the terms acid and conjugate acid using the Brønsted-Lowry theory.
- **10** Define the terms conjugate base and base using the Brønsted–Lowry theory.
- **11** Identify the acid/conjugate base and base/conjugate acid pairs in each of the following neutralisation reactions.
- **a**  $H_2SO_4(aq) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq)$ **b**  $CH_3COOH(aq) + OH^-(aq)$

 $\rightarrow CH_3COO^-(aq) + H_2O(l)$ c  $CO_3^{2-}(aq) + CH_3COOH(aq)$  $\rightarrow HCO_2^-(aq) + CH_2COO^-(aq)$ 

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

## 8.4 Concentration and strength

### Dilute and concentrated

The terms dilute and concentrated have no relationship to the strength of an acid or a base. These terms only describe the amount of acid or base dissolved in a specified volume of solution.

For example, concentrated hydrochloric acid would have a large amount of hydrogen chloride dissolved in a fixed volume of water. A dilute solution of hydrochloric acid would only have a small amount of hydrogen chloride dissolved in a fixed volume of water. Both solutions would contain a strong acid, but the more concentrated solution will contain more hydrogen ions per litre of solution.

### Strong and weak

The strength of acids is determined by their ability to ionise in solution. When a strong acid such as hydrochloric acid is dissolved in water it forms hydronium and chloride ions.

	HCl(aq) hydrochloric acid	+ +	H <sub>2</sub> O(l) water	$\rightarrow$ $\rightarrow$	H <sub>3</sub> O <sup>+</sup> (aq) hydronium ion	+ +	Cl <sup>–</sup> (aq) chloride ion
]		ſ					
	• • -	- H <sub>2</sub>	2 <mark>0(I)</mark>				
	• •	- Ha	<sub>3</sub> 0+(aq)				
	• • •	- Ch	-(aq)				
	• • •			fi C	gure 8.7 Strong a ompletely in solution	acide 1.	like HCI will ionise

Because it ionises completely, hydrochloric acid is referred to as a strong acid. Weaker acids such as vinegar (acetic acid) only partially ionise in solution and are described as weak acids.  $\cap$ 

Acid-base reactions



**figure 8.8** A concentrated strong acid (HCI) and a concentrated weak acid ( $CH_3COOH$ ). You can see the number of hydrogen ions is higher in the strong acid solution.

СН<sub>3</sub>СОО<sup>—</sup>
 СН<sub>3</sub>СООН

Strong acids react faster and are more corrosive than weak acids of the same concentration. A strong acid is a better electrolyte than a weak acid, i.e. a strong acid will conduct electricity much better than weak acid solution of the same concentration. This is because there would be more dissolved ions in a solution of strong acid which are able to conduct a current.

Most acids are **monoprotic** and only donate one proton per molecule. Monoprotic acids can be weak or strong also. Hydrochloric acid is a strong monoprotic acid and acetic acid (vinegar) is a weak monoprotic acid.

Sulfuric acid is referred to as a diprotic acid because it donates two protons.

$$\begin{split} H_2SO_4(aq) + H_2O(l) &\rightarrow HSO_4^-(aq) + H_3O^+(aq) \\ HSO_4^-(aq) + H_2O(l) &\rightarrow SO_4^{2-}(aq) + H_3O^+(aq) \end{split}$$

CIT(aq)

Sulfuric acid is a strong acid because it ionises to a large extent in aqueous solution, not because it is diprotic.

Phosphoric acid is a **triprotic acid** and can donate three protons. It is still only a weak acid because only a small proportion of phosphoric acid will ionise when reacting with a base.

$$\begin{split} H_{3}PO_{4}(aq) + H_{2}O(l) &\rightarrow H_{2}PO_{4}^{-}(aq) + H_{3}O^{+}(aq) \\ H_{2}PO_{4}^{-}(aq) + H_{2}O(l) &\rightarrow HPO_{4}^{2-}(aq) + H_{3}O^{+}(aq) \\ HPO_{4}^{2-}(aq) + H_{2}O(l) &\rightarrow PO_{4}^{3-}(aq) + H_{3}O^{+}(aq) \end{split}$$

Whether an acid is monoprotic, diprotic or triprotic does not determine its strength. The **strength of an acid** is determined by the extent to which it ionises in aqueous solution.



Methyl violet indicator is added to test tubes containing 1 M CH<sub>3</sub>COOH, 1 M HCl, 0.1 M HCl and 0.01 M HCl. The colour of the indicator in the 1 M CH<sub>3</sub>COOH most closely matches the colour in the 0.01 M HCl.

#### Purpose

To compare the extent of ionisation of 1 M CH<sub>3</sub>COOH and 1 M HCl.

#### Method

- Prepare a solution of approximately 0.1 M HCl by adding 10 mL of 1 M HCl to 90 mL of water.
- 2 Prepare a 0.01 M HCl solution by diluting the 0.1 M HCl solution in the same way.

An **electrolyte** is a substance that dissolves in water to form ions that are free to move and hence conduct electricity.

#### materials

- $3 \times 100$  mL beakers
- 4 × test tubes
  test-tube rack
- 10 mL measuring
- cylinder
- 100 mL measuring cylinder
- 10 mL of 1 M CH<sub>3</sub>COOH

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10 mL of 1 M HCl
methyl violet indicator

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- **3** Place solutions of 1 M, o.1 M and o.01 M HCl in test tubes to a depth of about 5 cm. To each, add three drops of methyl violet indicator.
- 4 Add three drops of methyl violet to a test tube containing a similar quantity of 1 M CH<sub>3</sub>COOH. Match the indicator colour in 1 M CH<sub>3</sub>COOH to one of the HCl solutions.

#### Theory

Unlike HCl, CH<sub>3</sub>COOH only ionises to a small extent in water:

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

Because just 1% of the CH<sub>3</sub>COOH molecules are present as CH<sub>3</sub>COO<sup>-</sup>, the concentration of H<sub>3</sub>O<sup>+</sup> ions in 1 M CH<sub>3</sub>COOH is about 0.01 M (pH 2). Methyl violet changes colour at a pH value of about 1.

#### Discussion

- 1 What is the concentration of  $H_3O^+$  ions in each of the HCl solutions?
- 2 Using your answer to Question 1, estimate the concentration of  $H_3O^+$  ions in 1 M CH<sub>3</sub>COOH.
- **3** Approximately what percentage of the CH<sub>3</sub>COOH molecules have been ionised?

#### Alternative activity

If two equal amounts of marble chips are simultaneously added to each of the acids in the test tubes, the rates of evolution of carbon dioxide gas may also be used as a measure of relative acidity. Alternatively, magnesium may be added and the rates of evolution of hydrogen gas compared.

The same principles apply for the strength of bases as well. A strong base such as sodium hydroxide will ionise completely to form sodium and hydroxide ions in solution.

NaOH(s)	+	$H_2O(l) \rightarrow$	Na <sup>+</sup> (aq)	+	OH <sup>-</sup> (aq)	+	$H_2O(l)$
sodium hydroxide		water	sodium ion		hydroxide ion		water

A weaker base such as ammonia will not ionise as readily as sodium hydroxide. Only a fraction of ammonia will react with water to form ammonium ions and hydroxide ions.

 $\begin{array}{rrrr} \mathrm{NH}_3(g) & + & \mathrm{H}_2\mathrm{O}(l) \rightleftharpoons & \mathrm{NH}_4{}^+(aq) & + & \mathrm{OH}^-(aq) \\ \mathrm{ammonia} & & \mathrm{water} & & \mathrm{ammonium\ ion} & & \mathrm{hydroxide\ ion} \end{array}$ 





safety

• Wear safety glasses and a laboratory coat for this experiment.

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Vorksheet 2

Acid-base reactions

Acid–base reactions

The double arrow indicates that a process is reversible. Not only do reactants form products but the products can also

### Questions

Square brackets [ ] are

used to represent

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LCHEMICAL REACTIONS

- 12 a What type of acid (monoprotic, diprotic, etc.) is H<sub>3</sub>AsO<sub>4</sub>?
  - **b** Write an equation(s) to show how it ionises in water.
  - c Identify the types of polyprotic acids in table 8.1.
- 13 What is the difference between a strong acid and a concentrated acid?
- **14** Why do strong acids conduct electricity better than weak acids?
- **15** What volume of 10 M hydrochloric acid would be required to prepare 250 mL of 0.30 M acid solution?

## 8.5 The pH scale

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A Danish scientist called Soren Sorenson proposed the pH scale in 1909. The concentration of hydrogen ions in a solution is used to compare the strength of an acid or a base. An acid solution contains a higher concentration of hydrogen ions and will have a lower pH. A basic solution contains a lower concentration of hydrogen ions and will have a higher pH.

The pH scale usually ranges from 1 to 14, but can be outside this range in cases of very strong, concentrated acids and bases. A pH of 7 indicates a solution is neutral and is neither an acid nor a base. It is possible to have a pH of less than 1 or greater than 14. The numbers merely provide a means of making a comparison between solutions. A pH of 0–3 can be described as very acidic, 3–6 as mildly acidic, 8–11 as mildly basic and 11–14 as very basic.

The pH of a solution is calculated using the negative logarithm of the concentration of hydrogen ions and is expressed as

 $pH = -log[H^+]$ 

Worked example 8.5A

If a solution of hydrochloric acid has a concentration of hydrogen ions equal to 1.0 M then the negative logarithm of this concentration defines this solution as having a pH of o.

```
pH = -log[H^+]
```

```
pH = -log[1.0] = 0.0
```

This would indicate a strongly acidic solution.

## Worked example 8.5B

Å solution of sodium hydroxide had a hydrogen ion concentration of  $1.0 \times 10^{-14}$  M. The negative logarithm of this solution defines the solution as having a pH of 14.

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- $pH = -log[H^+]$
- $pH = -log[1 \times 10^{-14}] = 14$

This would indicate a very alkaline (or basic) solution.



The pH scale is used widely throughout industry and in the home. Pool testing kits, used to maintain water quality in swimming pools, use the pH scale. Soap makers monitor the pH of their product to ensure it won't be too caustic for your skin and eyes.

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The pH of blood should remain at around 7.35–7.45 and stomach acid should be between 1–2 for an individual to remain healthy. If the pH of a lake drops from 6–7 to 3–4 then all the fish and plant life will die. The pH scale makes communicating the acidity level of a substance very easy.

### 三次perilmenな 8-4 Measuring pH

#### materials

- several different 50 mL water samples collected from local streams, drains, dams or ponds and from the local water supply
- pH meter or pH paper and pH colour code reference chart
- beaker
- test tubes

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safety

 Wear safety glasses and a laboratory coat for this experiment.

#### Purpose

To measure the pH of samples of water from several different sources.

#### Method

#### A. Using a pH meter

- 1 If necessary calibrate the pH meter using the instructions provided with the instrument.
- 2 Insert the probe of the pH meter into a beaker containing one of the 50 mL water samples. Allow to stand for 30 seconds. Record the pH reading.
- **3** Repeat this procedure for each water sample.

#### B. Using pH paper

Add a 2 cm length of pH paper to a test tube containing about 20 mL of one of the water samples. Estimate the pH of the sample by matching the colour of the pH paper with the colour code reference chart.

#### Discussion

- 1 What might lead to a sample of reservoir water having a pH value less than 7?
- 2 What is the pH of a solution in which the concentration of hydrogen ions is:
  - **a** 10<sup>-2</sup> M?
  - **b** 0.000 01 M?

### Questions

- **16** Determine the pH of the solutions described below.
  - **a**  $[H^+] = 0.01 \text{ M}$
  - **b**  $[H^+] = 1 \times 10^{-11} \text{ M}$
  - **c**  $[H^+] = 10^{-5} M$
  - **d**  $[H^+] = 1 \times 10^{-7} \text{ M}$
  - **e**  $[H^+] = 2.5 \times 10^{-7} \text{ M}$
  - **f**  $[H^+] = 2.3 \times 10^{-1} \text{ M}$
  - **g**  $[H^+] = 0.5 \text{ M}$ **h**  $[H^+] = 5 \times 10^{-8} \text{ M}$
- **17** Determine the [H<sup>+</sup>] of the following solutions.
  - **a** pH = 6.0
  - **b** pH = 7.0

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- **c** pH = 13.0 **d** pH = 3.5
- **e** pH = 12.7
- **f** pH = 5.4
- **g** pH = 1.6
- **h** pH = 8.1

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- **18** Calculate the pH of a solution that contains 50 g of  $HNO_3$  dissolved in enough water to create 1 L of solution.
- **19** Coca-Cola has a pH of 3 and black coffee has a pH of 5. How many more times acidic is Coca-Cola than black coffee?



When aqueous solutions of acids and bases are mixed, a reaction occurs in which the hydrogen ion from the acid and the hydroxide ion from the base combine in a neutralisation process that produces a **salt** and **water**. After a neutralisation reaction, the salt solutions consist of a mixture of positive and negative ions (and their names are in the salt name). For example, sodium chloride (NaCl) is a mixture of Na<sup>+</sup> and Cl<sup>-</sup> ions, calcium chloride (CaCl<sub>2</sub>) is a mix of Ca<sup>2+</sup> and Cl<sup>-</sup> ions etc.

Although all acid–base reactions are referred to generally as neutralisation reactions, strictly speaking **neutralisation** involves mixing an acid (pH < 7) with a base or alkali (pH > 7), which react to form a **neutral** salt solution of pH 7. This is not the case in the majority of acid–base reactions, as the salts can undergo hydrolysis (react with water) either accepting or donating a proton to form conjugate acid–base pairs and elevating or lowering the pH.

### Acidity of salt solutions

Salts are a class of compounds that consist of a cation other than  $H^+$  and an anion other than  $OH^-$  or  $O^{2-}$ . The acidity (pH) of salt solutions depends on whether or not their anions and cations hydrolyse. If a cation or anion donates a proton to water it forms hydronium ions ( $H_3O^+$ ) that causes the salt solution to be acidic. If an anion accepts protons from water, hydroxide ( $OH^-$ ) ions are formed, causing the salt solution to be basic.

### Acidic salts

Examples of acidic salts include NaHSO<sub>4</sub> and NH<sub>4</sub>Cl.

When combined with water, the hydrogen sulfate ion  $(HSO_4^-)$  and the ammonium ion  $(NH_4^+)$  will donate a proton to the water to form a hydronium ion.

$$\begin{split} HSO_4^-(aq) + H_2O(l) &\rightarrow SO_4^{2-}(aq) + H_3O^+(aq) \\ NH_4^+(aq) + H_2O(l) & NH_3(aq) + H_3O^+(aq) \end{split}$$

### **Basic salts**

Some anions of salts are able to accept protons from water molecules. In these cases the salt will be alkaline. Cations cannot accept protons and therefore cannot make a salt alkaline.

Examples of basic salts include Na<sub>2</sub>SO<sub>4</sub> and KCH<sub>3</sub>COO.

When combined with water the sulfate ion  $(SO_4^{2-})$  accepts a proton from water.

 $SO_4^{2-}(aq) + H_2O(l)$   $HSO_4^{-}(aq) + OH^{-}(aq)$ 

The ethanoate ion (CH $_3$ COO<sup>-</sup>) accepts a proton from water to form ethanoic acid molecules.

 $CH_3COO^{-}(aq) + H_2O(l)$   $CH_3COOH(aq) + OH^{-}(aq)$ 

Table 8.4 classifies common ions according to whether they cause aqueous solutions to be acidic, basic or neutral.

Small highly charged metal ions such as iron(III), zinc and aluminium are weakly acidic in aqueous solution. For example, the hydrated iron(III) ion hydrolyses according to the following reaction:

 $[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \qquad [Fe(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$ 

Two examples of how salts are useful in chemistry are as **buffers**, to regulate the pH of a solution, and as **indicators**, in monitoring the pH of a substance.

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Hydrolysis is a reaction i which an aqueous ion accepts or donates a proton to water.



table 8.4 Acid-base properties of some common ions in aqueous solution.					
Type of ion	Acidic	Basic	Neutral		
cation	NH4 <sup>+</sup> Fe <sup>3+</sup> Al <sup>3+</sup> Zn <sup>2+</sup>	none	metal ions from Group 1 and Group 2		
anion	HSO <sub>4</sub> <sup>-</sup> H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	F <sup>-</sup> , S <sup>2-</sup> , SO <sub>4</sub> <sup>2-</sup> , ClO <sup>-</sup> , CH <sub>3</sub> COO <sup>-</sup> CO <sub>3</sub> <sup>2-</sup> , HCO <sub>3</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , HPO <sub>4</sub> <sup>2-</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	Cl <sup>−</sup> , NO <sub>3</sub> <sup>−</sup> , Br <sup>−</sup> , I <sup>−</sup>		

### **Buffers**

**Buffers** are substances that resist changes in pH despite the addition of small amounts of acids or bases to a solution.

They usually consist of a weak acid or base, and work by removing any hydrogen and hydroxide ions from a solution. By removing both of these ions, the pH will remain constant.

Buffers are used in industries where fluctuations in pH are harmful to the manufacturing process. An example of this is the dyeing of fabrics. The dyes will not bind to the fabric as effectively if the pH is not maintained at the correct level. Our bodies have natural buffers in our blood and gastric juice to maintain the pH at healthy levels. Even the ocean maintains a healthy pH by removing excess acid using a buffer. Excessive addition of an acid or base can overpower a buffering system.

### Indicators

The most common way to determine the pH of an acid or base is with a substance called an **indicator**. Indicators change colour depending on the presence or the strength of an acid or base.

Indicators can also give an indication of the pH of a particular substance and are used in a chemical technique called titration to determine the exact concentration of acid or base in a particular solution.

Indicators are actually conjugate acids and bases that form different colours. The indicator phenolphthalein, for example, remains colourless in acidic solutions but turns pink in alkaline solutions.

HIn(aq)	+	OH-(aq)	$\rightarrow$	In <sup>-</sup> (aq)	+	$H_2O(l)$	(HIn = indicator)
colourless				pink			

This colour change occurs around a pH of 8–10.

Other indicators are different colours and change colour at a different pH range. Methyl red changes from red to yellow at pH range of 4–6. Bromocresol green changes from red to blue at a pH range of 4–6. Others such as litmus change from red to blue at pH range of 5–8

When an indicator gains or releases a hydrogen ion it changes how that substance absorbs and reflects different colours of light, causing a colour change.

There are some limitations that govern the use of indicators. First, changes in temperature will marginally affect the pH at which they will change colour. Second, indicators will also only give a rough guide to the pH because they usually change colour over a range of two pH points.

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Indicators are chemical substances that change

colour according to the pH

A **buffer** is a solution that

resists changes in pH by neutralising both acids and



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table 8.5 Common inc	licators.	
Indicator	Colour of acid form	Colour of base form
phenolphthalein	colourless	pink
methyl orange	pink	yellow
bromothymol blue	yellow	blue



### Purpose

To use the indicator methyl orange to identify each one of four different solutions as either water, 0.1 M HCl, 0.01 M HCl or 0.1 M NaOH.

#### Method

Devise a method to identify the four solutions.

#### Theory

Methyl orange is pink at pH less than 3 and yellow at pH greater than 4.

#### Discussion

- 1 Describe the method you used to identify the four solutions.
- 2 Estimate the pH of each solution.
- **3** Phenolphthalein is an indicator which changes from colourless at pH less than 8 to pink at pH greater than 10. What observations would you expect to make if you used phenolphthalein instead of methyl orange to identify the four solutions?
- 4 Sodium hydroxide is a strong alkali. Strong alkalis may be neutralised with strong acids. When sodium hydroxide is spilled onto clothes or skin the correct safety procedure is to wash immediately with water. Why should a strong acid not be used to neutralise the alkali in this situation?

### Experiment 8.6 Universal indicator colour display

*Two red solutions are mixed. The colour of the mixture changes from red to yellow to green to blue to purple.* 

#### Purpose

To show the change in colour of universal indicator as the pH changes in a chemical reaction.

### Method

#### Prior to the demonstration

- 1 Prepare a 500 mL solution containing 0.5 g Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O, 18.5 g KI and 3 mL of 0.1 M CH<sub>3</sub>COOH and enough universal indicator to produce a strong red colour. The solution is stable for about 6 hours.
- 2 Prepare a 500 mL solution containing 3 mL of 0.1 M CH<sub>3</sub>COOH, 5 mL of 20 vol  $H_2O_2$  and enough universal indicator to produce a strong red colour.

## materials

- 10 mL of each unknown solution
- methyl orange indicator
- test tubes
- test-tube rack

#### safety

- Wear safety glasses and a laboratory coat for this experiment.
- Any spillages should be mopped up immediately, and if the solution is splashed onto clothes or skin it should be washed off using plenty of water.

#### materials

- 2 × 600 mL beakers
  250 mL measuring cylinder (or 600 mL tall beaker)
- 2 × 10 mL measuring cylinders
- glass stirring rod
- white cardboard
- 0.5 g Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O
  18.5 g KI
- 6 mL of 0.1 M
- universal indicator
- 5 mL of 20 vol H<sub>2</sub>O<sub>2</sub>

Acid-base reactions

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#### safety

Wear gloves, safety glasses and a laboratory coat for this experiment.
 Avoid contact of H<sub>2</sub>O<sub>2</sub> with the eyes and skin.

#### For the demonstration

Pour equal volumes of the two solutions into a measuring cylinder and observe the colour changes. A white card behind the cylinder is helpful.

#### Theory

A series of reactions is involved:

 $H_2O_2(aq) + 2I^{-}(aq) \rightarrow 2OH^{-}(aq) + I_2(aq)$ 

 $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$ 

As the  $\mathrm{OH}^{\scriptscriptstyle-}$  is formed, it reacts with the ethanoic acid:

 $CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$ 

causing the pH to increase and the indicator colour to change.

#### Discussion

- 1 What does the colour of the universal indicator in the original solutions tell you about their pH?
- 2 What colour do you expect to observe when the two solutions are mixed?
- **3** Suggest reasons for the colour changes observed when the solutions are mixed.
- 4 Use the equations of the reactions involved in this process to explain the increase in pH observed.
- 5 Many indicators have a single acid colour and a single base colour. Suggest why universal indicator shows a number of colours.

#### Alternative activities

- This demonstration is particularly effective when carried out in a Petri dish on an overhead projector.
- The rate of the reaction is determined by the concentration of H<sub>2</sub>O<sub>2</sub>. Different concentrations of H<sub>2</sub>O<sub>2</sub> may be used to show the effect of concentration of reactants on reaction rate.

### Questions

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- 20 Write equations for the hydrolysis of the following ions.
  - a fluoride
  - **b** ammonium
  - **c** ethanoate
  - d dihydrogenphosphate
  - e hypochlorite
  - f aluminium

LCHEMICAL REACTIONS

- **21** Predict whether aqueous solutions of the following salts will be acidic, basic or neutral.
  - a aluminium iodide
  - **b** calcium hydrogensulfate
  - c potassium sulfate
  - d potassium hydrogenphosphate
  - e sodium carbonate
  - **f** sodium sulfide

### Summary **DDDD**

- Acids and bases are very common substances.
- Bases that dissolve in water are called **alkalis**.
- Acids and bases will react to form a salt and water in a neutralisation reaction.
- Acids undergo characteristic reactions.
- Acids and bases can be defined by the Arrhenius and Brønsted–Lowry theories.
- The Brønsted–Lowry theory defines acids as proton donors that form conjugate bases, and bases as proton acceptors that from conjugate acids.
- Amphiprotic substances can act as acids or bases.
- Acids and bases can be strong or weak. Strong acids make excellent electrolytes.

- Most acids are monoprotic, but some can be polyprotic—diprotic or triprotic.
- The strength of acids and bases can be compared on the pH scale. The pH of a solution is the negative logarithm of the concentration of hydrogen ions.
- **Buffers** are solutions that resist changes in pH.
- Indicators are substances that change colour depending on the pH.
- The salt of an acid–base reaction may be acidic, basic or neutral. If the anion or cation can donate a proton to water in solution, the salt is acidic. If the anion can accept a proton from water then the salt is basic.

### Key terms

- acid acidic salt alkali amphiprotic Arrhenius theory base
- basic salt Brønsted–Lowry theory buffers conjugate acid conjugate base diprotic
- electrolyte indicators monoprotic neutral salt neutralisation reaction pH
- pH scale polyprotic proton acceptors proton donor salt triprotic
- resist changes in that change cold eaction may be a **on** or **cation** can ion, the salt is **ac proton** from wate

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### **Chapter Review**

### 8.1 Introducing acids and bases

- **22** Which of the following is the formula of a common base?
  - A HCl
  - **B** HNO<sub>3</sub>
  - C NH<sub>3</sub>
  - D CH<sub>3</sub>COOH
- 23 What amount (in mol) of sulfuric acid is needed to exactly neutralise 0.01 mol of sodium hydroxide?A 0.2
  - **B** 0.02
  - C 0.01
  - **D** 0.005
- 24 a Give the name and formula of a common base.
  - **b** Give the name and formula of a common acid.
  - **c** Write an equation showing a reaction between the acid and base you have chosen.
- 25 Acids and bases have different characteristics.
  - a List three characteristics of an acid.
  - **b** List three characteristics of a base.
  - c You are given a clear solution in a beaker. Briefly outline how you would safely determine if it was an acid or a base.

### 8.2 Reactions involving acids

- **26** Which of the following gases is produced when dilute acid solution reacts with a metal?
  - $A H_2O$
  - B H<sub>2</sub>
  - **C** CO<sub>2</sub>
  - **D**  $0_2$
- **27** Which of the following reactions represents a neutralisation reaction?
  - **A** NaOH(aq) + HCl(aq)  $\rightarrow$  NaCl(aq) + H<sub>2</sub>O(l)
  - **B**  $C(g) + O_2(g) \rightarrow CO_2(g)$
  - C  $2NaOH(aq) + CuSO_4(aq) \rightarrow Cu(OH)_2(s) + Na_2SO_4(aq)$
  - **D**  $_{2}H_{2}O_{2}(l) \rightarrow O_{2}(g) + _{2}H_{2}O(l)$
- 28 Which of the following is not a likely product when an acid reacts with a metal carbonate?A H<sub>2</sub>O

  - **B** CO<sub>2</sub>
  - $H_2CO_3$

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- **D** CuCO<sub>3</sub>
- Which of the following equations correctly represents an acid reacting with a metal oxide?
   A HNO<sub>3</sub>(aq) + NaOH(aq) → NaNO<sub>3</sub>(aq) + H<sub>2</sub>O(l)

- **B**  $HNO_3(aq) + NaOH(aq)$ 
  - $\rightarrow \text{NaNO}_2(\text{aq}) + \text{H}_2(\text{g}) + \text{O}_2(\text{g})$
- **C** HNO<sub>3</sub>(aq) + Na<sub>2</sub>O(aq)  $\rightarrow$  2NaNO<sub>2</sub>(aq) + H<sub>2</sub>(g)
- **D**  $2HNO_3(aq) + Na_2O(aq) \rightarrow 2NaNO_3(aq) + H_2O(l)$
- **30** Which of the following is most likely to be produced when an acid reacts with a metal sulfide?
  - $A H_2$
  - B H<sub>2</sub>S
  - $C SO_2$
  - **D** SO<sub>3</sub>
- **31** Carbon dioxide can be produced in the laboratory by reacting dilute sulfuric acid with sodium carbonate.
  - **a** Write a full balanced chemical equation for the reaction that occurs.
  - **b** If 50.0 g of sodium carbonate is reacted with excess dilute sulfuric acid, calculate the mass of carbon dioxide produced.
  - c If 3.00 kg of carbon dioxide is produced, calculate the mass of sodium carbonate reacted.
  - **d** Suggest two safety precautions that should be followed during the procedure.
- **32** Magnesium metal reacts with hydrochloric acid.
  - **a** Write a full balanced chemical equation for the reaction.
  - **b** Calculate the mass of hydrogen gas produced when 5.0 g of magnesium reacts.
  - **c** 0.50 g of magnesium is added to 150 mL of 0.10 M hydrochloric acid.
    - i Which reactant will be in excess and by how much?
    - ii Calculate the mass of hydrogen gas produced.

### 8.3 Defining acids and bases

- **33** Which of the following substances is both amphiprotic and polyprotic?
  - A  $H_2SO_4$
  - B HCO<sub>3</sub>
  - $C H_2 PO_4^-$
  - $D H_3PO_4$
- **34 a** Write concise definitions for the following terms.
  - i Brønsted-Lowry base
  - ii strong acid
  - iii molarity

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- iv conjugate acid
- b Explain, with the aid of equations, why HCO<sub>3</sub> is classified as amphiprotic.

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- 35 The following equation represents a Brønsted-Lowry acid-base reaction:  $HNO_3(aq) + NH_3(aq) \rightarrow NH_4NO_3(aq)$ 
  - a Which reactant is acting as an acid?
  - **b** Give a reason for your answer to part a.
  - c Estimate the pH of a weak NH<sub>3</sub> solution. Explain your reasoning.
- 36 Write balanced equations for the three ionisation stages of phosphoric acid.

### 8.4 Concentration and strength

- 37 If 250.0 mL of 2.0 M HCl is diluted to 1 L, what amount of HCl (in mol) is present in 80.0 mL of diluted solution?
- 38 Calculate the concentration of each of the following diluted solutions.
  - a 20 mL of water is added to 6 mL of 0.5 M HCl.
  - **b** 1.0 L of water is added to 8.0 L of 0.5 M HCl.
  - **c** 3 L of water is added to 4 L of 0.5 M  $H_2SO_4$ .
  - d 50 mL of 2 M HCl is added to 180 mL of water.
- **39** Calculate the amount (in mol) of solute in: a 1.6 L of 0.75 M hydrochloric acid solution (HCl) **b** 3.0 L of 0.3 M nitric acid solution (HNO<sub>3</sub>)
  - c a mixture of 70 mL of 1.0 M HCl and 150 mL of o.3 M HCl.

### 8.5 The pH scale

40 Human gastric juice has a pH of 1. What is the concentration of hydrogen ions in gastric juice?

- **41** 2.7% of a 2.0 M monoprotic acid is ionised in a solution. Calculate the pH of the solution.
- **42** Human blood has a pH of 7.4. Is blood acidic, basic or neutral? What assumption have you made?
- **43** A solution of hydrochloric acid has a pH of 2.
  - a What is the molar concentration of hydrogen ions in the solution?
  - b What amount of hydrogen ions (in mol) would be present in 500 mL of this solution?
- **44** Calculate the pH of:
  - a a solution made by dissolving 0.100 mol of HNO<sub>3</sub> in water to make 100 mL of solution
  - **b** a solution made by adding 10 mL of 1.5 M HCl to 90 mL water
  - c a solution made by adding 50.0 mL water to a 100 mL solution of HCl with a pH of 2.00.

### 8.6 Salts

- 45 Classify the following salts as acidic, basic or neutral.
  - a BaCl<sub>2</sub>
  - **b**  $K_2SO_4$
  - c NaH<sub>2</sub>PO<sub>4</sub>
  - d Na<sub>2</sub>CO<sub>2</sub>
  - e NaHSO
  - NH<sub>4</sub>Cl f
  - $g K_3 PO_4$ h Cal<sub>2</sub>
  - i KHCO<sub>3</sub>

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Acid-base reactions

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## Organic chemistry

# 9.1 Organic compounds and functional groups

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Originally **organic compounds** were described as only those substances that came from living things. This idea has since been modified as a result of the work of the German chemist Friedrich Wöhler. In 1838 he synthesised the organic compound urea from the inorganic compound ammonium cyanate. Urea is a natural waste product of the metabolism of proteins and is excreted in our urine. Organic compounds can be the products of living processes or they can be synthesised in the laboratory. Wöhler inadvertently started a new industry.

Organic compounds made only of the elements carbon and hydrogen are called **hydrocarbons**. These compounds were studied in detail in Chapter 2. Carbon can form covalent bonds with itself and with hydrogen and many other elements to produce a huge variety of compounds.

Organic compounds contain covalent bonds and most molecules are non-polar. As a result organic compounds tend to be non-electrolytes. Their reaction rates are usually slow, while their carbon and hydrogen components seem to have an affinity for oxygen. This is demonstrated by their slow oxidation in air and more dramatically by their rapid oxidation when heated. The stability of organic compounds seems to be restricted to normal temperatures, with most decomposing at high temperatures. The properties and chemical reactions of organic compounds are very closely related to the types of atoms and groups of atoms attached to the hydrocarbon chains. Compounds with similar attachments of atoms can be grouped together and studied as families of compounds. The atoms or groups of atoms that influence the properties of compounds forming these families or homologous series are called **functional groups**.

**Organic compounds** are all substances that contain carbon, except carbonates and the oxides of carbon.



Electrolytes are substances that produce ions in aqueous solution and as a result can conduct an electric current.

### **Functional groups**

Functional groups include the double and triple bonds of alkenes and alkynes, the hydroxyl group (OH) of alcohols, the carbonyl group (=O) of the ketones, and the halogen of haloalkanes. All these functional groups are chemically reactive. Organic compounds are classified by their functional group (table 9.1). Worked examples 9.1A and 9.1B show you how to name organic compounds with functional groups.



A **functional group** is an atom or group of atoms that influence the properties of organic compounds.

Family (homologous series)	General formula	Functional group	Example
alkenes	C <sub>n</sub> H <sub>2n</sub>	C=C	ethene: $H_2C=CH_2$ H C=C H
alkynes	$C_nH_{2n-2}$	C≡C	ethyne: HC≡CH
haloalkanes	R−X X = a halogen	F, prefix fluoro Cl, prefix chloro Br, prefix bromo I, prefix iodo	chloromethane: CH <sub>3</sub> Cl H Cl H
alcohols (alkanols)	R-OH	–OH suffix ol prefix hydroxy	methanol: CH <sub>3</sub> OH
aldehydes (alkanals)	R-CHO	R-C o suffix al	methanal: $CH_2O$ HC
ketones (alkanones)	R-CO-R'	R R'    0 suffix one	propanone: $CH_3COCH$ $H_3C \longrightarrow C \longrightarrow CH_3$ $\parallel$ O
carboxylic acids (alkanoic acids)	R-COOH	R-C OH suffix oic (acid)	methanoic acid: HCOOH HC
amines (alkanamines)	R-NH <sub>2</sub>	−NH₂ suffix amine prefix amino	methanamine: $CH_3NH_2$ $H_3C$ $H_3C$ $H_$

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### Nomenclature

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#### Naming organic compounds

Organic compounds are named in a systematic way using rules established by the International Union of Pure and Applied Chemistry (IUPAC). In Chapter 2, section 2.5 Organic compounds, the procedures for naming saturated and unsaturated hydrocarbons were outlined. Table 2.15 lists the prefixes used in the systematic naming of hydrocarbons. Worked example 9.1A takes you through the steps of naming organic compounds with more than one functional group.



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#### Drawing organic compounds

By applying the rules used when naming organic compounds their structural formulas can be identified and drawn. Worked example 9.1B takes you through the steps for drawing organic compounds.



## Questions

**1** Define:

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- **a** organic compounds
- **b** functional groups.

Worksheet

Organic compounds

2 Give the functional group structure and an example, not in table 9.1, of each of the following: aldehyde, alcohol, ketone, carboxylic acid,

amine

- Classify the following compounds according to the functional group they contain: C<sub>2</sub>H<sub>5</sub>OH, HCOOH, CH<sub>3</sub>CH<sub>2</sub>CHO, CH<sub>3</sub>COOCH<sub>3</sub>, CH<sub>3</sub>COCH<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>
- 4 Name the compounds listed in Question 3. Table 2.15 will help with the prefixes needed when naming the carbon chains.
- **5** Draw structural formulae of the following organic compounds.
  - a 2-methylpropanal
  - **b** 3-hexanone
  - **c** 4,4-dichloro-1-butanol
  - **d** 3-amino-4-hydroxybutanoic acid

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# 9.2 Organic reactions

Organic reactions are of great importance in the modern world. Plastics, cosmetics, perfumes, pharmaceuticals, synthetic fibres and food additives represent important organic products. Reactions of organic molecules involve the breaking of relatively strong covalent bonds. As a result they tend to be slower than reactions of inorganic molecules and ions. Organic reactions are often complex and produce more than one product. The slow rate of organic reactions together with multiple products is of economic and environmental concern for manufacturers of organic reactions and restrict the number of waste products. There is an emerging field of chemistry known as 'green chemistry', in which work is being done to improve the types of reactions in processing industries, including organic reactions.

Three very important reactions of organic molecules are combustion, substitution and addition reactions.

## **Combustion reactions**

This is an important reaction. A very important example is the reaction of fuels with air to produce energy that provides power for many uses in our industrial world. Hydrocarbons burn in air (oxygen) to produce carbon dioxide and water and release large quantities of energy. An example of this is the combustion of octane in petrol.

 $2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g) + energy$ 

Organic molecules containing atoms other than oxygen and hydrogen will release other products. For example, a chlorohydrocarbon will produce chlorine gas as well as water and carbon dioxide.

The simplest formula, the empirical formula, of organic compounds can be analysed in the laboratory using data collected from their complete combustion. When a known mass of an organic compound is burnt in excess oxygen and the mass of the water and carbon dioxide products is recorded, the empirical formula can be calculated.



The **empirical formula** is the simplest whole number ratio of the elements in a compound. The **molecular formula** is the actual number of atoms of each element in the compound.

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$$n(C) = n(CO_2) = \frac{m}{M(CO_2)} = \frac{14.9 \text{ g}}{44.0 \text{ g mol}^{-1}} = 0.339 \text{ mol}$$
  
 $m(C) = n \times M(C) = 0.339 \times 12.0 = 4.07 \text{ g}$ 

Step 2: Determine the number of moles and mass of H atoms from the water,  $\mathrm{H_2O}.$ 

$$n(H) = 2n(H_2O) = 2\left(\frac{4.55}{18.0}\right) = 0.506 \text{ mol}$$
  
 $m(H) = n \times M(H) = (0.506)(1.00) = 0.506 \text{ g}$ 

Step 3: Determine the mass and number of moles of O atoms, oxygen.

m(0) = m(compound) - M(C) - m(H)= 10.0 - 4.07 - 0.506 = 5.42 g  $n(0) = \frac{m}{M(0)} = \frac{5.42}{16.0}$ 

Step 4: Determine the mole ratio of the elements.

	С	:	Н	:	0
n	0.339		0.506		0.339
$\div$ by the smallest number	0.339		0.506		0.339
	0.339		0.339		0.339
	= 1		= 1.49		= 1
Find the simplest whole nur	nber ratio:				
	2	:	3	:	2

Step 5: State the empirical formula of the compound.

**a** The empirical formula is the simplest whole number ratio of the elements:

EF is  $C_2H_3O_2$ 

Step 6: Determine the ratio of empirical formula mass and molecular mass. EFM is  $(C_2H_3O_2) = 2(12.0) + 3(1.0) + 2(16.0)$ 

M(molar mass) = 118 g mol<sup>-1</sup>

$$n = \frac{M}{\text{EFM}} = \frac{118}{59.0} =$$

**b**  $\therefore$  Molecular formula is  $(C_2H_3O_2)_2$ , which is  $C_4H_6O_4$ .

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## Substitution reactions

Saturated organic compounds can undergo substitution reactions. The molecule can have one or more atoms substituted by another type or group of atoms. Halogen atoms can substitute for hydrogen atoms as shown by the reaction between chlorine and ethane.







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Substitution reactions involve the replacement of an atom or group of atoms by another atom or group of atoms.

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Alkanes are very unreactive with many laboratory reagents. They will readily undergo combustion reactions and some substitution reactions under the right conditions. Substituted alkanes are more reactive and the substituted group can often undergo further substitution reactions. For example, methyl bromide can be produced from the halogenation of methane, and in turn can be converted to methanol.



figure 9.2 Substituted alkanes readily undergo further substitution reactions.

### Addition reactions

Unsaturated hydrocarbons can undergo addition reactions. An addition reaction occurs when two or more atoms or groups of atoms are added across a double or triple carbon–carbon bond. For example, hydrogenation reactions are important in the refining of petroleum. Hydrogenation is the addition of hydrogen to unsaturated hydrocarbons.



figure 9.3 The hydrogenation of ethene to form ethane.

It follows that halogenation is the addition of a halogen atom (F, Cl, Br, I) to an unsaturated hydrocarbon and hydration is the addition of water to an unsaturated hydrocarbon.

Unsaturated molecules are more reactive than saturated molecules.



figure 9.4 The addition of bromine to ethene.



figure 9.5 Ethene undergoes an addition reaction with steam to form ethanol.

Addition reactions involve the breaking of a double or triple bond and the addition of atoms or groups of atoms to each of the carbon atoms involved in the multiple

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- test tubes
- suggested hydrocarbons in dropper bottles heptane or octane hexene or any other alkene cyclohexene cyclohexane toluene freshly prepared bromine water in a dropper bottle

safety

- Wear safety glasses.
- Handle the liquids with care.
- Carry out the experiment in a fume cupboard or wellventilated area.
- Do not ingest the bromine or fumes from the organic materials.
- Always replace the lids after use.
- Most of the hydrocarbons are flammable, keep away from flames.
- All organic material should be collected in a beaker containing perlite or cat litter and kept in a fume cupboard to evaporate. Then wrap the perlite in plastic and dispose of in the garbage bin.

Reactivity of hydrocarbons

#### Purpose

To investigate the reactivity of saturated and unsaturated hydrocarbons.

#### Method

- 1 If available use semi-micro test tubes, if not use small test tubes.
- 2 Add 2.0 mL of hydrocarbon to a test tube and 1.0 mL of bromine water and shake.
- **3** Observe and record all observations.

#### Discussion

- 1 According to your observations, what functional group reacts with bromine water?
- 2 Classify any reactions that occurred as either an addition reaction or a substitution reaction.
- Bromine water contains HOBr(aq), Br<sup>-</sup>(aq) and H<sup>+</sup>(aq). It is the HOBr that reacts with the hydrocarbons forming OH and Br functional groups. Write balanced chemical equations for each observable reaction of hydrocarbon with bromine water.
- **4** If, instead of bromine water, the reactions were carried out with liquid bromine, write the balance equations for each of the reactions you described in Question 2.



## Questions

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- 6 Consider the following reactions.
   i burning butane (C<sub>4</sub>H<sub>10</sub>)
  - **ii** the chlorination of propene ( $CH_3CH=CH_2$ )
  - iii the chlorination of methane (CH<sub>4</sub>) to form chloromethane (CH<sub>3</sub>Cl)
  - iv the hydrogenation of butene (CH<sub>3</sub>CH<sub>2</sub>CH=CH<sub>2</sub>)
  - a Classify the reactions as either combustion, substitution or addition reactions.
  - **b** Write a balanced equation for each of the reactions.
- 7 An organic compound was known to contain only carbon and hydrogen. Complete combustion of a 2.49 g sample of the compound gave 3.87 g of water and 7.55 g of carbon dioxide. Calculate the empirical formula of the compound.
- 8 A compound contains 40.0% carbon, 6.7% hydrogen and 53.3% oxygen.
  - a Calculate its empirical formula.

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**b** The molar mass of this compound is 180 g mol<sup>-1</sup>. Determine its molecular formula.

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Alcohols contain the hydroxyl functional –OH group. It is the –OH functional group that gives the alcohols similar chemical properties. However, this hydroxyl group does not form hydroxide ions in aqueous solution, so they are not bases like NaOH. The hydroxyl functional group makes the molecules polar and allows them to form hydrogen bonds in addition to dispersion forces.

The two most well-known and important alcohols are also the two smallest: methanol and ethanol. Methanol is a clear, colourless, volatile liquid (boiling point 64.7°C) and dissolves readily in water. Ethanol, the most used of all alcohols, is, like methanol a clear, colourless, volatile liquid (boiling point 78.3°C) that is miscible in water. Although having similar chemical properties their effect on humans is quite different. Methanol is very poisonous and can cause blindness or death if consumed in large quantities. Ethanol on the other hand is the alcohol in alcoholic drinks such as wine, beer and bourbon (table 9.2). Methanol and ethanol are both used as solvents and as fuel, but ethanol has a wider variety of uses in cosmetics, varnishes, and various drugs, perfumes and dyes.

table 9.2 Ethanol content of some alcoholic beverages.				
Beverage	Alcohol content by volume (%)			
light beer	0.9–3.5			
beer	5			
table wine (red or white)	12			
fortified wines (sherry, port etc.)	20			
spirits (whisky, gin etc.)	35-50			

There are three types of alcohols—primary alcohols, secondary alcohols and tertiary alcohols—determined by the location of the –OH group on the carbon chain.

• **Primary alcohols** (1°) have an –OH group attached to an end carbon (figure 9.6). They have a general formula R–OH. Primary alcohols are the most reactive type of alcohol.



figure 9.6 Butanol is an example of a primary alcohol.

• Secondary alcohols (2°) have an –OH group attached to a carbon atom that is bonded to two other carbon atoms (figure 9.7). Secondary alcohols are less reactive than primary alcohols.



figure 9.7 2-Butanol is an example of a secondary alcohol.

Organic chemistry

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• **Tertiary alcohols** (3°) have an –OH group attached to a carbon atom that is bonded to three other carbon atoms (figure 9.8). Tertiary alcohols are relatively unreactive.



figure 9.8 2-Methyl-2-propanol is an example of a tertiary alcohol.

Experiment 9.2 Ethanol from fermentation

## materials

As selected by student

## safety

LCHEMICAL REACTIONS

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- Students prepare safety information prior to carrying out the experiment.
- Ethanol produced should not be ingested. It is flammable so keep away from any flame.

#### Introduction

The sugar industry is a thriving Australian industry. A byproduct of sugar cane processing is molasses, which is rich in sucrose and other sugars. The fermentation of molasses produces ethanol. Ethanol produced in this reaction is widely used as a solvent.

In this experiment you will design your own investigation that will enable you to produce ethanol from sucrose and to monitor any mass changes during the process.

#### Purpose

To investigate the production of ethanol from the fermentation of sucrose. Read the introduction again and write one or more questions or hypotheses to test in this investigation.

#### Method

- 1 Investigate the most suitable equipment to use and how to set it up for the fermentation of sugar.
- 2 Select the appropriate reagents.
- **3** Plan the procedure for carrying out the fermentation, monitoring mass changes and identifying the gaseous products.
- 4 Using material safety data sheets (MSDS) or other sources, find out the hazards and control measures for all selected reagents. Complete a safety information and risk assessment for the investigation before beginning the experiment.
- **5** Set up your control.
- 6 Plan your own results table for recording all measurements and observations.
- 7 Draw a labelled diagram of your experimental set-up.
- 8 Plan a test you will carry out to prove that ethanol has been produced.
- **9** Present a scientific report that includes the answers to the Discussion questions.

#### Discussion

- **1 a** What gas is produced in fermentation and how did you identify it?
- **b** Write a balanced equation for the fermentation reaction.
- 2 Explain the purpose of the control set-up.
- **3 a** What evidence did you gather about mass changes during the fermentation?
  - **b** Account for these changes.
- 4 Explain any modifications you made to your experimental design or set-up.
- 5 Describe the test you used to identify ethanol as one of the products. Explain your results.
- **6** Determine the approximate percentage of ethanol obtained in your fermentation.
- 7 What is the function of yeast in fermentation?
- 8 List the optimum conditions in which the fermentation of sugars is promoted.

Experimenでもの。 Investigating the solvent properties of ethanol

#### Purpose

To identify the solubility of different classes of substances in ethanol.

#### Method

- 1 Add 2 mL of ethanol to a small test tube.
- 2 Add a pea-sized amount of salt.
- **3** Stopper the test tube and shake.
- 4 Allow the mixture to settle and record your observations.
- **5** Dispose of the mixture in the waste container provided.
- 6 Repeat for the other solids.
- **7** Follow the same procedure for the liquids, adding 5 drops to the ethanol.

#### Discussion

- 1 Ethanol is a polar molecule. Explain what this means using the structure of ethanol to illustrate your answer.
- 2 Classify the solids as ionic or covalent molecular. Discuss their degree of solubility in ethanol in terms of bonding and structure.
- **3** Classify the liquids as ionic, polar covalent or non-polar covalent. Discuss their degree of solubility in ethanol in terms of intermolecular forces.
- 4 Some solutes dissolved to form a clear solution, but some seemed to produce new products as indicated by a colour change. From your observations of the solubility in ethanol of the substances tested, give one example of a solute that dissolves to form a clear solution and one example in which new products were formed. Explain the mechanism of dissolving.

#### materials

- stoppered test tubes, one for each test
   ethanol
- ethanoi
   0.25 teaspoon each of salt (NaCl), sugar (sucrose or glucose),
- iodine, sulfur
  a few drops of each of water, acetone, oil, kerosene, ethyl
- ethanoate
  O.1 M solutions of hydrochloric acid, ethanoic acid, sodium hydroxide

#### safety

- Wear safety glasses and laboratory coat.
- Use gloves when handling iodine.
- Ethanol and acetone are flammable, keep away from flames.
- Acids and sodium hydroxide are corrosive, handle with care.
- Dispose of all reactant and product mixtures in the container provided.

#### Organic chemistry

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## Questions

- 9 Write the structural formula of ethanol showing all bonds. Explain its polarity by referring to the bonds in the molecule, particularly those involving the –OH functional group.
- **10** Explain, with the aid of diagrams, why ethanol is highly soluble in water.
- 11 Ethanol has a boiling point of 79°C while its corresponding alkane, ethane, has a boiling point of -88.6°C. Explain this difference.
- **12** List differences between primary, secondary and tertiary alcohols. Present your answer in a table.

**13** Complete the following table, The first row has been done for you as an example.

alcohol			
Name	Structure	Type of alcohol	
ethanol	CH₃CH₂OH	primary	
2-propanol			
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> OH		
3-methyl-3-hexanol			

**14** List the alcohols in Question 13 in order from most reactive to least reactive.

# 9.4 Derivatives of alcohols

Aldehydes, ketones and carboxylic acids can be produced by the oxidation of alcohols. Alcohols can be oxidised by a number of oxidising agents, such as potassium permanganate and potassium dichromate, as shown in figure 9.9.



**figure 9.9** Primary alcohols can be oxidised to aldehydes and carboxylic acids. Secondary alcohols can be oxidised to ketones, while tertiary alcohols are difficult to oxidise. R, R' and R'' can be the same or different alkyl groups, or they can be hydrogen atoms in the case of aldehydes and carboxylic acids.

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#### Worked example 9 Write the equation for the oxidation of propanol to propanal using potassium dichromate. Step 1: Write the reduction half equation for potassium dichromate (Use the standard reduction potentials table 7.2 to identify the reduction half equation). Reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ Step 2: Write the oxidation half equation for propanol to propanal. Oxidation: $CH_3CH_2CH_2OH(l) \rightarrow CH_3CH_2CHO + 2H^+(aq) + 2e^-$ Step 3: Multiply the half equations if necessary so that the number of electrons produced during the reduction process is equal to the number of electrons required in the oxidation process. In this example the oxidation half equation needs to be multiplied by 3. Oxidation: $3CH_3CH_2CH_2OH(l) \rightarrow 3CH_3CH_2CHO + 6H^+(aq) + 6e^-$ Step 4: Add the two half equations so the electrons cancel to give the net equation for the overall redox reaction. Reduction: $Cr_2O_7^{2-}(aq) + {}^8/_4H^+(aq) + {}^{6}/_{e}^{+} \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ Oxidation: $3CH_3CH_2CH_2OH(l) \rightarrow 3CH_3CH_2CHO + 6 H^{+}(aq) + 6 e^{+}$ $Cr_2O_7^{2-}(aq) + 3CH_3CH_2CH_2OH(l) + 8H^+(aq) \rightarrow$ Redox: $2Cr^{3+}(aq) + 7H_2O(l) + 3CH_2CH_2CHO$

# / Worked example 9.43

Write the equation for the oxidation of 2-propanol to propanone using potassium permanganate.

Step 1: Write the reduction half equation for potassium permanganate (Use the standard reduction potentials (table 7.2) to identify the reduction half equation).

Reduction:  $MnO_4^{-}(aq) + 8H^{+}(aq) + 5e^{-} \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ 

Step 2: Write the oxidation half equation for 2-propanol to propanone.

Oxidation:  $CH_3CHOHCH_3 \rightarrow CH_3COCH_3 + 2H^+(aq) + 2e^-$ 

Step 3: Multiply the half equations if necessary so that the number of electrons produced during the reduction process is equal to the number of electrons required in the oxidation process. In this example the oxidation half equation needs to be multiplied by 5, while the reduction half equation needs to be multiplied by 2.

Reduction:  $2MnO_4^{-}(aq) + 16H^+(aq) + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)$ Oxidation:  $5CH_3CHOHCH_3 \rightarrow 5CH_3CHOCH_3 + 10H^+(aq) + 10e^-$ 

Step 4: Add the two half equations so the electrons cancel to give the net equation for the overall redox reaction.

Reduction:  $2MnO_4^{-}(aq) + {}^{6}\not{1} \notin H^{+}(aq) + \not{1} \notin e^{\not{+}} \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)$ Oxidation:  $5CH_3CHOHCH_3 \rightarrow 5CH_3COCH_3 + \not{1} \# H^{\not{+}}(aq) + \not{1} \# e^{\not{+}}$ 

 $\label{eq:Redox: 5CH_3CHOHCH_3 + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow$ 

 $5CH_3COCH_3 + 2Mn^{2+}(aq) + 8H_2O(l)$ 

#### materials

- 3 test tubes
- 250 mL beaker5 mL measuring
- cylinder • acidified potassium
- permanganate solutionbutanol
- 2-butanol
- 2-methyl-2-propanol

#### safety

- Wear safety glasses.
- Carry out the experiment in a wellventilated area.
- Avoid contact with the skin.
- Dispose of wastes in the container provided.

# Experiliment 9.4 Oxidation of alcohols

#### **Purpose**

To investigate the oxidation of a primary, a secondary and a tertiary alcohol.

#### Method

- 1 Prepare a hot water bath by adding boiling water from a kettle to a 250 mL beaker.
- **2** Add 2–5 mL of each of the three alcohols to three separate labelled test tubes and place the test tubes in the hot water bath.
- **3** Add 1–2 mL of acidified potassium permanganate solution to each of the alcohols, shake well and return to the hot water bath.
- 4 Record all observations.

#### Discussion

- 1 Why is a hot water bath used?
- 2 Classify the alcohols as primary, secondary or tertiary and list them from most reactive to least reactive.
- **3** Use your observations and text to predict products for any reactions.
- 4 Write the half equation for the reduction of the permanganate ion.
- 5 Write oxidation half equations for alcohol/s that reacted.
- 6 Write the overall redox reaction for the alcohol/s that reacted.
- 7 Predict the outcome if ethanol were tested. Explain your prediction. If possible test your prediction.

# Properties of aldehydes, ketones and carboxylic acids

Aldehydes, ketones and carboxylic acids are polar functional groups. The ketones are the least polar, while the carboxylic acids are the most polar of the three functional groups. In fact the carboxylic acids can form hydrogen bonds, making them very soluble in water. Hydrogen bonds are the strongest of the intermolecular forces. This gives carboxylic acids higher boiling points than similar molar mass aldehyde and ketone molecules. The aldehydes and ketones form the weaker dipole–dipole forces between their polar molecules. The polarity and strength of the hydrogen and polar bonds decrease as the size of the hydrocarbon chain increases. This means that the solubility of these molecules in water also decreases. The nature of the bonding and the location of the functional groups on the molecules influence their reactivity. Chemical reactivity follows a similar trend to the physical properties mentioned, with the carboxylic acids being the most reactive of the three functional groups.

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## Questions

- **15** List the three types of organic products that can be obtained from the oxidation of alcohols and draw their functional groups.
- **16** Methanol cannot be oxidised to a ketone. Explain.
- **17** Describe any observable changes and write oxidation and reduction half equations and the net redox equation for the following reactions.
- a the oxidation of methanol to methanal using potassium permanganate
- **b** the oxidation of ethanol to ethanoic acid using potassium permanganate
- c the reaction of potassium dichromate with 2-pentanol

Alcohols

**18** Use equations to help describe how you could prepare 2-butanone.

# 9.5 Reactions of organic acids

In the previous section we saw that organic acids contain the carboxyl functional group, –COOH (figure 9.9). Carboxylic acids are named by replacing the -e from the hydrocarbon name with the suffix -oic acid. For example, the carboxylic acid of ethane is ethanoic acid, which is the acid in vinegar and is responsible for the distinctive vinegar smell.



Organic acids are weak acids because they only partly ionise in aqueous solution to give a carboxylate ion and a proton, as shown in the equation below. This means that very few ions are formed in solution and the acid is mainly present as the molecule.

Ethanoic acid is a weak acid.

 $CH_3COOH(aq) \rightarrow CH_3COO^{-}(aq) + H^{+}(aq)$ 

or

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

Carboxylic acids undergo similar reactions to the inorganic acids. For example, they can react with a hydroxide to form a salt or with a reactive metal such as sodium to form a salt and hydrogen.

The reaction of ethanoic acid and potassium hydroxide is:

 $CH_3COOH(aq) + K^+(aq) + OH^-(aq) \rightarrow CH_3COO^-K^+(aq) + H_2O(l)$ 

The reaction of butanoic acid and sodium metal is:

 $2CH_{3}CH_{2}CH_{2}COOH(aq) + 2Na(s) \rightarrow 2CH_{3}CH_{2}COO^{-}Na^{+}(aq) + H_{2}(g)$ 

Carboxylic acids react with alcohols to produce an ester. Butanoic acid reacts with methanol to produce the ester methyl butanoate, the smell of apples.

 $CH_{3}CH_{2}CH_{2}COOH + CH_{3}OH \rightarrow CH_{3}CH_{2}CH_{2}COOCH_{3} + H_{2}O$ 

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## **Esters**

The reaction between a carboxylic acid and an alcohol is called an **esterification** reaction. An ester and water are produced. Esterification reactions are slow and reversible.

The structural formula of methyl butanoate above shows the ester functional group, RCOOR'.

When naming an ester, the first part of the name is from the alcohol reactant and the second part of the name comes from the acid. The -oic acid part of the name of the acid is replaced with the suffix -oate (figure 9.11).



Esters are an important functional group. They are responsible for fragrances and flavours in fruit. They can be manufactured synthetically or concentrated from natural sources to make perfumes, flavours and fragrances in foods. The more common esters are low melting point liquids with pleasant smells. There are many esters that are solids. Fats and waxes are solid esters (figure 9.12). Fats are used to make soap. The reaction of a fat (a triglyceride) with a strong base such as sodium hydroxide is called a **saponification reaction**. The saponification reaction is almost the reverse process to the esterification reaction. The products are an alcohol and the salt of a fatty acid—soap.



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## Questions

- **19** Draw the structural formula for the carboxylic acid and ester functional groups.
- **20** Use equations and diagrams to explain why organic acids are weak acids.
- **21** Write a balanced equation for the reaction of methanoic acid with:
  - a sodium hydroxide solution
  - **b** magnesium metal.

- **22 a** What is the name given to the reaction of a carboxylic acid with an alcohol?
  - **b** What are the products?
  - **c** Write a general equation to describe this reaction.
- **23** Identify the functional group of each of the following compounds and name them.
  - a CH<sub>3</sub>CH<sub>2</sub>COOH
  - **b** CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOH
  - c  $CH_3(CH_2)_4CH_2OH$ d  $CH_3(CH_2)_4COOCH_2CH_3$

# 9.6 Derivatives of ammonia

Amines and amides are families of organic compounds containing nitrogen (figure 9.13).



figure 9.13 (a) Ammonia, NH3, (b) an amine, RNH2, and (C) an amide, RCONH2.

## Amines

Amines, like alcohols, are classified as primary, secondary and tertiary. This is determined by the number of carbons attached to the nitrogen (figure 9.14). When one of the hydrogen atoms on the ammonia molecule is replaced by an alkyl group, a primary amine is formed. If a second hydrogen atom is also replaced by an alkyl group, a secondary amine is formed. A tertiary amine is made by replacing the third and final hydrogen atom of ammonia by an alkyl group.



figure 9.14 (a) A primary amine, (b) a secondary amine and (C) a tertiary amine.

Amines can be synthesised by the reaction of ammonia with a haloalkane such as iodomethane as shown.

 $\rm NH_3 + \rm CH_3 I \rightarrow \rm CH_3 \rm NH_2 + \rm HI$ 

When excess ammonia is used, a mixture of primary, secondary and tertiary amines is produced (see p. 251).

Amines are bases. Like the nitrogen atom of an ammonia molecule, the nitrogen atom of a primary amine has a lone pair of electrons (figure 9.14(a)), which enables it to form a bond with a hydrogen ion. That is, the amine can accept a proton and is therefore a base.

 $NH_3(aq) + H^*(aq) \rightarrow NH_4{}^*(aq)$ 

Ethylamine, like ammonia, can accept a proton and is basic.

 $\rm CH_3\rm CH_2\rm NH_2 + \rm H^+ \rightarrow \rm CH_3\rm CH_2\rm NH_3^+$ 

## Amides

Amides can be prepared by reacting ammonia or a primary or secondary amine with an acyl group, RCO–, from an acid chloride or an ester (figure 9.15). The acyl group displaces a hydrogen atom on the ammonia molecule.

propanoyl chloride + ammonia ----> propanamide + ammonium chloride

figure 9.15 Preparing an amide.

### Amino acids

The  $-NH_2$  group is often found in biological molecules, especially proteins. **Proteins** are long-chain molecules, natural polymers, made up of amino acids. **Amino acids** contain two functional groups: an amine and a carboxylic acid group (figure 9.16). Because of these two functional groups, amino acids have both acid and base properties. They are **amphoteric** and can react with an acid or a base to form a salt.



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Amino acids are twenty naturally occurring amino acids. Amino acids are the building blocks of proteins. Proteins are the building blocks of life.

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LCHEMICAL REACTIONS When two amino acids react with one another a special amide is formed called a dipeptide. The bond between the two amino acids is called a **peptide bond** (figure 9.17). A second and third peptide bond can occur at the available amino group and carboxyl group of the newly formed dipeptide. When this occurs many times a very large molecule called a polypeptide is formed. Very large polypeptides are called proteins.





figure 9.17 Two amino acids bond to form a peptide bond.



- **25** Use structural formulae to show the difference between an amine, an amide and an amino acid.
- **26** Write an equation to describe the production of butanamine (butylamine) from the reaction of chlorobutane and ammonia.
- 27 What does amphoteric mean?
- **28** Using the general formula of an amino acid in figure 9.16, show how it can act as an acid and as a base.
- 29 What is a peptide bond?



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## Summary DODD

- Any substance that contains carbon, except the oxides of carbon and carbonates, is an **organic compound**.
- A **functional group** is an atom or group of atoms that influences the properties of an organic compound. Functional groups include the double and triple bonds of **alkenes** and **alkynes**.
- The **combustion** of **hydrocarbons** in air produces carbon dioxide, water and energy.
- Saturated organic compounds can undergo substitution reactions. The molecule can have one or more atoms substituted by another type or group of atoms. When a halogen such as chlorine is substituted for a hydrogen atom, a haloalkane is formed.
- Unsaturated hydrocarbons can undergo addition reactions. An addition reaction occurs when two or more atoms or groups of atoms are added across a double or triple carbon–carbon bond.
- Alcohols contain the hydroxyl functional group, –OH group. Alcohols are polar solvents and can form hydrogen bonds with molecules such as water. Primary alcohols have an –OH group

attached to an end carbon and are the most reactive type of alcohol. **Secondary alcohols** have an –OH group attached to a carbon atom that is bonded to two other carbon atoms. **Tertiary alcohols** have an –OH group attached to a carbon atom that is bonded to three other carbon atoms and are the least reactive of the alcohols.

- Aldehydes and carboxylic acids can be produced from the oxidation of primary alcohols, while ketones can be produced from the oxidation of secondary alcohols. Carboxylic acids are weak acids because they only partly ionise in solution. They react with alcohols in an esterification reaction to produce an ester.
- Amines and amides are families of organic compounds containing nitrogen. Like the alcohols, amines are classified as primary, secondary and tertiary amines. The bond between the two amino acids is called a **peptide bond**. **Proteins** are polypeptides, natural polymers, made up of **amino acids**. Amino acids are **amphoteric** and can react with both an acid and a base.

### Key terms

- addition reaction alcohol aldehyde alkene alkyne amide amine amino acid
- amphoteric carboxylic acid combustion reaction ester esterification reaction functional group haloalkane hydrocarbon
- hydrogen bond ketone organic compound oxidation peptide bond primary alcohol protein saturated
- secondary alcohol substitution reaction tertiary alcohol unsaturated weak acid





## Chapter **Review**

## 9.1 Organic compounds and functional groups

- **30** Which of the following is not an organic compound?
  - A CH<sub>4</sub> B CaCO<sub>3</sub> C CH<sub>3</sub>COOH  $D H_2CO$
- **31** Which of the following statements about homologous series are correct? Homologous series have:
  - I the same functional groups
  - II similar chemical properties
  - III the same molecular formula
  - IV the same general formula
  - A All of the statements are correct.
  - **B** I, II & IV only **C** I & II only **D** I only
- 32 a Name the functional group and draw structural formulae of the following compounds (for example, propene: ene, an alkene,  $H_2C=CH_2$ ). propyne, butanoic acid, pentanone, ethanol, propanamine, ethanal
  - **b** Name the following organic compounds: i CH<sub>3</sub>CH<sub>2</sub>CHO ii H<sub>2</sub>C=CHCH<sub>3</sub>



**33** a Identify all the different functional groups on the structural formula of vitamin C below.



- **b** Complete the following: Vitamin C
- -OH groups (i.e. how many?) contains
- molecules are (nonpolar/polar) \_ in water (insoluble/soluble) • is

## 9.2 Organic reactions

- 34 Write a balanced equation for the combustion of the following: **b** pentene  $(C_5H_{10})$ 
  - a butane  $(C_4H_{10})$
  - **c** heptyne  $(\dot{C}_7 H_{12})$
- 35 Explain the difference between a substitution reaction and an addition reaction.
- **36** Write balanced equations for the following reactions:
  - a the synthesis of tetrachloromethane from the reaction of chlorine and methane
  - **b** the addition of bromine to ethene, and name the product
  - c the hydrogenation of ethyne
- 37 Calculate the empirical formula of the hydrocarbon containing 32.0 g of carbon and 2.6 g of hydrogen.
- **38** An organic ester used in a perfume contains only carbon, hydrogen and oxygen. When a 2.845 g sample was burned in excess oxygen. 1.868 g of water and 7.612 g of carbon dioxide were collected.
  - a Determine the empirical formula of the ester.
  - **b** If the molecular mass was found to be twice the empirical formula mass, determine its molecular formula.
  - c Draw a possible structural formula for the ester, given that it contains a benzene ring.

## 9.3 Alcohols

- 39 Distinguish between primary, secondary and tertiary alcohols. Include examples to support your explanations.
- 40 Propane is a gas at room temperature while propanol is a liquid. Explain.
- **41** Complete the following table.

Name of alcohol	Formula of alcohol	Type of alcohol	
ethanol	CH₃CH₂OH		
	CH <sub>3</sub> CHOHCH <sub>3</sub>	secondary	
2-methyl-2-butanol			
	$CH_3CH_2CH_2CH_2OH$		
2,3-hexanediol			

42 Describe a test that you could use to distinguish between a primary, a secondary and a tertiary alcohol.



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## 9.4 Derivatives of alcohols

- **43** Describe how each of the following organic compounds can be produced from an alcohol.
  - a aldehvde
  - **b** ketone
  - c carboxylic acid
- 44 Write equations for the following reactions. Include oxidation and reduction half equations.
  - a the oxidation of methanol by potassium permanganate to form methanoic acid
  - **b** the oxidation of 2-butanol using potassium dichromate
  - **c** the preparation of ethanal
- **45** Complete the following table.

Name of compound	Formula of compound	Type of compound
methanol		alcohol
CH₃CHO		
2-butanone		
	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	carboxylic acid
butanal		

46 Describe a test that you could use to distinguish between these three colourless liquids: propanol, propanoic acid and propanone.

## 9.5 Reactions of organic acids

- 47 Which of the following statements about carboxylic acids are correct?
  - I They turn red litmus blue.
  - II They are weak acids.
  - III They react with reactive metals to produce hydrogen gas.
  - IV They react with a base to form a salt and water.
  - A All of the statements are correct.
  - B I. II & III only
  - C II, III & IV only
  - **D** I only
- **48** Name the following.
  - a CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOH
  - **b** CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>COOH
  - c CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOCH<sub>3</sub>
  - d CH<sub>3</sub>COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

- 49 Write equations for the following carboxylic acids reactions. Describe any observations expected.
  - a  $CH_3CH_2CH_2CH_2COOH + NaOH \rightarrow$
  - **b** CH<sub>3</sub>CH<sub>2</sub>COOH + Mg  $\rightarrow$
  - c  $CH_3CH_2CH_2CH_2COOH + CH_3CH_2OH \rightarrow$

- 50 Write a balanced equation for the esterification reaction of methanoic acid and butanol. Name the ester formed.
- 51 Identify the alcohol and acid used to form the following esters:
  - a ethyl methanoate
  - **b** butyl ethanoate
  - c CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
  - d CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOCH<sub>2</sub>CH<sub>3</sub>

### 9.6 Derivatives of ammonia

- 52 Distinguish between an amine and an amide.
- 53 Show how methyl amine, CH<sub>3</sub>NH<sub>2</sub>, can form hydrogen bonds.
- 54 Write equations for the following reactions:
  - a  $NH_3 + CH_3CH_2Cl \rightarrow$
  - **b**  $NH_3 + CH_3CH_2CH_2COCl \rightarrow$
  - **c**  $NH_3 + HCOCl \rightarrow$
  - d  $NH_3 + CH_3CH_2CHClCH_3 \rightarrow$
- 55 Amines are basic. Explain.
- 56 The amino acid glycine has the structural formula shown.



- a Identify the amine and carboxylic acid functional groups.
- Using two glycine amino acids, show the b formation of a peptide bond.
- 57 In which of the following equations is the amino acid glycine acting as
  - a an acid?
  - **b** a base?

$$\begin{array}{ccc} A & CH_2 - COOH + H_2O \longrightarrow & CH_2 - COO^- + H_3O^+ \\ & & & \\ & & & \\ & NH_2 & & NH_2 \end{array}$$

**B**  $CH_2 - COOH + H_2O \longrightarrow CH_2 - COOH + OH^-$ 

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NH<sub>2</sub><sup>+</sup> C  $CH_2 - COOH + H_2O \longrightarrow CH_2 - COO^- + H_2O$ 

NH<sub>2</sub><sup>+</sup>

NH<sub>2</sub>

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