

1

Fundamentals

▼ MRSA bacteria can be detected by growing on a dish containing mannitol agar medium. Yellow areas show the presence of MRSA.
Image source: CDC/Science Photo Library.



Making substances: keeping ahead in the fight against bacteria

Antibiotic-resistant bacteria are one of the most serious threats to world health, killing nearly a million people a year. We have become used to the idea that bacterial diseases and infections, like tuberculosis (TB) and septicaemia, can be relatively easily cured with antibiotics, though in Victorian times they would have been deadly. But bacteria are fighting back and chemists are at the forefront of that battle against them. In fact, antibiotic resistance is spreading faster than new antibiotics can be introduced. This is a challenge for biomedical science across the world, and chemistry will lead the way in finding the solution.

One promising new molecule is plazomicin, whose discovery and potential as an antibiotic was reported in 2010 by the Achaogen company in California. A team of 16 chemists at the company synthesized over 400 analogues of the broad-spectrum antibiotic sisomicin. These 400 new compounds were screened for antibacterial activity and plazomicin

was found to be the most promising and selected for further development as an antibiotic. Plazomicin was finally approved for use by the Food and Drug Administration in the US in 2018 under the tradename Zemdri. Plazomicin has provided a new treatment for previously antibiotic-resistant urinary tract infections caused by Enterobacteriaceae. It has also been found to work synergistically with the antibiotics daptomycin or ceftobiprole against methicillin-resistant *Staphylococcus aureus* (MRSA). MRSA bacteria are present on the skin, nose, and throat of many healthy people where they seem to cause few problems. It is when MRSA gets into the lungs of frail or seriously ill patients that the infections become life-threatening.

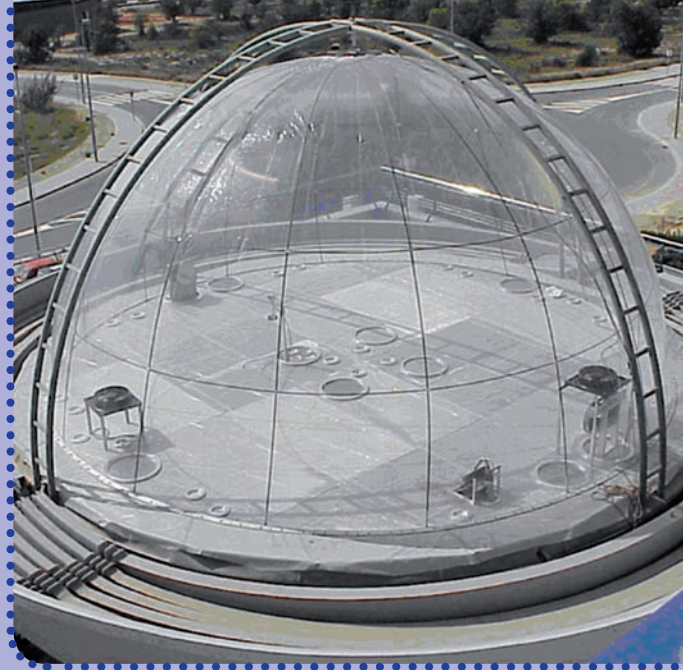
Carrying out measurements and mathematical modelling: studying the atmosphere

Most of the world's population lives in cities, and cities can be very polluted places. Chemists are finding ways to measure the concentration of pollutants such as hydrocarbons and nitrogen oxides on a street-by-street basis. These high-resolution measurements help city planners to decide better policies for preventing health damage by pollution.

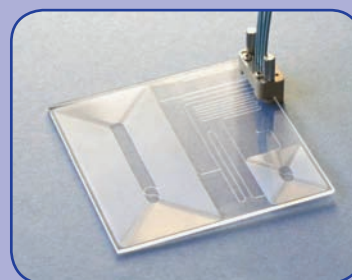
On a global scale, an understanding of the chemical reactions that take place in the atmosphere is needed to tackle the environmental problems associated with pollution.

Atmospheric chemists measure the concentrations of substances in the air at a range of locations near the ground, or at different altitudes using balloons, aircraft, and satellites. The results are analysed to look for patterns in behaviour and their causes. To make sense of the thousands of reactions that take place in the atmosphere, individual reactions are studied in detail in laboratory experiments. The way that chemicals in the air interact to form photochemical smogs is studied using smog-simulation chambers—huge reactors in which air, containing carefully controlled mixtures of pollutants, is exposed to sunlight.

Some atmospheric chemists work as computer modellers, combining the vast amount of information from experimental studies to produce models that are used to make predictions and to inform government policies on air pollution locally, nationally, and internationally.

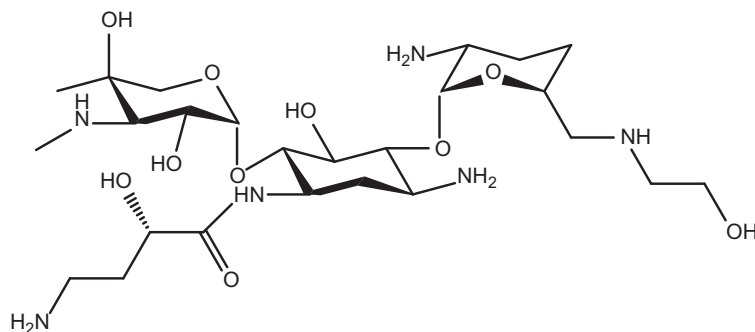


▲ The European smog-simulation chamber in Valencia, Spain. Image courtesy of Prof. Ally Lewis, Department of Chemistry, University of York.



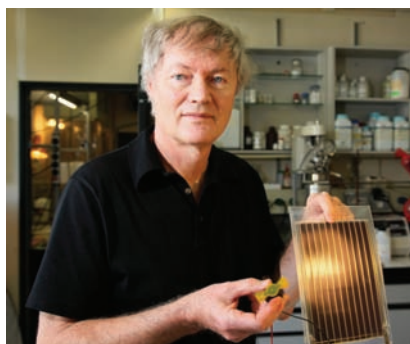
▲ This 'lab on a chip' carries a miniature gas chromatograph (see Section 11.3). It is used to analyse air samples to assess their quality. There are actually two gas chromatography columns arranged in series: the silvery lines are the columns the gases flow through. Image courtesy of Fundación CEAM, Valencia, Spain.

The structure of plazomicin. ►





Lithium-ion batteries power many devices, including some electric cars. Chemists are looking for alternatives to lithium-ion batteries that are safer and more quickly charged. A promising possibility is the aluminium-ion battery: aluminium is cheaper than lithium and less flammable, and ionizing aluminium releases three electrons compared with lithium's one. Image source: Janaka Dharmasena.



The Swiss photochemist Michael Graetzel invented the dye-sensitized solar cell. Image courtesy of Michael Graetzel. Photo credit: Alain Herzog.

i **Nanoparticles** have diameters from 1 nm to 100 nm (where 1 nm = 1×10^{-9} m).

» The hydrogen bonding in DNA is discussed in Box 25.5 (p.1160).

1.1 Chemistry: the central science

The traditional division of chemistry into physical, inorganic, organic, and analytical is an arbitrary one and the majority of chemists work across these divides. Most real problems also require chemists to interact with scientists in other disciplines. For example, chemists, physicists, mathematicians, and meteorologists work together on the vital problem of predicting the extent of future global warming and its effect on climate.

Many of the devices that we use every day—including mobile phones—depend on batteries. Electric cars offer a low pollution future, but a big limitation is the size and cost of their batteries. Chemistry is at the heart of research to find new, lighter, long-life, low-cost batteries that are quickly charged.

In the area of materials, inorganic chemists, materials scientists, bioscientists, engineers, and medics all work together on the design and production of new materials, such as a magnesium alloy battery embedded in a biocompatible polymer for use in implanted medical devices. The development of organic light-emitting diodes (OLEDs) has revolutionized the technology of display screens with the production of thin, light-weight monitors for use in computers, televisions, and the display screens on mobile phones.

In the field of renewable energy, dye-sensitized solar cells are being developed that will provide a cheaper alternative to silicon-based products. Light-harvesting dyes containing ruthenium are adsorbed onto a thin film of titanium dioxide (TiO_2) nanoparticles in contact with a redox electrolyte. The dye molecules absorb solar radiation shining on them. The resulting excited dye molecules pass on their energy by transferring electrons to the titanium dioxide, so generating an electric current. The system is arranged so that the electrolyte supplies electrons back to the dye so that the cycle can be repeated over and over again.

Many molecules in biological systems, such as DNA (the carrier of the genetic code), ATP (the source of energy in cells), and chlorophyll (the pigment that captures the energy used to drive photosynthesis), contain inorganic as well as organic components. Figure 1.1 shows the structure of part of a DNA molecule. To explain how such molecules work, biochemists need to understand ideas from physical chemistry such as thermodynamics, kinetics, and electrochemistry. Chemists, biochemists, and biologists collaborate to provide a complete picture. Box 1.1 describes how chemistry is central to understanding the role of DNA and underpins genomics.

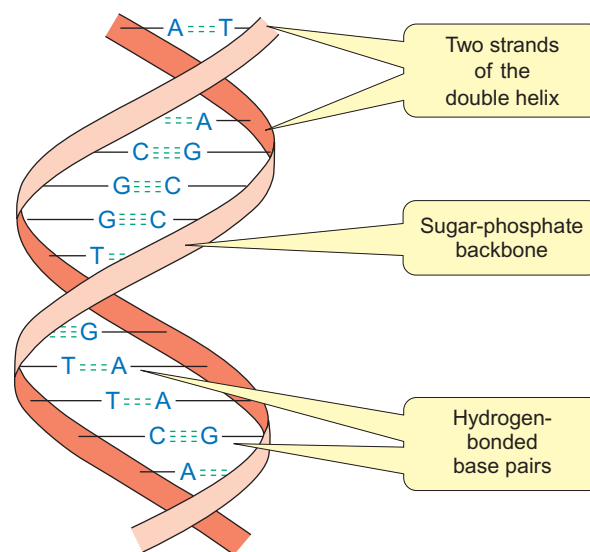


Figure 1.1 The structure of part of a DNA molecule. 'Organic' deoxyribose sugar units alternate with 'inorganic' phosphate groups to make up the backbones of the two strands of the double helix. Hydrogen bonding between the four organic bases, thymine (T), cytosine (C), adenine (A), and guanine (G), bonded to the deoxyribose units, links the two strands together.



Box 1.1 The hundred thousand genomes project

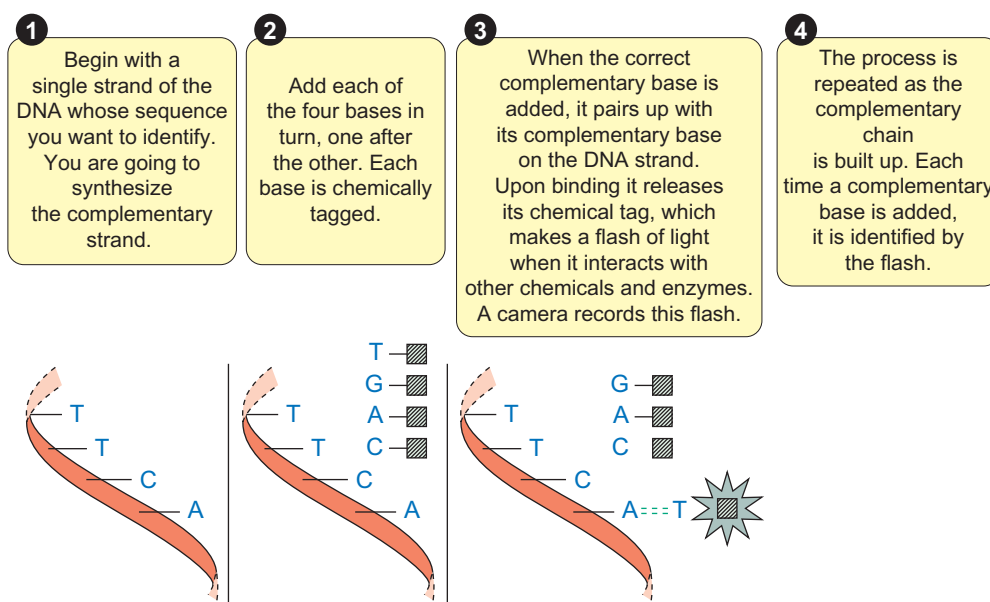
The full set of genes for an organism is called its **genome**. Mapping out the complete sequence of base pairs comprising a genome, and how these are organized into genes, is one of the aims of **genomics**—and it's all chemistry.

An international project, the Human Genome Project, was set up in 1990 to map out the 3 billion (3×10^9) base pairs in a human genome. Working out the sequence of bases involved a huge database of information and took 16 years to complete at a total cost of nearly \$3 billion. In 2016, thanks to advances in the technology of genome sequencing, a human genome could be mapped in about 24 hours at a cost of under \$1000.

How genome sequencing works

The extraordinary progress in genome sequencing is down to interdisciplinary collaboration with chemistry at its centre. Sequencing technology is changing all the time, but the methods all involve chemistry and computing.

One method is shown below—it is called 'sequencing by synthesis' and it is fully automated in a DNA sequencer. A complementary strand of DNA is built on to a single strand of the original DNA whose sequence you want to identify. Chemists have designed a system that emits a flash of light when the correct base joins the growing complementary strand. The four bases (A, T, G, and C) are added one after the other, and when the correct one is added, you get a flash of light. A camera, linked to a computer, records the flash, and then the machine moves on to the next base in the DNA chain and the process is repeated. By knowing the sequence of bases being joined to the complementary strand, we can then deduce the sequence of our original DNA strand. Massive computing power has made it possible to automate the process. It is this combination of chemistry with computing power that has driven the dramatic increase in sequencing speed and the reduction of cost.



▲ One method for sequencing DNA by synthesizing the complementary strand.

100 000 Genomes Project

As genome sequencing becomes faster and cheaper, scientists are realizing the enormous potential of genomics. Apart from identical twins, every person has their own unique genome, but the differences between individuals' genomes are very small—each human shares about 99.9% of their genome with everyone else. But the differences are interesting and tell us a lot. If scientists look closely at the genomes of people who suffer from particular diseases, they can learn about the influence of genetics on disease, and even develop therapeutic strategies that are tailored to individuals carrying particular genes.

► The logo of the original Human Genome Project shows its interdisciplinary nature. This is the thinking behind the 100 000 Genomes Project, a research effort established to sequence 100 000 genomes from around 85 000 patients of the British National Health Service. The 100 000th sequencing was completed in December 2018. So far, actionable findings have been identified for around 25% of the patients with rare diseases.





Cancerous tumours start to grow when the DNA in normal cells changes in particular ways. 50 000 of the genomes in the 100 000 Genomes Project will be from people suffering from cancer. Each one of 25 000 cancer sufferers will give two samples of DNA: one from normal cells and one from a tumour. By comparing the DNA of tumours with the DNA of normal cells, scientists can find out more about what genetic changes might have stimulated the development of the tumours—and how to treat them. New treatments for cancer could be just one of the many valuable outcomes from the 100 000 Genomes Project.

Editing genes

The 2020 Nobel Prize for chemistry was jointly awarded to Emmanuelle Charpentier and Jennifer Doudna for 'the development of a method for genome editing'.

Charpentier and Doudna discovered the Crispr-Cas9 genome editing technique which enables scientists to cut a DNA molecule at a chosen site, thus editing the genetic code of living organisms. Crispr, which stands for clustered regularly interspaced short palindromic repeats, is a relatively cheap and simple tool that has led to an explosion in the application of gene editing to a wide range of problems, such as tackling genetic illnesses, producing disease resistant crops, and modification of mosquitoes to stop malaria.

In cancer treatment, Crispr-edited immune cells are being investigated. Crispr-editing of bone marrow cells has led to patients with

▼ **Figure 1** Emmanuelle Charpentier and Jennifer Doudna



Source: dpa picture alliance / Alamy Stock Photo

sickle cell disease no longer requiring regular blood transfusions. Crispr is being investigated as a means to edit pig DNA so that their organs can be transplanted into humans.

Genome editing is not without its critics and there are serious ethical considerations. The genome is very complex and the results of editing genes cannot always be predicted. Genes may have multiple functions so solving one problem could inadvertently cause new ones. This is particularly important for those genes that can be inherited by future generations. Despite the undoubted ethical challenges Crispr and gene editing have enormous potential for providing new medical treatments and boosting food production.

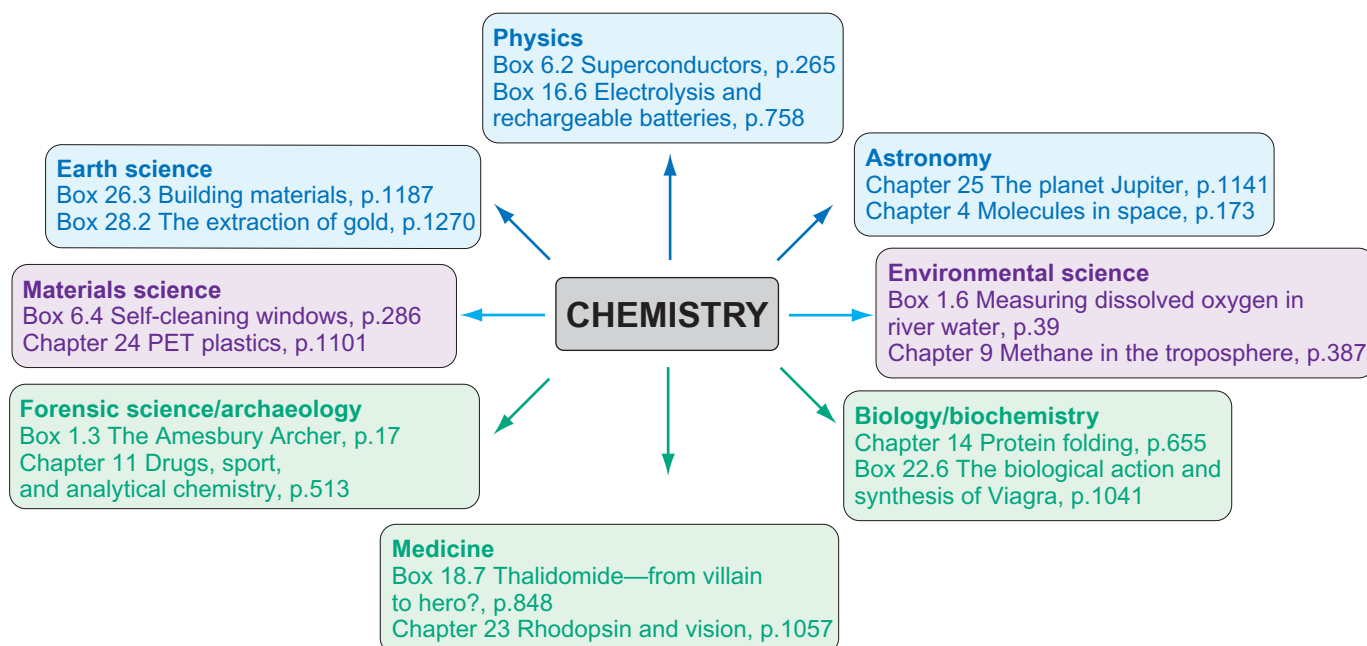


Figure 1.2 Chemistry as the central science, showing examples from chapters in the book.

In this book, we have highlighted the role of chemistry as the central science by including examples of applications of chemistry in many related fields. Some of these are shown in Figure 1.2.

1.2 Measurement, units, and nomenclature

Chemical knowledge is constantly increasing. New compounds are constantly being synthesized and data on the behaviour of chemical systems are being collected and analysed in research laboratories around the world. To allow chemists to communicate and compare their work effectively, there has to be an internationally agreed set of rules for them to work by. One of the roles of the International Union of Pure and Applied Chemistry (IUPAC) is to make recommendations for the naming of chemical compounds, the use of units and symbols, and the use of chemical terminology.

SI units

When scientists make measurements, they report each physical quantity (mass, volume, pressure, etc.) as a number and a defined unit multiplied together.

For example,

$$p = 1.00 \times 10^5 \text{ Pa}$$

In general,

$$\text{physical quantity} = \text{number} \times \text{unit}$$

SI units (Système International d'Unités) are an internationally accepted system of metric units. The system is based on seven **base units**, of which six are commonly used in chemistry. These are shown in Table 1.1. Note that the symbol for the physical quantity is printed in italics. By convention variables are written in italics, labels are written in Roman text. The names of units that are named after scientists, such as the kelvin, start with a lower-case letter rather than a capital letter, though the symbol for the unit does start with an upper-case (capital) letter. Thus, the symbol for kelvin is **K**, not k.

All other units can be derived from the base units and are called **derived units**. Most of the commonly used derived units have their own name. Some of these are listed in Table 1.2.

A unit can be modified by a prefix, which denotes multiplication or division by a power of ten. Table 1.3 shows the prefixes commonly used in chemistry. So, for example, $1 \text{ kg} = 1 \times 10^3 \text{ g} = 1000 \text{ g}$, and $1 \text{ }\mu\text{m} = 1 \times 10^{-6} \text{ m}$. To avoid confusion over duplication of symbols, the symbols for mega, giga, and tera are in upper-case letters, and the symbol for micro is μ (mu, Greek letter m). Note that there is a space between the number and its unit.



The International Union of Pure and Applied Chemistry (IUPAC) is a non-governmental body that advances aspects of the chemical sciences worldwide. Image reproduced by permission of the IUPAC.

Table 1.1 SI base quantities and base units used in chemistry

SI base quantity	Symbol for quantity	Name of SI unit	Symbol for SI unit
Mass	<i>m</i>	kilogram	kg
Length	<i>l</i>	metre	m
Time	<i>t</i>	second	s
Temperature	<i>T</i>	kelvin	K
Amount of substance	<i>n</i>	mole	mol
Electric current	<i>I</i>	ampere	A

1

i Always keep the number and the unit of a physical quantity together. One is meaningless without the other. For example, what is meant by the statement: 'The volume of the box is 17?' It could be 17 cm^3 , 17 dm^3 , 17 m^3 , or any other unit of volume.

Length

Chemists deal with matter on a macroscopic scale in the laboratory, but explain its behaviour in terms of atoms and molecules. This requires a wide range of distances (see Figure 1.3). You will need to become familiar with the multiplication prefixes in Table 1.3 used to describe lengths on atomic and molecular scales.

A typical C–H bond length in a hydrocarbon is 0.000000000109 m . Using scientific notation, it can be written as $1.09 \times 10^{-10} \text{ m}$, though this is still rather cumbersome.

Table 1.2 SI derived units commonly used in chemistry

Physical quantity	Name of SI unit	Symbol for SI unit	Written in terms of SI base units
Frequency	hertz	Hz	s^{-1}
Force	newton	N	kg m s^{-2}
Pressure	pascal	Pa	$\text{kg m}^{-1} \text{s}^{-2}$ ($= \text{N m}^{-2} = \text{J m}^{-3}$)
Energy, heat, work	joule	J	$\text{kg m}^2 \text{s}^{-2}$ ($= \text{N m} = \text{Pa m}^3$)
Celsius temperature*	degree Celsius	$^{\circ}\text{C}$	K
Electric charge	coulomb	C	A s
Electric potential	volt	V	$\text{kg m}^2 \text{s}^{-3} \text{A}^{-1}$ ($= \text{J C}^{-1}$)

*The Celsius temperature, θ , is defined by: $\theta/^{\circ}\text{C} = T/\text{K} - 273.15$ (where T is the temperature on the kelvin scale).

Table 1.3 Some SI multiplication prefixes

Multiplication factor	10	10^3	10^6	10^9	10^{12}		
Name	deca	kilo	mega	giga	tera		
Abbreviation	da	k	M	G	T		
Multiplication factor	10^{-1}	10^{-2}	10^{-3}	10^{-6}	10^{-9}	10^{-12}	10^{-15}
Name	deci	centi	milli	micro	nano	pico	femto
Abbreviation	d	c	m	μ	n	p	f

i Useful conversions

$$\begin{aligned}
 1 \text{ m} &= 100 \text{ cm} \\
 &= 1000 \text{ mm} \\
 &= 1 \times 10^6 \mu\text{m} \\
 &= 1 \times 10^9 \text{ nm} \\
 &= 1 \times 10^{12} \text{ pm} \\
 1 \text{ mol} &= 1 \times 10^3 \text{ mmol} \\
 &= 1 \times 10^6 \mu\text{mol}
 \end{aligned}$$

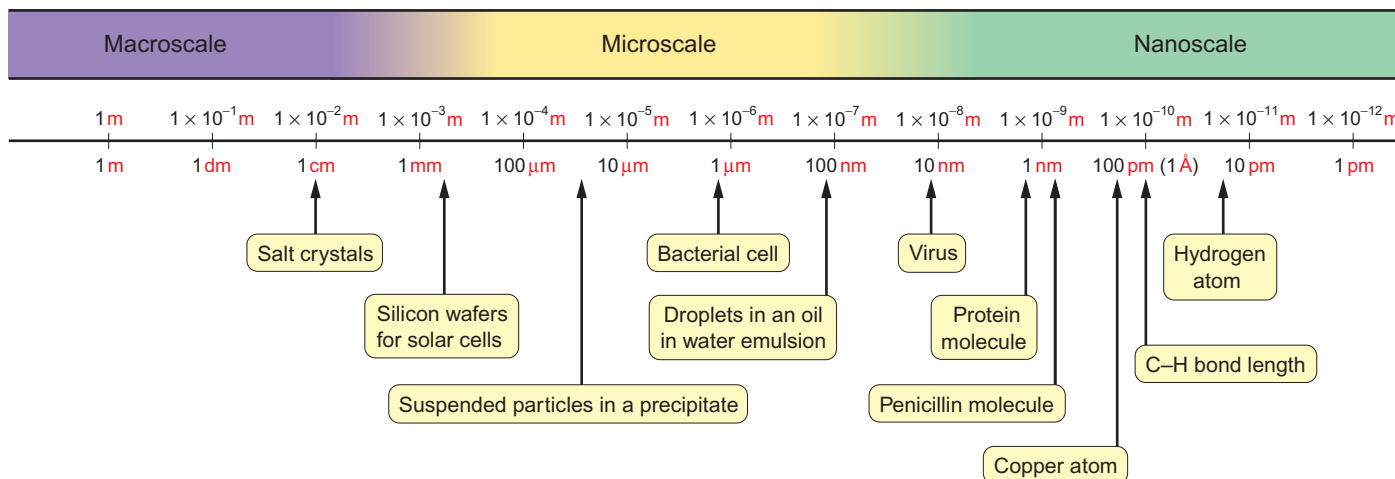


Figure 1.3 Units of distance from macroscale to microscale and nanoscale.

The value of the bond length becomes more manageable if you express it in nanometres (0.109 nm) or in picometres (109 pm). Most bond lengths are roughly the same order of magnitude and a convenient, non-SI, unit is the angstrom, Å (where $1 \text{ Å} = 1 \times 10^{-10} \text{ m}$), because most bonds are between 1 Å and 3 Å in length. So the C–H bond length can be written as 1.09 Å. The angstrom is less used these days in favour of SI units, but you will see all three units, nanometres, picometres, and angstroms, for atomic and molecular distances in chemistry textbooks. This book uses mainly picometres.

Temperature

Two temperature scales are commonly used in chemistry. The Celsius temperature scale is the one used in everyday life. Temperatures are reported in the weather forecast in degrees Celsius; pure water normally boils at 100°C and freezes at 0°C . Temperatures, however, can go much lower than this. The lowest temperature possible is -273.15°C —known as **absolute zero** on the kelvin scale. This is the scale adopted for the international standard in science. It is often called the **thermodynamic scale** or, sometimes, the **absolute scale** of temperature.

The symbol for temperatures in kelvin is T . The symbol θ (Greek theta) is used for temperatures in degrees Celsius. To convert between the two scales, you need to use the expression below.

$$T = \theta + 273.15$$

in degrees Celsius

in kelvin

So, to obtain a temperature in kelvin, you add 273.15 to the temperature in degrees Celsius. (The 273.15 is exact, but often this degree of accuracy is not warranted by the data and it is enough to add 273.) Another way of writing this relationship is

$$T/\text{K} = \theta/^\circ\text{C} + 273.15 \quad (1.1)$$

Note that the degree symbol ($^\circ$) is not used with temperatures in kelvin. T is a product of a number and the unit K, so T/K is a pure number; similarly, $\theta/^\circ\text{C}$ is a pure number. This means that Equation 1.1 is a relationship between pure numbers. Pure numbers are dimensionless quantities. The magnitude of a degree Celsius is the same as that of a kelvin and so temperature *differences* on the two scales are numerically the same.

The units of any physical quantity can be derived from the expression for the quantity in terms of SI base quantities. You just substitute the base units for these quantities into the expression. For example, for the volume of the rectangular reaction chamber shown in the margin

$$\begin{aligned} \text{volume} &= \text{width} \times \text{depth} \times \text{height} \\ &= (2 \text{ m}) \times (1 \text{ m}) \times (3 \text{ m}) \\ &= 6(\text{m} \times \text{m} \times \text{m}) \times 6 \text{ m}^3 \end{aligned}$$

So, the SI unit of volume is m^3 . However, 1 m^3 is a large volume for most laboratory chemistry, where volumes are usually measured in dm^3 or cm^3 .

The type of analysis used above in working out the unit of volume is called **dimensional analysis** (or sometimes **quantity calculus**, though it has nothing to do with calculus). Worked example 1.1 illustrates the use of dimensional analysis in working out derived units. Dimensional analysis is also useful as a check that a calculation has been carried out correctly.

Some non-SI units, such as the litre (L) for volumes (instead of m^3) and the atmosphere (atm) or bar (bar) for pressures (instead of Pa), are still used and you will need to be familiar with these.

i C-H bond length

$$1.09 \times 10^{-10} \text{ m}$$

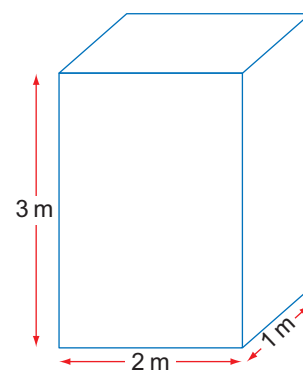
$$1.09 \text{ Å}$$

$$0.109 \text{ nm}$$

$$109 \text{ pm}$$

Σ **Scientific notation** (sometimes called **standard form**) is a convenient way of writing very large, or very small, numbers. The number is written as a number between 1 and 10 (expressed as a decimal) multiplied by an appropriate power of 10.

» You can see in Chapter 13 why temperatures in kelvin are called thermodynamic temperatures.



Rectangular reaction chamber.



Worked example 1.1 Derived units

Work out the SI derived unit for density.

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

Strategy

Insert SI base units into the expression for density.

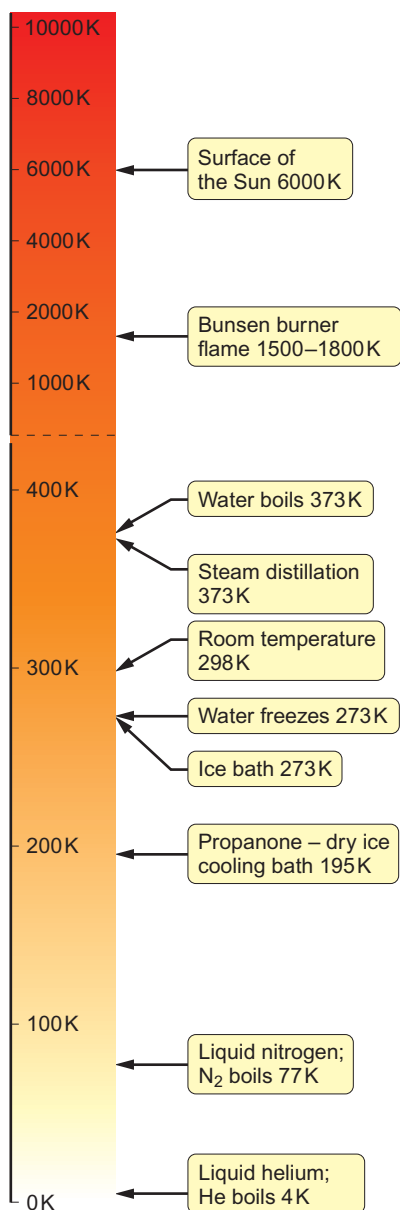
Solution

$$\begin{aligned} \text{SI unit of density} &= \frac{\text{SI unit of mass}}{\text{SI unit of volume}} \\ &= \frac{\text{kg}}{\text{m}^3} = \text{kg m}^{-3} \end{aligned}$$

(Note, however, that densities are often quoted in g cm^{-3} .)

Now try this

Work out the SI derived unit for molar mass (the mass of one mole of a substance).



The thermodynamic temperature scale.

Useful conversions

Volume

$$\begin{aligned} 1 \text{ L} &= 1 \text{ dm}^3 \\ &= 1000 \text{ cm}^3 \\ &= 1 \times 10^{-3} \text{ m}^3 \end{aligned}$$

$$\begin{aligned} 1 \text{ mL (millilitre)} &= 1 \times 10^{-3} \text{ L} = 1 \text{ cm}^3 \\ 1 \text{ }\mu\text{L (microlitre)} &= 1 \times 10^{-6} \text{ L} = 0.001 \text{ cm}^3 \end{aligned}$$

Pressure

$$\begin{aligned} 1 \text{ atm} &= 1.01325 \times 10^5 \text{ Pa} \\ 1 \text{ bar} &= 1.00000 \times 10^5 \text{ Pa} \end{aligned}$$

Carrying out calculations

Below are five rules that will help you to carry out calculations successfully. Dimensional analysis is very important and will prevent many of the common errors with units.

- ALWAYS set out your working clearly to avoid careless errors.
- ALWAYS include both the *number* and the *unit* of physical quantities in your working—not just in the answer.
- Units must be consistent (e.g. all volumes must be in the same units, so if volumes are in m^3 , density must be in kg m^{-3}).
- Convert quantities to the correct units *before* you substitute them into an expression.
- Make sure you quote the answer to the appropriate number of significant figures, rather than the number that comes up on your calculator.

Significant figures give an indication of the precision of a measurement. The rules for identifying significant figures are explained briefly here. Firstly, all non-zero digits are significant. For example, 52 has two significant figures (5 and 2), whereas 52.167 has five significant figures (5, 2, 1, 6, and 7). Zeros between non-zero digits are significant. So, 202.3408 has seven significant figures. Any zeros to the left of the non-zero digits are not significant. For example, 0.00036 has two significant figures, 3 and 6. Zeros after the non-zero digits are significant if they are justified by the precision of the measurement or calculation. So, 12.300 has five significant figures. In calculations, if you are multiplying or dividing, the significant figures in the answer should be the same as the smallest number of significant figures in the data you have used in the calculation. See the sample calculation below.

In this book, the units in worked examples are printed in red. Any cancelling out of units is shown using diagonal strikethroughs as shown below. This method may take longer but allows you to spot errors in units. All the information you need is in the example.

Sample calculation

Use the ideal gas equation, $pV = nRT$, to work out the volume (V) of 1.00 mol (n) of a gas at temperature $T = 298 \text{ K}$ and pressure $p = 1.00 \times 10^5 \text{ Pa}$. The gas constant R has a value of $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

Rearrange the equation to give an expression for the volume, V , of the gas.

$$V = \frac{nRT}{p}$$

Substitute values for n , R , T , and p in the equation. Remember to include units.

$$V = \frac{(1.00 \text{ mol}) \times (8.316 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{1.00 \times 10^5 \text{ Pa}}$$

Check that the units are consistent. (If they are not, convert to consistent units.) In this case, use Table 1.2 (p.8) to write joules in terms of pascals and metres ($1 \text{ Pa} = 1 \text{ J m}^{-3}$ so $1 \text{ J} = 1 \text{ P m}^3$).

$$V = \frac{(1.00 \text{ mol}) \times (8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{1.00 \times 10^5 \text{ Pa}}$$

Cancel out the units to give the units for volume and work out the answer.

$$\begin{aligned} V &= \frac{(1.00 \cancel{\text{ mol}}) \times (8.314 \cancel{\text{ Pa}} \text{ m}^3 \cancel{\text{ K}^{-1}} \cancel{\text{ mol}^{-1}}) \times (298 \cancel{\text{ K}})}{1.00 \times 10^5 \cancel{\text{ Pa}}} \\ &= 0.248 \text{ m}^3 \end{aligned}$$

The answer is quoted to 3 significant figures to correspond with the smallest number of significant figures in the data.

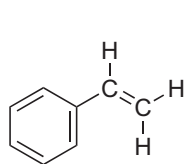
Nomenclature

In the early days of chemistry, names of compounds were often based on the source, or on a property, of the compound. For example:

- limestone (source of calcium carbonate);
- acetic acid (Latin: *acetum*, vinegar);
- putrescine (smell of rotting animal flesh).

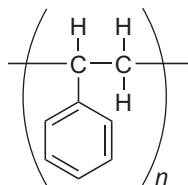
Many natural products are still named from their sources. For example, the name penicillin comes from the name of the mould, *Penicillium notatum*, that produces it (Figure 1.4). Unfortunately, these **common names** (sometimes called **trivial names**) do not help you to work out the structure of the compound. To do this, IUPAC has devised a systematic method for naming organic and inorganic compounds. The rules for naming compounds are called **nomenclature**.

The rules for naming inorganic compounds are discussed in Section 1.4. Chapter 2 shows you how to work out systematic **IUPAC names** for organic compounds. Practising chemists, however, tend to use a mixture of common names and IUPAC names, so you will become familiar with both. For example, you probably know the compound phenylethene by its systematic name, rather than by its common name styrene, but you are likely to know the addition polymer formed from it as polystyrene, rather than poly(phenylethene).



Common name: styrene

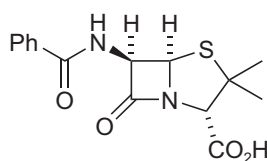
IUPAC name: phenylethene



Common name: polystyrene

IUPAC name: poly(phenylethene)

(where n is a very large number)



Common name: penicillin G

IUPAC name: (2*S*,5*R*,6*R*)-6-(benzamido)-3,3-dimethyl-7-oxo-4-thia-1-aza-bicyclo[3.2.0]heptane-2-carboxylic acid

Σ You can find help with working with numbers in the Maths Toolkit MT1 (p.1306). Rearranging equations is discussed in Maths Toolkit MT2 (p.1314).

» You can find out more about the ideal gas equation and this type of calculation in Sections 8.1 and 8.2.



Figure 1.4 Penicillin gets its name from the mould *Penicillium notatum*. Its antibiotic action was first observed by Alexander Fleming in 1928. Image source: Crulina 98/ CC-BY-SA.

i In chemistry, a **natural product** is a chemical compound or substance produced by a living organism.

» The IUPAC rules for naming organic compounds are discussed in Sections 2.4–2.8. A list of frequently used common names is included at the end of Chapter 2 (p.111). The naming of inorganic compounds is discussed in Section 1.4.

» Conventions for drawing the structures of organic compounds are discussed in Section 2.2.

In this book, both common and systematic names are generally given when a compound is first introduced. For simple compounds, such as ethene and ethanoic acid, the IUPAC names (rather than ethylene and acetic acid, respectively) are used subsequently. For more complex compounds, IUPAC names can be cumbersome so common names are used where these are available. In the case of penicillin, for example, the common name is certainly more convenient than the IUPAC name of (2*S*,5*R*,6*R*)-3,3-dimethyl-7-oxo-6-[(2-phenoxyacetyl)amino]-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid. Note that names of elements and compounds are not proper nouns and so don't start with a capital letter.



Summary

- SI units are based on seven base units; other units are derived from these and are called derived units.
- Bond lengths are conveniently measured in picometres ($1 \text{ pm} = 1 \times 10^{-12} \text{ m}$).
- Temperature can be measured in degrees Celsius or in kelvin. The kelvin scale is the international standard in science and is called the thermodynamic temperature scale or the absolute temperature scale.
- Many compounds have both a common name and a systematic IUPAC name.

? For practice questions on these topics, see questions 1–4 at the end of this chapter (p.67).

1.3 Atoms and the mole

We are all familiar with the white crystal of sodium chloride, or common salt. Its constituent elements, however, couldn't be more different from it. Sodium is a soft, silvery metal made up of sodium atoms. Elemental chlorine is a green gas with a characteristic, choking smell. The gas is made up of chlorine atoms bound together in pairs as Cl_2 molecules. Sodium metal and chlorine gas are both very reactive elements and are toxic to humans. Yet, when they react together (Figure 1.5), they produce white crystals of sodium chloride which is an essential component of our diet.

The reaction described above illustrates the difference between elements and compounds. Sodium metal and chlorine gas are **elements** because they contain only one kind of atom (see margin note). Sodium chloride is a compound. **Compounds** are made up of atoms of more than one element. The atoms in compounds are bonded together in molecules or in network structures. The bonding in network structures can be ionic (as in the case of sodium chloride) or covalent.

i Atoms of an element all have the same number of protons in the nucleus. They may not be identical as some may have different numbers of neutrons. **Isotopes** of elements are discussed on p.14.

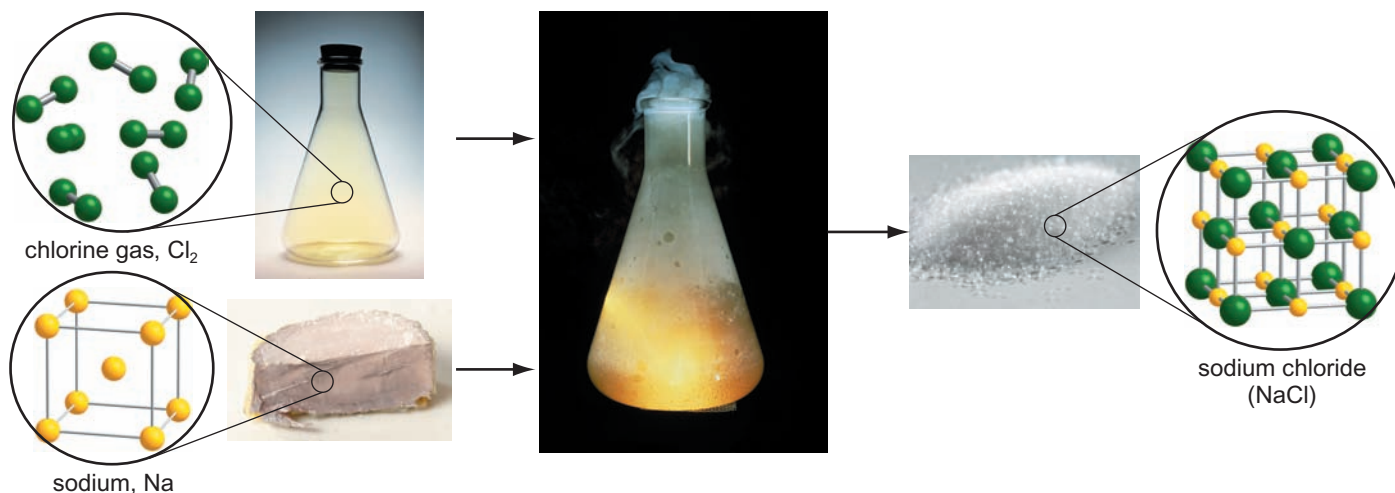


Figure 1.5 Reaction of sodium metal and chlorine gas to form sodium chloride. Image source: Charles D Winters/Science Photo Library and IDPS, University of Bath.

The properties of a compound bear no resemblance to those of the constituent elements—an idea that is often poorly understood by non-chemists. Important issues, such as the presence of mercury in some injections given to babies, are frequently misreported in the media. In this case, the toxic properties of mercury metal (the *element*) were commonly quoted, when a *compound* of mercury (ethylmercury) was actually being used as the preservative in the injection. Similarly, many people on ‘low sodium’ diets may not realize that they are cutting down on sodium *ions* not sodium *atoms*. Iron and calcium are both essential elements in the human diet but certainly not in their elemental metallic forms.

Structure of the atom

A simple classical model of the atom is shown in Figure 1.6. A tiny dense positively charged **nucleus** is surrounded by negatively charged **electrons**. The nucleus is made up of positively charged **protons** and (except for hydrogen atoms) uncharged **neutrons**, held together by a strong nuclear force. This force overcomes the electrostatic repulsion between the positively charged protons. Overall, an atom is electrically neutral which tells us that it has the same number of electrons and protons. Properties of the electron, proton, and neutron are summarized in Table 1.4.

During the twentieth century other subatomic particles, such as neutrinos, muons, and quarks, were discovered. These particles tell physicists about the fundamental nature of matter, but their existence has little impact on chemistry. This is because chemical reactivity is largely related to the arrangements and movements of electrons.

In the classical model of atomic structure, the orbiting electrons are arranged in shells around the nucleus. Electrons in the outermost shell (**valence electrons**) are usually the ones involved in chemical reactions. This simple model is sufficient to explain many observations. It does, however, have severe limitations, and Chapters 3 and 4 elaborate on this model using the ideas of quantum mechanics.

Elements differ from each other by the number of protons they contain in the nucleus. This number of protons is the **atomic number** (proton number) of an element, and it is given the symbol Z .

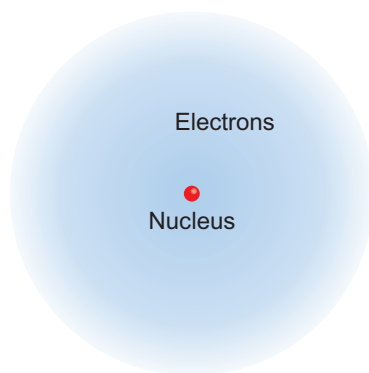


Figure 1.6 A simple classical model of the atom. Negatively charged electrons surround a positively charged nucleus, so overall the atom is electrically neutral.

Table 1.4 Properties of subatomic particles

Particle	Relative mass	Relative charge	Location in atom
Electron, e	1	-1	Around nucleus
Proton, p	1836	+1	In the nucleus
Neutron, n	1839	0	In the nucleus



‘Table salt contains the deadly poisons chlorine and cyanide!’—or does it? It is important to know whether an ingredient is an element or a compound and exactly how the atoms or ions are bound. Cl^- ions are safe but Cl_2 is not; $[\text{Fe}(\text{CN})_6]^{3-}$ is added as a drying agent and is safe, but free CN^- ions are not. Image source: Adrian Hughes/iStock.

» You can find all the known chemical elements in the Periodic Table inside the cover of this book. Covalent molecules are discussed in Chapters 4 and 5, and network structures in Chapter 6.

i There are four fundamental forces in nature—electromagnetic, weak nuclear, strong nuclear, and gravitational.

» You can read about the historical development of ideas about atomic structure in Section 3.1.

i **Atomic number (Z)**
This is the number of protons in the nucleus of an atom and is characteristic of an element. For example:

Hydrogen $Z = 1$
Helium $Z = 2$
Carbon $Z = 6$
Uranium $Z = 92$

Elements are arranged in the Periodic Table in order of increasing atomic number (see Section 3.6). Values of Z for all the elements are given on the inside back cover.

Isotopes

Although the number of protons is fixed for an element, the number of neutrons can vary. Atoms of the same element with different numbers of neutrons in their nuclei are known as **isotopes**. The existence of isotopes was predicted by Frederick Soddy in 1911, and later demonstrated by Francis Aston by the effect of magnetic fields on ions. This led Aston to the invention of the mass spectrometer. Box 1.2 describes how a simple mass spectrometer works.

The **mass number** of an isotope is the total number of protons and neutrons in the nucleus. Hydrogen has three isotopes, with mass numbers of 1, 2, and 3. About 99% of hydrogen atoms have nuclei containing just a single proton. This isotope of hydrogen is the only isotope of any element not to have any neutrons in its nucleus. About 1% of the hydrogen atoms have nuclei that contain a neutron in addition to the proton, so have a mass number of 2. There is also a radioactive isotope of hydrogen, atoms of which have two neutrons in their nuclei and, therefore, a mass number of 3. The isotopes of hydrogen are unusual in that they are given special names and symbols. The isotope with a mass number of 2 is called deuterium (D) and that with mass number 3 is called tritium (T).

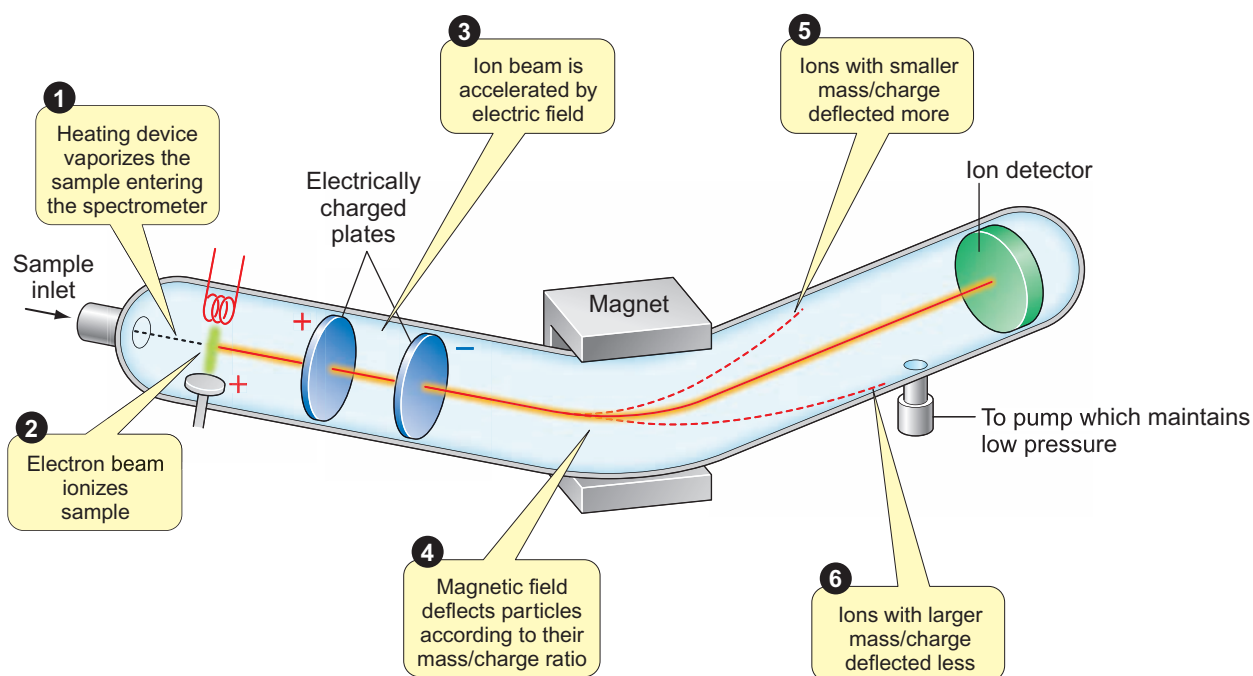
Isotopes are represented by atomic symbols in which the **atomic number** is given as a subscript, and the mass number as a superscript, both written before the chemical symbol for the element. Normal hydrogen is therefore represented as ${}^1_1\text{H}$, deuterium as ${}^2_1\text{H}$,



Box 1.2 Mass spectrometry

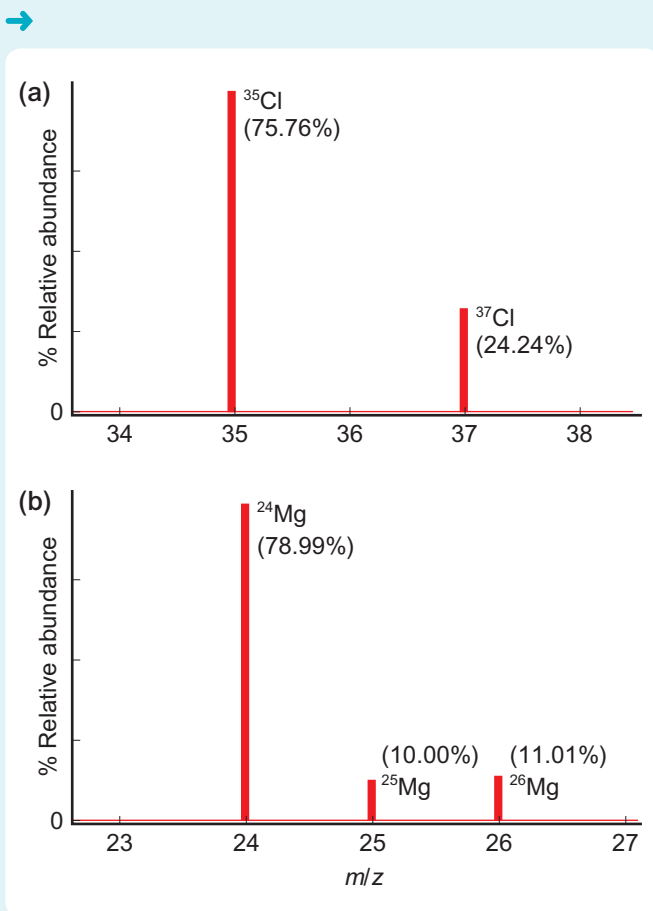
A good way to learn the principles of mass spectrometry is to look at the magnetic mass spectrometer shown in Figure 1 — though as we explain later, most modern mass spectrometers are ‘time-of-flight’ machines.

In the basic spectrometer in Figure 1, a substance is placed in a vacuum and vaporized. The sample is then bombarded with electrons to form ions, which are accelerated using an electric field. The accelerated ions pass through a magnetic field, and the extent to



▲ **Figure 1** Diagram of a simple mass spectrometer.

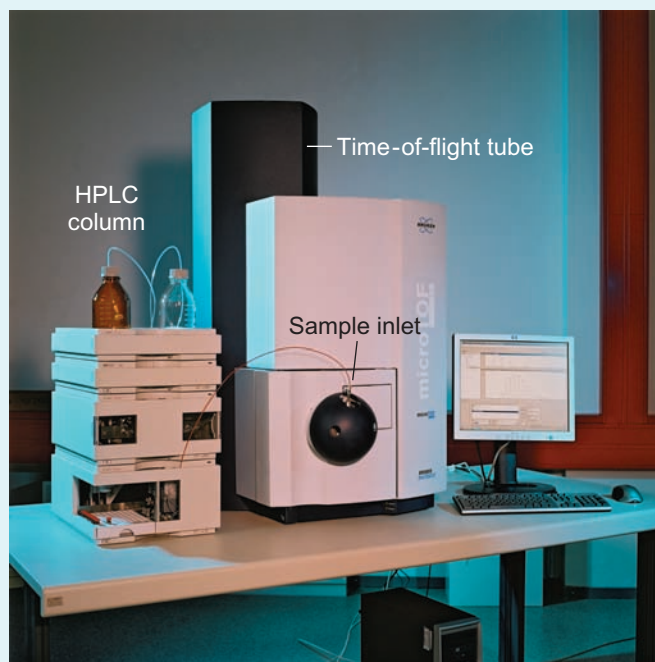




▲ **Figure 2** Mass spectra of (a) chlorine and (b) magnesium, showing the presence of isotopes.

which they are deflected depends on m/z , their mass to charge ratio—the greater the mass to charge ratio, the smaller the deflection. The ions that strike the detector produce an electric current. The magnetic field is gradually increased so that ions with different m/z values are targeted at the detector. The detector signal is recorded as the magnetic field is varied producing a **mass spectrum**. (Alternatively, the magnetic field can be kept fixed and the accelerating electric field varied.) The mass spectra for atomic chlorine and magnesium in Figure 2 show their isotopic compositions. Original mass spectrometers used bombardment with electrons to form ions but nowadays other techniques are also used (Section 12.1).

The mass spectra of molecules are more complex than those of atoms, because the ion formed from the molecule (the **molecular ion**) can break into fragments, giving rise to characteristic peaks in



▲ **Figure 3** A time-of-flight mass spectrometer linked to a high-performance liquid chromatography (HPLC) column. Image courtesy of Bruker Daltonik.

the spectrum. The mass spectrum of a molecule, therefore, gives information about both its molecular mass and its structure.

Most modern mass spectrometers operate in a different way that does not require a magnetic field. In a **time-of-flight mass spectrometer** (Figure 3), ions are accelerated by an electric field and the time it takes for the ions to reach a detector is measured. The time taken depends on m/z —heavier ions move more slowly—so all ions with the same m/z value arrive at the detector at the same time.

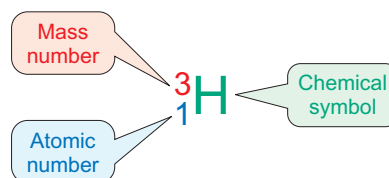
Complex mixtures can be analysed by linking a mass spectrometer to a gas chromatograph or a high-performance liquid chromatography column. The components of the mixture are first separated by chromatography and then fed directly into the mass spectrometer for identification. Examples of these techniques are described in Box 11.1 (p.515) and Section 11.3. Section 12.1 discusses the use of mass spectrometry in determining the structures of organic compounds.

Now try this

Look at the mass spectrum of magnesium in Figure 2(b). How many protons and neutrons are there in the nuclei of each of the three isotopes?

and tritium as ^3_1H . Since the atomic number is constant for a particular element and can be worked out from the chemical symbol, the subscript is often omitted. These symbols then become ^1H , ^2H , and ^3H , respectively. They are sometimes written as hydrogen-1, hydrogen-2, and hydrogen-3. You can practise writing and using atomic symbols in Worked example 1.2.

Atomic symbol for tritium



Worked example 1.2 Atomic symbols

An isotope of molybdenum has 54 neutrons. What is its atomic symbol?

Strategy

Use the table on the inside back cover to determine the chemical symbol for molybdenum and its atomic number, Z .

Add the number of protons to the number of neutrons to give the mass number.

Solution

Molybdenum (Mo) has an atomic number of 42 so it has 42 protons. The mass number of the isotope is given by the number of protons (42) plus the number of neutrons (54).

The mass number is 96, and the atomic symbol is ${}_{42}^{96}\text{Mo}$.

Now try this

Element X has the atomic symbol ${}_{90}^{203}\text{X}$. What is the name of the element and how many protons and neutrons are there in the nucleus?

» Box 8.4 (p.371) explains how the difference in physical properties of two isotopes is used in the enrichment of uranium.

i **Atomic mass units and daltons**
IUPAC defines an atomic mass unit (u) as $1/12$ the mass of an atom of ${}^{12}\text{C}$. The atomic mass unit has a value of 1.661×10^{-27} kg, which corresponds closely to the mass of a proton or neutron. More recently, these units have been called daltons (Da); they are used particularly by biochemists. So, $1 \text{ Da} = 1 \text{ u}$, and the mass of one ${}^{12}\text{C}$ atom is 12 Da . (Note that atomic mass units and daltons are non-SI units.)

i Sometimes the Avogadro constant is given the symbol L .

Σ An **integer** is a whole number.

i The term **relative molar mass** (M_r) is often used as this applies to both molecular and non-molecular substances.

The different isotopes of an element normally react chemically in an identical manner. However, since their masses are different, their physical properties show some variation. These differences are usually small, but for the isotopes of hydrogen they are more marked, because of the large proportionate difference between the masses of the isotopes. Box 1.3 describes an example of isotope analysis in an archaeological investigation.

Relative atomic mass and moles of atoms

The mass of a hydrogen atom is very small, approximately 1.674×10^{-27} kg. This is not a practical value to use to compare atomic masses, so instead a relative scale is used. This **relative atomic mass** (A_r) is defined as the mass of a substance that contains exactly $6.02214076 \times 10^{23}$ atoms (or molecules in the case of compounds). This number of atoms is called a **mole of atoms** and is called the **Avogadro constant**, N_A . Note that A_r values have no units.

The mole and Avogadro's constant used to be defined in terms of the mass of 12 g of carbon. Exactly 12 g of ${}^{12}\text{C}$ contain 6.022×10^{23} atoms. The relative atomic mass weighed out in grams of any element contains the same number of atoms—whatever the element.

The relative atomic masses of many elements are close to an integer as they contain mainly one isotope. However, there are exceptions. The relative atomic mass of chlorine is 35.453 due to the presence of ${}^{35}\text{Cl}$ (abundance 75.76%) and ${}^{37}\text{Cl}$ (abundance 24.24%). Worked example 1.3 shows how the relative atomic mass is calculated.

The masses of individual isotopes (**relative isotopic masses**) are not exactly whole numbers. Some values for selected elements are given in Table 1.5.



Box 1.3 The Amesbury Archer

The grave of a man known as the Amesbury Archer was discovered near to Stonehenge in southern England in 2002. This grave dates from the early Bronze Age and is the richest grave from this time ever found in Britain. The wealth of the objects found there, including the country's first known gold objects, indicate that the archer was a man of status. Oxygen isotope analysis of the man's dental enamel gave an insight into his origin.

Most of the oxygen that goes into the formation of tooth and bone comes from water, which is ultimately derived from rain or snow. Although the most abundant isotope of oxygen is ^{16}O , there are two other stable isotopes, ^{17}O and ^{18}O , present in minor amounts. The ratio of the isotopes depends on a number of environmental factors such as temperature and altitude. Drinking water in warm climates has a higher ratio of $^{18}\text{O}:^{16}\text{O}$ than that in cold climates. Determination of this $^{18}\text{O}:^{16}\text{O}$ ratio in teeth provides a means of determining where a person might have lived at the time their teeth formed.

Oxygen isotope analysis revealed a relatively low $^{18}\text{O}:^{16}\text{O}$ ratio for the Amesbury Archer, indicating that the man came from a colder climate region than was found in Britain at the time. He most likely came from somewhere in the Alps region, probably Switzerland, Austria, or Germany.

Box 3.9 on p.154 describes how the Amesbury Archer was dated using radiocarbon dating.

Now try this

- How do the three isotopes of oxygen vary in the number of protons, neutrons, and electrons present?
- Why do you think that analysis of the $^{18}\text{O}:^{16}\text{O}$ ratio can be useful in the analysis of orange juice that is suspected of being adulterated with water?



▲ The grave of the Amesbury Archer, dating from around 2300 BC. It was discovered in 2002. Image courtesy of Wessex Archaeology.



Worked example 1.3 Relative atomic mass of magnesium

Use the information from the mass spectrum in Figure 2(b) in Box 1.2 (p.15) to work out the relative atomic mass, A_r , of naturally occurring magnesium. (Assume that the relative mass of ^{24}Mg is exactly 24, that of ^{25}Mg is 25, and that of ^{26}Mg is 26.)

Strategy

Use the percentage abundances in the mass spectrum to work out the average relative mass of 100 atoms. Hence find the average mass of one atom (the 'weighted average').

Solution

$$\begin{aligned} \text{Average relative mass of 100 atoms of magnesium} \\ &= (24 \times 78.99) + (25 \times 10.00) + (26 \times 11.01) \\ &= 1895.76 + 250.00 + 286.26 = 2432.02 \end{aligned}$$

$$\begin{aligned} \text{Average relative mass of one atom of magnesium, } A_r(\text{Mg}) \\ &= 24.32 \end{aligned}$$

(Note. The calculations in this worked example are simplified because the isotopic masses are not exactly whole numbers (see Table 1.5).)

Now try this

Naturally occurring bromine contains ^{79}Br (abundance 50.69%) and ^{81}Br (abundance 49.31%). Calculate the relative atomic mass of naturally occurring bromine.

Table 1.5 Relative masses and natural abundances of some isotopes of selected elements

Element	Isotope	Relative isotopic mass	Abundance/%
H	^1H	1.0078	99.9885
	^2H	2.0141	0.0115
C	^{12}C	12	98.93
	^{13}C	13.0034	1.07
N	^{14}N	14.0031	99.64
	^{15}N	15.0001	0.36
O	^{16}O	15.9949	99.757
	^{17}O	16.9991	0.038
	^{18}O	17.9992	0.205
F	^{19}F	18.9984	100
Mg	^{24}Mg	23.9850	78.99
	^{25}Mg	24.9858	10.00
	^{26}Mg	25.9826	11.01
P	^{31}P	30.9738	100
Cl	^{35}Cl	34.9689	75.76
	^{37}Cl	36.9659	24.24
Br	^{79}Br	78.9183	50.69
	^{81}Br	80.9163	49.31
I	^{127}I	126.9045	100

i Use the correct symbol

- M_r is the symbol for the relative formula mass (or relative molecular mass) of a substance. **No units.**
- M is the symbol for the molar mass of a substance. Units: g mol^{-1} (or kg mol^{-1}).
- m is the symbol for the actual mass of one atom or molecule or one formula unit of a substance. Units: **g** (or **kg**).

i **The mole**
A **mole** (1 mol) of a substance is the **amount of substance** that contains $6.02214076 \times 10^{23}$ formula units (atoms, molecules, groups of ions, etc.). The number of formula units in a mole is $6.022 \times 10^{23} \text{ mol}^{-1}$, N_A , the **Avogadro constant**.

Relative formula mass

In the same way that relative atomic mass is used to compare the masses of atoms of elements, **relative formula mass** is used to compare the formula masses of compounds. Where the formula represents a discrete molecule (such as CH_4 or H_2SO_4), the relative formula mass is called the **relative molecular mass**. Both relative formula mass and relative molecular mass are given the symbol M_r .

The relative formula mass of a substance is worked out by first writing down the formula of the substance and then adding together the relative atomic masses of each of the atoms in the formula. For example,

$$M_r(\text{H}_2\text{SO}_4) = (1.01 \times 2) + (32.07 \times 1) + (16.00 \times 4) = 98.09$$

Amount of substance and molar mass

The unit of **amount of substance** is the **mole** (symbol **mol**). A mole of a substance always contains 6.022×10^{23} (N_A) entities. These entities may be atoms, molecules, or groups of ions in a formula unit, so it is important to indicate whether you are dealing with a mole of atoms, a mole of molecules, etc. The easiest way to do this is to give the formula of the entity the mole refers to. For example, 'a mole of chlorine (Cl_2)' or 'a mole of atomic chlorine (Cl)'. A mole of Cl_2 molecules contains twice as many atoms as a mole of Cl atoms.

The mole is important because chemists need to know when the amounts of different compounds are the same, not in terms of their masses but in terms of the number of atoms or molecules each contains, since chemical reactions take place between atoms and molecules in specific stoichiometric ratios.

Chemical amounts are defined so that the mass of one mole (the **molar mass**, M) is equal to the relative atomic mass, or the relative formula mass, in grams (or kg). Thus, the molar mass of ^{12}C is exactly 12 g mol^{-1} (0.012 kg mol^{-1}) and the molar mass of H_2SO_4 is 98.09 g mol^{-1} ($0.09809\text{ kg mol}^{-1}$). In this book, molar mass is quoted in g mol^{-1} . In general,

$$\text{amount (in mol)} = \frac{\text{mass (in g)}}{\text{molar mass (in g mol}^{-1}\text{)}} \quad (1.2)$$

We can use analysis of the units to check that this relationship is correct:

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

Equation 1.2 is used in Worked example 1.4 to calculate the amount in moles in a given mass of glucose.



Stoichiometry

The relationship between the amounts of reactants and products is called the stoichiometry of the reaction. A balanced chemical equation shows the stoichiometry of a reaction.



Millimoles

For small quantities of a substance, you may see the chemical amount quoted in millimoles (mmol), where $1\text{ mmol} = 1 \times 10^{-3}\text{ mol}$.



Worked example 1.4 Amount of substance

How many moles of molecules are contained in 25.4 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$)?

From Equation 1.2

$$\begin{aligned} \text{amount (in mol)} &= \frac{\text{mass (in g)}}{\text{molar mass (in g mol}^{-1}\text{)}} \\ &= \frac{25.4\text{ g}}{180.18\text{ g mol}^{-1}} = 0.141\text{ mol} \end{aligned} \quad (1.2)$$

Strategy

Work out the relative formula mass (M_r) of glucose.

The molar mass of glucose is the relative formula mass in grams per mole.

Use Equation 1.2 to work out the amount in moles.

Solution

$$M_r(\text{C}_6\text{H}_{12}\text{O}_6) = (12.01 \times 6) + (1.01 \times 12) + (16.00 \times 6) = 180.18$$

Now try this

- What mass of sodium chloride contains 5.82 mol of NaCl?
- How many moles of silicon are there in a 99.999% pure 100 mm square silicon wafer of 500 μm thickness weighing 10 g?

Chemical formulas

- The **empirical formula** of a substance tells you the *ratio* of the numbers of different types of atom in the substance.
- A **molecular formula** tells you the actual number of different types of atom in a molecule.
- A **structural formula** shows how the atoms in a molecule are bonded together. This is sometimes also called a **displayed formula**.
- Skeletal formulas** use lines to represent the carbon framework in an organic compound.

Worked example 1.5 shows how the empirical formula of a compound is calculated from its composition by mass. The formula of a compound, such as sodium chloride (NaCl), which has an extended network structure, is an empirical formula. For a molecular compound, such as benzene, you can write both an empirical formula (CH) and a molecular formula (C_6H_6).

CH Empirical formula
 C_6H_6 Molecular formula



Skeletal structural formula, usually shown in this book as



Chemical formulas for benzene.

» You can find more about drawing the structural formulas of organic compounds in Section 2.2.

Interestingly, the empirical formula of a human was first calculated in 2020. The following 22-element empirical formula was reported: $\text{H}_{375,000,000}\text{O}_{132,000,000}\text{C}_{85,700,000}\text{N}_{6,430,000}\text{Ca}_{1,500,000}\text{P}_{1,020,000}\text{S}_{206,000}\text{Na}_{183,000}\text{K}_{177,000}\text{Cl}_{127,000}\text{Mg}_{40,000}\text{Si}_{38,600}\text{Fe}_{2,680}\text{Zn}_{2,110}\text{Cu}_{7,614}\text{Mn}_{13}\text{F}_{13}\text{Cr}_7\text{Se}_4\text{Mo}_3\text{Co}_1$. So there are 375 million H atoms to every Co atom in your body.



Worked example 1.5 Empirical formulas and molecular formulas

An organic compound contains 52.2% carbon, 13.1% hydrogen, and 34.7% oxygen by mass.

- (a) Work out its empirical formula.
 (b) Mass spectrometry shows the compound has a relative molecular mass of 46. What is its molecular formula?

Strategy

(a) You are given the mass composition in percentages, so write down the masses of C, H, and O in 100 g of the compound. Set out your working in columns as shown below.

Work out the number of moles of atoms of C, H, and O in these masses.

Find the simplest ratio of moles of atoms of C:H:O by dividing each amount by the smallest value. The ratio gives the empirical formula.

(b) Work out the relative formula mass corresponding to the empirical formula and compare this with the relative formula mass of the compound obtained from mass spectrometry.

Solution

(a)

	C	H	O
% Mass	52.2%	13.1%	34.7%
Mass in g in 100 g compound	52.2 g	13.1 g	34.7 g
Amount (in mol)	$\frac{52.2 \cancel{\text{g}}}{12.01 \cancel{\text{g mol}^{-1}}}$ = 4.35 mol	$\frac{13.1 \cancel{\text{g}}}{1.01 \cancel{\text{g mol}^{-1}}}$ = 13.0 mol	$\frac{34.7 \cancel{\text{g}}}{16.0 \cancel{\text{g mol}^{-1}}}$ = 2.17 mol
Simplest ratio (divide by smallest)	$\frac{4.35 \cancel{\text{mol}}}{2.17 \cancel{\text{mol}}} = 2.00$	$\frac{13.0 \cancel{\text{mol}}}{2.17 \cancel{\text{mol}}} = 5.99$	$\frac{2.17 \cancel{\text{mol}}}{2.17 \cancel{\text{mol}}} = 1.00$

Ratio of moles of atoms C:H:O is 2 : 6 : 1.

Empirical formula is $\text{C}_2\text{H}_6\text{O}$.

(b) $M_r(\text{C}_2\text{H}_6\text{O}) = (12.0 \times 2) + (1.01 \times 6) + (16.0 \times 1) = 46$. This corresponds to the M_r obtained from mass spectrometry, so the molecular formula of the compound is also $\text{C}_2\text{H}_6\text{O}$.

Now try this

- (a) A compound was found to contain 1.18% hydrogen, 42.00% chlorine, and 56.82% oxygen by mass. What is its empirical formula?
 (b) Elemental analysis of a contaminant extracted from a sample of soy sauce showed a composition of 40.24% carbon, 6.87% hydrogen and 52.89% oxygen. Determine the empirical formula of the contaminant.



Summary

- Elements contain atoms that all have the same number of protons.
- Compounds are made up of atoms of more than one element; the atoms are bonded together in molecules or in extended network structures.
- A simple classical model of the atom consists of a tiny dense positively charged nucleus surrounded by electrons.
- The atomic number Z of an element is the number of protons in an atom. The mass number is the total number of protons and neutrons in an atom.
- Many elements have more than one isotope. Isotopes are atoms of an element that contain different numbers of neutrons in their nuclei. An isotope can be represented by an atomic symbol showing the mass number and atomic number.
- A mole (1 mol) of a substance is the amount of substance that contains as many formula units (atoms, molecules, groups of ions, etc.) as there are in exactly 12 g of ^{12}C . The number of formula units in a mole is $6.022 \times 10^{23} \text{ mol}^{-1}$, N_A , the Avogadro constant.
- The empirical formula of a substance gives the *ratio* of the numbers of different types of atom in the substance; the molecular formula gives the actual number of different types of atom in a molecule. The structural formula shows how the atoms in a molecule are bonded together.

? For practice questions on these topics, see questions 5–9 at the end of this chapter (p.67).

1.4 Chemical equations

Chemical equations summarize what happens in a chemical reaction. They tell you:

- what substances react;
- what products are formed;
- the relative amounts of the substances involved.

If an equation is balanced, you can use it to work out how much of each reactant is needed to react exactly, and how much of each product to expect if the reaction goes to completion.

When you balance an equation, you are really doing an atom count (or a count of ions and electrons if it is an ionic equation; see p.27). Atoms are neither created nor destroyed in a chemical change—simply rearranged into new molecules or new network structures. This is one of the fundamental laws of chemistry and is known as the **law of conservation of mass**. A balanced chemical equation is a sort of balance sheet of where each atom starts and where it ends up. There must be the same number of atoms at the end of the reaction as there was at the start.

Balancing equations

The first step in constructing a balanced equation is to write down the correct formula for each of the substances involved. If the substance is molecular, you need the molecular formula (e.g. water H_2O , methane CH_4 , ethanol $\text{C}_2\text{H}_5\text{OH}$). If the compound is ionic, you can work out the empirical formula from the formulas of the ions involved (see Table 1.6). For example, calcium chloride contains Ca^{2+} ions and Cl^- ions, so the formula of calcium chloride is CaCl_2 . Note that an ion made up from several atoms is written in brackets when there is more than one in the formula of the compound. For example, ammonium sulfate contains NH_4^+ ions and SO_4^{2-} ions, so the formula of ammonium sulfate is $(\text{NH}_4)_2\text{SO}_4$. The

i **The law of conservation of mass**
The French chemist, Antoine Lavoisier, noted in 1774 that, if nothing is allowed to enter or leave a reaction vessel, the *total* mass is the same after a chemical reaction has taken place as it was before the reaction.



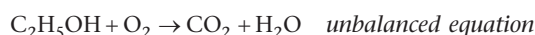
Brandy contains ethanol which burns in oxygen with a blue flame. Image source: Paul Cowan/iStock.

Table 1.6 Names and formulas of some common ions. For metallic elements where there is more than one common ion, the oxidation state is given (e.g. iron(II) and iron(III)). For some anions the systematic IUPAC name is given in brackets, although the non-systematic versions are still in use (e.g. see Figure 27.28 in Section 27.6, p.1246).

Positive ions (cations)		Negative ions (anions)	
Charge 1+		Charge 1-	
H ⁺	hydrogen	H ⁻	hydride
Li ⁺	lithium	F ⁻	fluoride
Na ⁺	sodium	Cl ⁻	chloride
K ⁺	potassium	Br ⁻	bromide
Cu ⁺	copper(I)	I ⁻	iodide
Ag ⁺	silver(I)	OH ⁻	hydroxide
NH ₄ ⁺	ammonium	N ₃ ⁻	azide
Charge 2+		NO ₂ ⁻	nitrite (nitrate(III))
Mg ²⁺	magnesium	NO ₃ ⁻	nitrate (nitrate(V))
Ca ²⁺	calcium	CN ⁻	cyanide
Sr ²⁺	strontium	OCN ⁻	cyanate
Ba ²⁺	barium	SCN ⁻	thiocyanate
Mn ²⁺	manganese(II)	HCO ₃ ⁻	hydrogencarbonate
Fe ²⁺	iron(II)	HSO ₄ ⁻	hydrogensulfate
Co ²⁺	cobalt(II)	H ₂ PO ₄ ⁻	dihydrogenphosphate
Ni ²⁺	nickel(II)	CH ₃ CO ₂ ⁻	ethanoate
Cu ²⁺	copper(II)	ClO ⁻	hypochlorite (chlorate(I))
Zn ²⁺	zinc	ClO ₂ ⁻	chlorite (chlorate(III))
Cd ²⁺	cadmium(II)	ClO ₃ ⁻	chlorate (chlorate(V))
Sn ²⁺	tin(II)	ClO ₄ ⁻	perchlorate (chlorate(VII))
Pb ²⁺	lead(II)	Charge 2-	
Charge 3+		O ²⁻	oxide
Al ³⁺	aluminium	S ²⁻	sulfide
Fe ³⁺	iron(III)	CO ₃ ²⁻	carbonate
Cr ³⁺	chromium(III)	C ₂ O ₄ ²⁻	ethanedioate
		SO ₃ ²⁻	sulfite (sulfate(IV))
		SO ₄ ²⁻	sulfate (sulfate(VI))
		S ₂ O ₃ ²⁻	thiosulfate
		Charge 3-	
		N ³⁻	nitride
		PO ₄ ³⁻	phosphate

subscripts in the formulas cannot be changed. Atoms or ions combine in fixed ratios to form compounds, so water is always H_2O , calcium chloride is always CaCl_2 , etc. Different numbers would create different substances.

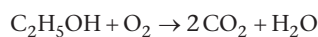
Ethanol burns in air or oxygen to form carbon dioxide and water. The unbalanced equation looks like this.



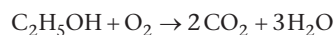
The equation is **unbalanced** because there are different numbers of each type of atom on either side. For example, there are two C atoms on the left but only one C atom on the right.

To balance the equation, you need to insert numbers *in front* of the formulas, so that there are equal numbers of each type of atom on either side of the equation. These numbers tell you the number of *formula units* involved in the reaction. Note that there should be a space between the number and the formula. For the reaction of ethanol with oxygen, you can do this in three steps, balancing the numbers of C, H, and O atoms in turn.

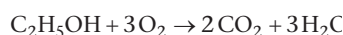
Step 1 We need more C on the right-hand side of the equation. Balance the number of C atoms by inserting a 2 before CO_2 (i.e. two molecules of CO_2).



Step 2 We need more H on the right-hand side of the equation. Balance the number of H atoms by inserting a 3 before H_2O (i.e. three molecules of H_2O).

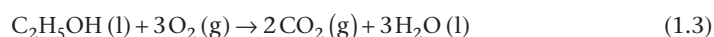


Step 3 We now need more O on the left-hand side of the equation. Balance the number of O atoms by inserting a 3 before O_2 (i.e. three molecules of O_2). Remember there is an O atom in $\text{C}_2\text{H}_5\text{OH}$, so there are a total of seven O atoms on either side of the equation.

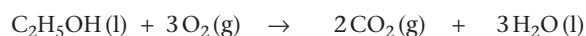


Finally Check you have equal numbers of each type of atom on either side. Both sides now have 2 C, 6 H, and 7 O.

State symbols are often included in an equation to show whether each substance is a gas, a liquid, or a solid, or is present in aqueous solution. For the reactants and products at room temperature, the balanced equation for the combustion of ethanol then becomes



Equation 1.3 tells you that one molecule of $\text{C}_2\text{H}_5\text{OH}$ reacts with exactly three molecules of O_2 to form two molecules of CO_2 and three molecules of H_2O . Because a mole of each substance contains the same number of molecules (N_A), the equation also tells you that 1 mol of $\text{C}_2\text{H}_5\text{OH}$ reacts exactly with 3 mol of O_2 to form 2 mol of CO_2 and 3 mol of H_2O . The amounts in moles allow you to work out the *masses* that react exactly (see Worked example 1.6).



Molecules:	1 molecule	3 molecules	2 molecules	3 molecules
Moles:	1 mol	3 mol	2 mol	3 mol
Masses:	46 g	$3 \times 32 \text{ g}$	$2 \times 44 \text{ g}$	$3 \times 18 \text{ g}$

The relationship between the amounts of reactants and products is called the **stoichiometry** of the reaction. The numbers before the formula units used to balance the equation are the **stoichiometric coefficients**.

i A balanced equation is one with equal numbers of each type of atom on either side of the equation. The charge must also be same on each side. This is particularly important in redox equations where electrons are added to balance the charges (see p.28).

i In older books, sulfur is spelt 'sulphur'. The spelling with 'f' is recommended by IUPAC. Older books also spell formulas as formulae. This version is falling out of common use.

i **State symbols**
State symbols are included in chemical equations to show the physical state (see Section 1.7) of the reactants and products.

- (g) gas
- (l) liquid
- (s) solid
- (aq) aqueous solution (solution in water)
- (sol) solution (in a solvent other than water)

i A balanced equation is sometimes called a stoichiometric equation.



Worked example 1.6 Using a balanced equation to work out reacting masses

Use the balanced equation for the combustion of ethanol to work out the mass of carbon dioxide produced when 25 g of ethanol are burned in a plentiful supply of air. We can assume there is an excess of oxygen present.

Strategy

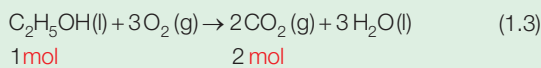
Write the balanced equation for the reaction (Equation 1.3).

Under the equation, state what the equation tells you about the amounts in moles of the substances you are interested in.

Change the amounts in moles to masses in grams.

Scale the masses to the ones in the question.

Solution



Change to mass by multiplying by formula mass.

$$46 \text{ g} \qquad (2 \times 44 \text{ g}) = 88 \text{ g}$$

Divide both sides by 46 to give 1 g ethanol.

$$1 \text{ g} \qquad \left(\frac{88}{46}\right) \text{ g}$$

Multiply both sides by 25 to give 25 g ethanol.

$$25 \text{ g} \qquad \left(\frac{88 \times 25}{46}\right) \text{ g} = 48 \text{ g}$$

So, 48 g of CO_2 are produced when 25 g of ethanol are burned.

Now try this

- What mass of oxygen is needed to react exactly with 25 g of ethanol?
- Butanol, $\text{C}_4\text{H}_9\text{OH}$, is being explored as a possible biofuel. Calculate the mass of carbon dioxide produced when 1 litre of butanol is burned in an combustion engine.

Types of chemical reaction

Chemical reactions can be classified in a number of ways. Below are four common types of chemical reaction that you need to be able to recognize.

- Acid–base reactions** involve the transfer of a proton (H^+ ion) from an acid to a base; see Sections 7.1 and 7.2. In Section 7.8 this definition is broadened to include other types of acids and bases.
- Redox reactions** involve the transfer of electrons in simultaneous oxidation and reduction reactions (see p.28).
- Precipitation reactions** involve the formation of a solid product when two solutions are mixed (see p.40).
- Complexation reactions** involve the formation of a complex ion (or an uncharged complex) in which, in almost all cases, a central metal ion is surrounded by electron-donating ligands; see Section 28.3.

Working out the yield of a reaction

The maximum mass of product that can be obtained from a chemical reaction can be worked out from the balanced equation and is called the **theoretical yield**. Some reactions go to completion and the mass of product that is actually obtained in the laboratory or in a chemical plant is very close to this. Often though, the **actual yield** is less than the theoretical yield. Some loss of product can occur during isolation from the reaction mixture and purification. There may be competing **side reactions** leading to other products. In addition, some reactions do not go to completion, but reach a state of equilibrium in which both reactants and products are present.

The **percentage yield** of a reaction tells you what percentage of the theoretical yield was actually obtained.

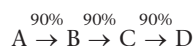
$$\text{Percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \quad (1.4)$$

» Chemical equilibrium is discussed in Section 1.9. These ideas are taken further in Chapter 15 (p.694).

i If a reaction is carried out with other than stoichiometric amounts of reactants, so that one or more of the reactants is in excess, the yield is calculated from the amount of the limiting reactant—the one that is completely used up in the reaction.

It is usual to quote percentage yields as integers (see Worked example 1.7).

In a synthesis involving several steps, a few steps with low yields can have a disastrous effect on the overall yield. Suppose a synthesis involves three steps, each of which gives a 90% yield of product.



The starting compound for each step is the product of the previous step. So the overall yield for the sequence $A \rightarrow D$ is:

$$\frac{90}{100} \times \frac{90}{100} \times \frac{90}{100} = \frac{729\,000}{100\,000} = \frac{72.9}{100} \times 100 \text{ or } 73\%$$

If, however, each step resulted in a 30% conversion to the required product, the overall yield after three stages would only be:

$$\frac{30}{100} \times \frac{30}{100} \times \frac{30}{100} = \frac{27\,000}{100\,000} = \frac{2.7}{100} \times 100 \text{ or } 3\%$$

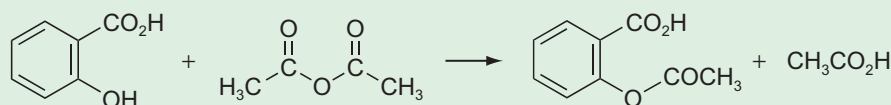
The percentage conversion to a required product tells you nothing about the amount of *waste* generated by the process—something that is particularly important in the chemical industry. Calculating the atom efficiency as in Box 1.4 helps in understanding the amount of waste in a reaction.

i Although a high percentage yield is desirable in an industrial process, sometimes, as in the case of the Haber process in Worked example 1.7, it is more economical to accept a lower yield if this means the rate of the reaction is higher. The reactants are separated from the product and recycled through the reactor.



Worked example 1.7 Percentage yield of a reaction

Suppose you prepare a sample of aspirin by heating 10 g salicylic acid (2-hydroxybenzoic acid) with an excess of ethanoic anhydride. You obtain 6.2 g of pure aspirin. What is the percentage yield of the reaction?



Strategy

Use the balanced equation above to work out the theoretical yield from 10 g salicylic acid.

Use Equation 1.4 to work out the percentage yield.

Solution

From the equation, 1 mol of salicylic acid gives 1 mol of aspirin.

138 g of salicylic acid gives 180 g of aspirin. These masses are the molecular masses of the starting material and product respectively.

1 g of salicylic acid gives $\frac{180}{138}$ g of aspirin.

10 g of salicylic acid gives $\left(\frac{180 \times 10}{138}\right)$ g = 13.0 g of aspirin. This is

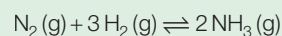
the theoretical yield. The actual yield was 6.2 g.

From Equation 1.4

$$\begin{aligned} \text{Percentage yield} &= \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% & (1.4) \\ &= \frac{6.2}{13.0} \times 100\% = 48\% \end{aligned}$$

Now try this

In the Haber process, nitrogen reacts with hydrogen to form ammonia:



The reaction does not go to completion and an equilibrium mixture of reactants and products is formed.

To investigate the equilibrium, 1.00 mol of nitrogen and 3.00 mol of hydrogen are sealed in a container at 100 atm pressure and 400 °C. The equilibrium mixture contains 8.57 g of ammonia. What is the percentage yield of the reaction?



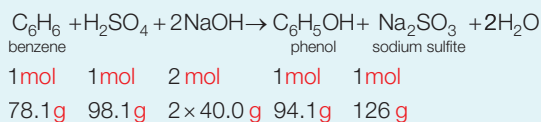
Box 1.4 Atom efficiency and green chemistry

Chemists make use of the law of conservation of mass to work out the **atom efficiency**, or **atom economy**, of a reaction. This is a way of assessing how efficiently a reaction makes use of the reactant atoms and is a good indicator of the *waste* generated by the reaction. Such considerations are becoming increasingly important as the chemical industry seeks to develop more economical and more sustainable manufacturing processes.

Atom efficiency is calculated from the stoichiometric equation for the overall process.

$$\text{Atom efficiency} = \frac{\text{molar mass of desired product}}{\text{sum of molar masses of reactants}} \times 100\% \quad (1.5)$$

Working out the atom efficiency of alternative production routes provides a convenient way of comparing economic and environmental factors. For example, at one time phenol was manufactured by sulfonating benzene with concentrated sulfuric acid and then treating the product with sodium hydroxide. The overall equation for the reaction is



Atom efficiency

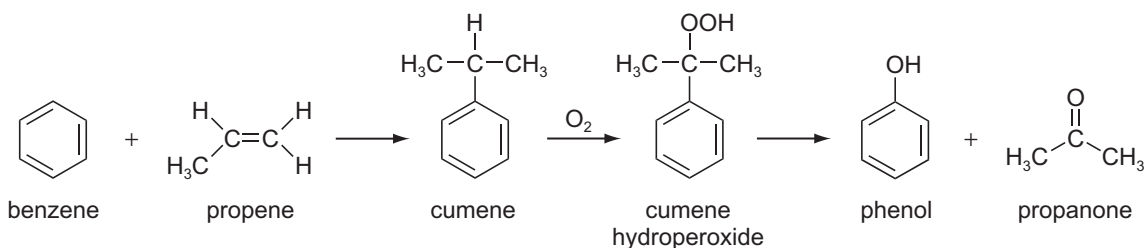
$$\begin{aligned} &= \frac{94.1 \text{ g mol}^{-1}}{78.1 \text{ g mol}^{-1} + 98.1 \text{ g mol}^{-1} + (2 \times 40.0 \text{ g mol}^{-1})} \times 100\% \\ &= \frac{94.1 \cancel{\text{ g mol}^{-1}}}{256.2 \cancel{\text{ g mol}^{-1}}} \times 100\% \\ &= 36.7\% \end{aligned}$$

This means that well under half the mass of the reactants ends up in the desired product. The rest is waste—unless uses can be found for the 126 g of sodium sulfite produced for every 94.1 g of phenol.

The calculation of atom efficiency assumes that all the reactants are converted to the products, as shown by the equation (i.e. there is 100% yield of the products). In practice, the yield was only about 88%, which brought the atom efficiency down to 32.3%. Some sodium sulfite is used in the wood pulp and paper industry, but most of it is waste.

This is one of the reasons why the sulfonation process has now been superseded by the **cumene process**. In the first stage of the cumene process, benzene reacts with propene to form 2-phenylpropane (cumene). The cumene is then treated with oxygen to form an unstable hydroperoxide, which breaks down to give phenol and propanone (acetone). (The conventions for drawing benzene rings are discussed in Section 22.1. The mechanism for this reaction is described in Box 22.2 (p.1009).)

▼ Ski and snowboard wear is usually made of nylon. Phenol is one of the feedstocks used in the production of nylon. Image source: Marco Maccarini/Stock.

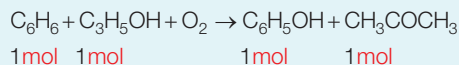


▲ The cumene process for the manufacture of phenol.





The overall equation for the three-stage process is



Atom efficiency of phenol production

$$= \frac{94.1 \text{ g mol}^{-1}}{78.1 \text{ g mol}^{-1} + 58.1 \text{ g mol}^{-1} + 36.0 \text{ g mol}^{-1}} \times 100$$

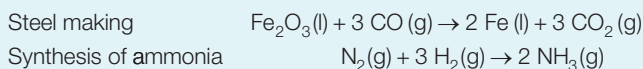
$$= \frac{94.1 \text{ g mol}^{-1}}{172.2 \text{ g mol}^{-1}} = 54.6\%$$

The atom economy for phenol is still relatively low. However, propanone is a valuable product of the reaction and is used to make plastics and industrial solvents. None is wasted, so the overall atom

efficiency of the process would be 100% if the conversion to products were complete. In practice, the atom efficiency is less than this because the obtained yield is only approximately 85%.

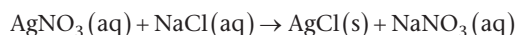
Now try this

- (a) Demand for propanone is rising at a lower rate than the demand for phenol. Calculate the atom efficiency of the cumene process if half the propanone is considered as waste and the overall conversion to products is 90%.
- (b) Calculate the atom efficiencies of the following two industrial processes:

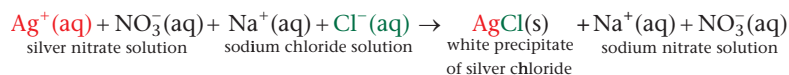


Ionic equations

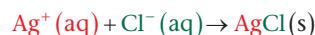
For reactions involving ionic compounds, the balanced equation is often shortened to include only the ions that take part in the reaction. For example, if you add a solution of silver nitrate to a solution of sodium chloride, a white precipitate of silver chloride forms (see Figure 1.7). (The white precipitate of silver chloride darkens on exposure to air as it decomposes.)



In a dilute solution of an ionic compound in water, the ions are surrounded by water molecules and behave independently of each other. So, a more accurate way to write the equation is



The Na^+ ions and NO_3^- ions are present in solution before and after the reaction. They do not take part in the reaction and so are called **spectator ions**. They can be left out of the equation, which then becomes



This type of equation, which excludes spectator ions and shows only the ions actually taking part in the reaction, is called an ionic equation. Note the importance of the state symbols, which clearly indicate that the above equation represents a precipitation reaction. An ionic equation can include non-ionic substances, such as metals, or covalent molecules, such as $\text{H}_2\text{O}(\text{l})$ or $\text{CO}_2(\text{g})$. State symbols are also useful for identifying these in the equation. You can practise writing ionic equations in Worked example 1.8.

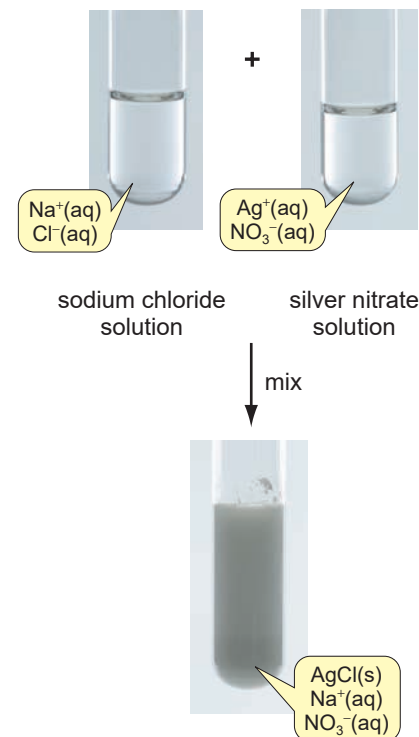


Figure 1.7 Precipitation of silver chloride. Image source: IDPS, University of Bath.



Always check when writing and balancing an ionic equation that the overall charge

on each side of the equation is the same.



Worked example 1.8 Ionic equations

Construct an ionic equation for the neutralization of hydrochloric acid by sodium hydroxide solution.

Strategy

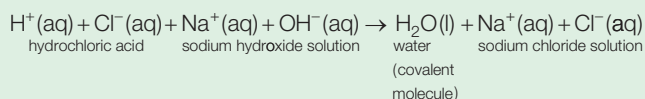
Write out a full, balanced equation for the reaction showing the ions present in the reactants and products. Identify any non-ionic substances and include state symbols in the equation.

Cross out the spectator ions that do not take part in the reaction.

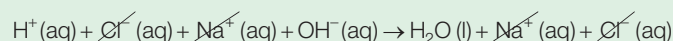
Include the remaining ions and any non-ionic substances in the ionic equation.

Solution

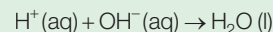
The full, balanced equation for the reaction is



Crossing out spectator ions



the ionic equation becomes



This ionic equation is the same for all neutralization reactions, whatever the acid and base used.

Now try this

Construct an ionic equation for the reaction of hydrofluoric acid (HF) with a solution of sodium carbonate (Na_2CO_3).

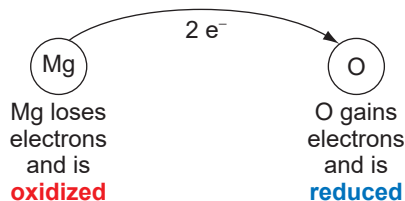
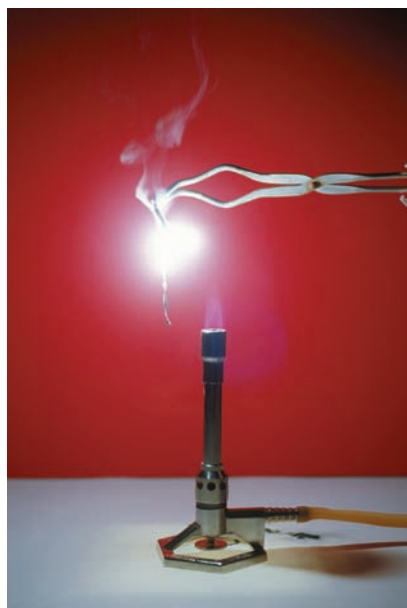
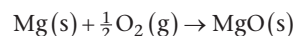


Figure 1.8 The burning of magnesium in air is a redox reaction. Image source: Charles D Winters/Science Photo Library.

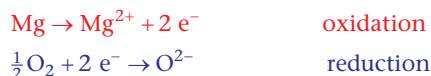
» The structures of ionic solids are discussed in Sections 6.4 and 6.5.

Oxidation and reduction

When a piece of magnesium burns in air (Figure 1.8), the magnesium gains oxygen and is oxidized. The product, magnesium oxide, is an ionic solid containing Mg^{2+} ions and O^{2-} ions.

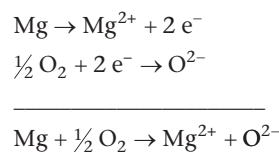


If you look at what is happening to the Mg atoms and to the O atoms in the reaction, you can describe the reaction by two **half equations**:



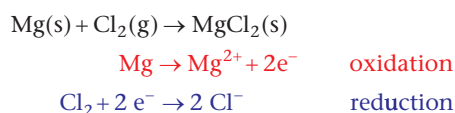
The magnesium loses electrons in one half reaction and oxygen gains electrons in the other. Another way of looking at **oxidation** is to say that oxidation is loss of electrons. **Reduction**, then, occurs when electrons are gained. So, in this reaction, the oxygen is being reduced and the magnesium is being oxidised. Reduction and oxidation occur simultaneously when magnesium burns in air. It is a reduction–oxidation, or **redox**, reaction.

Half equations express two contributions to an overall redox reaction. If you add the two half equations above together and cancel the 2e^- , you get the overall equation for the reaction.



Remember the half equations are just a schematic representation—the electrons are not actually free in the reaction mixture.

These definitions of oxidation and reduction allow reactions to be classed as redox reactions even if they do not involve oxygen. For example, the burning of magnesium in chlorine closely resembles the reaction of magnesium with oxygen. Magnesium chloride is an ionic solid containing Mg^{2+} and Cl^- ions.

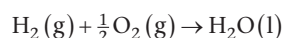


The magnesium atoms lose electrons and are oxidized. The chlorine atoms gain electrons and are reduced.

In the above reactions, O_2 and Cl_2 remove electrons from magnesium atoms and are called **oxidizing agents**. Similarly, the Mg atoms give electrons to O or Cl atoms and are **reducing agents**.

Oxidation states

Sometimes when a redox reaction involves non-ionic compounds, it is not possible to break the reaction down into half reactions involving electron transfer. For example, when hydrogen burns in air, water is formed



The equation is similar to the magnesium–oxygen one. Hydrogen is gaining oxygen and is being oxidized, but the product, water, is a covalent molecule.

To extend the idea of redox to reactions like this, chemists use the idea of **oxidation states** (sometimes called **oxidation numbers**). The atoms of each element in a substance are assigned oxidation states to show how much they are oxidized or reduced.

Rules for assigning oxidation states

- 1 The oxidation state of atoms in a pure element is zero.
- 2 In an uncharged compound, the sum of all the oxidation states is zero.
- 3 For simple ions containing only one element, such as Na^+ or Cl^- , the oxidation state is the same as the charge on the ion.
- 4 For ions containing more than one element, the sum of all the oxidation states is equal to the charge on the ion.
- 5 In compounds and ions, some elements have oxidation states that rarely change. These are:
 - F: -1 (always);
 - O: -2 (except in O_2^{2-} , O_2^- , OF_2 , O_2F_2 , and some metal oxides);
 - H: $+1$ (except when combined with metals as H^-);
 - Cl: -1 (except when combined with O and F);
 - Group 1 metals: $+1$;
 - Group 2 metals: $+2$.

Note that oxidation states always have a *sign* and a *number*. (The sign is written *before* the number to avoid confusion with charges.)


Applying the rules—some examples

Water (H_2O):

- Hydrogen is in oxidation state $+1$ (*rule 5*); oxygen is in oxidation state -2 (*rule 5*).
- There are two hydrogen atoms and one oxygen atom, so, for the compound, the sum of the oxidation states is $2 \times (+1) + (-2) = 0$ (*rule 2*).


Sulfate ion (SO_4^{2-}):


- Oxygen is in oxidation state -2 (*rule 5*).
- There are four O atoms, so the total contribution of the O atoms to the oxidation state of the ion is $4 \times (-2) = -8$.
- The sum of the oxidation states in the ion is -2 (the charge on the ion) (*rule 4*), so the oxidation state of S in the ion must be $+6$.

 The following mnemonic is helpful in remembering the definitions of oxidation and reduction.

OILRIG

Oxidation Is Loss of electrons; Reduction Is Gain of electrons.

 **Oxidation** is loss of electrons. An **oxidizing agent** removes electrons from something else. **Reduction** is gain of electrons. A **reducing agent** gives electrons to something else.

 An element is oxidized when its oxidation state increases. An element is reduced when its oxidation state decreases.

i The naming of organic compounds is covered in Chapter 2.

i An alternative approach to naming cations is to place the charge on the ion in brackets. Using this method, the ions are called the iron(2+) ion and the iron(3+) ion, respectively.

Table 1.7 Examples of polyatomic cations

Formula	Name
O ₂ ⁺	dioxygen ion
H ₃ O ⁺	oxonium ion
NH ₄ ⁺	ammonium ion
NMe ₄ ⁺	tetramethylammonium ion

Table 1.8 Naming the oxoanions of chlorine

Formula	Name	Oxidation state of chlorine
ClO ₄ ⁻	Perchlorate	+7
ClO ₃ ⁻	Chlorate	+5
ClO ₂ ⁻	Chlorite	+3
ClO ⁻	Hypochlorite	+1

Dichromate ion (Cr₂O₇²⁻):

- Oxygen is in oxidation state -2 (*rule 5*).
- There are seven O atoms, so the total contribution of the O atoms to the oxidation state of the ion is $7 \times (-2) = -14$.
- The sum of the oxidation states in the ion is -2 (the charge on the ion) (*rule 4*), so the combined oxidation state of the two Cr atoms in the ion must be $+12$. So each Cr has an oxidation state of $+6$.

Oxidation states and naming inorganic compounds

Most inorganic compounds have systematic names (see Section 1.2) that tell you which elements are present, in what combination, and in what oxidation states.

Cations

Cations containing a single element have the same name as the element. For example, H⁺ is the hydrogen ion and Na⁺ is the sodium ion. When an element can form more than one ion, the oxidation state of the element is given in brackets as a Roman numeral after the element name. Iron can form Fe²⁺ and Fe³⁺ ions, and these are called the iron(II) ion and the iron(III) ion, respectively (see Table 1.6 on p.22). Note that there is no space between the element name and the oxidation state. Examples of cations containing more than one atom are given in Table 1.7.

Anions

Anions containing a single element have the same stem as the element name, but the ending changes to *-ide*. For example, Cl⁻ is the **chloride** ion and O²⁻ is the **oxide** ion. There are a large number of polyatomic anions, and examples of these are given in Table 1.6 (p.22).

The endings *-ate* and *-ite* usually indicate that the ions contain oxygen, and these ions are called oxoanions. The thiocyanate ion (SCN⁻) has an *-ate* ending even though it contains no oxygen. The thio- prefix shows that a sulfur atom has replaced the oxygen atom in cyanate (OCN⁻).

Some elements form more than one oxoanion. For example, Table 1.8 shows how the four oxoanions of chlorine are named. The names give an indication of the numbers of oxygen atoms present:

- *-ate* anions contain more oxygen than *-ite* anions;
- the *per-* prefix implies more oxygen than the *-ate* anion;
- the *hypo-* prefix implies less oxygen than the *-ite* anion.

i As with cations, the charge on an anion can be placed in brackets at the end of the name. This is useful when more than one anion is

possible. For example, the superoxide ion (O₂⁻) is also known as the dioxide(1-) ion.

Alternatively, longer systematic names can be used to unambiguously provide the formula. For example, the IUPAC name for the perchlorate ion (ClO₄⁻) is tetraoxidochlorate(1-) (see Figure 27.28 in Section 27.6, p.1246). Using this nomenclature, the sulfate ion (SO₄²⁻) is tetraoxidosulfate(2-). In this book, you will see the simplest names, such as perchlorate, sulfate, sulfite, nitrate, and nitrite.

Compounds

The name of an ionic compound consists of the cation name followed by the anion name. In this way, NaCl is sodium chloride, MgBr₂ is magnesium bromide, (NH₄)₂SO₄ is ammonium sulfate, and FeCl₂ is iron(II) chloride. Note that even though in, for example, MgBr₂ there are two bromide ions they are not indicated in the name. This is because magnesium

only forms compounds in the +2 oxidation state so the number of bromide ions can be inferred from the charge on Mg^{2+} .

Covalently bonded binary compounds are named in a similar way to ionic compounds, with the more electropositive element given first with its element name, followed by the more electronegative element with its element name changed to use the anionic -ide ending. For example, HCl is hydrogen chloride and H_2S is hydrogen sulfide. When the elements can combine in more than one way, the compounds are distinguished by indicating the numbers of atoms of the elements present in the formula using the prefixes shown in Table 1.9. For example, SO_2 is sulfur dioxide and SO_3 is sulfur trioxide. Normally, when only one atom of an element is present, the prefix 'mono-' is omitted. An exception to this is CO, which is called carbon monoxide. Sometimes prefixes are needed for both elements so, for example, N_2O_5 is dinitrogen pentoxide. Some further examples are given in Worked example 1.9.

i A **binary compound** is a compound containing only two different elements.

i **Electronegativity** is the tendency of an atom in a molecule to attract electrons to itself. An atom with low electronegativity is said to be electropositive. See Section 4.3.

Table 1.9 Prefixes indicating the numbers of atoms present

Number of atoms	Prefix	Example*
1	mono-	carbon monoxide (CO)
2	di-	carbon dioxide (CO_2)
3	tri-	sulfur trioxide (SO_3)
4	tetra-	silicon tetrachloride (SiCl_4)
5	penta-	dinitrogen pentoxide (N_2O_5)
6	hexa-	sulfur hexafluoride (SF_6)
7	hepta-	iodine heptafluoride (IF_7)
8	octa-	triuranium octoxide (U_3O_8)
9	nona-	tetraphosphorus nonasulfide (P_4S_9)
10	deca-	disulfur decafluoride (S_2F_{10})

*When the element name begins with a- or o-, the a- or o- of the prefix is usually dropped to make pronunciation easier. For example, it is pentoxide not pentaoxide.



Worked example 1.9 Naming inorganic compounds

What are the systematic names for

(a) BrF_5 , (b) CaI_2 , and (c) $\text{Fe}(\text{NO}_3)_2$?

Strategy

For binary compounds, change the name of the more electronegative element so that it ends in -ide. For ionic compounds, indicate the oxidation state using Roman numerals if more than one oxidation state is possible. For covalently bonded compounds, use prefixes to indicate the numbers of atoms in the formula if the elements can combine in different combinations.

Solution

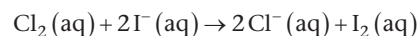
- (a) Bromine and fluorine can combine in more than one way, so the numbers of atoms in the formula need to be identified. Fluorine is more electronegative, so the compound is bromine pentafluoride.
- (b) Calcium only forms the +2 oxidation state. The compound is calcium iodide.
- (c) Iron forms more than one type of ion, so the oxidation state needs to be indicated. The anion is nitrate (NO_3^-) so the compound is iron(II) nitrate.

Now try this

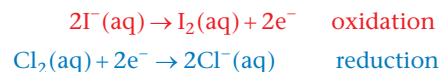
What are the systematic names for (a) SeF_4 and (b) $\text{Fe}(\text{ClO}_4)_3$?

Changes of oxidation state

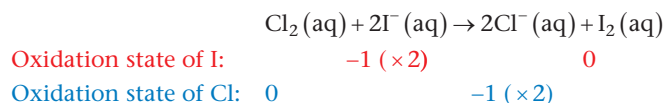
We can use oxidation states to find out what has been oxidized and what has been reduced in a reaction. For example, consider the reaction between chlorine and iodide ions.



Half reactions:



In terms of electron transfer, chlorine is reduced and iodine is oxidized. Now look at the oxidation states:



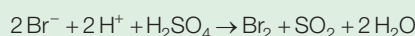
- The oxidation state of iodine **increases** from **-1 to 0**, and iodine has been **oxidized**.
- The oxidation state of chlorine **decreases** from **0 to -1**, and chlorine has been **reduced**.

Note that the overall increase in oxidation states balances the overall decrease. Another example is given in Worked example 1.10.



Worked example 1.10 Changes of oxidation state

When concentrated sulfuric acid is added to solid potassium bromide, red-brown fumes of bromine vapour are seen and sulfur dioxide gas is also given off. The ionic equation is shown below. Assign oxidation states to the elements in each of the reactants and products in the equation. Use these values to decide what has been oxidized and what reduced.

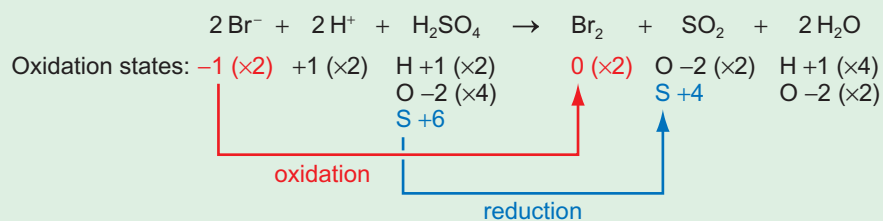


Strategy

Use the rules on p.29 to assign oxidation states for each element in the equation.

Write the values under the reactants and products in the equation. Elements for which the oxidation state increases have been oxidized in the reaction; elements for which the oxidation state decreases have been reduced.

Solution



▲ Addition of concentrated sulfuric acid to potassium bromide. Red-brown fumes of bromine vapour (Br_2) are produced.
Image source: IDPS, University of Bath.

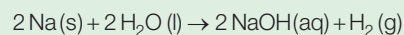




- H is +1 in reactants and products, so no redox.
- O is -2 in reactants and products, so no redox.
- Br **increases** from -1 in 2Br^- to 0 in Br_2 , so it has been **oxidized**. The overall increase in oxidation numbers is 2.
- S **decreases** from +6 in H_2SO_4 to +4 in SO_2 , so it has been **reduced**. The overall decrease in oxidation numbers is 2.

Now try this

- (a) Use oxidation states to decide what has been oxidized and what reduced in the reaction of sodium with water.



- (b) Use changes in oxidation states to produce a balanced equation for the reaction between magnesium and oxygen.


Constructing and balancing redox equations from half equations

Constructing an overall equation from the two half equations can be tricky at first and requires some practice. Here are the steps to follow. You can practise using them in Worked example 1.11.

- Step 1** Identify what is being oxidized and what reduced, and then write the two unbalanced half equations for oxidation and reduction.
- Step 2** Balance all the elements in the half equations except O and H.
- Step 3** Balance O by adding H_2O . Then, in *acidic solution*, balance H by adding H^+ . In *alkaline solution*, balance H by adding H_2O to the side of the half equation that needs H (just *one* H_2O for each H needed) whilst adding OH^- to the other side. Then cancel out any surplus water.
- Step 4** Balance electric charges in the half equations by adding electrons to the left-hand side for the reduction reaction and to the right-hand side for oxidation reaction.
- Step 5** Multiply the half equations, if necessary, by factors so that each equation transfers the same number of electrons.
- Step 6** Add the two half equations together so that the numbers of electrons transferred cancel out.
- Step 7** Simplify the overall equation, if necessary, by cancelling species that appear on both sides.
- Step 8** Check that atoms and charges on each side of the equation balance. Check that you have no electrons left in the overall equation.

i When combining half equations to give an overall equation, make sure that the number of electrons released in oxidation is the same as the number of electrons gained in reduction.

» Redox reactions are important in electrochemistry. Section 16.3 shows how you can predict whether one compound will oxidize or reduce another. Redox reactions of p-block elements and their compounds are discussed in Chapter 27 and those of d-block elements and their compounds in Chapter 28.

 Visit the online resources to view [Screencast 1.1](#), which walks you through [Worked example 1.11](#), constructing and balancing a redox equation from half equations.



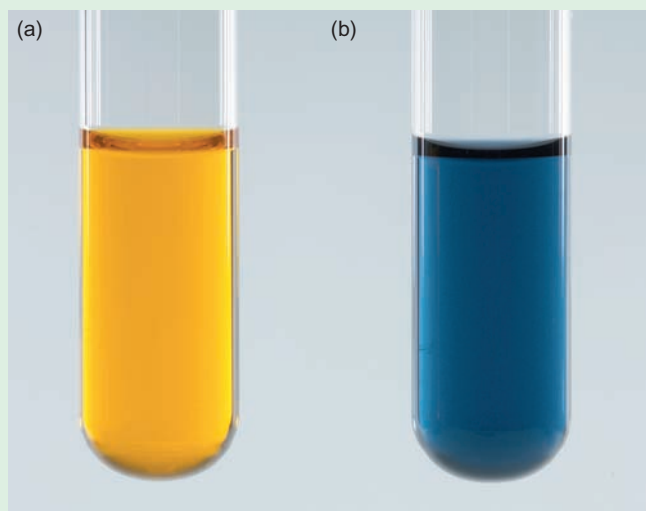
Worked example 1.11 Constructing and balancing a redox equation from half equations

Sulfur dioxide gas turns an acidified solution of potassium dichromate from orange to blue-green. The SO_2 is oxidized to SO_4^{2-} ions. The orange $\text{Cr}_2\text{O}_7^{2-}$ ions are reduced to blue-green Cr^{3+} ions. Construct half equations and a balanced overall equation for the reaction.

Strategy

Start by writing unbalanced half equations for the oxidation of SO_2 and the reduction of $\text{Cr}_2\text{O}_7^{2-}$ ions. Then follow through the steps 1–8 above.

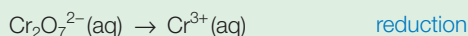
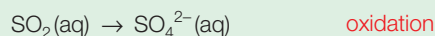




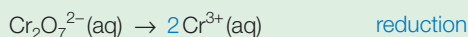
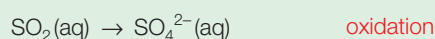
▲ Another redox reaction involving $\text{Cr}_2\text{O}_7^{2-}$ ions. Ethanol reduces the orange $\text{Cr}_2\text{O}_7^{2-}$ ions in (a) to blue-green Cr^{3+} ions in (b). The ethanol is oxidized to ethanal and then to ethanoic acid. This reaction was the basis of early breath tests for ethanol (see Box 11.6, p.542). Image source: IDPS, University of Bath.

Solution

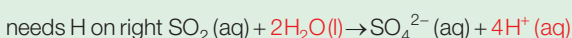
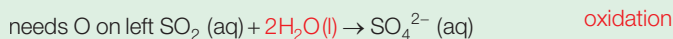
Step 1 Unbalanced half equations.



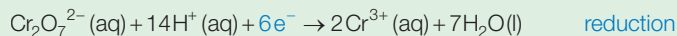
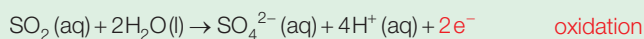
Step 2 Balance elements other than O and H.



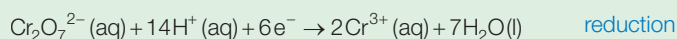
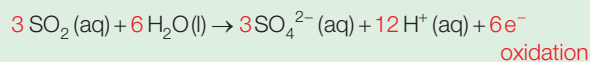
Step 3 Balance O and H by adding H_2O and H^+ ions (in acidic solution).



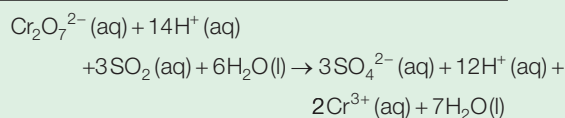
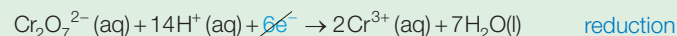
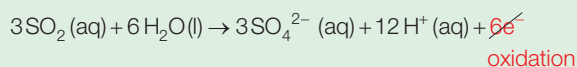
Step 4 Balance electric charge by adding electrons.



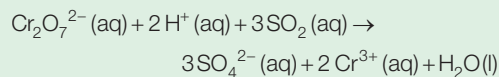
Step 5 Multiply the oxidation half equation $\times 3$, so that the number of electrons transferred is the same in half equations.



Step 6 Add the two half equations and cancel out the electrons.



Steps 7 and 8 Simplify the equation by cancelling out $\text{H}^+(\text{aq})$ ions and $\text{H}_2\text{O}(\text{l})$ molecules that occur on both sides of the equation. Atoms and charges on each side of the equation balance and no free electrons are left over.



Now try this

- (a) Fe^{2+} ions are oxidized to Fe^{3+} by MnO_4^- ions in acidic solution. The MnO_4^- ions are reduced to Mn^{2+} ions. Construct half equations and a balanced overall equation for the reaction.
- (b) Use the change in oxidation states of Fe^{2+} and MnO_4^- to construct a balanced overall equation.

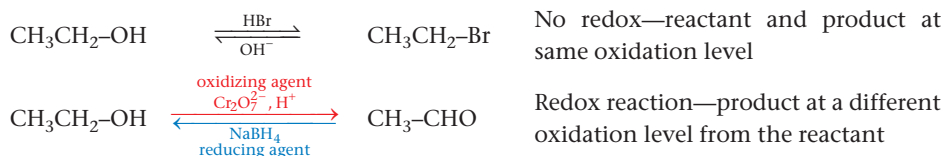
» A functional group, such as $-\text{Cl}$ and $-\text{OH}$, on the hydrocarbon skeleton of an organic molecule gives the molecule characteristic properties; see Section 2.3.

» You can read about the rules for assigning oxidation levels in organic compounds in Section 19.2. The oxidation of alcohols is discussed in Box 23.2 (p.1066). There is a list of common oxidizing and reducing agents in organic chemistry in Appendix 4 (p.1342).

Redox in organic reactions: oxidation levels

Carbon has nine oxidation states ranging from -4 in CH_4 to $+4$ in CO_2 and CCl_4 . For most organic molecules, however, it is not helpful to assign oxidation states to individual atoms. What, for example, are the oxidation states of carbon and hydrogen in ethane (C_2H_6) and in propane (C_3H_8)? Organic chemists use a system of oxidation levels based on the extent of oxidation or reduction of *the carbon atom that is part of, or attached to, the functional group*. Thus, alcohols and halogenoalkanes are at the same oxidation level because they can be interconverted without using oxidizing or reducing agents.

To convert an alcohol into an aldehyde or a ketone requires an oxidizing agent, so aldehydes and ketones are at a higher oxidation level than alcohols. Aldehydes can be oxidized to carboxylic acids, so carboxylic acids are at a higher oxidation level still. For example,



Summary

- A balanced equation is one with equal numbers of each type of atom on either side of the equation. It is a balance sheet of where each atom starts and where it ends up. For an ionic equation, the total charge on either side of the equation must be the same.
- The relationship between the amounts of reactants and products is called the stoichiometry of the reaction. It allows you to calculate the masses that react exactly and the masses of the products formed.
- The percentage yield of a reaction tells you what percentage of the theoretical yield is actually obtained.
- An ionic equation shows only the ions that take part in the reaction, plus any non-ionic substances involved. Spectator ions are not included.
- Oxidation is loss of electrons or increase in oxidation state. Reduction is gain of electrons or decrease in oxidation state.
- Redox reactions can be formally represented by two half equations, one for oxidation and the other for reduction.
- Systematic names for inorganic compounds tell you which elements are present, in what combination, and in what oxidation states.
- For organic compounds, oxidation levels are more useful than oxidation states.

For practice questions on these topics, see questions 10–15 at the end of this chapter (p.68).

1.5 Working out how much you have

Concentrations of solutions

Many chemical reactions take place in solution. The substance dissolved is called the **solute**, and the liquid it dissolves in the **solvent**. The **concentration** of a solution tells you how much of the solute is dissolved in a particular volume of the solution.

Concentrations can be expressed in various units depending on the circumstances. Sometimes units of grams per dm^3 (grams per litre) are used. A solution containing 20 g of sodium chloride dissolved in 1 dm^3 of solution has a concentration of 20 g dm^{-3} . You may sometimes see the solubility of a substance quoted in grams per 100 g of solvent.

Usually, however, chemists are more interested in the *chemical amount* of substance present rather than the mass. The amount in moles tells you the number of formula units present and relates to the chemical equation for a reaction. So, the preferred units for measuring concentrations are mol dm^{-3} .

The molarity of a solution is the amount (in moles) of solute dissolved per dm^3 of *solution* (not solvent). The volume of the solution includes the volume of the dissolved solute. The units are mol dm^{-3} .

To convert g dm^{-3} to mol dm^{-3} , you need to know the molar mass of the solute.

$$\text{Concentration (mol dm}^{-3}\text{)} = \frac{\text{concentration (g dm}^{-3}\text{)}}{\text{molar mass (g mol}^{-1}\text{)}} \quad (1.6)$$

The use of Equation 1.6 is illustrated in Worked example 1.12. Box 1.5 describes an alternative way of expressing very low concentrations.

The **solubility** of a solid in a solvent is the maximum mass that will dissolve in a given mass (or volume) of the solvent, at a particular temperature, in the presence of excess undissolved solid, so that the solution is **saturated**. For example, the solubility of sodium chloride at 298 K is 36.0 g per 100 g of water.

A solution with a concentration of 1 mol dm^{-3} is sometimes called a one molar solution, abbreviated to 1 M.



Box 1.5 Measuring low concentrations: parts per million

It is often more convenient to express low concentrations in parts per million (**ppm**) or even parts per billion (**ppb**; where 1 billion = 1×10^9). If you use these units, it is important to be clear about what they refer to.

Parts per million by mass

This unit is often used for low concentrations of an impurity in a liquid or a solid. For example, the concentration of a pesticide in a ground water sample may be quoted as 1 **ppm (by mass)**. This means that 1 g of the water sample contains 1×10^{-6} g (1 **µg**) of the pesticide. Another way of thinking about ppm is as a concentration of 1 mg in 1 kg or 1 mg in 1 litre.

Concentration in ppm (by mass)

$$= \frac{\text{mass of component}}{\text{total mass of liquid or solid}} \times 10^6 \text{ ppm} \quad (1.7)$$

if both masses are in the same units

Parts per million by volume

For gases, ppm by volume is used. For example, the concentration of carbon dioxide in the atmosphere in 2019 was 409 **ppm (by volume)**. To understand what this means it helps to remember that, for an ideal gas, the volume is proportional to the number of moles (or molecules). Thus, in this example one mole of air contains 409×10^{-6} mol (409 **µmol**) of CO₂. In terms of molecules, one million molecules of air contain 409 molecules of CO₂.



▲ The Mauna Loa Observatory in Hawaii has been recording atmospheric CO₂ concentrations since 1958, when the concentration of CO₂ was 316 **ppm by volume** (see Box 10.5, p.485). In 2019, the CO₂ concentration was 409 **ppm by volume**. Image source: National Oceanic and Atmospheric Administration (NOAA).

Concentration in **ppm (by volume)**

$$= \frac{\text{mass of component}}{\text{total moles of gas}} \times 10^6 \text{ ppm} \quad (1.8)$$

Percentage composition

409 **ppm (by volume)** is the same as 0.0409 % **by volume**.

Now try this

- (a) The label on a bottle of mineral water says it contains '27 mg calcium per litre'.
- What is the concentration of Ca²⁺ ions in **ppm (by mass)** and the **percentage by mass** of Ca²⁺ ions?
 - What is the concentration of Ca²⁺ ions in **mol dm⁻³**?
- (b) The world's oceans contain around 1 **ppt** of dissolved gold. The approximate volume of the combined oceans is 1.4×10^{23} **dm³**. What is the approximate mass of gold in the world's oceans and what is its value at today's price of gold?



Worked example 1.12 Units of concentration

2.54 g of sodium chloride were dissolved in water and the solution made up to 100 cm³. What is the concentration of the solution in mol dm⁻³?

Strategy

Work out the concentration of the solution in g dm⁻³. (Remember: 1 dm³ = 1000 cm³.)

Use Equation 1.6 to convert g dm⁻³ to mol dm⁻³.

Solution

100 cm³ contain 2.54 g of NaCl, so 1000 cm³ contain 25.4 g of NaCl.

$$\begin{aligned} M_r(\text{NaCl}) &= 22.99 + 35.45 \\ &= 58.44 \end{aligned}$$

From Equation 1.6,

$$\begin{aligned} \text{Concentration (mol dm}^{-3}\text{)} &= \frac{\text{concentration (g dm}^{-3}\text{)}}{\text{molar mass (g mol}^{-1}\text{)}} \quad (1.6) \\ &= \frac{25.4 \text{ g dm}^{-3}}{58.44 \text{ g mol}^{-1}} \\ &= 0.435 \text{ mol dm}^{-3} \end{aligned}$$

Now try this

43.7 g of anhydrous copper(II) sulfate (CuSO₄) were dissolved in water and the solution was made up to 2.00 dm³. What is the molarity of the solution?

If you know the concentration (*c*) of a solution, you can work out the amount (*n*) of solute in a particular volume (*V*).

$$\text{Amount (n) = concentration (c) } \times \text{ volume of solution (V)}$$

$$\text{mol} \qquad \text{mol dm}^{-3} \qquad \text{dm}^3$$

So,

$$n = c \times V \quad (1.9)$$

If you use this equation, remember to convert the volume of solution into dm³.

Volumetric analysis: titrations

For a chemical reaction taking place between two solutions, if you know the stoichiometric equation for the reaction and the concentration of one of the reactants, you can carry out a **titration** to find the concentration of the other reactant. This involves adding small amounts of one solution from a burette to a known volume of the other solution in a conical flask until the reaction is just complete.

The procedure is called **volumetric analysis** because it involves making accurate measurements of volumes of solutions. The **equivalence point** is the point in a titration when the amount of added reagent has reacted exactly with the solution in the flask. An **indicator** is usually added so that a colour change indicates when this has happened. The point at which the indicator changes colour is the **end-point** of the titration.

i A solution whose concentration is known exactly is called a **standard solution**.



Worked example 1.13 Finding how much solute is in a given volume of solution

What mass of sodium carbonate (Na₂CO₃) must be dissolved in water to give 75.0 cm³ of a solution with a concentration of 2.05 mol dm⁻³?

Strategy

(a) Work out the amount of Na₂CO₃ in 75.0 cm³ of the 2.05 mol dm⁻³ solution. You can do this from first principles or by using Equation 1.9 (but remember to convert the volume of the solution to dm³). (1 dm³ = 1000 cm³.)

(b) Use Equation 1.2 (p.19) to convert the amount in moles to the mass in grams.

Solution

(a) **Working out the amount of Na₂CO₃ from first principles:**
1000 cm³ (1 dm³) of solution contain 2.05 mol of Na₂CO₃
1 cm³ of solution contains $\frac{2.05}{1000}$ mol of Na₂CO₃





75.0 cm^3 of solution contain $\frac{2.05 \times 75.0}{1000} \text{ mol} = 0.1538 \text{ mol}$ of Na_2CO_3

or,

Working out the amount of Na_2CO_3 using Equation 1.9:

$$n = c \times V$$

$$\text{amount of Na}_2\text{CO}_3 = 2.05 \text{ mol dm}^{-3} \times 0.0750 \text{ dm}^3 \quad (1.9)$$

$$= 0.1538 \text{ mol}$$

$$(b) M_r(\text{Na}_2\text{CO}_3) = (2 \times 22.99) + 12.01 + (3 \times 16.00) = 106.0$$

Use Equation 1.2,

$$\text{amount (in mol)} = \frac{\text{mass (in g)}}{\text{molar mass (in g mol}^{-1}\text{)}} \quad (1.2)$$

and rearrange to give an expression for the mass.

$$\text{Mass of Na}_2\text{CO}_3 \text{ needed} = \text{amount} \times \text{molar mass}$$

$$= 0.1538 \text{ mol} \times 106.0 \text{ g mol}^{-1}$$

$$= 16.3 \text{ g}$$

Now try this

- (a) A solution of sodium carbonate has a concentration of $0.157 \text{ mol dm}^{-3}$. What volume of solution contains exactly 1.00 g of sodium carbonate?
- (b) What mass of sodium thiosulfate crystals ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) must be dissolved in 250 cm^3 of water to give a solution with a concentration of $0.0750 \text{ mol dm}^{-3}$?

» The pH changes during acid–base titrations are explained in Section 7.4.

Figure 1.9 shows a typical titration apparatus that you may have used in the laboratory. The unknown concentration is calculated by following the steps in Worked example 1.14. An automated titration apparatus used for routine titrations in industry is shown in Figure 1.10. It monitors the pH of the solution as the titration proceeds and detects the equivalence point by responding to a rapid change in pH that occurs at that point.



Figure 1.9 Typical apparatus for a titration, showing a burette, pipette, and a volumetric flask used for making up a standard solution. Image source: IDPS, University of Bath.



Figure 1.10 Automated titration apparatus used to carry out routine acid–base titrations in industry. Image courtesy of Metrohm AG/Brinkmann Instruments Inc.



Worked example 1.14 An acid–base titration

A standard solution of sulfuric acid can be used to find the concentration of a solution of sodium hydroxide, whose concentration is unknown. In a titration, $0.100 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ was added from a burette to 25.0 cm^3 of NaOH containing a few drops of phenolphthalein as the indicator. The solution changed from pink to colourless after the addition of 21.4 cm^3 of the sulfuric acid. What is the concentration of the sodium hydroxide solution?

Strategy

The steps below can be adapted for any titration calculation.

- Step 1** Write down the stoichiometric equation for the reaction.
- Step 2** State what the equation tells you about the amounts of the substances you are interested in.
- Step 3** Use the concentration of the standard solution to work out the number of moles that have reacted.
- Step 4** From your answer to Step 2, find the number of moles of the other reactant present in the volume of solution used. This is the amount that reacted exactly.
- Step 5** Convert this to the amount in 1 dm^3 of solution to give the concentration in mol dm^{-3} .

Solution

- Step 1** The stoichiometric equation for the reaction is
 $\text{H}_2\text{SO}_4(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
- Step 2** The equation tells you that 1 mol of H_2SO_4 reacts exactly with 2 mol of NaOH.
- Step 3** 21.4 cm^3 of $0.100 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ were added.

Working out the amount of H_2SO_4 added from first principles:

1000 cm^3 of $\text{H}_2\text{SO}_4(\text{aq})$ contain 0.100 mol of H_2SO_4

1 cm^3 of $\text{H}_2\text{SO}_4(\text{aq})$ contains $\frac{0.100}{1000} \text{ mol}$ of H_2SO_4

21.4 cm^3 of $\text{H}_2\text{SO}_4(\text{aq})$ contain $\frac{0.100 \times 21.4}{1000} \text{ mol}$
 $= 2.14 \times 10^{-3} \text{ mol H}_2\text{SO}_4$

or,

Working out the amount of H_2SO_4 added using Equation 1.9 (p.37):

$$n = c \times V$$

$$\text{Amount of H}_2\text{SO}_4 = 0.100 \text{ mol dm}^{-3} \times 0.0214 \text{ dm}^3 \\ = 2.14 \times 10^{-3} \text{ mol}$$

(When using Equation 1.9, remember to convert the volume of the solution to dm^3 .)

- Step 4** From Step 2, amount of NaOH to react exactly
 $= 2 \times (2.14 \times 10^{-3} \text{ mol})$

This was contained in 25.0 cm^3 of solution.

- Step 5** Concentration of NaOH solution
 $= \frac{2 \times (2.14 \times 10^{-3} \text{ mol})}{0.025 \text{ dm}^3}$
 $= 0.171 \text{ mol dm}^{-3}$

Now try this

14.8 cm^3 of $0.00105 \text{ mol dm}^{-3}$ nitric acid ($\text{HNO}_3(\text{aq})$) reacted exactly with 9.85 cm^3 of calcium hydroxide solution ($\text{Ca}(\text{OH})_2(\text{aq})$). Calculate the concentration of the calcium hydroxide solution (a) in mol dm^{-3} and (b) in g dm^{-3} .

Sometimes it is necessary to add an *excess* of a standard reagent to the solution of unknown concentration and then determine the amount of the standard reagent remaining after the reaction by a **back titration** using a second standard solution. This technique is used when the rate of reaction is slow, making the determination of the end-point difficult, or when the solution of unknown concentration is unstable. An example of a back titration in the analysis of river water is described in Box 1.6.



Visit the online resources to view Screencast 1.2, which walks you through Worked example 1.14, the stages in carrying out the calculation for a typical titration.



Box 1.6 Measuring dissolved oxygen in river water

In the UK, analysis of the dissolved oxygen in river water is carried out routinely by the water industry. A 'healthy' river has dissolved oxygen concentrations ranging from around 5 mg dm^{-3} to 10 mg dm^{-3} . (The EC standard for a salmon river requires 50% of

samples to be at least 9 mg dm^{-3} and never less than 6 mg dm^{-3} .) In heavily polluted water, oxygen is used up by aerobic bacteria decomposing the organic material in the river. The concentration of oxygen falls and the river becomes lifeless.

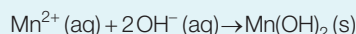




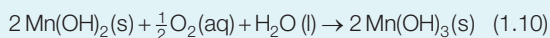
Measurements are taken on site using electronic probes, which are pre-calibrated in the laboratory at regular intervals.

One method used to pre-calibrate the electronic probes involves performing a **Winkler titration**. This is a back titration that takes place in three stages.

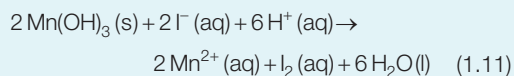
Stage 1 The water sample is treated with a solution of manganese(II) sulfate (MnSO_4 (aq)) followed by an alkaline solution of potassium iodide (KI (aq)). Both these solutions are present in excess to ensure that all the dissolved oxygen reacts. The following reaction takes place.



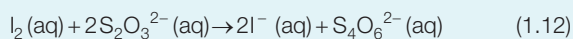
A precipitate of manganese(II) hydroxide forms which is oxidized by the dissolved oxygen to form manganese(III) hydroxide.



Stage 2 The precipitate of manganese(III) hydroxide is allowed to settle and the solution is acidified with sulfuric acid. The flask is swirled gently until all the precipitate dissolves. In the acidified solution, the liberated Mn^{3+} (aq) ions are rapidly reduced back to Mn^{2+} (aq) by the I^{-} (aq) ions.



Stage 3 The mixture is transferred to a conical flask and the I_2 (aq) is titrated with a standard solution of sodium thiosulfate in the presence of a starch indicator. The blue colour changes to a pale yellow colour at the end-point.



▲ Adequate dissolved oxygen is essential for good water quality. Analysis is carried out on site using an electronic probe. Image courtesy of David Preston, Environment Agency.

Now try this

A Winkler titration was performed on a 150 cm^3 sample of river water. 12.2 cm^3 of a $0.0100 \text{ mol dm}^{-3}$ sodium thiosulfate solution were required.

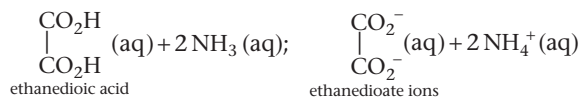
- Calculate the concentration of the dissolved oxygen in mg dm^{-3} .
- Suggest why a back titration is used in this determination, rather than a direct titration of O_2 against Mn^{2+} (aq).

i Measurement of mass is one of the simplest but most accurate measurements that can be made in the laboratory.

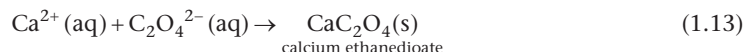
Gravimetric analysis

Analytical methods that are based on accurate measurements of mass rather than volume are known as gravimetric analyses. One technique involves reacting the substance being analysed in solution so that a precipitate of known composition is produced. The precipitate is then separated by filtration, washed, dried, and accurately weighed.

For example, one way of determining the calcium content of natural waters is to treat a sample of water with an excess of ethanedioic acid (oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$) followed by a solution of ammonia.



The ammonia reacts with the ethanedioic acid to produce ethanedioate ions and ensures that all the calcium ions in the water sample are precipitated as calcium ethanedioate (calcium oxalate)



The precipitate of calcium ethanedioate is collected in a weighed filtering crucible (see Figure 1.11), dried, and heated strongly in air. The calcium ethanedioate is converted to calcium oxide



When the crucible is cool, the crucible and remaining solid are weighed. Then the crucible and contents are heated, cooled, and weighed again, to check that the conversion to calcium oxide is complete. Hence, the mass of CaO produced from the calcium ions in a given volume of water can be found. Worked example 1.15 shows how the results are calculated.



Figure 1.11 A sintered glass weighing crucible. Image source: IDPS, University of Bath.



Worked example 1.15 Gravimetric analysis

In an analytical laboratory, a 250.0 cm^3 sample of river water was treated with excess ethanedioic acid and ammonia solution to precipitate all the Ca^{2+} ions present as CaC_2O_4 . The precipitate was filtered, washed, dried, and heated strongly in a crucible whose empty mass was 24.3782 g . The mass of the crucible and CaO was 24.5186 g . Calculate the concentration of Ca^{2+} ions in the water in **g per 100 cm^3** of water.

Strategy

Calculate the mass of CaO formed.

Calculate the amount of CaO formed.

Use Equations 1.13 and 1.14 to work out the stoichiometric relationship between the Ca^{2+} ions in the water and the CaO produced.

Work out the amount in moles of Ca^{2+} ions in the 250.0 cm^3 water sample.

Convert this to **g per 100.0 cm^3** of water.

Solution

$$\begin{aligned} \text{Mass of CaO formed} &= 24.5186\text{ g} - 24.3782\text{ g} \\ &= 0.1404\text{ g} \end{aligned}$$

$$M_r(\text{CaO}) = 40.08 + 16.00 = 56.08$$

From Equation 1.2 (p.19),

$$\begin{aligned} \text{amount of CaO formed} &= \frac{0.1404\text{ g}}{56.08\text{ g mol}^{-1}} \\ &= 2.5036 \times 10^{-3}\text{ mol} \end{aligned}$$

From Equations 1.13 and 1.14, **1 mol** of CaO is formed from **1 mol** of Ca^{2+} ions in the water sample.

250.0 cm^3 of the water sample contain $2.5036 \times 10^{-3}\text{ mol}$ of $\text{Ca}^{2+}(\text{aq})$.

Divide by 250 cm^3 to find the amount in 1 cm^3 . Then multiply by 100 cm^3 to find the amount in that volume. 100.0 cm^3 of the water sample contains

$$\begin{aligned} &\frac{(2.5036 \times 10^{-3}\text{ mol}) \times 100.0\text{ cm}^3}{250.0\text{ cm}^3} \\ &= 1.0014 \times 10^{-3}\text{ mol of Ca}^{2+}(\text{aq}) \end{aligned}$$

Now try this

- (a) A 4.500 g sample of an oil containing the pesticide DDT ($\text{C}_{14}\text{H}_9\text{Cl}_5$) was heated with sodium in alcohol to liberate all the chlorine present as Cl^- ions. The mixture was treated with silver nitrate solution and 1.509 g of solid AgCl were recovered. Calculate the percentage (by mass) of DDT in the sample.
- (b) Lawn fertilizer contains ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$. The ammonium sulfate content was analysed by precipitating 1.7764 g of barium sulfate, BaSO_4 from a solution of 1.0234 g of the lawn fertilizer in water. Calculate the weight percent (w/w%) of ammonium sulfate in the fertilizer.



Summary

- The molarity of a solution is the amount (in mol) of solute dissolved in 1 dm³ of solution.
- The amount (in mol) of solute (n) dissolved in a volume (V) of solution (in dm⁻³) is given by:
 $n = c \times V$, where c is the concentration of the solution in mol dm⁻³.
- Volumetric analysis involves accurate measurements of volumes of solutions.
- Gravimetric analysis involves accurate measurements of mass.

? For practice questions on these topics, see questions 16 and 17 at the end of this chapter (p.68).

1.6 Energy changes in chemical reactions

Transfer of energy

Energy is the capacity to do work. **Work** is done when motion occurs against a force. For example, when you lift up a book, you are doing work against the force of gravity and this requires energy. The plunger in the syringe in Figure 1.12 is pushed back against gravity and against the atmosphere so that work is done.

The transfer of energy is a familiar occurrence in everyday life. When a fossil fuel, such as coal or oil, is burned in a power station, chemical energy is converted to thermal energy, which is used to heat water. The steam generated produces motion in a turbine and the mechanical energy of the rotating turbine is converted to electrical energy. The electrical energy is delivered to your home where it can produce motion in an electric motor, or heat in an electric fire, or light from a lamp.

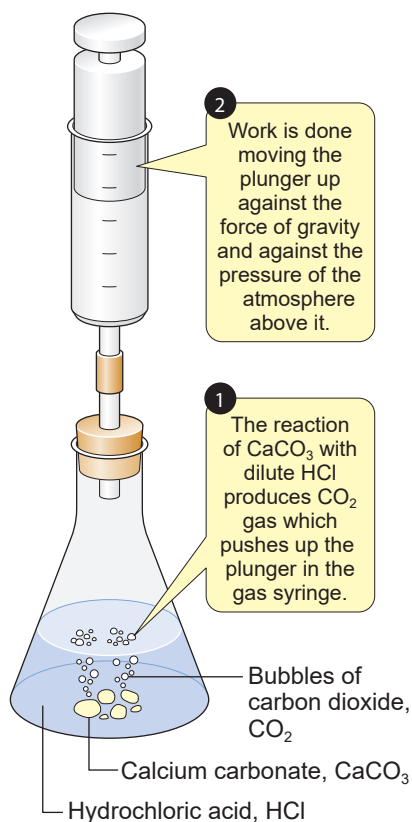


Figure 1.12 A simple chemical reaction that produces motion. When the reaction is carried out in an open flask, work is done pushing back the atmosphere.

i The unit for **work**, and hence for energy, is the joule, J. The work done is one joule when a force of one newton acts over a distance of one metre:

$$1 \text{ J} = 1 \text{ Nm} = 1 (\text{kg ms}^{-2})\text{m} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

(Newtons and joules are both derived SI units; see Table 1.2 (p.8).)

Think about the bungee jumper in Figure 1 in Box 1.7 (p.43). The height of the platform gives the jumper a large potential energy. When the jumper dives off the platform, the potential energy is converted into kinetic energy. Towards the end of the fall, the cord starts to stretch and slows down the descent. As the cord stretches, the kinetic energy of the jumper is converted into potential energy—this time stored in the stretched out molecules of the cord. Potential energy and kinetic energy are discussed in more detail in Box 1.7.

Thermochemistry

Energy changes are a characteristic feature of chemical reactions. Many chemical reactions give out energy and some take energy in. Usually the energy is in the form of heat or work, but reactions (such as the one in Figure 1.13) can also emit light or sound. In an electrochemical cell, a chemical reaction is arranged so that chemical energy is converted directly to electrical energy; see Section 16.3.

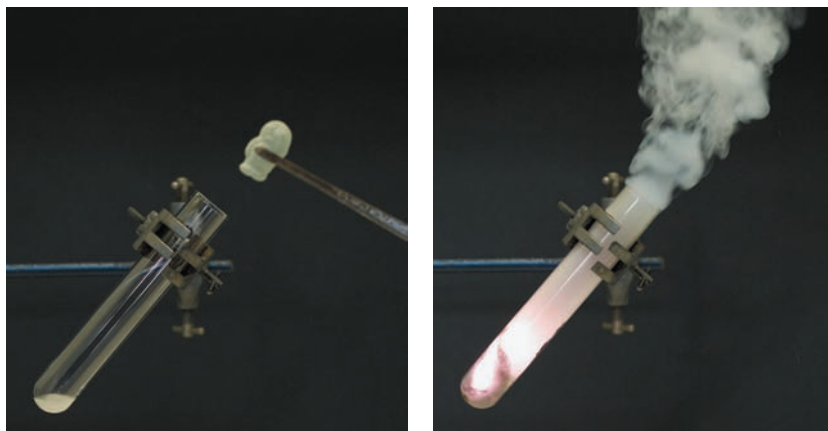


Figure 1.13 The screaming jelly baby. Potassium chlorate is heated strongly until it decomposes and gives off oxygen. When the jelly baby is added, the sugar it contains is oxidized to carbon dioxide and water in a violent reaction. Chemical energy is converted to heat, light, and sound (hence the name of the demonstration), and work is done by the expanding gases pushing against the atmosphere. A similar, but less violent, reaction takes place in your body when you metabolize glucose. Image courtesy of Oxford University Press.



Box 1.7 Potential energy and kinetic energy

The potential energy (E_{PE}) stored in an object can be measured by the energy needed to get it to its current position. This energy is equivalent to the work done in moving the object to its present position. Work is defined as the product of the force (F) and the distance (d) over which it operates, as shown in Equation 1.15

$$\begin{aligned} \text{work} &= \text{force} \times \text{distance} \\ &= F \times d \end{aligned} \quad (1.15)$$

Newton's second law of motion defines force as

$$\begin{aligned} \text{force} (F) &= \text{mass} \times \text{acceleration} \\ &= m \times a \end{aligned}$$

The SI unit of force is the newton. 1 N is the force that gives a mass of 1 kg an acceleration of 1 m s^{-2} .



▲ Figure 1 Transfer of potential energy to kinetic energy during a bungee jump. Image source: Matej Michelizza/iStock.

For the bungee jumper in Figure 1, the force acting is that of gravity—given from Newton's second law by the mass (m) of the person multiplied by the acceleration due to gravity, $g = 9.81 \text{ m s}^{-2}$ so that

$$F = m \times g$$

Combining this with Equation 1.15, the potential energy of a bungee jumper standing on the platform at a height h above the surface of the Earth is given by Equation 1.16.

$$\text{Potential energy} = E_{PE} = mgh \quad (1.16)$$

The kinetic energy (E_{KE}) of an object depends on its mass, m , and the speed, v , at which it is moving.

$$\text{Kinetic energy} = E_{KE} = \frac{1}{2}mv^2 \quad (1.17)$$

Later in this book, you will meet the terms potential energy and kinetic energy applied to atoms and molecules. The potential energy of an atom or molecule is related to its position. The forces acting arise from interactions between atoms in a molecule, or between atoms or ions in a network structure, or between molecules (see Section 17.3). The kinetic energy is related to motion, such as the random motion of molecules in gases (see Section 8.4). In Section 10.5, there is a discussion of the interconversion of kinetic and potential energy during the vibration of a chemical bond.

Now try this

- Calculate the minimum energy needed for a bungee jumper weighing 65.0 kg to climb from the ground to a platform 35.0 m high.
- Calculate the kinetic energy of a nitrogen molecule travelling at 500 m s^{-1} .

» The relationship between heat and work is known as thermodynamics and is discussed in Chapters 13 and 14. Thermodynamics is fundamental to much of chemistry and biochemistry.

A reaction that gives out energy and heats the surroundings (the air, the reaction flask, the car engine, etc.) is described as **exothermic**. The reacting system loses energy; the products end up with less energy than the reactants had—but the surroundings end up with more and get hotter. A reaction that takes in energy and cools the surroundings is **endothermic**. In this case, the reacting system gains energy; the products end up with more energy than the reactants had—but the surroundings end up with less and get cooler.

The heat transferred between the reaction and the surroundings in an open container is the **enthalpy change** for the reaction (see Box 1.8). The enthalpy change for a reaction can be shown on an **enthalpy level diagram** (see Figures 1.14 and 1.15, which show enthalpy level diagrams for an exothermic reaction and for an endothermic reaction, respectively).

There is no way to measure the enthalpy, H , of a substance. All we can do is measure the *change* in enthalpy, ΔH , when a reaction occurs.

$$\text{Change in enthalpy} = \Delta H = H(\text{products}) - H(\text{reactants})$$

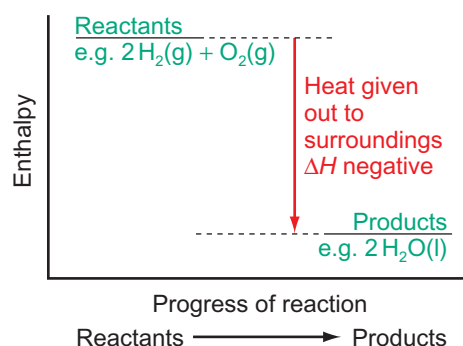


Figure 1.14 Enthalpy level diagram for an exothermic reaction, for example, the reaction of hydrogen and oxygen to form water:
 $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$.

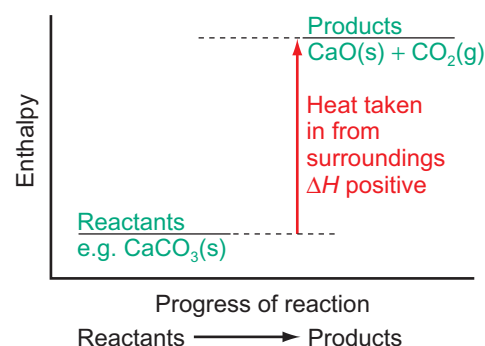


Figure 1.15 Enthalpy level diagram for an endothermic reaction, for example, the decomposition of calcium carbonate:
 $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$.



The Greek symbol Δ

Δ (Delta) is used to mean 'a change in'. For any property or quantity, X ,

$$\begin{aligned}\Delta X &= X(\text{after the change}) \\ &\quad - X(\text{before the change}) \\ &= X_{(\text{final})} - X_{(\text{initial})}\end{aligned}$$

Δ is commonly used in chemistry to represent a change in X during a chemical reaction, so

$$\Delta X = X_{(\text{products})} - X_{(\text{reactants})}$$



Box 1.8 Enthalpy and internal energy

Enthalpy change is the heat transferred between a reaction and the surroundings at *constant pressure*. This applies to many reactions carried out in the laboratory in open containers. If you seal the container, so that the reaction takes place at *constant volume*, the heat transferred is called the **internal energy change**.

If the reaction involves a change in the number of moles of gas present, the internal energy change is different from the enthalpy change.

Suppose, for example, that a gas is given off from an exothermic reaction taking place in an open container. The gas does work pushing back the atmosphere. Some of the chemical energy from the reaction is used to do work—the rest is converted to heat. If the same reaction takes place in a sealed container, no work is done against the atmosphere and all the chemical energy is converted to heat. You can find out more about enthalpy and internal energy in Section 13.5.

For an exothermic change, the value of ΔH is *negative*. This is because, from the point of view of the chemical system, energy is *lost* to the surroundings. Conversely, for an endothermic change, the value of ΔH is *positive*, because the system *gains* energy from the surroundings.

Enthalpy change for a chemical reaction is denoted by the symbol $\Delta_r H$. For common types of reactions, other subscripts may be used, for example, $\Delta_c H$ for the enthalpy change of a combustion reaction (see Section 13.3).

Standard conditions and thermochemical equations

The value of $\Delta_r H$ depends on the temperature and pressure at which the reaction occurs, as well as on the physical state of the components. For example, if water is a reactant or product, the value of $\Delta_r H$ depends on whether the water is liquid or steam.

A set of **standard conditions** (denoted by the superscript $^\ominus$) is defined to allow comparisons between values. Standard conditions are:

- a pressure of 1 bar ($1.00 \times 10^5 \text{ Pa} = 100 \text{ kPa}$);
- the reactants and products in their standard states (pure compound at 1 bar pressure or concentration for a solution of exactly 1.00 mol dm^{-3}).

Values of $\Delta_r H^\ominus$ are quoted at a specific temperature, usually 298 K (25 °C) and *always* have a sign to show whether the reaction is exothermic or endothermic. The units of enthalpy changes are usually kJ mol^{-1} (or sometimes J mol^{-1} for smaller changes).

Using symbols such as these, a great deal of information can be conveyed in a straightforward manner. For example, for the reaction of hydrogen and oxygen, the equation

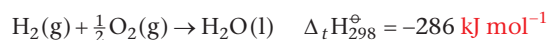


can be translated into words as ‘when 2 mol of hydrogen gas react with 1 mol of oxygen gas to form 2 mol of liquid water at 298 K and 1 bar pressure, 572 kJ of energy are transferred to heat the surroundings’. This type of equation linking an enthalpy change to the molar amounts in a balanced equation is known as a **thermochemical equation**.

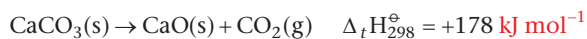
Note that the enthalpy change for the reverse reaction (under the same conditions of temperature and pressure) has the same magnitude but the opposite sign.

$$\Delta_r H(\text{forward reaction}) = -\Delta_r H(\text{backward reaction}) \quad (1.18)$$

Note too that, in this context, the units kJ mol^{-1} mean **kJ per molar amounts as stated in the equation**. If you use 1 mol of hydrogen, rather than 2 mol, then $\frac{1}{2} \times 572 \text{ kJ} = 286 \text{ kJ}$ of energy are transferred. So,



For the thermal decomposition of calcium carbonate in Figure 1.15 (p.44)

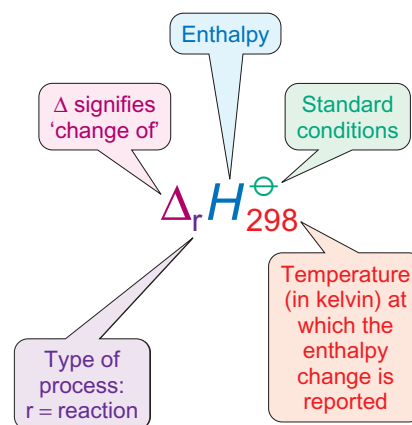


You can practise using a thermochemical equation to calculate the heat transferred in a reaction in Worked example 1.16 and in Box 1.9.

i You should get into the habit of *always* showing the sign when you write a ΔH value, whether it is positive or negative.

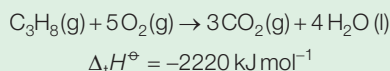
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i The standard enthalpy change of reaction, $\Delta_r H^\ominus$, is the enthalpy change for a reaction at 1 bar and 298 K (25 °C) with all components in their standard states. Values are usually quoted at 298 K (25 °C), $\Delta_r H_{298}^\ominus$



Worked example 1.16 Using thermochemical equations

A portable camp stove burns propane fuel. The thermochemical equation for the combustion of propane is



How much heat energy is supplied when 500 g of propane burn in a plentiful supply of air so that combustion is complete?

Strategy

Use the thermochemical equation to write down the heat energy released when 1 mol of propane burns.

Use Equation 1.2 to work out the amount in moles of propane burned:

$$\text{amount (in mol)} = \frac{\text{mass (in g)}}{\text{molar mass (in g mol}^{-1}\text{)}} \quad (1.2)$$

Find the energy released when this amount of propane burns. →



Solution

From the thermochemical equation, 2220 kJ of energy are supplied when 1 mol propane reacts with oxygen.

$$M_r(\text{C}_3\text{H}_8) = 44.1$$

$$500 \text{ g propane} = \frac{500 \cancel{\text{g}}}{44.1 \cancel{\text{g mol}^{-1}}} = 11.3 \text{ mol}$$

$$\begin{aligned} \text{Heat supplied by burning 500 g propane} &= 2220 \text{ kJ mol}^{-1} \times 11.3 \cancel{\text{mol}} \\ &= 25200 \text{ kJ} \end{aligned}$$

(Note that the answer does not have a sign because the direction of heat transfer is indicated by saying 'heat supplied'. When you quote a value for an *enthalpy change*, $\Delta_r H$, however, you must always include a sign.)

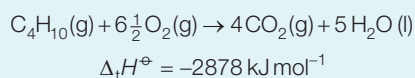
Now try this

When 1 mol of pentane burns in a plentiful supply of air, 3537 kJ of energy are transferred as heat to the surroundings at 298 K. Write a balanced thermochemical equation for the reaction, and use it to work out the enthalpy change when 500 g of pentane are burned.



Box 1.9 Butane hair stylers

In cordless butane hair stylers, heat is generated by the oxidation of butane by air in the presence of a catalyst.



The catalyst is often platinum powder, which is dispersed on an aluminium oxide support. The butane is supplied as a liquid in a small pressurized container. When the container is pierced, the butane gas released passes over the catalyst and oxidizes exothermically. When the hair styler is first switched on, the catalyst is heated by a battery, but the temperature quickly rises as the reaction takes place and no further external heating is needed.

Now try this

- (a) The label on a 'butane' refill for a hair styler states that it contains 14 g of 'isobutane'. The formula of 'isobutane' is C_4H_{10} .
- Assuming the fuel burns completely, according to the thermochemical equation above, calculate the heat energy supplied from 14 g of 'isobutane'.
 - Suggest a structural formula (see Section 1.3) for 'isobutane' and give its systematic IUPAC name.

A cordless hair styler uses liquid butane as the fuel. Image courtesy of Braun. ►

(You can read about structural isomers and naming hydrocarbons in Section 2.5. You will be able to calculate enthalpy changes under temperatures other than 298 K after studying Section 13.4.)

- (b) Butanol is being investigated as a possible biofuel. The enthalpy of combustion of butanol is $-2670 \text{ kJ mol}^{-1}$. Assuming complete combustion, calculate the energy released on combustion of 1 litre of butanol. The density of butanol is 0.81 g cm^{-3} .



Where does the energy come from?

Chemical reactions involve breaking and making chemical bonds. Bonds break in the reactants, the atoms rearrange, and new bonds form in the products. The energy changes in chemical reactions come from the energy changes when bonds are broken and made.

A chemical bond arises from an electrostatic attraction between the electrons and nuclei of the atoms or ions forming the bond. Breaking a bond requires an input of energy to overcome this attraction and separate the atoms or ions. When a bond is formed, energy is released.

- Bond breaking is an endothermic process.
- Bond formation is an exothermic process.

The difference in energy between the bond-breaking and bond-forming processes in a chemical reaction determines whether the overall change is exothermic or endothermic. Thus the reaction of hydrogen with oxygen is exothermic because more energy is released when the new bonds are formed in H_2O than was taken in to break the bonds in H_2 and O_2 (Figure 1.16).

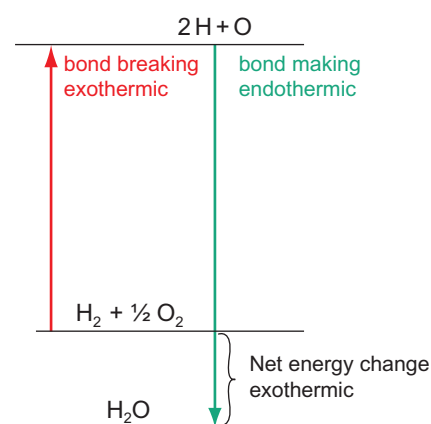



Figure 1.16 Bond breaking and bond making in the reaction of H_2 with O_2 .

Enthalpy profiles for exothermic and endothermic processes

Figure 1.17 shows the **enthalpy profile** for an exothermic reaction. The **progress of reaction** as reactants are converted to products is plotted on the x -axis. Enthalpy is plotted on the y -axis. Figure 1.18 shows the enthalpy profile for an endothermic reaction.

The energy barrier is called the activation enthalpy, sometimes called the activation energy. It arises because energy is needed to start the bond-breaking process. This is why some reactions need heating to get them started. When you use a match to ignite methane or a spark to ignite petrol vapour in a car engine, you are supplying the energy that is needed to break bonds. Once the reaction gets under way, the energy released from making the new bonds supplies energy for further bond breaking. For some reactions with a small energy barrier, there is enough energy in the surroundings at room temperature to get them started and no heating is necessary. Other reactions, such as the endothermic decomposition of calcium carbonate, need continuous heating.

The height of the energy barrier is related to the *rate* of the reaction. It is the energy that molecules must possess before they can react. The greater the proportion of molecules with this energy, the faster the reaction takes place. This is why raising the temperature increases the rate of reaction—it increases the proportion of molecules with enough energy to overcome the energy barrier.

 Visit the online resources to view **Screencast 1.4**, which walks you through drawing an enthalpy level diagram relating bond breaking and bond making.

» Progress of reaction is sometimes called the extent of reaction or the reaction coordinate. See Sections 9.1 and 9.7.

» Rates of reaction (kinetics) are discussed in Chapter 9. Section 9.7 looks at energy barriers and the effect of temperature on the rate of a reaction.

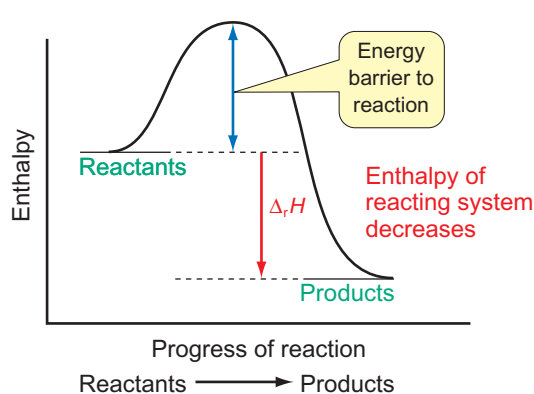


Figure 1.17 Enthalpy profile for an exothermic reaction.

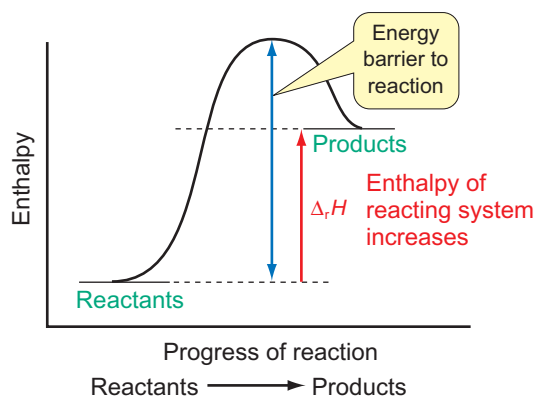


Figure 1.18 Enthalpy profile for an endothermic reaction.



Summary

- An exothermic reaction gives out energy and heats the surroundings; an endothermic reaction takes in energy and cools the surroundings.
- The enthalpy change, ΔH , for a reaction is the heat transferred between the reacting system and the surroundings at *constant pressure*; the value of ΔH is negative for an exothermic reaction and positive for an endothermic reaction.
- The standard enthalpy change of reaction, $\Delta_r H_{298}^\ominus$, is the enthalpy change for a reaction at 1 bar and 298 K (25 °C) with all components in their standard states.
- A thermochemical equation links an enthalpy change to the molar amounts in a balanced equation for the reaction.
- Bond breaking is an endothermic process; bond formation is an exothermic process.

? For a practice question on these topics, see question 18 at the end of this chapter (p.69).

i Fluids

The molecules in a fluid have enough energy to overcome the forces between molecules and move past one another so that the substance flows. A liquid flows under the influence of gravity from one container to another. A gas spreads out to fill the space containing it.

i Gases and vapours

The term 'vapour' is often used for the gaseous state of a substance that is normally a solid or a liquid at room temperature. For example, chemists talk about water vapour and sodium vapour lamps, but oxygen gas and carbon dioxide gas. This definition is refined in Section 8.6.

i Solids and liquids

Structurally, liquids are much closer to solids than to gases. A typical liquid contains only about 3% more empty space than a close-packed solid. Solids and liquids are known as condensed phases.

» The structure and properties of solids are discussed in Chapter 6. The behaviour of gases is covered in Chapter 8, and that of liquids and solutions in Chapter 17.

1.7 States of matter and phase changes

At room temperature and pressure, oxygen is a gas, water is a liquid, and copper is a solid. The different physical states (gas, liquid, and solid) are called **states of matter**.

- A **solid** is a rigid form of matter. It has a shape and occupies a fixed volume (at a particular temperature and pressure).
- A **liquid** is a fluid form of matter. It occupies a fixed volume (at a particular temperature and pressure) but has no fixed shape. It has a well-defined, horizontal surface and, below this surface, it takes up the shape of the container.
- A **gas** is also a fluid form of matter. It spreads out to fill the space containing it and takes up the shape of the container.

Solids and liquids do not expand very much when you heat them, but gases expand a lot. Gases can be compressed by increasing the pressure, whereas liquids and solids cannot easily be compressed except at high pressures.

These *macroscopic* properties of the states of matter can be explained on a *molecular scale* in terms of the arrangement and motion of the molecules. This is called the **kinetic-molecular model** for the structure of matter and is summarized in Figure 1.19. Note that the term 'molecule' is used rather loosely here to mean the basic units making up the matter, which may be molecules, atoms, or ions.

A solid is rigid because the molecules cannot easily move past one another due to strong interactions between them. The molecules do vibrate, though, about fixed average positions. The vibrations become more vigorous as the temperature is raised, until the molecules have enough energy to move from their fixed positions and the solid melts to form a liquid. The molecules in a liquid are still very close together but they are able to move around in a restricted way. There is relatively little 'free space' in a liquid and collisions are very frequent. On further heating, the molecules gain more energy and move around faster. Eventually, they have enough energy to overcome completely the attractions of the other molecules in the liquid and escape from the surface to form a gas. (Remember that, when a molecular solid changes from solid \rightarrow liquid \rightarrow gas, it is only the intermolecular attractions *between* the molecules that are broken, not the covalent bonds *within* the molecules—see Section 1.8.)

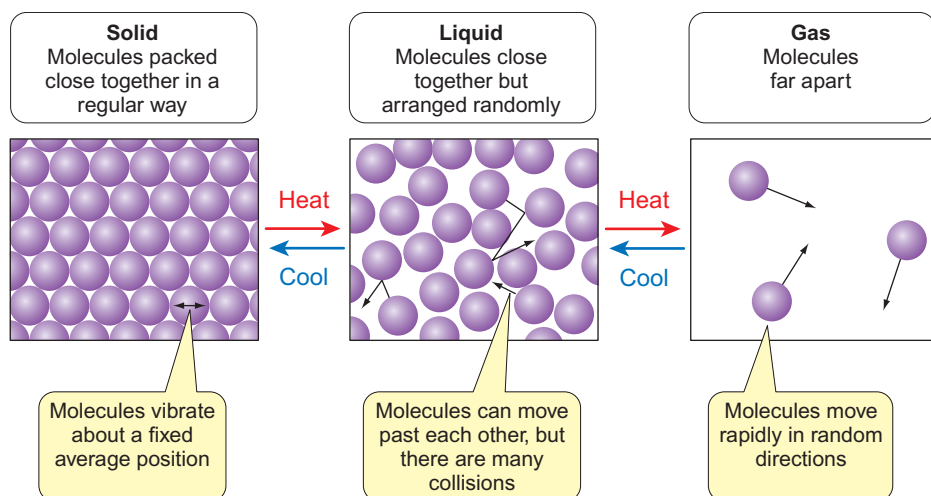


Figure 1.19 Kinetic-molecular model for the structure of matter.

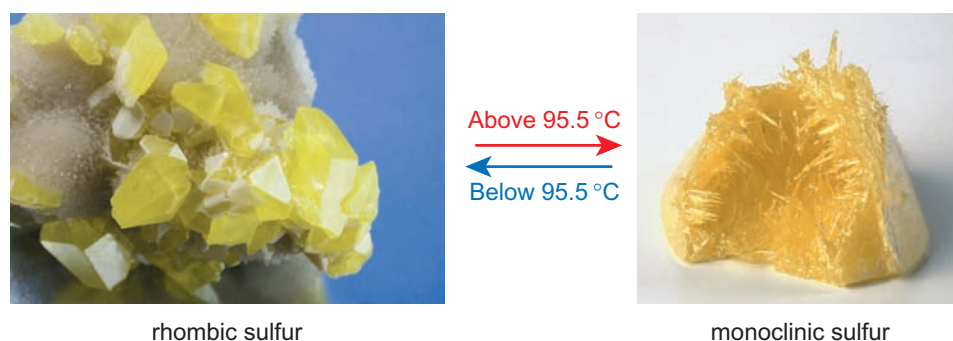


Figure 1.20 The two solid phases (allotropes) of sulfur. The transition temperature is 95.5 °C at atmospheric pressure. Image source: Melissa Carol/Stock and Clive Streeter/Dorling Kindersley.

Phase changes

The three states of matter are different **phases**. A transition from one phase to another is called a **phase change** or **phase transition**. The melting of ice to form liquid water is an example of a phase change. Within the solid state, there may be more than one phase. Sulfur can exist as two different solid phases, rhombic and monoclinic (Figure 1.20). The sulfur molecules are packed differently in the two forms to give different crystal structures. At atmospheric pressure, rhombic sulfur changes into monoclinic sulfur at 95.5 °C. Below this **transition temperature**, rhombic sulfur is the more stable phase. Above the transition temperature, monoclinic sulfur is the more stable phase. In practice, the transition from one solid phase to the other has a high energy barrier (see Section 1.6) and is relatively slow.

In contrast, the transitions between the three states of matter usually take place quickly. At 1 atm pressure, the temperature at which:

- a solid changes into a liquid is called its **normal melting point (m.p. or T_m)**;
- a liquid changes into a gas is called its **normal boiling point (b.p. or T_b)**.

Values for m.p. and b.p. are usually quoted in °C rather than in kelvin; T_m and T_b are *always* quoted in kelvin. Note that ‘normal’ here has a precise scientific sense, meaning 1 atm pressure, and does not simply mean ‘ordinary’.

i A **phase** is a form of matter that is uniform throughout, both in chemical composition and its physical state.

i The $^\ominus$ superscript signifies that these are standard enthalpy changes; see Section 1.6.

i Reverse sublimation is sometimes called solid deposition or vapour deposition.

» The conditions of temperature and pressure under which two phases exist in equilibrium can be plotted on a graph to give a phase diagram. Phase diagrams are discussed in Section 1.7.1. You can find more about enthalpy changes of state in Section 1.3.2.



Figure 1.21 Iodine crystals sublime on heating to give purple iodine vapour. Reverse sublimation takes place when the vapour cools and iodine crystals are deposited around the mouth of the tube. Image source: IDPS, University of Bath.

At pressures other than 1 atm, the temperatures at which these transitions take place are called the **melting temperature** and the **boiling temperature**, respectively.

Melting and freezing

Melting (also known as **fusion**) is an endothermic process. Energy is taken in from the surroundings to overcome intermolecular attractions so that the molecules can move past one another. The enthalpy change for 1 mol of the substance is called the **enthalpy change of fusion**, $\Delta_{\text{fus}}H^\ominus$, and values always have a positive sign. The enthalpy change for the reverse process, **freezing**, is called the **enthalpy change of freezing**, $\Delta_{\text{freezing}}H^\ominus$. This is an exothermic process and values always have a negative sign. Since the enthalpy changes for a process and its reverse process have the same magnitude but opposite signs (Equation 1.18 (p.45)), we can say:

$$\Delta_{\text{fus}}H^\ominus = -\Delta_{\text{freezing}}H^\ominus$$

Vaporization and condensation

Vaporization is an endothermic process taking in energy from the surroundings. Energy is needed to overcome intermolecular attractions in the liquid and so separate the molecules. The enthalpy change for 1 mol of the substance is called the **enthalpy change of vaporization**, $\Delta_{\text{vap}}H^\ominus$, and values always have a positive sign. The enthalpy change for the reverse process, condensation, is called the **enthalpy change of condensation**, $\Delta_{\text{cond}}H^\ominus$, and values always have a negative sign. When a gas condenses to form a liquid, intermolecular attractions are re-formed. So, condensation is an exothermic process and heat is released into the surroundings.

$$\Delta_{\text{vap}}H^\ominus = -\Delta_{\text{cond}}H^\ominus$$

Evaporation and boiling both involve molecules in the liquid overcoming the attraction of neighbouring molecules and escaping into the vapour phase. However, there are differences between the two processes. Evaporation happens only at the surface of the liquid. It can take place at any temperature and is relatively slow. At the same time, molecules in the vapour are colliding with the liquid surface and condensing. After a time, if the liquid is in a sealed container, evaporation and condensation take place at the same rate and the system reaches equilibrium (see Section 1.9). The **vapour pressure** of a liquid is the pressure of the vapour in equilibrium with the liquid at a particular temperature.

A liquid boils when its vapour pressure is equal to the external pressure above the liquid. Boiling is a much more rapid process than evaporation and takes place at a fixed temperature (for a given pressure). Bubbles of gas form in the body of the liquid and molecules escape from inside the liquid as well as from the surface.

Sublimation and reverse sublimation

When crystals of iodine are heated *gently*, purple iodine vapour is given off from the solid (Figure 1.21). No liquid iodine is formed. As the vapour reaches the cooler part of the tube, solid iodine is deposited. The conversion of a solid directly to vapour is called **sublimation**. The enthalpy change for 1 mol of the substance is called the **enthalpy change of sublimation**, $\Delta_{\text{sub}}H^\ominus$, and values always have a positive sign. The reverse process is known as reverse sublimation and the enthalpy change is called the **enthalpy change of reverse sublimation**, $\Delta_{\text{reverse sub}}H^\ominus$, and values always have a negative sign.

$$\Delta_{\text{sub}}H^\ominus = -\Delta_{\text{reverse sub}}H^\ominus$$

Figure 1.22 shows the transitions between the three states of matter and the **enthalpy changes of state** involved. The phase changes of water and the enthalpy changes involved are discussed in Box 1.10.

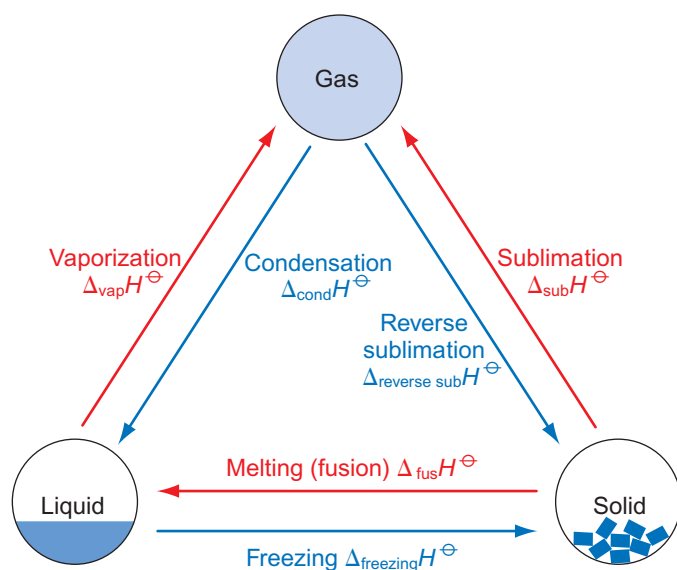


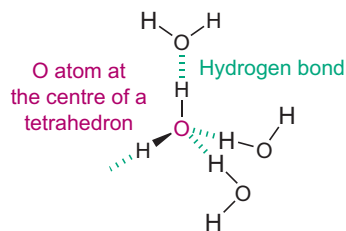
Figure 1.22 Transitions between the three states of matter and the enthalpy changes involved. (Red arrows represent endothermic phase changes and blue arrows exothermic phase changes.)



Box 1.10 Phase changes of water

The phase changes in the water cycle are central to life on Earth. They have a controlling influence on the climate—the formation of dew, rain, snow, and frost and the evaporation of water from rivers and the oceans are all phase changes of water. The enthalpy changes of state accompanying these changes affect the temperature of the atmosphere and the surface of the Earth and, together with ocean currents, are responsible for moving huge quantities of energy around the planet. The Gulf Stream, for example, carries warm water from the Caribbean north-eastwards and warms the seas to the west of Great Britain and Ireland.

The phase changes are accompanied by changes in the structure of water. In ice, each water molecule forms hydrogen bonds to four other water molecules (Figure 1). (Hydrogen bonds are discussed in Section 1.8.)



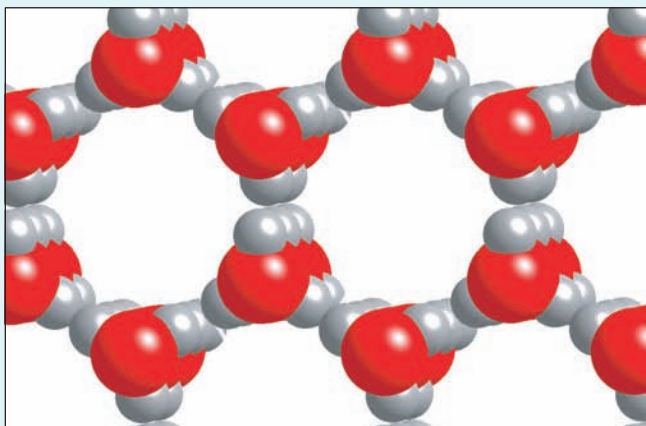
▲ **Figure 1** Hydrogen bonding in ice.

The result is the open, regular structure shown in Figure 2(a). For ice to melt, the molecules must have enough energy to overcome the attraction of the hydrogen bonds and break away from their neighbours. Hydrogen bonding is still present in liquid water (Figure 2(b)) but it is more transient—the molecules in liquid water are tumbling past each other and hydrogen bonds are constantly forming and breaking. At 0 °C, the molecules are closer together in liquid water than in ice, so the water is denser than the ice—and ice floats on water.

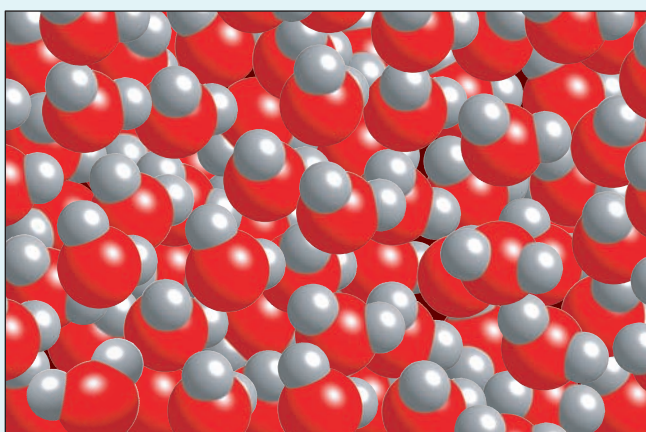
Figure 2(c) shows molecules escaping from the surface of liquid water to form water vapour. The enthalpy change of vaporization of water is very high (compared to the values for molecules with a similar molar mass, such as methane (CH₄) and ammonia (NH₃)). You appreciate this when you sweat in hot weather. Evaporation of sweat produces a cooling effect on your skin. Conversely, condensation of water is an exothermic process. Steam scalds badly because the energy released as it condenses to water is passed to your skin. Figure 3 shows an enthalpy level diagram for the phase changes of water.

The formation of frost directly from water vapour in the air is reverse sublimation (Figure 4). When the frost vanishes as vapour without first melting, it is by sublimation.

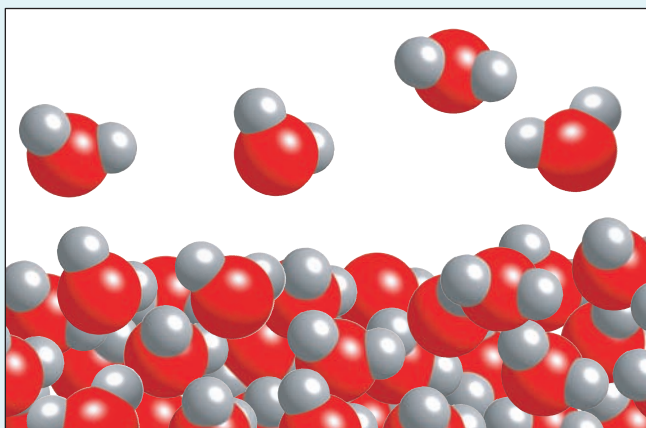




(a) The open structure of ice

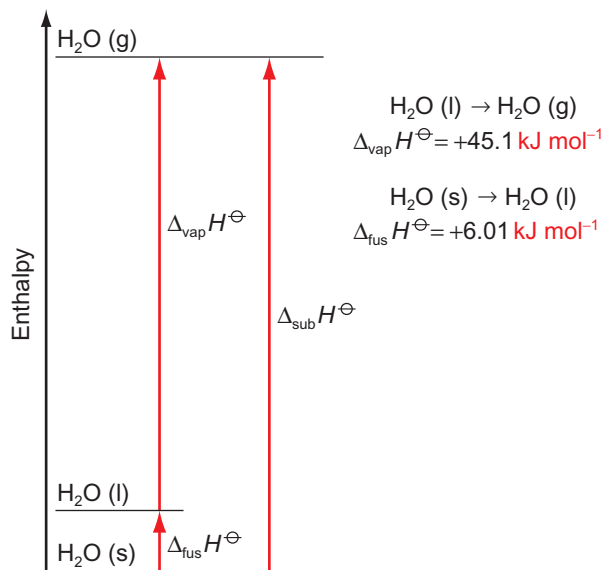


(b) The denser structure of liquid water



(c) Evaporation from the surface of liquid water

▲ **Figure 2** Molecular models showing the structure of the three phases of water.



▲ **Figure 3** Enthalpy level diagram for the phase changes of water. (The values have been adjusted to 0 °C so only enthalpy changes associated with phase changes are involved.)



▲ **Figure 4** Light, feathery hoar frost forms by reverse sublimation of water vapour from cold, relatively dry air. Frost formed from the freezing of dew (liquid water) is denser and more icy. Image source: Digital Vision.

Now try this

- In warm countries, water can be kept cool by storing it in unglazed earthenware pots. Explain the process involved.
- Suggest why wet clothes dry on a washing line but not in a plastic bag.
- Using the data in Figure 3, write down values at 0 °C for:
 - $\Delta_{\text{sub}}H^\ominus(\text{H}_2\text{O})$; (ii) $\Delta_{\text{cond}}H^\ominus(\text{H}_2\text{O})$; (iii) $\Delta_{\text{freezing}}H^\ominus(\text{H}_2\text{O})$.
- Suggest why the value of $\Delta_{\text{vap}}H^\ominus(\text{H}_2\text{O})$ is very much more endothermic than the value of $\Delta_{\text{fus}}H^\ominus(\text{H}_2\text{O})$.



Summary

- There are three common states of matter: solid; liquid; and gas.
- The three states of matter are phases. Within the solid state, there may be more than one phase.
- The kinetic–molecular model for the structure of matter explains macroscopic properties in terms of the arrangement and motion of the molecules.
- Transitions between states of matter are called phase changes.
- The enthalpy changes accompanying phase changes are called enthalpy changes of state. Values refer to 1 mol of the substance.
- Melting (fusion), vaporization, and sublimation all involve the breaking of intermolecular attractions and are endothermic processes. The reverse processes—freezing, condensation, and reverse sublimation, respectively—involve the formation of intermolecular interactions and are exothermic processes.
- $\Delta_{\text{fus}}H^\ominus = -\Delta_{\text{freezing}}H^\ominus$
 $\Delta_{\text{vap}}H^\ominus = -\Delta_{\text{cond}}H^\ominus$
 $\Delta_{\text{sub}}H^\ominus = -\Delta_{\text{reverse sub}}H^\ominus$

? For a practice question on Sections 1.7 and 1.8, see question 19 at the end of this chapter (p.69).

1.8 Non-covalent interactions

When a molecular substance changes from solid \rightarrow liquid \rightarrow gas, the transitions require an input of energy to overcome attractions between the molecules. The molecules in a gas are far apart and move independently of one another but, even here, there are some attractive forces between the molecules. **Intermolecular interactions** (sometimes called intermolecular forces) are very much weaker than the covalent bonds holding the atoms together within the molecule (Figure 1.23). They do not involve the sharing of electron pairs and are sometimes called **non-covalent interactions**.

There are different types of non-covalent interactions depending on the molecules involved. The strength of the interactions affects the enthalpy changes of fusion and vaporization (and hence the melting and boiling temperatures) of the substance (see Section 1.7). Table 1.10 summarizes the various types of non-covalent interactions. It includes interactions between ions and molecules and between ionic groups in molecules.

The attraction between molecules is always the result of an electrostatic attraction between opposite charges. One type of interaction occurs between *all* molecules, including the atoms in monatomic gases, such as helium, neon, and argon. These interactions are called **London dispersion interactions** (or sometimes just **London interactions** or **dispersion interactions**). They arise because, at a particular instant, the electrons in a molecule are unevenly distributed. The molecule has an instantaneous dipole, which then induces a dipole in an adjacent molecule. (A longer, but more descriptive, name for these interactions is **instantaneous dipole-induced dipole interactions**.) Figure 1.24 shows how these interactions arise between two isolated neon atoms—but you can draw similar diagrams for any pair of atoms or molecules.

When a molecule has a permanent dipole, adjacent molecules align themselves to maximize the attractions between positive and negative charges. Such **dipole–dipole interactions** are more marked in the solid state where molecules have fixed positions (Figure 1.25) but are also present in liquids and gases. In addition, there will be London dispersion forces between the molecules. The total attraction between two molecules is the sum of the different types of attractions possible.



Non-covalent interactions

This term is normally used to include all attractions other than covalent, ionic, and metallic bonding. When the attraction is between two molecules, it is called an **intermolecular interaction**.



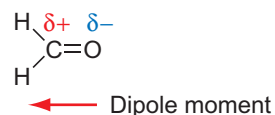
Previously, you may have used the term **van der Waals interactions** (or **van der Waals forces**) to describe London dispersion interactions. You may also see this term in some textbooks. However, the van der Waals term is sometimes used to include all the different types of interactions and is best avoided; see Sections 8.6 and 17.3.

i Polar molecules and molecular dipoles

A polar molecule is one that has a permanent separation of charge and, hence, a dipole moment. For example, the molecule HCl has a dipole moment because the Cl atom is more electronegative than the H atom and the covalent bond is polarized.



Similarly, the C=O bond in methanal, HCHO, is polarized and the methanal molecule has a dipole moment.



» Electronegativity is discussed in Section 4.3. There is more about polar molecules and molecular dipoles in Section 5.3. Polarization in organic molecules is discussed in Section 1.9.1.

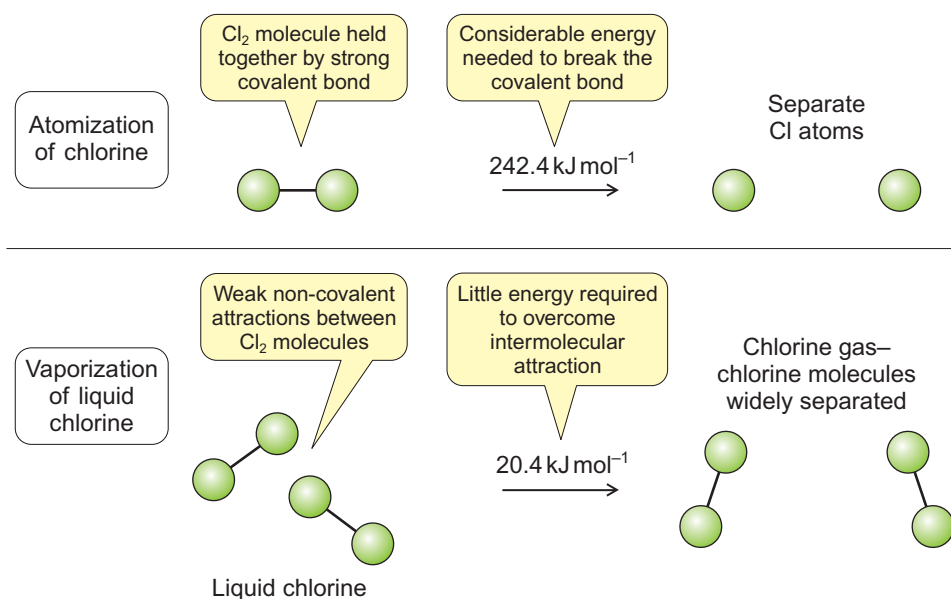


Figure 1.23 Covalent bonds within a molecule are much stronger than the attractions between molecules.

Table 1.10 Types of non-covalent interactions. For comparison, the energies of covalent bonds lie in the range 150 kJ mol^{-1} to 1000 kJ mol^{-1} .

Interaction	Acts between	For example	Typical energy/ kJ mol^{-1}
London dispersion	All types of molecules	Ne, H ₂ , CH ₄ , Cl ₂ , HCl	~ 5
Dipole-dipole	Polar molecules	HCl	2
Dipole-induced dipole	A polar molecule and a molecule that may or may not be polar	Between HCl and Cl ₂ or between HCl and CH ₄	< 2
Ion-dipole	An ion and a polar molecule	A metal ion dissolved in water	15
Hydrogen bond	A molecule containing the electronegative atoms O, N, or F bound to H and a molecule containing O, N, or F. The H atom forms a link between the two electronegative atoms	H ₂ O, NH ₃ , HF	10–40*
Ion-ion	Ionic groups	Between -NH_3^+ and -CO_2^- groups in proteins	250

* The hydrogen bond in the ion $[\text{HF}_2]^-$ is particularly strong, 165 kJ mol^{-1} ; see Section 25.3.

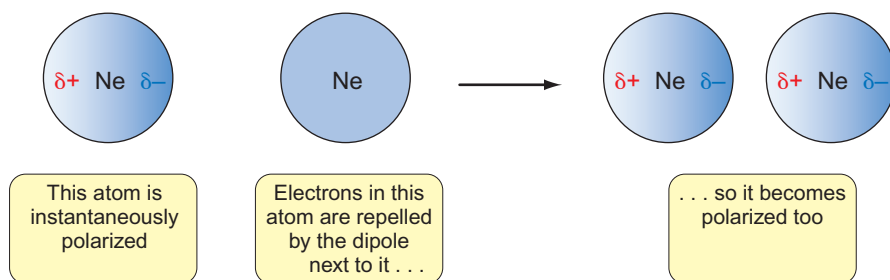


Figure 1.24 London dispersion interactions between neon atoms.

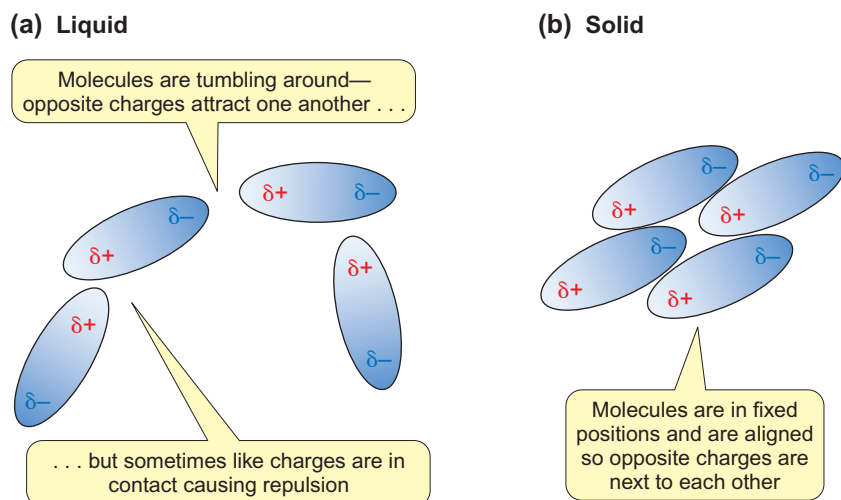


Figure 1.25 Dipole-dipole interactions between polar molecules in (a) the liquid state and (b) the solid state.

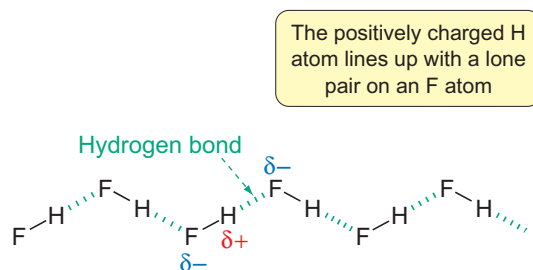


Figure 1.26 Hydrogen bonding in HF.

A molecule with a permanent dipole, such as HCl, can *induce* a dipole in an adjacent non-polar molecule. The positive end of the permanent dipole attracts electrons in the non-polar molecule, making it temporarily polar. The result is called a **dipole-induced dipole interaction**. This type of interaction is important in mixtures of molecules (e.g. between HCl and Cl₂ molecules).

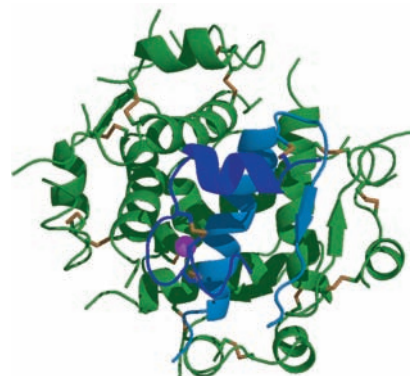
Hydrogen bonding is an extreme form of dipole-dipole interaction. A hydrogen atom attached to an electronegative atom, O, N, or F, is attracted to an electronegative atom on an adjacent molecule. The hydrogen atom carries a partial positive charge and forms a link between the two electronegative atoms. Figure 1.26 shows hydrogen bonding in solid HF.

Non-covalent interactions can occur between different parts of the same molecule, in which case they are called **intramolecular** interactions. Intramolecular interactions are very important in large biochemical molecules. Intramolecular hydrogen bonding, for example, causes a protein chain to fold into either a helical or a sheet structure. Other non-covalent interactions, including attractions between ionic groups, are then responsible for further folding to give the biochemically active shape. Extensive hydrogen bonding is one of the reasons why the polymer Kevlar® is so strong (see Box 1.11).

Ion-dipole interactions are responsible for the hydration of ions in water (Figure 1.27). The attachment of water molecules to a central ion is known as **hydration**. The interactions are particularly strong for small ions with high charges, such as Al³⁺ ions, which are strongly hydrated in water. Other polar solvents behave in a similar way. The general process is called **solvation**.

i **Hydrogen bonding** is discussed in more detail in Section 25.3 where the definition is broadened to include examples of hydrogen bonding involving atoms other than O, N, and F.

i **Intra** means within a single molecule; **inter** means between separate molecules.

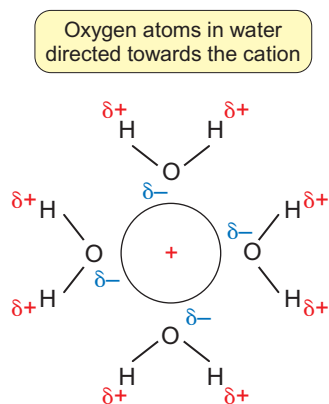


Ribbon structure of the monomer of the protein, insulin. Non-covalent interactions cause protein chains to fold into the biochemically active shape. Image courtesy of Chen Ho at Pittsburgh Supercomputing Centre.

» You can find more about intermolecular interactions in Sections 8.6 (gases), 17.3 (liquids and solutions), and 6.1 (solids). Hydrogen bonding is discussed in detail in Section 25.3. Hydrogen bonding governs the structure and reactions of many organic compounds, for example, see Section 23.3.

» The hydration of ions affects the behaviour of ions in aqueous solution, for example; see Section 16.2. Solvation effects in organic chemistry are discussed in Chapter 19. Energy changes on solvation are described in Section 17.4. The hydration of Group 1 ions is discussed in Section 26.3.

(a) Hydration of a cation



(b) Hydration of an anion

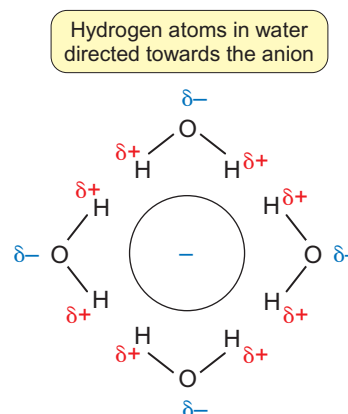
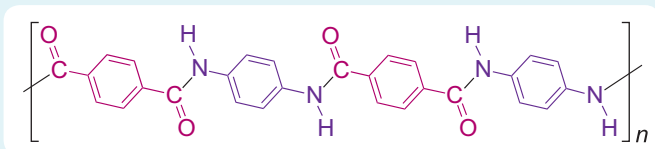


Figure 1.27 Hydration of ions in water. (a) A cation is surrounded by water molecules with their oxygen atoms directed towards the ion. (b) An anion is surrounded by water molecules with hydrogen atoms directed toward the ion. (Both hydrogen atoms in each water molecule will not always be directed towards the ion.)



Box 1.11 Why is Kevlar® so strong?

The polymer Kevlar® was first made in 1965 by Stephanie Kwolek while working in the DuPont Laboratories in the USA. Since then uses for the polymer have multiplied and it is now used in a wide variety of applications ranging from bulletproof vests to tennis racquets and other sporting equipment.



▲ Kevlar®

The polymer is lightweight, flexible, and resistant to heat, fire, and chemicals. Ropes and cables made from Kevlar® are five times stronger than steel on an equal weight basis, so small diameter ropes can be used to moor large ships. The secret of Kevlar®'s remarkable properties lies in its highly ordered, crystalline structure.

There are three main reasons for the strength of Kevlar®. First, the benzene rings, linked by amide groups, give each polymer chain a rigidity due to limited bond rotation. Second, strong hydrogen bonding *between* the chains fixes them into position and prevents individual chains from slipping past one another. Finally, when Kevlar® is spun into fibres, the polymer chains orientate themselves along the fibre axis with hydrogen bonds linking adjacent chains. The flat sheets of linked



▲ The combination of light weight and strength in Kevlar® means that it is used for sporting equipment and protective wear for the police and the armed forces. Image source: simonkr/iStock.

chains are stacked along the radii giving a highly ordered, crystalline structure (Figure 1). The polymer is processed in the liquid crystal phase (see Box 17.1, p.773)—the result is an extremely strong fibre.

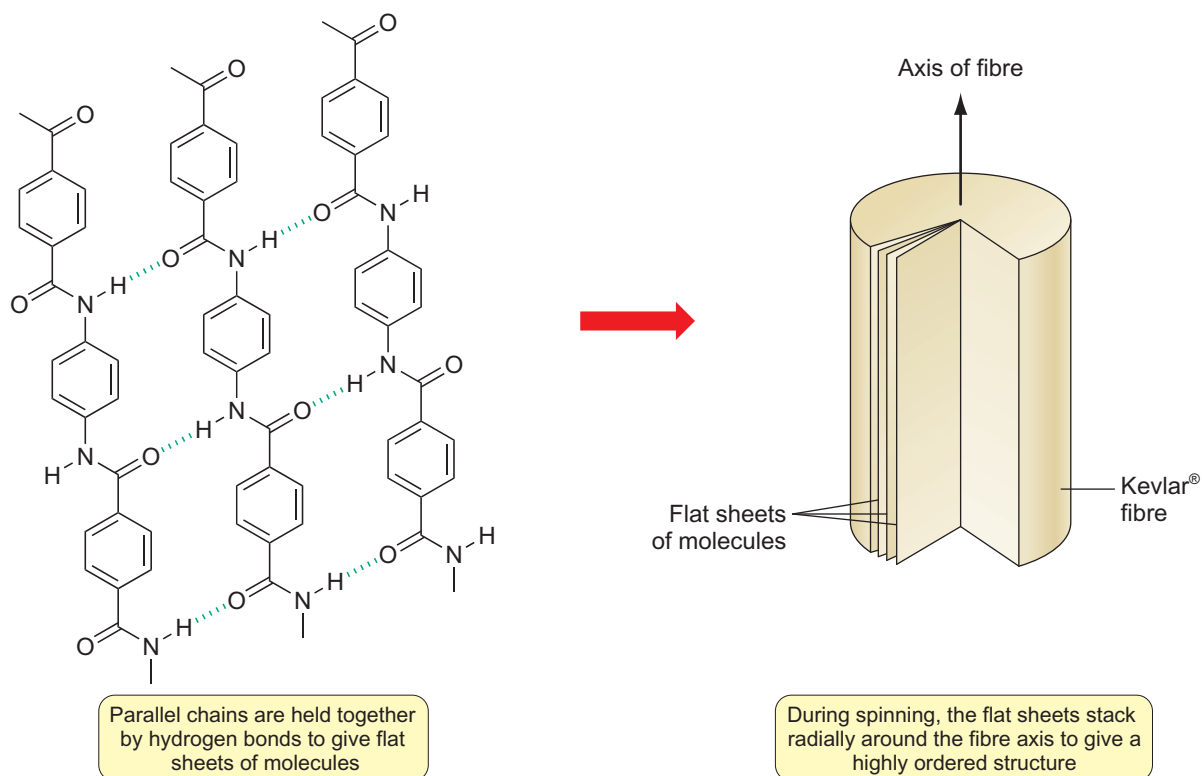
.....
Now try this

In terms of intermolecular attractions, suggest why it is possible to make strong ropes out of Kevlar® or nylon, but not from polythene (poly(ethene)).





▼ **Figure 1** The crystalline structure of Kevlar®



Summary

- Non-covalent interactions include interactions between molecules, between ions and molecules, and between ionic groups within molecules.
- London dispersion interactions are present in all molecules and in monatomic gases. They arise from the electrostatic attraction between an instantaneous dipole in a molecule and an induced dipole in an adjacent molecule.
- Other types of interactions include:
 - dipole–dipole interactions;
 - dipole–induced dipole interactions;
 - ion–dipole interactions;
 - hydrogen bonds;
 - ion–ion interactions.
- These types of interactions are summarized in Table 1.10 (p.54).



For a practice question on Sections 1.7 and 1.8, see question 19 at the end of this chapter (p.69).



A dynamic equilibrium is established between carbon dioxide and water in a stoppered bottle of sparkling water or fizzy drink. Image courtesy of Nestlé Waters.

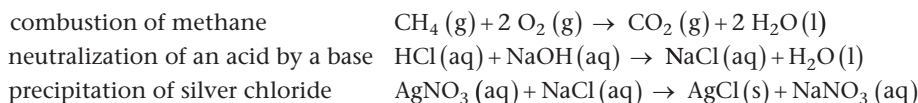
i Dynamic equilibrium

The amounts of reactants and products at equilibrium are constant because the forward reaction is taking place at the same rate as the reverse reaction.

1.9 Chemical equilibrium: how far has a reaction gone?

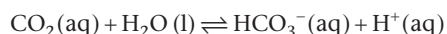
Dynamic equilibrium

Some reactions *go to completion* and are represented by a single arrow in the chemical equation. This tells you that virtually all the reactants are converted into products. For example,



Many other reactions do not go to completion in this way, but instead reach a **state of equilibrium** in which both reactants and products are present. This is a state of balance in which no further net change in the amounts of reactants and products takes place.

For example, when carbon dioxide gas dissolves in water, some of the dissolved gas reacts with the water to form hydrogencarbonate ions (HCO_3^- (aq)) and hydrogen ions (H^+ (aq)). The reaction comes to equilibrium when just a small proportion of the CO_2 (aq) has reacted. The equilibrium mixture contains all four species in solution.



On a *molecular scale*, CO_2 molecules are still reacting with H_2O molecules to form HCO_3^- ions and H^+ ions. At the same time, HCO_3^- ions and H^+ ions are constantly reacting together to reform CO_2 and H_2O molecules. At equilibrium, the rates of the forward and backward reactions are equal, so that, on the *macroscopic scale*, nothing *seems* to happen. This is why chemical equilibrium is called **dynamic equilibrium**. It is represented by the symbol \rightleftharpoons in the chemical equation.

Position of equilibrium

There are many equilibrium mixtures possible for a given reaction system, depending on the concentrations of the substances mixed at the start and the reaction conditions, such as temperature and pressure. Chemists often talk about the **position of equilibrium**. This means one particular set of equilibrium concentrations for the reaction. If the conditions, or one of the concentrations, are changed, the system is no longer in equilibrium and the concentrations of reactants and products change until a new position of equilibrium is reached. If this change results in the formation of more products, you say that the position of equilibrium *moves to the right* (meaning towards the products on the right-hand side of the equation). Conversely, if the change results in the formation of more reactants, you say that the position of equilibrium *moves to the left* (meaning towards the left-hand side of the equation).

The position of equilibrium can be altered by changing the:

- concentrations of reacting substances (in solution);
- pressures of reacting gases;
- temperature.

Henri Le Chatelier studied data from many equilibrium reactions and, in 1888, proposed a series of rules enabling him to make qualitative predictions about the effects of changes on an equilibrium. The rules are summarized in **Le Chatelier's principle** which states that:

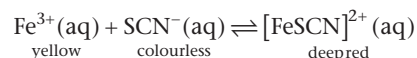
when an external change is made to a system in dynamic equilibrium, the system responds to minimize the effect of the change.

» Le Chatelier's principle is a useful way of *remembering* how an equilibrium system responds to external changes, but it does not *explain* these changes. For explanations of the way equilibrium position changes, see Section 15.5.

Applying Le Chatelier's principle

Changing the concentration

Yellow iron(III) ions ($\text{Fe}^{3+}(\text{aq})$) react with colourless thiocyanate ions ($\text{SCN}^{-}(\text{aq})$) to form deep red $[\text{Fe}(\text{SCN})]^{2+}(\text{aq})$ ions. The reaction is reversible and an equilibrium is set up



The intensity of the red colour of the solution is a good indication of the concentration of $[\text{Fe}(\text{SCN})]^{2+}(\text{aq})$ in the mixture. If the concentration of either $\text{Fe}^{3+}(\text{aq})$ or $\text{SCN}^{-}(\text{aq})$ is increased, the solution goes a darker red, showing the position of equilibrium has moved to the right. This is in accordance with Le Chatelier's principle because moving to the right reduces the concentrations of the reactants and minimizes the effect of the imposed change. The concentration of $\text{Fe}^{3+}(\text{aq})$ can be reduced by adding ammonium chloride, as chloride ions react with $\text{Fe}^{3+}(\text{aq})$ to form $[\text{FeCl}_4]^{-}(\text{aq})$ ions. If you do this, the red colour of the solution becomes paler, indicating that the position of equilibrium has moved to the left.

Preparative chemistry is all about turning reactants into products, and chemists usually want to shift the position of equilibrium as far to the right as possible when dealing with reversible reactions. One way to do this is to remove one of the products from the reaction vessel, so that the reaction is constantly being shifted towards the product side. This is simple if one of the products is a gas. For example, when limestone is heated in an open container and the carbon dioxide is allowed to escape, the reaction goes to completion. If the reaction is carried out in a sealed container, however, the system comes to equilibrium.

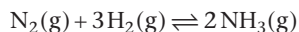


In Box 1.12, the effects of changes in concentration on a series of related equilibria are discussed.

Changing the pressure

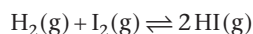
Many important industrial processes involve reversible reactions that take place in the gas phase. Increasing the pressure at which the reaction is carried out moves the position of equilibrium towards the side of the equation with fewer gas molecules, as this reduces the pressure and minimizes the effect of the imposed change.

For example, ammonia is made industrially from nitrogen and hydrogen by the Haber process.



There are 4 molecules of gaseous reactants on the left-hand side of the equation, but only 2 molecules of gaseous product on the right-hand side. So, an increase in pressure causes the position of equilibrium to shift towards the right and increases the yield of ammonia. For this reason, the Haber process is carried out at high pressure, between 25 atm and 150 atm.

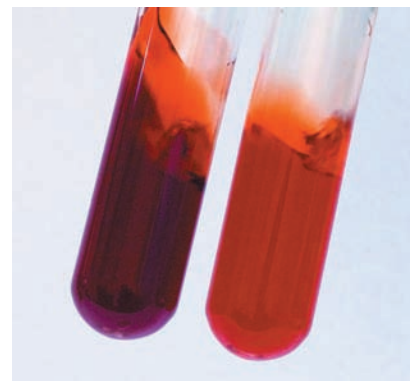
Note that pressure only has an effect on the position of equilibrium when there is a change in the number of gaseous molecules during the reaction. For a reaction such as



where there is the same number of gaseous molecules on each side of the equation, a change of pressure does not affect the position of equilibrium.

Changing the temperature

The enthalpy changes for a reaction and its reverse reaction have the same magnitude but opposite signs (Equation 1.18, p.45). If the temperature is increased, the position of equilibrium moves in the direction of the endothermic change because this lowers the temperature and minimizes the effect of the imposed change.



A solution containing $[\text{Fe}(\text{SCN})]^{2+}(\text{aq})$ is a deep red colour (tube on left). On addition of NH_4Cl , the solution becomes paler (tube on the right).

i The **Haber process** is sometimes referred to as the Haber-Bosch process. The synthetic method was developed by Fritz Haber in 1909. The process was then scaled up by Carl Bosch, a chemical engineer employed by BASF near Mannheim in Germany. The first industrial plant went into production in 1913.

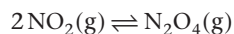
i By convention, when a ΔH value is quoted alongside the equation for a reversible reaction, the value given refers to the forward reaction, that is, left to right as written.

1

Visit the online resources to view Video 1.1, which illustrates the effect of temperature on the $\text{NO}_2/\text{N}_2\text{O}_4$ equilibrium.

Visit the online resources to view Video 1.2, which uses Le Chatelier's principle to explain how the $\text{NO}_2/\text{N}_2\text{O}_4$ equilibrium responds to changes of pressure.

For example, the dark brown gas, nitrogen dioxide (NO_2), is in equilibrium with its colourless dimer, dinitrogen tetroxide (N_2O_4). (See Chapter 15 for photographs of this reaction.) The forward reaction is exothermic.



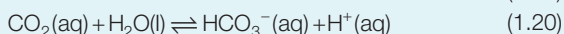
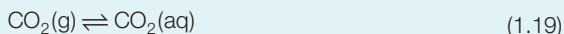
If a sealed glass container of the brown equilibrium mixture is placed in boiling water, the brown colour deepens, because the position of equilibrium moves in the direction of the endothermic change towards the reactant. When the container is cooled in ice, the gas mixture turns almost colourless as the position of equilibrium moves in the direction of the exothermic change towards the product.



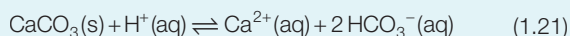
Box 1.12 Connecting equilibria and cave chemistry

In many systems, particularly naturally occurring systems, two or more equilibria are linked together, so that the product of the first equilibrium is the reactant in the next, and so on. You can use Le Chatelier's principle to predict the effect of changing the concentration of a substance, in one equilibrium reaction, on concentrations in the other linked equilibria.

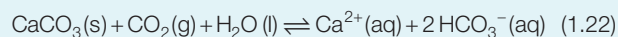
When carbon dioxide in the air comes into contact with water, the equilibria in Equations 1.19 and 1.20 are established.



As a result, rainwater is slightly acidic. As rainwater slowly percolates through limestone rocks, a third equilibrium (Equation 1.21) becomes involved.



Combining these three equilibria, the overall reaction is



The reversible reaction in Equation 1.22 is responsible for the spectacular caves and potholes found in limestone country. The direction in which the reaction proceeds depends on the conditions. The concentration of carbon dioxide in the air in contact with the water seeping through the limestone rocks is 10–40 times higher than the normal atmospheric concentration. This is because water percolating through the ground dissolves carbon dioxide from decomposing organic matter. The calcium carbonate in the rocks dissolves — creating fissures and caves.



▲ Stalactites and stalagmites in an underground cave. Image source: Ken Rygh Creative Art & Design/iStock.





The temperature inside the caves is approximately the same as in the limestone rocks, but the concentration of carbon dioxide is now similar to that in the atmosphere. When the percolating water drips from the roof of a cave, carbon dioxide escapes from solution into the surrounding air and solid calcium carbonate precipitates out from the solution. Stalactites made from the precipitated calcium carbonate slowly grow down from the ceiling. Similarly, stalagmites grow up from the cave floor at the point where the drops land.

Now try this

- Use Le Chatelier's principle and Equation 1.22 to explain both the formation of caves and the presence of stalactites and stalagmites in limestone areas.
- The concentration of carbon dioxide in the atmosphere is currently increasing from year to year. What effect does this increase in carbon dioxide concentration have on the acidity of rainwater?

Equilibrium constant K_c

When a reaction reaches equilibrium, the concentrations of reactants and products are related. For the reaction of hydrogen and iodine to produce hydrogen iodide

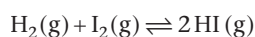


Table 1.11 shows the equilibrium concentrations of $\text{H}_2(\text{g})$, $\text{I}_2(\text{g})$, and $\text{HI}(\text{g})$ for different initial reaction mixtures at 730 K. In the first three experiments, mixtures of hydrogen and iodine were placed in sealed reaction vessels and allowed to come to equilibrium. In the final two experiments, hydrogen iodide alone was sealed in the reaction vessel.

The experiments show that, for this reaction, at 730 K, the ratio

$$\frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})] \times [\text{I}_2(\text{g})]}$$



The multiplication sign between the square brackets is often omitted.

is constant at about 46.7. The constant is called the **equilibrium constant, K_c** .

Table 1.11 Initial and equilibrium concentrations for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

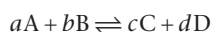
Experiment	Initial concentration/mol dm ⁻³			Equilibrium concentration/mol dm ⁻³			K_c
	$[\text{H}_2(\text{g})]$	$[\text{I}_2(\text{g})]$	$[\text{HI}(\text{g})]$	$[\text{H}_2(\text{g})]$	$[\text{I}_2(\text{g})]$	$[\text{HI}(\text{g})]$	
1	2.40×10^{-2}	1.38×10^{-2}	0	1.14×10^{-2}	$0.1-2 \times 10^{-2}$	2.52×10^{-2}	46.4
2	2.44×10^{-2}	1.98×10^{-2}	0	0.77×10^{-2}	0.31×10^{-2}	3.34×10^{-2}	46.7
3	2.46×10^{-2}	1.76×10^{-2}	0	0.92×10^{-2}	0.22×10^{-2}	3.08×10^{-2}	46.9
4	0	0	3.04×10^{-2}	0.345×10^{-2}	0.345×10^{-2}	2.35×10^{-2}	46.9
5	0	0	7.58×10^{-2}	0.86×10^{-2}	0.86×10^{-2}	5.86×10^{-2}	46.4

Values of K_c are constant for a particular temperature, so you should always state the temperature when you quote an equilibrium constant.

$$K_c = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})] \times [\text{I}_2(\text{g})]} = 46.7 \text{ at } 730 \text{ K}$$

Under the same conditions, the same position of equilibrium is reached whether the equilibrium is approached from the reactants or from the products. In fact, once a system is at equilibrium, it is impossible to tell whether the equilibrium was arrived at by starting with the reactants or with the products. Figure 1.28 shows how the concentrations of reactants and products change as the reaction approaches equilibrium.

For the general reaction



The **square brackets** in the expression for the equilibrium constant mean the concentration in mol dm⁻³. Do not confuse these with the square brackets used for complex ions, such as $[\text{FeCl}_4]^-$. **Equilibrium concentrations** (the concentrations when the reaction has reached equilibrium) are sometimes indicated by a subscript 'eqm' after the square brackets $[\]_{\text{eqm}}$, though this can become quite cumbersome and the subscripts are often omitted.

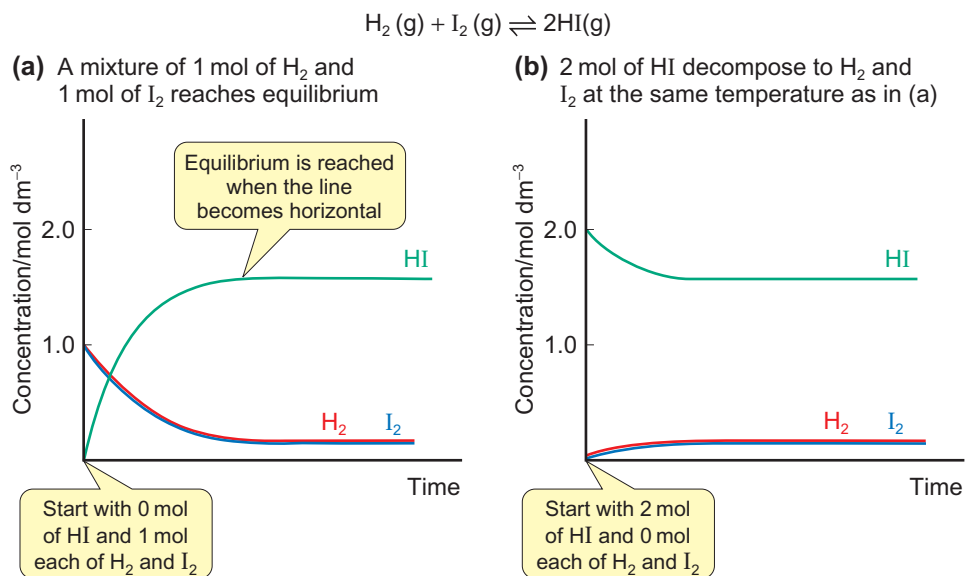


Figure 1.28 Equilibrium is reached in a sealed vessel from either (a) a mixture of hydrogen and iodine, or from (b) pure hydrogen iodide.

the equilibrium constant, K_c , for the reaction is given by the expression:

Equilibrium constant in terms of concentrations

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \quad (1.23)$$

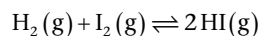
Concentrations of products raised to powers of the coefficients in the equation

Concentrations of reactants raised to powers of the coefficients in the equation

Units of K_c

The units of K_c vary depending on the reaction.

Example 1

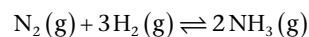


$$K_c = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}$$

$$\text{Units of } K_c \text{ are given by } \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})}$$

So, for this reaction, K_c has **no units**, since the units on the top and bottom of the expression cancel out.

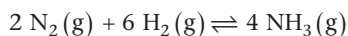
Example 2



$$K_c = \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3}$$

$$\text{Units of } K_c \text{ are given by } \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})^3} = \text{mol}^{-2} \text{ dm}^6$$

Example 3



$$K_c = \frac{[\text{NH}_3(\text{g})]^4}{[\text{N}_2(\text{g})]^2[\text{H}_2(\text{g})]^6}$$

$$\text{Units of } K_c \text{ are given by } \frac{(\text{mol dm}^{-3})^4}{(\text{mol dm}^{-3})^2(\text{mol dm}^{-3})^6} = \text{mol}^{-4} \text{ dm}^{12}$$

You can see that the units for K_c vary from reaction to reaction and must be worked out from the equation for the reaction and the expression for K_c . Examples 2 and 3 show why, whenever you quote a value for K_c , you must always give the stoichiometric equation for the reaction it refers to. You should also give the temperature at which the measurements were made. Worked example 1.17 illustrates the use of the equilibrium constant, K_c .

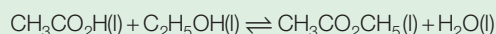


Visit the online resources to view Screencast 1.3, which discusses the use of equilibrium constants in terms of concentrations and in terms of partial pressures.



Worked example 1.17 Equilibrium constants in terms of concentrations

The ester, ethyl ethanoate, can be prepared by reacting the carboxylic acid, ethanoic acid, with the alcohol, ethanol. The reaction is reversible and comes to equilibrium



- Write an expression for K_c for the reaction and comment on the units of K_c .
- The table below shows equilibrium concentrations of the reactants and products at 373 K.

	Equilibrium concentration/mol dm ⁻³
ethanoic acid	0.0342
ethanol	7.033
ethyl ethanoate	0.981
water	0.981

Calculate the equilibrium constant for the reaction at 373 K.

Strategy

- Use Equation 1.23 to write the expression for K_c and then use this expression to work out the units of K_c .
- Substitute the equilibrium concentrations into the expression for K_c to find its value at 373 K.

Solution

- Using Equation 1.23,

$$K_c = \frac{[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5(\text{l})][\text{H}_2\text{O}(\text{l})]}{[\text{CH}_3\text{CO}_2\text{H}(\text{l})][\text{C}_2\text{H}_5\text{OH}(\text{l})]}$$

$$\text{Units of } K_c \text{ are given by } \frac{(\text{mol dm}^{-3})(\text{mol dm}^{-3})}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})}$$

so K_c for this reaction has **no units**.

$$\begin{aligned} \text{(b)} \quad K_c &= \frac{(0.981 \text{ mol dm}^{-3}) \times (0.981 \text{ mol dm}^{-3})}{(0.0342 \text{ mol dm}^{-3}) \times (7.033 \text{ mol dm}^{-3})} \\ &= 4.00 \end{aligned}$$

Now try this

An equimolar mixture of ethanoic acid and ethanol was heated at 373 K. At equilibrium, the concentration of ethanoic acid was found to be 0.820 mol dm⁻³. Calculate the concentration of ethyl ethanoate in the equilibrium mixture. (*Hint*. Use the stoichiometric equation for the reaction to determine the concentration of ethanol in the equilibrium mixture.)

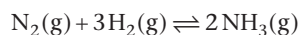
Equilibrium constant K_p

For a reaction taking place in the gas phase, it is often more convenient to write the equilibrium constant in terms of partial pressures of the gases, rather than in terms of their concentrations.

If you assume that each gas in the equilibrium mixture behaves independently of the other gases present, the total pressure of the mixture, p_{total} , is equal to the sum of the partial pressures of the gases present. The **partial pressure**, p , of a gas in a mixture is the pressure the gas would exert if it were present alone.

» Partial pressures are covered in more detail in Section 8.3.

For the reaction of nitrogen and hydrogen to form ammonia,



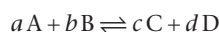
$$p_{\text{total}} = p_{\text{N}_2} + p_{\text{H}_2} + p_{\text{NH}_3}$$

At constant temperature, the partial pressure of each gas is proportional to its concentration (see Equation 1.25 below), so you can write an expression for an equilibrium constant, K_p

$$K_p = \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} p_{\text{H}_2}^3}$$

For this reaction, the units of K_p are $\frac{\text{Pa}^2}{\text{Pa Pa}^3} = \text{Pa}^{-2}$ (if the pressures are measured in pascals), or $\frac{\text{atm}^2}{\text{atm atm}^3} = \text{atm}^{-2}$ (if the pressures are measured in atmospheres).

For the general reaction



the equilibrium constant, K_p , is given by the expression

$$K_p = \frac{p_{\text{C}}^c p_{\text{D}}^d}{p_{\text{A}}^a p_{\text{B}}^b} \quad (1.24)$$

For gaseous reactions, either K_p or K_c can be used. As with K_c , the **units** of K_p vary from reaction to reaction and need to be worked out from each K_p expression. Worked example 1.18 illustrates the use of the equilibrium constant, K_p .

Relationship between concentration and partial pressure of a gas

You can use the ideal gas equation, $pV = nRT$, to work out the relationship between concentration and partial pressure of a gas, where p = partial pressure of the gas, V = volume, n = amount in moles, T = temperature, and R (the gas constant) = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. The concentration of the gas is given by n/V .

$$\text{For an ideal gas, } p = \frac{nRT}{V} = \text{concentration} \times RT \quad (1.25)$$

At constant T , $p \propto \text{concentration}$.

Relationship between K_p and K_c

In general, $K_p = K_c(RT)^{\Delta n}$, where Δn is the change in the number of moles of gas on going from reactants to products and R is the gas constant. For the ammonia reaction,

$$\Delta n = 2 \text{ mol} - 4 \text{ mol} = -2 \text{ mol, so } K_p = K_c(RT)^{-2}$$

You can derive this relationship by substituting expressions for the partial pressures in terms of concentrations using Equation 1.25 into the expression for K_p (e.g. $p_{\text{NH}_3} = [\text{NH}_3] \times RT$).

» The ideal gas equation is discussed in Sections 8.1 and 8.2.



Worked example 1.18 Equilibrium constants in terms of partial pressures

A 1:3 molar mixture of N_2 and H_2 is heated at 673 K and 50 atm so that it comes to equilibrium. The equilibrium mixture contains 15.3% NH_3 (by volume). Calculate a value for K_p for the reaction at this temperature.

Strategy

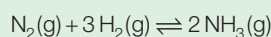
Write the balanced equation for the reaction.

Work out the equilibrium percentages of N_2 and H_2 . (They react in the ratio 1:3, so the unreacted gases will still be present in this ratio at equilibrium.)

Use the equilibrium percentages to work out the partial pressure of each gas present at equilibrium. (Note that the equilibrium percentages *by volume* are also the equilibrium percentages *by amount in moles*.)

Substitute these values into the expression for K_p .

Solution



At equilibrium, the percentage of NH_3 (by volume) is 15.3% (0.153 as a fraction). The remaining 84.7% must be N_2 and H_2 in the ratio 1 : 3.

Equilibrium % of $N_2 = \frac{1}{4} \times 84.7\% = 21.18\%$ (0.2118 as a decimal)

Equilibrium % of $H_2 = \frac{3}{4} \times 84.7\% = 63.53\%$ (0.6353 as a decimal)

$$\text{Total pressure} = 50 \text{ atm} = p_{N_2} + p_{H_2} + p_{NH_3}$$

$$p_{N_2} = 0.2118 \times 50 \text{ atm} = 10.59 \text{ atm}$$

$$p_{H_2} = 0.6352 \times 50 \text{ atm} = 31.77 \text{ atm}$$

$$p_{NH_3} = 0.153 \times 50 \text{ atm} = 7.65 \text{ atm}$$

Substituting these values into the expression for K_p (Equation 1.24)

$$K_p = \frac{p_{NH_3}^2}{p_{N_2} p_{H_2}^3} = \frac{(7.65 \text{ atm})^2}{(10.59 \text{ atm}) \times (31.77 \text{ atm})^3}$$

$$= 1.7 \times 10^{-4} \text{ atm}^{-2} \text{ (at 673 K)}$$

(Note that $p_{N_2} = (\text{mole fraction of } N_2) \times p_{\text{total}}$; see Section 8.3. The answer is given to 2 significant figures to correspond with the smallest number of significant figures in the data.)

Now try this

A second investigation was carried out at the same temperature (673 K) but at a higher pressure. At equilibrium, the partial pressure of N_2 was 18.7 atm and the partial pressure of H_2 was 56.1 atm.

- Calculate the partial pressure of NH_3 in the equilibrium mixture.
- What was (i) the total pressure for the second investigation and (ii) the percentage of NH_3 in the equilibrium mixture?

Values of equilibrium constants vary enormously (see Table 1.12). Note, in particular, the effect on the value of K_p of expressing the value in pascals rather than atmospheres (1 atm = 1.01×10^5 Pa). It is vital to quote units alongside values of K_c and K_p .

All reactions can be considered as equilibrium reactions. Even reactions that seem to go to completion actually have a very small amount of reactant left in equilibrium with the products. In some cases, the position of equilibrium is so far towards the products it is impossible to detect any reactants left in the reaction mixture. Such reactions have very large equilibrium constants. Similarly, a reaction that is observed not to go at all may be regarded as having a vanishingly small equilibrium constant.

» You can find out more about chemical equilibria in Section 15.1, where a *thermodynamic equilibrium constant*, K , is defined in terms of *activities*, rather than concentrations or partial pressures. This equilibrium constant is used in thermodynamics and has the advantage of not having units.

Table 1.12 Some values of K_c and K_p for gaseous reactions at 298 K

Reaction	K_c		K_p			
	Value	Unit	Value	Unit	Value	Unit
$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$	3.4×10^{81}	$\text{mol}^{-1} \text{ dm}^3$	1.4×10^{75}	Pa^{-1}	1.4×10^{80}	atm^{-1}
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	3.6×10^8	$\text{mol}^{-2} \text{ dm}^6$	5.8×10^{-5}	Pa^{-2}	6.0×10^5	atm^{-2}
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	620	—	620	—	620	—
$2NO_2(g) \rightleftharpoons N_2O_4(g)$	170	$\text{mol}^{-1} \text{ dm}^3$	6.7×10^{-5}	Pa^{-1}	6.8	atm^{-1}
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	4.6×10^{-31}	—	4.6×10^{-31}	—	4.6×10^{-31}	—



Summary

- A chemical equilibrium is a dynamic equilibrium in which the forward and reverse reactions are taking place at the same rate, so concentrations remain constant.
- Le Chatelier's principle summarizes the effects of external changes on an equilibrium: when an external change is made to a system in dynamic equilibrium, the system responds to minimize the effect of the change.
- Equilibrium constants can be expressed in terms of concentrations, K_c , or, for gaseous reactions, in terms of partial pressures, K_p , where $K_p = K_c(RT)^{\Delta n}$.
- For a general reaction: $aA + bB \rightleftharpoons cC + dD$, $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ and $K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$

Table 1.13 summarizes the effect of changing conditions on the composition of equilibrium mixtures and on equilibrium constants. The important thing to remember is that K_c and K_p are constant unless the temperature changes. Note that catalysts do not affect the position of equilibrium or the equilibrium constant. They increase the *rates* of both the forward and reverse reactions so that the same position of equilibrium is reached—but it is reached more quickly.

Table 1.13 The effect of changing conditions on the composition of equilibrium mixtures and equilibrium constants

Change in	Composition	K_c or K_p
Concentration	Changes	Unchanged
Partial pressure	Changes	Unchanged
Total pressure	May change	Unchanged
Temperature	Changes	Changes
Catalyst	Unchanged	Unchanged

? For practice questions on these topics, see questions 20 and 21 at the end of this chapter (p.69).



Concept review

By the end of this chapter, you should be able to do the following.

- Understand and be able to use IUPAC base units and derived units.
- Describe the structure of an atom in terms of protons, neutrons, and electrons.
- Understand the terms mass number and atomic number and write atomic symbols for chemical elements.
- Describe how a simple mass spectrometer can be used to show the isotopic composition of an element.
- Understand and use the terms: relative atomic mass (A_r); relative formula (or molecular) mass (M_r); Avogadro constant (N_A); the mole (mol) as a unit of amount of substance.
- Work out the empirical formula of a compound from its elemental composition and understand the relationship between empirical formula and molecular formula.
- Write a balanced equation for a reaction, including state symbols, and use it to calculate reacting masses.
- Work out the yield of a chemical reaction.
- Write ionic equations.
- Understand and use the terms redox, oxidation and reduction, oxidizing agent, and reducing agent.
- Write half equations for a redox reaction and use them to construct a balanced overall equation for the reaction.

- Assign oxidation states and use changes of oxidation state to decide what has been oxidized and what reduced in a redox reaction.
- Perform calculations involving concentrations of compounds in solution.
- Understand the techniques of volumetric analysis and gravimetric analysis and be able to carry out relevant calculations.
- Understand what is meant by the terms: exothermic; endothermic; enthalpy change of a reaction; standard conditions; and thermochemical equation.
- Draw an enthalpy level diagram and relate enthalpy changes to bond-breaking and bond-formation processes.
- Describe the states of matter and phase changes in terms of a kinetic-molecular model of matter.
- Recognize different types of non-covalent (intermolecular) interactions.
- Understand that chemical equilibrium is a dynamic equilibrium and use Le Chatelier's principle to predict the effect of changes on the position of equilibria.
- Write expressions for the equilibrium constants, K_c and K_p , and carry out simple calculations.

Key equations

Temperature in kelvin	$T / K = \theta / ^\circ\text{C} + 273.15$	(1.1)
Chemical amount	$\text{amount (in mol)} = \frac{\text{mass (in g)}}{\text{molar mass (in g mol}^{-1}\text{)}}$	(1.2)
Percentage yield	$\text{Percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$	(1.4)
Molarity of a solution	$\text{Concentration (mol dm}^{-3}\text{)} = \frac{\text{concentration (g dm}^{-3}\text{)}}{\text{molar mass (g mol}^{-1}\text{)}}$	(1.6)
The relationship between concentration (c) in mol dm^{-3} , amount in moles (n), and the volume of solution (V) in dm^3	$n = c \times V$	(1.9)
Potential energy	$\text{Potential energy} = E_{\text{PE}} = mgh$	(1.16)
Kinetic energy	$\text{Kinetic energy} = E_{\text{KE}} = \frac{1}{2}mv^2$	(1.17)
Thermochemical equations	$\Delta_r H$ (forward reaction) = $-\Delta_r H$ (backward reaction)	(1.18)
Equilibrium constant for the reaction: $aA + bB \rightleftharpoons cC + dD$	In terms of concentrations: $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$	(1.23)
	In terms of partial pressures: $K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b}$	(1.24)

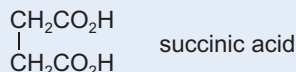
Questions

More challenging questions are marked with an asterisk *.

- The C–C bond length in a crystal of diamond is 0.154 nm. What is this distance in (a) metres, (b) picometres, (c) angstroms? (Section 1.2)
- Oxygen gas liquefies at -183.0°C and freezes at -218.4°C . Work out its melting point, T_m , and boiling point, T_b , in kelvin. (Section 1.2)
- A sealed flask holds 10 dm^3 of gas. What is this volume in (a) cm^3 , (b) m^3 , (c) litres? (Section 1.2)
- What is the SI derived unit for the speed of a molecule? (Section 1.2)
- How many moles of atoms are contained in the following masses: (a) 22.0 g of magnesium; (b) 43.2 g of chlorine; (c) 126 mg of gold; (d) 1.00 kg of mercury? (Section 1.3)

6. Calculate the amount of each substance contained in the following masses: (a) 89.2 g of carbon dioxide (CO₂); (b) 43.2 g of chlorine (Cl₂); (c) 0.48 kg of calcium hydroxide (Ca(OH)₂); (d) 25 tonnes of water, H₂O (1 tonne = 1 × 10⁶ g). (Section 1.3)
7. What is the mass (in g) of (a) 5.46 mol of CuO; (b) 0.107 mol of KMnO₄; (c) 2.85 mmol of C₂H₅OH; (d) 1.95 μmol of HCN? (Section 1.3)

8. The structure of succinic acid is shown below. (Section 1.3)

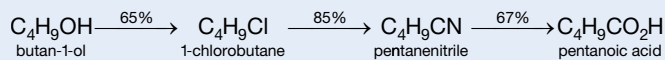


- (a) Write down the molecular formula of succinic acid and work out its molar mass.
- (b) What is the empirical formula of succinic acid?
- (c) What is the percentage of carbon in succinic acid?
- (d) Calculate the amount of succinic acid in a 0.125 g sample of the pure acid.
- (e) How many molecules of succinic acid are present in the 0.125 g sample?
- (f) How many carbon atoms are present in the 0.125 g sample?
9. Write down the formulas for sodium azide and sodium nitride. Use these to explain the difference between the N₃⁻ ion and the N³⁻ ion. (Section 1.3)
10. The fertilizer, ammonium nitrate, is made by reacting ammonia with nitric acid. (Section 1.4)

- (a) Write a balanced equation, with state symbols, for the reaction of ammonia gas with nitric acid to form a solution of ammonium nitrate.
- (b) Rewrite the equation to show the ions present in the reactants and products, and hence write an ionic equation for the reaction.
- (c) What *type* of chemical reaction does your equation represent?

Nitric acid is manufactured from ammonia. The first stage in this process involves burning ammonia in oxygen on the surface of a platinum gauze catalyst. The products are NO and H₂O.

- (d) Construct a balanced equation for the burning of NH₃ in O₂.
- (e) Calculate the maximum mass of NO that could be obtained by burning 1.00 kg of NH₃ and the mass of oxygen required.
- (f) In practice, 1.45 kg of NO were obtained from the reaction in (e). What was the percentage yield of the reaction?
11. Pentanoic acid (C₄H₉CO₂H) can be synthesized in three steps from butan-1-ol (C₄H₉OH) as shown below (Section 1.4):



- (a) What is the overall yield for the conversion of butan-1-ol to pentanoic acid?

- (b) If you carried out the synthesis starting with 20.0 g of butan-1-ol, what mass of pentanoic acid would you obtain?
- (c) Even when there are no side reactions in an organic reaction, a 100% yield of product is rarely obtained. Suggest reasons why this might be.

12. A stream running out from a copper mine contains a dilute solution of copper sulfate. As it passes over an iron grid, copper metal deposits on the grid. (Section 1.4)

- (a) Write a balanced equation, with state symbols, for the reaction taking place.
- (b) Write an ionic equation for the reaction.
- (c) Assign oxidation states to the elements in each of the reactants and products in the equation in (b). Use these values to decide what has been oxidized and what reduced.

13. (a) What are the systematic names for (i) CS₂; (ii) Cl₂O₇; (iii) XeF₆; (iv) (NH₄)₂SO₄; (v) CrCl₃; (vi) KIO₄?

- (b) Write the formula of each of the following compounds: (i) sodium sulfite; (ii) barium carbonate; (iii) iron(II) chloride; (iv) sodium thiosulfate; (v) diiodine pentoxide; (vi) dinitrogen oxide. (Section 1.4)

14. In most compounds, H has an oxidation state of +1 and O has an oxidation state of -2. The following compounds are exceptions to this rule. Assume each metal has the oxidation state of its most common ion and that F has an oxidation state of -1. Find the oxidation state of H or O in each compound: (a) KO₂; (b) Na₂O₂; (c) MgH₂; (d) LiAlH₄; (e) OF₂. (Section 1.4)

- 15.* Sodium chromate (Na₂CrO₄) can be prepared by oxidizing a chromium(III) salt with sodium peroxide (Na₂O₂) in alkaline solution. The Cr³⁺ ions are oxidized to CrO₄²⁻ ions. The O₂²⁻ ions are reduced to OH⁻ ions. Construct half equations and a balanced overall equation for the reaction. (Section 1.4)

- 16.* To prepare a very dilute solution, it is more accurate to make up a more concentrated standard solution, and carry out a series of successive dilutions, than to weigh out a very small mass of the solute.

A solution was made by dissolving 0.587 g of KMnO₄ in dilute sulfuric acid and making the volume of solution up to 1 dm³ in a volumetric flask. 10.0 cm³ of this solution were transferred to a second 1 dm³ volumetric flask and diluted to the mark with water. The dilution process was then repeated once, that is, 10.0 cm³ of this solution were transferred to a 1 dm³ volumetric flask and diluted to the mark with water. (Section 1.5)

- (a) What mass (in mg) of KMnO₄ would you have had to weigh out to make 500 cm³ of a solution with the same concentration as the final dilute solution?
- (b) What is the concentration of the final dilute KMnO₄ solution in mol dm⁻³?

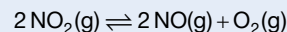
- 17.* The most common type of kidney stone is formed from calcium ethanedioate (CaC₂O₄) which precipitates out in the urinary tract when concentrations of Ca²⁺ ions and C₂O₄²⁻ ions

become too high. Magnesium ions are known to inhibit the formation of kidney stones. To analyse the concentrations of Ca^{2+} (aq) and Mg^{2+} (aq) in a sample of urine, the ions were precipitated as ethanedioates and the mixed precipitate of CaC_2O_4 and MgC_2O_4 was analysed by gravimetric analysis.

The solid ethanedioates were first heated to form a mixture of CaCO_3 and MgO . The mass of this mixture was 0.0433 g. This solid was then heated more strongly to give a mixture of CaO and MgO . The mass of the solid residue from this process was 0.0285 g. What was the mass of the Ca^{2+} ions in the original sample of urine? (Section 1.5)

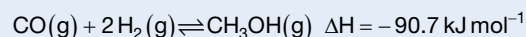
18. The standard enthalpy change of combustion of heptane, C_7H_{16} , at 298 K, is $-4817 \text{ kJ mol}^{-1}$. (Section 1.6)
- Write a thermochemical equation for the complete combustion of heptane to carbon dioxide and water.
 - What is the enthalpy change when 50 g of heptane are burned?
 - What mass of heptane would be needed to provide 100 MJ of energy?
- 19.*
- List the non-covalent interactions present in liquid water. Which is responsible for the strongest interactions between the molecules?
 - Explain why the value of $\Delta_{\text{vap}}H^\ominus(\text{H}_2\text{O})$ is unusually high for a molecule of its size.
 - In a storm, 3 cm of rain falls on the city of Leeds, which has an area of approximately 500 km^2 . Estimate the energy released as heat when this quantity of water condenses from vapour to form rain. (Density of water is 1.00 g cm^{-3} ; $\Delta_{\text{vap}}H^\ominus(\text{H}_2\text{O}) = +40.7 \text{ kJ mol}^{-1}$ at 298 K.)
 - The output from a large 2000 MW power station is 2000 MJ s^{-1} . How long would it take the power station to deliver the same quantity of energy as was released by the condensation of the rain in (c)? (Sections 1.7 and 1.8)

- 20.* Nitrogen dioxide gas is heated in a sealed container at 700 K until the system comes to equilibrium. The nitrogen dioxide dissociates into nitrogen monoxide and oxygen in an endothermic process (Section 1.9):



The equilibrium constant at 700 K is $2.78 \times 10^{-2} \text{ mol dm}^{-3}$.

- Write an expression for K_c .
 - State how the position of equilibrium would be affected by:
 - an increase in temperature
 - an increase in the total pressure.
 - At equilibrium at 700 K, the concentration of nitrogen monoxide was found to be $0.017 \text{ mol dm}^{-3}$. What was the concentration of nitrogen dioxide in the equilibrium mixture?
- 21.* One stage in the manufacture of methanol from methane involves the conversion of synthesis gas (a mixture of CO and H_2) to methanol. The conversion is carried out over a catalyst at a temperature of around 500 K and a pressure of 100 atm. (Section 1.9)



- Write an expression for K_p for the reaction.
- At 500 K and 100 atm pressure, an equilibrium mixture contains 42% CH_3OH and 48% CO . Calculate a value for K_p at this temperature.
- Use Le Chatelier's principle to predict what would happen to the percentage of methanol in the mixture if:
 - the temperature increases;
 - the pressure increases;
 - hydrogen is added at constant temperature and pressure.



Online resources

Access the online resources at www.oup.com/he/burrows4e to try out self-test questions. You can also view additional supporting material relevant to the topics in this chapter, including:

- Screencasts
- Videos

- Chapter summaries, learning outcomes, and key equations
- Solutions manual