1

Some basic concepts

1.1 What is chemistry and why is it important?

Matter, be it animal, vegetable or mineral, is composed of chemical elements or combinations thereof. Over a hundred elements are known, although not all are abundant by any means. The vast majority of these elements occur naturally, but some, such as technetium and curium, are artificial.

Chemistry is involved with the understanding of the properties of the elements, how they interact with one another, and how the combination of these elements gives compounds that may undergo chemical changes to generate new compounds.

Life has evolved systems that depend on carbon as a fundamental element; carbon, hydrogen, nitrogen and oxygen are particularly important in biological systems. A true understanding of biology and molecular biology must be based upon a full knowledge of the structures, properties and reactivities of the molecular components of life. This basic knowledge comes from the study of chemistry.

The line between physical and chemical sciences is also a narrow one. Take, for example, the rapidly expanding field of superconducting materials – compounds that possess negligible resistance to the flow of electrons. Typically, this property persists only at very low temperatures but if the super-conducting materials are to find general application, they must operate at ambient temperatures. Although a physicist may make the conductivity measurements, it is the preparation and study of the *chemical* composition of the materials that drive the basic research area.
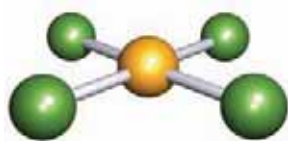
Chemistry plays a pivotal role in the natural sciences. It provides the essential basic knowledge for applied sciences, such as astronomy, materials science, chemical engineering, agriculture, medical sciences and pharmacology. After considering these points, the answer to the question '*why study chemistry as a first*

year university science?' should not cause you much problem. Whatever your final career destination within the scientific world, an understanding of chemical concepts is essential.
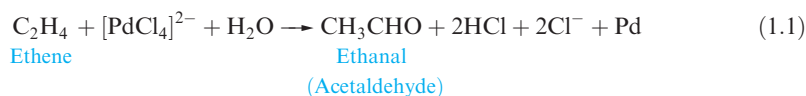
It is traditional to split chemistry into the three branches of inorganic, organic and physical; theoretical chemistry may be regarded as a division of the physical discipline. However, the overlap between these branches of the subject is significant and real. Let us consider a case study – the Wacker process, in which ethene is oxidized to ethanal (equation 1.1).
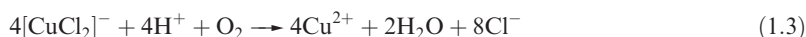
$$C_2H_4 + [PdCl_4]^{2-} + H_2O \longrightarrow CH_3CHO + 2HCl + 2Cl^- + Pd \qquad (1.1)$$

Ethene   Ethanal (Acetaldehyde)

(1.1)

Until recently, this was a significant industrial method for the preparation of ethanal. The reaction occurs in water in the presence of the palladium(II)-containing ion, $[PdCl_4]^{2-}$ **1.1**. The palladium(0) formed in reaction 1.1 is converted back to $[PdCl_4]^{2-}$ by reaction with copper(II) and chloride ions (equation 1.2). The copper(I) so formed (as $[CuCl_2]^-$) is reoxidized by O_2 (equation 1.3). In this way, the $[PdCl_4]^{2-}$ and Cu^{2+} function as *catalysts* since they undergo no *overall* change through the cycle of reactions.

$$2Cu^{2+} + Pd + 8Cl^- \longrightarrow [PdCl_4]^{2-} + 2[CuCl_2]^- \qquad (1.2)$$

$$4[CuCl_2]^- + 4H^+ + O_2 \longrightarrow 4Cu^{2+} + 2H_2O + 8Cl^- \qquad (1.3)$$

The basic reaction (ethene to ethanal) is an organic one. The catalyst is inorganic. Physical chemistry is needed to interpret the kinetics and understand the mechanism of the reaction and to work out the most effective conditions under which it should take place in an industrial setting. All three branches of chemistry are used to understand the Wacker process. This is just one of a myriad of cases in which a discussion of a chemical process or concept requires the interplay of two or more areas of chemistry.

In *Chemistry*, topics have been arranged to provide a natural progression through the chemistry that a first year science undergraduate student needs to assimilate. There are no artificial barriers placed between areas of chemistry although the traditional areas of inorganic, organic and physical are distinguishable. By studying chemistry from a single book in which the branches of chemistry are clearly linked, we hope that you will learn to apply the concepts to new situations more easily.

The aim of the rest of this chapter is to review some essential topics and to provide you with a source of reference for basic definitions.

1.2   What is the IUPAC?

As chemistry continues to expand as a subject and as the number of known chemical compounds continues to grow at a dramatic rate, it becomes increasingly vital that a set of ground rules be accepted for the naming of compounds. Not only accepted, but, probably more importantly, *used* by chemists.

The International Union of Pure and Applied Chemistry (IUPAC) is, among other things, responsible for making recommendations for the naming of both inorganic and organic compounds, as well as for the numbering system and the collective names that should be in common use for groups of elements in the periodic table.

Throughout this text, we will be using recommended IUPAC nomenclature wherever possible, but old habits die hard and a host of trivial names persists in the chemist's vocabulary. Where use of only the IUPAC nomenclature may cause confusion or may not be generally recognized, we have introduced both the recommended and trivial names. Some basic rules and revision for organic and inorganic nomenclature are dealt with in Section 1.18. As new classes of compounds are introduced in this textbook, we detail the systematic methods of naming them.

1.3 SI units

A system of internationally standardized and recognized units is as important as a system of compound names. The Système International d'Unités (SI units) provides us with the accepted system of measurement.

Base SI quantities

There are seven base SI quantities (Table 1.1). In addition there are two supplementary units, the radian and the steradian. The *radian* is the SI unit of angle and its symbol is *rad*. For solid geometry, the unit of solid angle is the *steradian* with the unit symbol *sr*. With the exception of the kilogram, all the base SI units are defined in terms of a physical constant, for example, the speed of light in a vacuum. The kilogram is defined as the mass of a prototype international platinum–iridium cylinder which is kept at the International Bureau of Weights and Measures in Paris. The Avogadro Project is an international collaboration which aims to measure the Avogadro constant more precisely and enable the kilogram to be defined with respect to this physical constant. The re-determination of the Avogadro constant may be complete by 2010.

Table 1.1 The base quantities of the SI system.

Physical quantity	Symbol for quantity	Base unit	Unit symbol
Mass	m	kilogram	kg
Length	l	metre	m
Time	t	second	s
Electrical current	I	ampere	A
Temperature (thermodynamic)	T	kelvin	K
Amount of substance	n	mole	mol
Luminous intensity	I_v	candela	cd

Degree Celsius, °C (instead of kelvin), is an older unit for temperature which is still in use; note the correct use of the notation °C and K, not °K.

Table 1.2 Some derived units of the SI system with particular names.

Unit	Name of unit	Symbol	Relation to base units
Energy	joule	J	$kg\,m^2\,s^{-2}$
Frequency	hertz	Hz	s^{-1}
Force	newton	N	$kg\,m\,s^{-2}$
Pressure	pascal	Pa	$kg\,m^{-1}\,s^{-2}$
Electric charge	coulomb	C	$A\,s$
Capacitance	farad	F	$A^2\,s^4\,kg^{-1}\,m^{-2}$
Electromotive force (emf)	volt	V	$kg\,m^2\,s^{-3}\,A^{-1}$
Resistance	ohm	Ω	$kg\,m^2\,s^{-3}\,A^{-2}$

An important feature of SI units is that they are completely self-consistent. From the seven base units, we can derive all other units as shown in worked examples 1.1, 1.2 and 1.11. Some of the most commonly used derived units have their own names, and selected units of this type, relevant to chemistry, are listed in Table 1.2.

Derived SI units

Whenever you are using an equation to calculate a physical quantity, the units of the new quantity can be directly determined by including in the same equation the units of each component. Consider the volume of a rectangular box of sides a, b and c (equation 1.4). The SI unit of length is the metre (Table 1.1) and so the SI unit of volume can be determined as in equation 1.5. Throughout this book, we combine quantities and units in equations. Thus, equations 1.4 and 1.5 are combined to give the calculation for the volume of the box in the form of equation 1.6.

$$\text{Volume of box} = \text{length} \times \text{width} \times \text{height} = a \times b \times c = abc \qquad (1.4)$$

$$\text{SI unit of volume} = (\text{SI unit of length}) \times (\text{SI unit of width})$$
$$\times (\text{SI unit of height})$$
$$= m \times m \times m = m^3 \qquad (1.5)$$

$$\text{Volume of box} = (\text{length in m}) \times (\text{width in m}) \times (\text{height in m})$$
$$= (a\,m) \times (b\,m) \times (c\,m)$$
$$= abc\,m^3 \qquad (1.6)$$

Some older units still persist, notably atmospheres, atm (instead of pascals), for pressure, and calories, cal (instead of joules), for energy, but on the whole, SI units are well established and are used internationally.

APPLICATIONS

Box 1.1 The importance of being consistent with units

In 1999, NASA lost the spacecraft 'Mars Climate Orbiter'. An investigation into its loss revealed that one team of scientists had been working in Imperial units of inches, feet and pounds, while their international collaborators had been using metric units. Data used in part of the ground-based navigation software was provided in Imperial units and were not converted into metric units before being fed into the on-board navigation system. The result of providing the flight information in data sets with inconsistent units was that the spacecraft was unable to manoeuvre into the correct orbit about Mars, and was consequently lost in space.
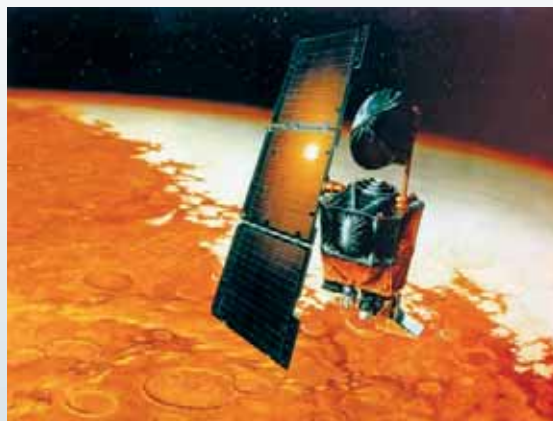
Artist's impression of the Mars Climate Orbiter.

Worked example 1.1   Defining units

Determine the SI unit of density.

Density is mass per unit volume:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$$\therefore \text{ the SI unit of density} = \frac{\text{SI unit of mass}}{\text{SI unit of volume}} = \frac{\text{kg}}{\text{m}^3} = \text{kg m}^{-3}$$

Large and small numbers

Scientific numbers have a habit of being either extremely large or extremely small. Take a typical carbon–carbon (C–C) single bond length. In the standard SI unit of length, this is 0.000 000 000 154 m. Writing this number of zeros is clumsy and there is always the chance of error when the number is being copied. The distance can be usefully rewritten as 1.54×10^{-10} m. This is a much neater and more easily read way of detailing the same information about the bond length. It would be even better if we could eliminate the need to write down the '$\times 10^{-10}$' part of the statement. Since bond lengths are usually of the same order of magnitude, it would be useful simply to be able to write '1.54' for the carbon–carbon distance. This leads us to the unit of the ångström (Å); the C–C bond distance is 1.54 Å. Unfortunately, the ångström is *not* an SI unit although it *is* in common use. The SI asks us to choose from one of the accepted multipliers listed in Table 1.3. The distance of 1.54×10^{-10} m is equal to either 154×10^{-12} m or 0.154×10^{-9} m, and from Table 1.3 we see that these are equal to 154 pm or 0.154 nm respectively. Both are acceptable within the SI. Throughout this book we have chosen to use picometres (pm) as our unit of bond distance.

Table 1.3 Multiplying prefixes for use with SI units; the ones that are most commonly used are given in pink.

Factor	Name	Symbol	Factor	Name	Symbol
10^{12}	tera	T	10^{-2}	centi	c
10^{9}	giga	G	10^{-3}	milli	m
10^{6}	mega	M	10^{-6}	micro	μ
10^{3}	kilo	k	10^{-9}	nano	n
10^{2}	hecto	h	10^{-12}	pico	p
10	deca	da	10^{-15}	femto	f
10^{-1}	deci	d	10^{-18}	atto	a

Consistency of units

A **word of warning** about the use of the multipliers in Table 1.3. In a calculation, you must work in a consistent manner. For example, if a density is given in $g\,cm^{-3}$ and a volume in m^3, you *cannot* mix these values, e.g. when determining a mass:

$$\text{Mass} = \text{Volume} \times \text{Density}$$

You must first scale one of the values to be consistent with the other as is shown in worked example 1.2. The most foolproof way of overcoming this frequent source of error is to convert all units into the scale defined by the base units (Table 1.1) *before* you substitute the values into an equation. We shall see many examples of this type of correction in worked examples throughout the book.

Worked example 1.2   Units in calculations

Calculate the volume occupied by 10.0 g of mercury if the density of mercury is $1.36 \times 10^4\,kg\,m^{-3}$ at 298 K.

The equation that relates mass (m), volume (V) and density (ρ) is:

$$\rho = \frac{m}{V} \qquad \text{or} \qquad V = \frac{m}{\rho}$$

Before substituting in the numbers provided, we must obtain consistency among the units.
Density is given in $kg\,m^{-3}$ but the mass is given in g, and should be converted to kg (or the density converted to $g\,m^{-3}$):

$$10.0\,g = 10.0 \times 10^{-3}\,kg = 1.00 \times 10^{-2}\,kg$$

Now we are a position to calculate the volume occupied by the mercury:

$$V = \frac{m}{\rho} = \frac{1.00 \times 10^{-2}\,kg}{1.36 \times 10^4\,kg\,m^{-3}} = 7.35 \times 10^{-7}\,m^3$$

Table 1.4 Properties of the proton, electron and neutron.

	Proton	Electron	Neutron
Charge / C	$+1.602 \times 10^{-19}$	-1.602×10^{-19}	0
Charge number (relative charge)	1	-1	0
Rest mass / kg	1.673×10^{-27}	9.109×10^{-31}	1.675×10^{-27}
Relative mass	1837	1	1839

1.4 The proton, electron and neutron

The basic particles of which atoms are composed are the *proton*, the *electron* and the *neutron*.[§] Some key properties of the proton, electron and neutron are given in Table 1.4. A neutron and a proton have approximately the same mass and, relative to these, the electron has a negligible mass. The charge on a proton is of equal magnitude, but opposite sign, to that on an electron and so the combination of *equal numbers* of protons and electrons results in an assembly that is neutral overall. A neutron, as its name suggests, is neutral – it has no charge. The arrangements and energies of electrons in atoms and ions are discussed in Chapter 3.

1.5 The elements

An *element* is matter, all of whose atoms are alike in having the same positive charge on the nucleus.

The recommended IUPAC definition of an *element* states that 'an element is matter, all of whose atoms are alike in having the same positive charge on the nucleus'. Each element is given a symbol and these are predominantly internationally accepted even though the names of the elements themselves are subject to linguistic variation (see Box 1.2).

Metals, non-metals and semi-metals

In the United States, Al is known as *aluminum*.

Elements can be classified as metals, non-metals or semi-metals. The names of *most* metals end in '-ium', e.g. lithium, sodium, magnesium, calcium, aluminium, scandium, chromium, titanium, vanadium, hafnium, ruthenium, rhodium, iridium, osmium and palladium. Common exceptions include tin, lead, iron, cobalt, copper, zinc, tungsten, platinum, silver and gold. Under IUPAC recommendations, the term 'semi-metal' is preferred over 'metalloid'. We look further at what constitutes a 'semi-metal' in Chapter 9.

Allotropes

Some elements exist in more than one structural form and this property is called *allotropy*. Consider carbon – two commonly quoted *allotropes* of

---

[§] These are the particles considered fundamental by chemists, although particle physicists have demonstrated that there are yet smaller building blocks. This continual subdivision recalls the lines of Jonathan Swift:
 'So, naturalists observe, a flea
 Hath smaller fleas that on him prey;
 And these have smaller fleas to bite 'em,
 And so proceed *ad infinitum*.'

Box 1.2 The elements: names with meanings

The origin of the names of the chemical elements and their variation between languages is fascinating. A wealth of chemical history and fact is hidden within the names, although changing from one language to another may obscure this information. Three examples illustrate this.

Mercury (Hg)

The silver-white, liquid metal mercury was known to the ancient Greeks as *liquid silver*. This name evolved into the Latin *hydrargyrum* from which our present-day symbol *Hg* arises. Mercury used to be known as *quicksilver* in English (*quick* means alive) and the element is called *Quecksilber* in German. The word *mercury* refers to the messenger of the Roman gods – anyone who has tried to 'catch' a globule of mercury will appreciate the analogy.

Cobalt (Co)

The *d*-block element cobalt (Co) is known as *Kobalt* in German. Nickel and cobalt occur in varying amounts in iron ores. When these ores were processed by early miners, ores containing significant amounts of cobalt gave inferior metallic products. These ores became known as *false ores* and were named after the malicious imps or *Kobold* who supposedly lived in the mines.

Tungsten (W)

Tungsten has the unexpected symbol W. In German, tungsten is called *Wolfram* and this refers to its ore *wolframite*. The other common ore is *scheelite*, which was named after Scheele, the discover of tungsten. Scheele was Swedish, and before the ore was called scheelite, it was known as *tungsten* which translates as 'heavy stone'.

Scheelite crystals on quartz.

Allotropes of an element are different structural modifications of that element.

carbon are graphite and diamond (Figure 1.1), both of which possess infinite structures. Both allotropes consist only of atoms of carbon and both burn in an excess of O_2 to give only carbon dioxide, CO_2. The physical appearances of these two allotropes are, however, dramatically different. Diamond is thermodynamically unstable at room temperature and pressure with respect to graphite but, fortunately, the interconversion is extremely slow and diamond is termed *metastable*. In the 1980s, further allotropes of carbon called the fullerenes were discovered. These are present in soot to the
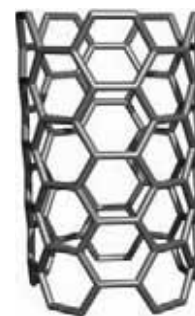

Graphite   Diamond   The fullerene C_{60} Carbon nanotube

Fig. 1.1 The structures of four allotropes of carbon; C_{60} is representative of the group of fullerenes. The nanotube shown is representative of a large family of single- and multi-walled tubes.

extent of a few per cent by mass, and the commonest component consists of discrete C_{60} molecules (Figure 1.1). Further allotropes of carbon, the carbon nanotubes (Figure 1.1), were discovered in 1991 and are some of the best known examples of *nanoparticles*; at least one dimension of a 'nanoscale' object should be of the order of 10^{-9} m (see Table 1.3). The semiconducting or metallic properties of single-walled and multi-walled carbon nanotubes and their high tensile strength, mean that they are currently being investigated, at both research and commercial level. Other common elements that exhibit allotropy are tin, phosphorus, arsenic, oxygen, sulfur and selenium.

1.6 States of matter

Solids, liquids and gases

At a given temperature, an element is in one of three *states of matter* – solid, liquid or vapour (Figure 1.2). A vapour is called a gas when it is above its *critical temperature*.

In a *solid*, the atoms are often arranged in a regular fashion. The solid possesses a fixed volume (at a stated temperature and pressure) and shape. A *liquid* also has a fixed volume at a given temperature and pressure, but has no definite shape. It will flow into a container and will adopt the shape of this vessel. The particles (atoms or molecules) in a *gas* move at random and can occupy a large volume. A gas has no fixed shape.

In Figure 1.2, the surface boundary of the solid is determined by the solid itself and is not dictated by the container. On the other hand, unless restricted by a container, the boundary of a gas is continually changing; this permits two (or more) gases to mix in a process called *diffusion* (Figure 1.3). In a liquid, the shape of the liquid mimics the shape of the container, but at the upper surface of the liquid the phenomenon of *surface tension* operates and this defines the surface boundary. When liquids mix they are said to be *miscible*; hexane and octane are miscible, as are water and ethanol. If liquids do not mix (e.g. water and oil, water and hexane), they are *immiscible*.

If two liquids mix, they are *miscible*. *Immiscible* liquids form distinct layers.

Fig. 1.2 The arrangement of particles (atoms or molecules) in a solid, a liquid and a gas. For the solid, the surface is determined by the solid itself. The shape of the liquid is controlled by the shape of the container; the liquid has a definite surface. The atoms or molecules of the gas are free to move throughout the container.
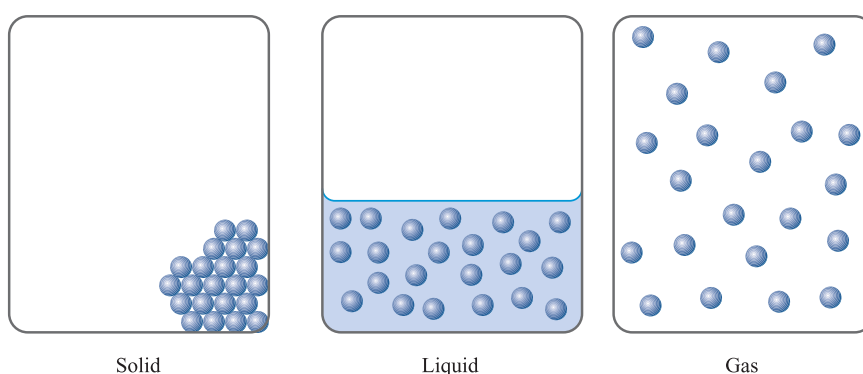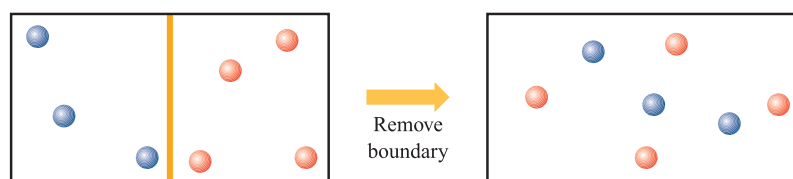

Solid   Liquid   Gas

Fig. 1.3 A gas is trapped within the boundaries of the vessel in which it is held. Two gases can mix together (*diffuse*) if the boundary between them is removed.

Remove boundary

In chemical equations, the states of substance are often included and the standard abbreviations are:

solid   (s)
liquid   (l)
gas   (g)

The use of (aq) refers to an aqueous solution; this is *not* a state of matter.

Phases

The three states of a substance are *phases*, but within one state there may be more than one phase. For example, each allotrope of carbon is a different phase but each is in the solid state. Each phase exists under specific conditions of temperature and pressure and this information is represented in a *phase diagram*. Figure 1.4 shows a pressure–temperature phase diagram for a one-component system. The solid blue lines represent the boundaries between the phases. At a given pressure (or temperature), the transformation from one phase to another takes place at a particular temperature (or pressure). Crossing a boundary corresponds to changing the phase of the substance, e.g. melting a solid or vaporizing a liquid. Most commonly, we are dealing with phase transitions at atmospheric pressure (see worked example 1.3). An element (or a single allotrope if the element possesses more than one allotrope) changes from solid to liquid at its *melting point*, and from liquid to vapour at its *boiling point* (Table 1.5). The terms *gas* and *vapour* are often used interchangeably, but there is a real distinction between them. The dashed line in Figure 1.4 illustrates this distinction: a vapour can be liquefied by increasing the pressure, but a gas cannot. Above the critical temperature, T_c, the gas can no longer be liquefied, no matter how high the pressure is increased.

When heated at a particular pressure, some elements transform directly from solid to vapour, and this process is called *sublimation*. Iodine readily sublimes when heated at atmospheric pressure.

At temperatures and pressures above the critical point, a substance becomes a *supercritical fluid* (Figure 1.4). If you observe a substance as it reaches its critical point, the meniscus at the liquid–gas interface disappears, illustrating that there is no longer a distinction between the two

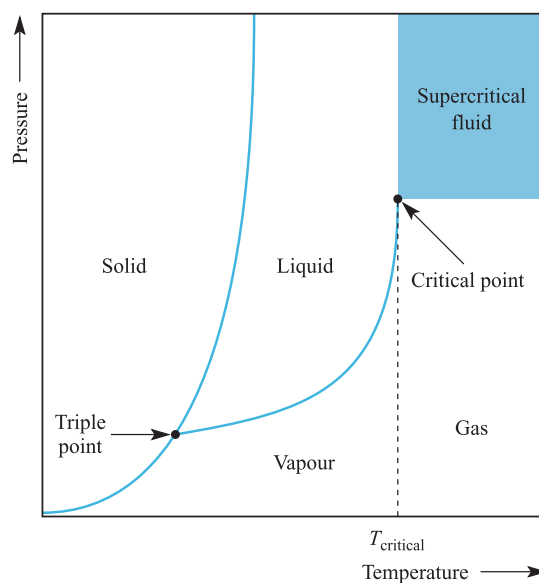**Fig. 1.4** A simple pressure–temperature phase diagram for a one-component system.

Table 1.5 Melting and boiling points (at atmospheric pressure) and appearance of selected elements. Carbon and sulfur are not included because neither undergoes a simple change of state.

Element (allotrope)	Symbol	Melting point / K	Boiling point / K	Physical appearance at 298 K
Aluminium	Al	933	2793	White metal
Bromine	Br	266	332.5	Brown-orange liquid
Calcium	Ca	1115	1757	Silver-white metal
Chlorine	Cl	172	239	Green-yellow gas
Chromium	Cr	2180	2944	Silver metal
Cobalt	Co	1768	3200	Silver-blue metal
Copper	Cu	1358	2835	Reddish metal
Fluorine	F	53	85	Very pale yellow gas
Gold	Au	1337	3081	Yellow metal
Helium	He	–	4.2	Colourless gas
Hydrogen	H	14	20	Colourless gas
Iodine	I	387	458	Black solid
Iron	Fe	1811	3134	Silver-grey metal
Lead	Pb	600	2022	Blue-grey metal
Lithium	Li	453.5	1615	Silver-white metal
Magnesium	Mg	923	1363	Silver-white metal
Manganese	Mn	1519	2334	Silver metal
Mercury	Hg	234	630	Silver liquid
Nickel	Ni	1728	3186	Silver metal
Nitrogen	N	63	77	Colourless gas
Oxygen	O	54	90	Colourless gas
Phosphorus (white)	P	317	550	White solid
Potassium	K	336	1032	Silver-white metal
Silicon	Si	1687	2638	Shiny, blue-grey solid
Silver	Ag	1235	2435	Silver-white metal
Sodium	Na	371	1156	Silver-white metal
Tin (white)	Sn	505	2533	Silver metal
Zinc	Zn	692.5	1180	Silver metal

phases. Supercritical carbon dioxide (scCO$_2$) has many commercial applications, notably in the food (e.g. decaffeination of coffee and tea), tobacco (nicotine extraction) and pharmaceutical industries. Extraction processes can be designed so that the supercritical fluid is recycled, making the use of scCO$_2$ environmentally friendly. New applications of scCO$_2$ are continually emerging, a recent development being the cleaning of antique textiles.

Worked example 1.3   Using a simple phase diagram
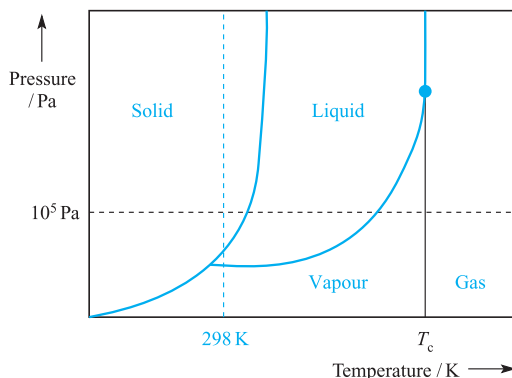
The phase diagram above is for a one-component system, X. The pressure of 10^5 Pa corresponds to atmospheric pressure (P_{atm}).

(a) At P_{atm}, does X melt above or below 298 K?
(b) Where on the diagram would you find the boiling point of X?
(c) What phase does X exist in at 298 K and 10^5 Pa?
(d) Under what conditions does X sublime?
(e) What happens to X at pressures and temperatures above the critical point?

All phase changes at atmospheric pressure occur along the dashed black line shown on the phase diagram. The blue dashed line corresponds to 298 K.

(a) Follow the P_{atm} line until it crosses the solid–liquid boundary. This is the melting point of **X**, i.e. above 298 K.
(b) Follow the P_{atm} line until it crosses the liquid–vapour boundary. This is the boiling point of **X**.
(c) At 298 K and 10^5 Pa (i.e. where the vertical and horizontal dashed lines cross), **X** is a solid.
(d) Sublimation is the direct change from solid to vapour. There is a boundary between these phases only at low temperatures and pressures.
(e) Above the critical point (i.e. the top right-hand corner of the phase diagram), **X** is a supercritical liquid.
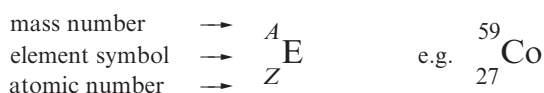

1.7   Atoms and isotopes

An ***atom*** is the smallest unit quantity of an element that is capable of existence, either alone or in chemical combination with other atoms of the same or another element.

Atoms and atomic number

An *atom* is the smallest unit quantity of an element that is capable of existence, either alone or in chemical combination with other atoms of the same or another element. It consists of a positively charged *nucleus* and negatively charged electrons. The simplest atom is hydrogen (protium) which is made up of one proton and one electron. The proton of a hydrogen

atom is its nucleus, but the nucleus of any other atom consists of protons *and* neutrons.

All atoms are neutral, with the positive charge of the nucleus exactly balanced by the negative charge of a number of electrons equal to the number of protons. The electrons are situated outside the nucleus. Each atom is characterized by its *atomic number*, Z. A shorthand method of showing the atomic number and *mass number*, A, of an atom along with its symbol, E, is used:

$$\begin{array}{ll}\text{mass number} & \longrightarrow \\ \text{element symbol} & \longrightarrow \quad {}^{A}_{Z}\text{E} \qquad \text{e.g.} \quad {}^{59}_{27}\text{Co} \\ \text{atomic number} & \longrightarrow \end{array}$$

Atomic number $= Z =$ number of protons in the nucleus $=$ number of electrons
Mass number $= A =$ number of protons $+$ number of neutrons

Relative atomic mass

The mass of an atom is concentrated in the nucleus where the protons and neutrons are found. If we were to add together the actual masses of protons and neutrons present, we would always be dealing with very small, non-integral numbers, and for convenience, a system of *relative atomic masses* is used. The *atomic mass unit* (u) has a value of $\approx 1.660 \times 10^{-27}$ kg, and this corresponds closely to the mass of a proton or a neutron (Table 1.4). Effectively, the mass of each proton and neutron is taken to be one atomic mass unit. The scale of relative atomic masses (A_{r}) is based upon measurements taken for carbon with all atomic masses stated *relative to* $^{12}\text{C} = 12.0000$.

Isotopes

For a given element, there may be more than one type of atom, and these are called *isotopes* of the element. *Do not confuse isotopes with allotropes*. Allotropes are different structural forms of a *bulk* element arising from different spatial arrangements of the atoms (Figure 1.1). Isotopes are atoms of the same element with *different numbers of neutrons*. Some isotopes that do not occur naturally may be produced artificially (see Box 1.3).

An element is characterized by the number of protons and, to keep the atom neutral, this must equal the number of electrons. However, the number of neutrons can vary. For example, hydrogen possesses three naturally occurring isotopes. The most abundant by far (99.985%) is protium, ^{1}H, which has one proton and one electron but no neutrons. The second isotope is deuterium, ^{2}H (also given the symbol D), which has one proton, one electron and one neutron. Deuterium is present naturally at an abundance of 0.015% and is sometimes called 'heavy hydrogen'. Tritium (^{3}H or T) occurs as fewer than 1 in 10^{17} atoms in a sample of natural hydrogen and is radioactive. The atomic mass of naturally occurring hydrogen reflects the presence of all three isotopes and is the weighted mean of the masses of the isotopes present. The relative atomic mass of hydrogen is 1.0080, and the value is close to 1 because the isotope ^{1}H with mass number 1 makes up 99.985% of the natural mixture of isotopes.

Isotopes of an element have the same atomic number, Z, but different atomic masses.

Other examples of elements that exist naturally as mixtures of isotopes are lithium ($^{6}_{3}\text{Li}$ and $^{7}_{3}\text{Li}$), chlorine ($^{35}_{17}\text{Cl}$ and $^{37}_{17}\text{Cl}$) and copper ($^{63}_{29}\text{Cu}$ and $^{65}_{29}\text{Cu}$). Elements that occur naturally as only one type of atom are *monotopic* and

THEORY

Box 1.3 Artificially produced isotopes and β-particle emission

Some isotopes, in particular those of the heaviest elements in the periodic table, are produced by the bombardment of one nucleus by particles which induce nuclear fusion. Typical particles used for the bombardment are neutrons.

An example of an artificially produced isotope is the formation of $^{239}_{94}Pu$, an isotope of plutonium, in a series of nuclear reactions beginning with the isotope of uranium $^{238}_{92}U$. The bombardment of $^{238}_{92}U$ with neutrons results in nuclear fusion:

$$^{238}_{92}U + ^{1}_{0}n \longrightarrow ^{239}_{92}U$$
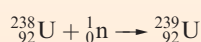
The relative atomic mass of the product is one atomic mass unit greater than that of the initial isotope because we have added a neutron to it. The isotope $^{239}_{92}U$ undergoes spontaneous loss of a β-particle (an electron, see below) to form an isotope of neptunium ($^{239}_{93}Np$) which again undergoes β-decay to give $^{239}_{94}Pu$:

$$^{239}_{92}U \longrightarrow ^{239}_{93}Np + \beta^{-}$$

$$^{239}_{93}Np \longrightarrow ^{239}_{94}Pu + \beta^{-}$$
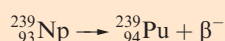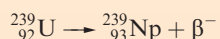
β-Decay

β-Particle emission (β-decay) occurs when an *electron* is lost *from the nucleus* by a complex process which effectively 'turns a neutron into a proton'.[§] The mass of the nucleus undergoing β-decay does not change because the β-particle has negligible mass. The atomic number of the nucleus undergoing the emission increases by one since, effectively, the nucleus has gained a proton:

$$^{1}_{0}n \longrightarrow ^{1}_{1}p + \beta^{-}$$
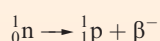
[§] This notation is not strictly correct. The decay of a nucleus by the loss of a β-particle is a complex process, the study of which belongs within the remit of the particle physicist. Of interest to us here is the fact that a nucleus that undergoes β-decay retains the same atomic mass but increases its atomic number by one.

include phosphorus ($^{31}_{15}P$) and cobalt ($^{59}_{27}Co$). Isotopes can be separated by *mass spectrometry* and Figure 1.5a shows the isotopic distribution in atomic chlorine. In the mass spectrum of Cl_2 (Figure 1.5b), three peaks are observed and are assigned to the possible combinations of the two isotopes of chlorine. The technique of mass spectrometry is described in Chapter 10.

In the shorthand notation for denoting an isotope, the atomic number is often omitted because it is a constant value for a given element, e.g. the two isotopes of copper can be distinguished by simply writing ^{63}Cu and ^{65}Cu.

Fig. 1.5 Mass spectrometric traces for (a) atomic chlorine and (b) molecular Cl_2.
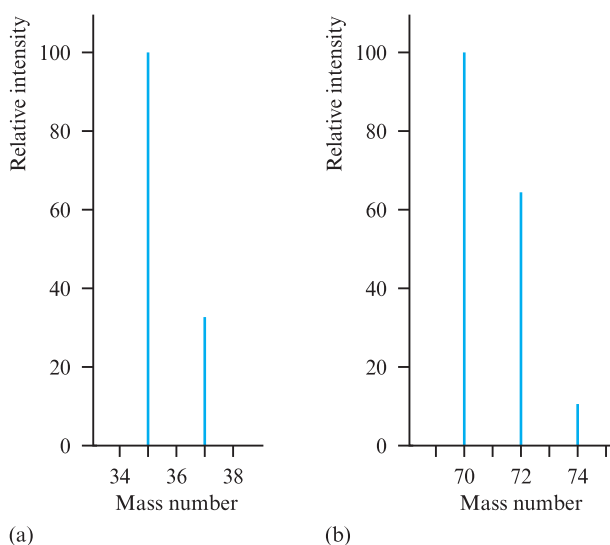
Worked example 1.4   Isotopes

An isotope of hydrogen, $^{7}_{1}$H, with a lifetime of 10^{-21} s, has been artificially produced. How many protons, electrons and neutrons does $^{7}_{1}$H possess?

The atomic number of every isotope of hydrogen is 1, and each isotope possesses one electron and one proton.
The mass number of $^{7}_{1}$H is 7. Therefore:

Number of protons + number of neutrons = 7
Number of neutrons = 7 − 1 = 6

Worked example 1.5   Relative atomic mass

Calculate the relative atomic mass A_r of naturally occurring magnesium if the distribution of isotopes is 78.7% $^{24}_{12}$Mg, 10.1% $^{25}_{12}$Mg and 11.2% $^{26}_{12}$Mg, and the accurate masses of the isotopes to three significant figures (sig. fig.) are 24.0, 25.0 and 26.0.

The relative atomic mass of magnesium is the weighted mean of the atomic masses of the three isotopes:

$$\text{Relative atomic mass} = \left(\frac{78.7}{100} \times 24.0\right) + \left(\frac{10.1}{100} \times 25.0\right) + \left(\frac{11.2}{100} \times 26.0\right)$$

$$= 24.3 \quad \text{(to 3 sig. fig.)}$$

Worked example 1.6   Abundance of isotopes

Calculate the percentage abundances of ^{12}C and ^{13}C if the relative atomic mass, A_r, of naturally occurring carbon is 12.011, and the accurate masses of the isotopes are 12.000 and 13.003 (to 5 sig. fig.).

Let the % abundances of the two isotopes be x and $(100 - x)$. The value of A_r is therefore:

$$A_r = 12.011 = \left(\frac{x}{100} \times 12.000\right) + \left(\frac{100 - x}{100} \times 13.003\right)$$

$$12.011 = \left(\frac{12.000x}{100}\right) + \left(\frac{1300.3 - 13.003x}{100}\right)$$

$$12.011 \times 100 = 12.000x + 1300.3 - 13.003x$$

$$1201.1 = 1300.3 - 1.003x$$

$$x = \frac{1300.3 - 1201.1}{1.003} = \frac{99.2}{1.003} = 98.9 \quad \text{(to 3 sig. fig.)}$$

The abundances of the isotopes ^{12}C and ^{13}C are 98.9% and 1.1%, respectively.

1.8   The mole and the Avogadro constant

In one mole of substance there are the **Avogadro number**, L, of particles:
$L \approx 6.022 \times 10^{23}\,\text{mol}^{-1}$

In Table 1.1 we saw that the SI unit of 'amount of substance' is the *mole*. This unit can apply to any substance and hence it is usual to find the statement 'a mole of x' where x might be electrons, atoms or molecules. In one mole of substance there are $\approx 6.022 \times 10^{23}$ particles, and this number is called the Avogadro constant or number, L. It is defined as the number of atoms of carbon in exactly 12 g of a sample of isotopically pure $^{12}_{6}\text{C}$. Since L is the number of particles in a mole of substance, its units are mol^{-1}.

| Worked example 1.7 | The mole and the Avogadro constant (1) |

Calculate how many atoms there are in 0.200 moles of copper. ($L = 6.022 \times 10^{23}\,\text{mol}^{-1}$)

The number of atoms in one mole of Cu is equal to the Avogadro constant $= 6.022 \times 10^{23}$.

Number of atoms in 0.200 moles of Cu $= (0.200\,\text{mol}) \times (6.022 \times 10^{23}\,\text{mol}^{-1})$

$= 1.20 \times 10^{23}$ (to 3 sig. fig.)

| Worked example 1.8 | The mole and the Avogadro constant (2) |

Calculate how many molecules of H_2O there are in 12.10 moles of water. ($L = 6.022 \times 10^{23}\,\text{mol}^{-1}$)

The number of molecules in one mole of water is equal to the Avogadro constant $= 6.022 \times 10^{23}$.

Number of molecules in

12.10 moles of water $= (12.10\,\text{mol}) \times (6.022 \times 10^{23}\,\text{mol}^{-1})$

$= 7.287 \times 10^{24}$ (to 4 sig. fig.)

1.9   Gas laws and ideal gases

In this section we summarize some of the important laws that apply to *ideal gases*.

The kinetic theory of gases

The kinetic theory of gases is a model that can explain the observed gas laws in terms of atoms and molecules. In an *ideal gas*, we assume the following (the *postulates of the kinetic theory of gases*):

- the volume occupied by the particles (atoms or molecules) is negligible;
- the particles are in continuous, random motion;

Fig. 1.6 A particle in a cubic box of side l collides with a wall at point A. The collision is elastic and no kinetic energy is lost. After impact the particle rebounds and travels across the box to the opposite wall where another collision occurs, and so on.
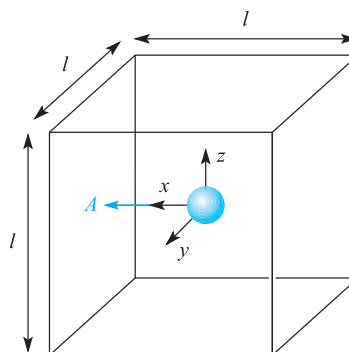
- there are no attractive or repulsive interactions between the particles;
- collisions of the particles with the walls of their container result in the pressure, P, exerted by the gas;
- collisions between particles are elastic and no kinetic energy is lost upon collision;
- the average kinetic energy, E_k, is directly proportional to the temperature of the gas.

By treating the kinetic theory of gases in a quantitative manner, we can derive the ideal gas law.

Consider a gaseous particle of mass m moving in a straight-line path within a closed cubic box of side l. The motion continues until there is an elastic collision with the wall of the container (Figure 1.6). The velocity, v, of the particle can be resolved into three directions coincident with the three Cartesian axes (x, y, z). If the particle is travelling in the x direction, it has a momentum of mv_x (equation 1.7) and on impact, it undergoes a change in momentum (equation 1.8). If the collision is elastic, the new velocity is $-v_x$.

$$\text{Momentum} = \text{mass} \times \text{velocity} \tag{1.7}$$

$$\text{Change in momentum} = (mv_x) - (-mv_x) = 2mv_x \tag{1.8}$$

Every time the particle travels across the container (distance l), a collision occurs (Figure 1.6). The number of collisions per second is given by equation 1.9 and it follows that the change in momentum per second is as shown in equation 1.10.

$$\text{Number of collisions per second} = \frac{\text{Velocity}}{\text{Distance}} = \frac{v_x}{l} \tag{1.9}$$

$$\text{Change in momentum per second} = (2mv_x)\left(\frac{v_x}{l}\right) = \frac{2mv_x^2}{l} \tag{1.10}$$

Our particle also has velocity components in the y and z directions. The velocity of the particle, c, is given by equation 1.11, and the total change in momentum per second for this particle is given by equation 1.12.

$$c^2 = v_x^2 + v_y^2 + v_z^2 \tag{1.11}$$

$$\text{Total change in momentum} = \frac{2mv_x^2}{l} + \frac{2mv_y^2}{l} + \frac{2mv_z^2}{l} = \frac{2mc^2}{l} \tag{1.12}$$

For a particles with velocities c_i, the total change in momentum per second is $\dfrac{2m}{l}\displaystyle\sum_{i=1}^{i=a} c_i^2$.

Defining the root mean square velocity, $\bar{c}$, such that:

$$\bar{c}^2 = \left(\frac{1}{a} \sum_{i=1}^{i=a} c_i^2 \right)$$

leads to the expression for the change in momentum given in equation 1.13.

$$\text{Total change in momentum} = \frac{2ma\bar{c}^2}{l} \tag{1.13}$$

By Newton's Second Law of Motion, the force exerted on the walls of the container by the impact of the particles equals the rate of change of momentum. From the force, we can find the pressure since pressure is force per unit area. The total area is equal to that of the six walls of the container (which is $6l^2$) and, so, the pressure is given by equation 1.14, where V is the volume of the cubic container.

$$\text{Pressure, } P = \frac{\text{Force}}{\text{Area}} = \frac{\left(\frac{2ma\bar{c}^2}{l} \right)}{6l^2} = \frac{2ma\bar{c}^2}{6l^3} = \frac{ma\bar{c}^2}{3V} \tag{1.14}$$

Pressure = Force per unit area

$$P = \frac{F(\text{newton})}{A(\text{m}^2)}$$

Let us now move from considering a particles to a molar scale. For n moles of particles, $a = nL$ where L is the Avogadro number. We can therefore rewrite equation 1.14 in the form of equation 1.15, and we shall return to this equation *obtained from a theoretical model* later in this section.

$$PV = \frac{nLm\bar{c}^2}{3} \tag{1.15}$$

Pressure and Boyle's Law

Pressure (P) is defined as force per unit area (equation 1.16) and the derived SI units of pressure are pascals (Pa) (Table 1.2).

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} \tag{1.16}$$

Although atmospheric pressure is the usual working condition in the laboratory (except when we are specifically working under conditions of reduced or high pressures), a pressure of 1 bar (1.00×10^5 Pa) has been defined by the IUPAC as the *standard pressure*.[§] Of course, this may not be the exact pressure of working, and in that case appropriate corrections must be made as we show below.

When a fixed mass of a gas is compressed (the pressure on the gas is increased) at a constant temperature, the volume (V) of the gas decreases. The pressure and volume are related by Boyle's Law (equation 1.17). From this inverse relationship we see that doubling the pressure halves the volume, and halving the pressure doubles the volume of a gas.

$$\text{Pressure} \propto \frac{1}{\text{Volume}}$$

$$P \propto \frac{1}{V} \qquad \textit{at constant temperature} \tag{1.17}$$

[§] Until 1982, the standard pressure was 1 atmosphere (1 atm $= 101\,325$ Pa) and this pressure remains in use in many textbooks and tables of physical data. The bar is a 'non-standard' unit in the same way that the ångström is defined as 'non-standard'.

Charles's Law

Boyle's Law is obeyed only under conditions of constant temperature because the volume of a gas is dependent on both pressure and temperature. The volume and temperature of a fixed mass of gas are related by Charles's Law (equation 1.18) and the direct relationship shows that (at constant pressure), the volume doubles if the temperature is doubled.

Volume $\propto$ Temperature

$$V \propto T \qquad \textit{at constant pressure} \tag{1.18}$$

A combination of Boyle's and Charles's Laws gives a relationship between the pressure, volume and temperature of a fixed mass of gas (equation 1.19), and this can be rewritten in the form of equation 1.20.

$$P \propto \frac{T}{V} \tag{1.19}$$

$$\frac{PV}{T} = \text{constant} \qquad P = \text{pressure},\ V = \text{volume},\ T = \text{temperature} \tag{1.20}$$

Corrections to a volume of gas from one set of pressure and temperature conditions to another can be done using equation 1.21; each side of the equation is equal to the *same* constant.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \tag{1.21}$$

Worked example 1.9   **Dependence of gas volume on temperature and pressure**

If the volume of a sample of helium is 0.0227 m³ at 273 K and 1.00×10^5 Pa, what is its volume at 293 K and 1.04×10^5 Pa?

The relevant equation is:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

First check that the units are consistent: V in m³, T in K, P in Pa. (In fact, *in this case* inconsistencies in units of P and V would cancel out – why?)

$P_1 = 1.00 \times 10^5 \text{ Pa} \qquad V_1 = 0.0227 \text{ m}^3 \qquad T_1 = 273 \text{ K}$

$P_2 = 1.04 \times 10^5 \text{ Pa} \qquad V_2 = ? \qquad\qquad T_2 = 293 \text{ K}$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{(1.00 \times 10^5 \text{ Pa}) \times (0.0227 \text{ m}^3)}{(273 \text{ K})} = \frac{(1.04 \times 10^5 \text{ Pa}) \times (V_2 \text{ m}^3)}{(293 \text{ K})}$$

$$V_2 = \frac{(1.00 \times 10^5 \text{ Pa}) \times (0.0227 \text{ m}^3) \times (293 \text{ K})}{(273 \text{ K}) \times (1.04 \times 10^5 \text{ Pa})} = 0.0234 \text{ m}^3$$

| Worked example 1.10 | Dependence of gas pressure on volume and temperature |

The pressure of a $0.0239\,m^3$ sample of N_2 gas is 1.02×10^5 Pa. The gas is compressed to a volume of $0.0210\,m^3$ while the temperature remains constant at $293\,K$. What is the new pressure of the gas?

The equation needed for the calculation is:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

but because $T_1 = T_2$, the equation can be simplified to:

$$P_1 V_1 = P_2 V_2$$

The data are as follows:

$$P_1 = 1.02 \times 10^5\,\text{Pa} \qquad V_1 = 0.0239\,\text{m}^3$$
$$P_2 = ? \qquad\qquad\quad V_2 = 0.0210\,\text{m}^3$$

$$(1.02 \times 10^5\,\text{Pa}) \times (0.0239\,\text{m}^3) = (P_2\,\text{Pa}) \times (0.0210\,\text{m}^3)$$

$$P_2 = \frac{(1.02 \times 10^5\,\text{Pa}) \times (0.0239\,\text{m}^3)}{(0.0210\,\text{m}^3)} = 1.16 \times 10^5\,\text{Pa}$$

Check to make sure that the answer is sensible: compression of a gas at constant temperature should lead to an increase in pressure.

Ideal gases

In real situations, we work with 'real' gases, but it is convenient to assume that most gases behave as though they were *ideal*. *If* a gas is ideal, it obeys the *ideal gas law* (equation 1.22) in which the constant in equation 1.20 is the *molar gas constant*, *R*, and the quantity of gas to which the equation applies is 1 mole.

$$\frac{PV}{T} = R = 8.314\,\text{J K}^{-1}\,\text{mol}^{-1} \tag{1.22}$$

For *n* moles of gas, we can rewrite the ideal gas law as equation 1.23.

$$\frac{PV}{T} = nR \quad \text{or} \quad PV = nRT \tag{1.23}$$

The molar gas constant has the same value for *all gases*, whether they are atomic (Ne, He), molecular and elemental (O_2, N_2) or compounds (CO_2, H_2S, NO).

We have already seen that the IUPAC has defined *standard pressure* as 1.00×10^5 Pa (1 bar) and a value of *standard temperature* has been defined as $273.15\,K$. For our purposes, we often use $273\,K$ as the standard temperature.[§] The volume of one mole of an ideal gas under conditions of standard pressure and temperature is $0.0227\,m^3$ or $22.7\,dm^3$ (equation 1.24). We consider the consistency of the units in this equation in worked example 1.11.

[§] The standard temperature of $273\,K$ is *different* from the *standard state temperature* of $298\,K$ used in thermodynamics; see Section 2.2 and Chapter 17.

$$\text{Volume of 1 mole of ideal gas} = \frac{nRT}{P}$$

$$= \frac{1 \times (8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (273\,\text{K})}{(1.00 \times 10^5\,\text{Pa})}$$

$$= 0.0227\,\text{m}^3 \qquad (1.24)$$

From Table 1.2: $\text{Pa} = \text{kg m}^{-1}\,\text{s}^{-2}$

$$\text{J} = \text{kg m}^2\,\text{s}^{-2}$$

and therefore the units work out as follows:

$$\frac{\text{kg m}^2\,\text{s}^{-2}\,\text{K}^{-1}\,\text{mol}^{-1} \times \text{K}}{\text{kg m}^{-1}\,\text{s}^{-2}} = \text{m}^3\,\text{mol}^{-1}$$

> The **molar volume** of an ideal gas under conditions of standard pressure $(1.00 \times 10^5\,\text{Pa})$ and temperature (273 K) is $22.7\,\text{dm}^3$.

You should notice that this volume differs from the $22.4\,\text{dm}^3$ with which you may be familiar! A molar volume of $22.4\,\text{dm}^3$ refers to a standard pressure of 1 atm (101 300 Pa), and $22.7\,\text{dm}^3$ refers to a standard pressure of 1 bar (100 000 Pa).

We now return to equation 1.15, derived from the kinetic theory of gases. By combining equations 1.15 and 1.23, we can write equation 1.25 for one mole.

$$RT = \frac{Lm\bar{c}^2}{3} \qquad (1.25)$$

We can now show the dependence of the kinetic energy of a mole of particles on the temperature. The kinetic energy, E_k, is equal to $\frac{1}{2}m\bar{c}^2$, and if we make this substitution into equation 1.25, we can write equation 1.26.

$$RT = \frac{2}{3}LE_k \qquad \text{or} \qquad E_k = \frac{3}{2}\frac{RT}{L} \qquad (1.26)$$

where E_k refers to one mole and R is the molar gas constant. The gas constant per molecule is given by the Boltzmann constant, $k = 1.381 \times 10^{-23}\,\text{J K}^{-1}$. The molar gas constant and the Boltzmann constant are related by equation 1.27, and hence we can express the kinetic energy per molecule in the form of equation 1.28.

$$\text{Boltzmann constant,}\, k = \frac{R}{L} \qquad (1.27)$$

$$E_k = \tfrac{3}{2}kT \quad \text{where } E_k \text{ refers to 1 molecule} \qquad (1.28)$$

Worked example 1.11   **Finding a derived SI unit**

Determine the SI unit of the molar gas constant, R.

The ideal gas law is:

$$PV = nRT$$

where P = pressure, V = volume, n = number of moles of gas, T = temperature.

$$R = \frac{PV}{nT}$$

The SI unit of $R = \dfrac{(\text{SI unit of pressure}) \times (\text{SI unit of volume})}{(\text{SI unit of quantity}) \times (\text{SI unit of temperature})}$

The SI unit of pressure is Pa but this is a *derived* unit. In base units, $Pa = kg\,m^{-1}\,s^{-2}$ (Tables 1.1 and 1.2):

$$\text{SI unit of } R = \frac{(kg\,m^{-1}\,s^{-2}) \times (m^3)}{(mol) \times (K)}$$

$$= kg\,m^2\,s^{-2}\,mol^{-1}\,K^{-1}$$

While this unit of R is correct in terms of the base SI units, it can be simplified because the joule, J, is defined as $kg\,m^2\,s^{-2}$ (Table 1.2). The SI unit of $R = J\,mol^{-1}\,K^{-1}$ or $J\,K^{-1}\,mol^{-1}$.

Exercise: Look back at equation 1.23 and, by working in SI *base units*, show that a volume in m^3 is consistent with using values of pressure in Pa, temperature in K and R in $J\,K^{-1}\,mol^{-1}$.

Worked example 1.12   Determining the volume of a gas

Calculate the volume occupied by one mole of CO_2 at 300 K and 1 bar pressure. ($R = 8.314\,J\,K^{-1}\,mol^{-1}$)

Assuming that the gas is ideal, the equation to use is:

$$PV = nRT$$

First ensure that the units are consistent – the pressure needs to be in Pa:

$$1\,bar = 1.00 \times 10^5\,Pa$$

To find the volume, we first rearrange the ideal gas equation:

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

$$V = \frac{nRT}{P} = \frac{1 \times (8.314\,J\,K^{-1}\,mol^{-1}) \times (300\,K)}{(1.00 \times 10^5\,Pa)}$$

$$= 0.0249\,m^3 = 24.9\,dm^3$$

The cancellation of units is as in equation 1.24.

NB: You should develop a habit of stopping and thinking whether a numerical answer to a calculation is sensible. Is its magnitude reasonable? In this example, we know that the molar volume of any ideal gas at $1.00 \times 10^5\,Pa$ and 273 K is $22.7\,dm^3$, and we have calculated that at $1.00 \times 10^5\,Pa$ and 300 K, the volume of one mole of gas is $24.9\,dm^3$. This increased volume appears to be consistent with a relatively small rise in temperature.

Gay-Lussac's Law

Gay-Lussac's Law states that when gases react, the volumes of the reactants (and of the products if gases) are in a simple ratio, provided that the volumes are measured under the same conditions of temperature and pressure. Gay-Lussac's observations (made at the end of the 18th century) are consistent with the ideal gas equation (equation 1.23). Since P, T and R are constants when the volume measurements are made, it follows that the volume of a gaseous component in a reaction is proportional to the number of moles present.

Worked example 1.13	Applying Gay-Lussac's Law

At standard temperature and pressure, it was observed that 22.7 dm^3 of N$_2$ reacted with 68.1 dm^3 of H$_2$ to give 45.4 dm^3 of NH$_3$. Confirm that these volumes are consistent with the equation:

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$
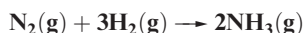
Work out the ratio of the volumes:

N$_2$		H$_2$		NH$_3$
22.7	:	68.1	:	45.4
1	:	3	:	2

This ratio is consistent with the stoichiometry of the equation given.

Dalton's Law of Partial Pressures

In a mixture of gases, the total pressure exerted by the gas on its surroundings is the sum of the *partial pressures* of the component gases. This is Dalton's Law of Partial Pressures and can be expressed as in equation 1.29.

$$P = P_A + P_B + P_C + \cdots \tag{1.29}$$

where P = total pressure, P_A = partial pressure of gas A, etc.

The partial pressure of each gas is directly related to the number of moles of gas present. Equation 1.30 gives the relationship between the partial pressure of a component gas (P_X) and the total pressure P of a gas mixture.

$$\text{Partial pressure of component X} = \frac{\text{Moles of X}}{\text{Total moles of gas}} \times \text{Total pressure} \tag{1.30}$$

One use of partial pressures is in the determination of equilibrium constants for gaseous systems and we look further at this in Chapter 16.

Worked example 1.14	Partial pressures of atmospheric gases

The atmosphere consists of 78.08% dinitrogen, 20.95% dioxygen and 0.93% argon, with other gases present in trace amounts. If atmospheric pressure is 101.3 kPa, what are the partial pressures of N$_2$, O$_2$ and Ar in the atmosphere?

Total pressure, $P_{atm} = 101.3$ kPa

$$P_{atm} = P_{N_2} + P_{O_2} + P_{Ar} + P_{\text{other gases}}$$

Because the other gases are present in trace amounts:

$$P_{atm} \approx P_{N_2} + P_{O_2} + P_{Ar}$$

78.08% of the atmosphere is N$_2$, therefore:

$$P_{N_2} = \frac{(78.08)}{100} \times 101.3 = 79.10 \text{ kPa}$$

BIOLOGY AND MEDICINE

Box 1.4 Diving to depths

The gas laws are of great importance to underwater divers. As a diver descends, the pressure increases. At sea level, a diver experiences atmospheric pressure ($\approx$1 bar). At a depth of 10 m, the hydrostatic pressure is about 2 bar, and when a diver reaches a depth of 40 m, the pressure is 5 bar. Deep-sea divers breathe compressed air. This is composed mainly of N_2 (78%) and O_2 (21%) (see Figure 21.1). Whereas dioxygen is essential for respiration, N_2 is inert with respect to the body's metabolism. As the total pressure increases, the partial pressures of the component gases increase according to Dalton's Law of partial pressures:

$$P_{total} = P_{O_2} + P_{N_2} + \cdots$$

When air is taken into the lungs, it is in close contact with the blood. At atmospheric pressure, the solubility of N_2 in blood is low, but its solubility increases as the pressure increases. This is quantified in Henry's Law, which states that the solubility of a gas is directly proportional to its partial pressure. For a deep-sea diver, the amount of N_2 entering the blood and body tissues increases as the depth of the dive increases. Once a diver begins to ascend from a dive, the partial pressure of N_2 decreases and N_2 that has built up in the bloodstream can escape.

Two medical problems are associated with the accumulation of N_2 in the body during a deep-sea dive. The first is *nitrogen narcosis*. The symptoms of nitrogen narcosis depend on depth and pressure, the onset being at a depth of about 25 m. Depending on the depth, the diver may be affected by an impaired ability to make reasoned decisions, or may suffer from drowsiness and confusion. The effects can be reversed by ascending to regions of lower pressure. The ascent can, however, result in another medical problem: decompression sickness. This is caused by bubbles of N_2. The amount of N_2 escaping as bubbles from body tissue into the bloodstream depends on both the depth of the dive and the length of time that a diver has been exposed to high partial pressures of N_2. Provided that the bubbles are transported in the blood and diffuse back into the lungs, the N_2 can be

A diver in a decompression chamber.

exhaled. However, if large bubbles of N_2 are trapped in the body, the diver begins to suffer from decompression sickness. This can be treated by using a decompression (hyperbaric) chamber. The diver is placed in the chamber and subjected to recompression, i.e. the pressure within the chamber in increased to simulate the deep-sea pressures. This assists the break-up of large N_2 bubbles which are able to enter the bloodstream. Slow decompression then follows and N_2 is released from the body in a controlled manner.

Given the problems associated with humans diving, how do marine mammals manage? For details on how they have evolved to cope with being in an oxygen-free environment and with high hydrostatic pressures, see: G. L. Koopman (2001) in *Encyclopedia of Ocean Sciences,* eds J. Steele, S. Thorpe and K. Turekian, Academic Press, San Diego, p. 1589 – 'Marine mammal diving physiology'.

Similarly:

$$P_{O_2} = \frac{(20.95)}{100} \times 101.3 = 21.22 \, \text{kPa}$$

$$P_{Ar} = \frac{(0.93)}{100} \times 101.3 = 0.94 \, \text{kPa}$$

Check: $P_{N_2} + P_{O_2} + P_{Ar} = 79.10 + 21.22 + 0.94 = 101.26 \, \text{kPa}$

| Worked example 1.15 | Partial pressures |

At 290.0 K and 1.000×10^5 Pa, a $25.00\,\text{dm}^3$ sample of gas contains 0.3500 moles of argon and 0.6100 moles of neon. (a) Are these the only components of the gas mixture? (b) What are the partial pressures of the two gases? ($R = 8.314\,\text{J K}^{-1}\,\text{mol}^{-1}$)

Part (a): The ideal gas law can be used to find the *total* number of moles of gas present:

$$PV = nRT$$

The volume must be converted to m^3: $25.00\,\text{dm}^3 = 25.00 \times 10^{-3}\,\text{m}^3$

$$n = \frac{PV}{RT} = \frac{(1.000 \times 10^5\,\text{Pa}) \times (25.00 \times 10^{-3}\,\text{m}^3)}{(8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (290.0\,\text{K})} = 1.037\,\text{moles}$$

From Table 1.2: $\text{Pa} = \text{kg m}^{-1}\,\text{s}^{-2}$

$$J = \text{kg m}^2\,\text{s}^{-2}$$

Total number of moles of gas $= 1.037$

Moles of argon $+$ moles of neon $= 0.3500 + 0.6100 = 0.9600$

Therefore there are $(1.037 - 0.9600) = 0.077$ moles of one or more other gaseous components in the sample.

Part (b): Now that we know the total moles of gas, we can determine the partial pressures of argon (P_{Ar}) and neon (P_{Ne}):

$$\text{Partial pressure of component X} = \frac{\text{moles of X}}{\text{total moles of gas}} \times \text{total pressure}$$

$$\text{For argon: } P_{\text{Ar}} = \frac{(0.3500\,\text{mol})}{(1.037\,\text{mol})} \times (1.000 \times 10^5\,\text{Pa}) = 33\,750\,\text{Pa}$$

$$\text{For neon: } P_{\text{Ne}} = \frac{(0.6100\,\text{mol})}{(1.037\,\text{mol})} \times (1.000 \times 10^5\,\text{Pa}) = 58\,820\,\text{Pa}$$

Graham's Law of Effusion

Consider the two containers shown in Figure 1.7; they are separated by a wall containing a tiny hole. The pressure of the gas in the left-hand container is higher than that in the right-hand container. If there are no gas molecules at all in the right-hand container, the pressure is zero and the right-hand chamber is said to be *evacuated*. (In practice, the lowest pressures attainable experimentally are of the order of 10^{-8} Pa.) Gas molecules (or atoms if it is a

Fig. 1.7 (a) A gas is contained in a chamber that is separated from another chamber at a lower pressure by a wall in which there is a pinhole. (b) Gas molecules or atoms will move from the region of higher to lower pressure, *effusing* until the pressures of the two containers are equal.
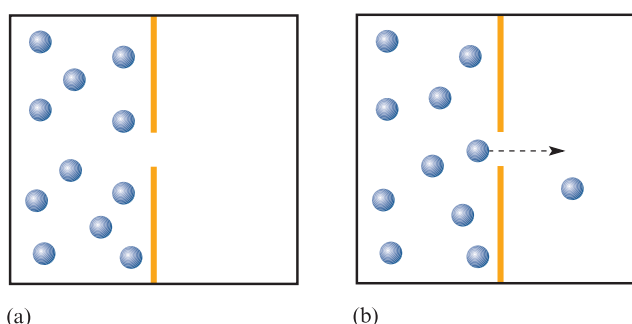

(a)   (b)

Table 1.6 Rates of effusion for a range of gases, determined experimentally in the same piece of apparatus.

Gaseous compound	Molecular formula	Rate of effusion / $cm^3 s^{-1}$
Methane	CH_4	1.36
Neon	Ne	1.22
Dinitrogen	N_2	1.03
Carbon dioxide	CO_2	0.83
Sulfur dioxide	SO_2	0.71
Dichlorine	Cl_2	0.65

monatomic gas such as neon or argon) will pass through the hole from the region of higher pressure to that of lower pressure until the pressures of the gases in each container are equal. This process is called *effusion*.

Graham's Law of Effusion (proven experimentally) is given in equation 1.31 where M_r is the relative molar mass of the gas.

$$\text{Rate of effusion of a gas} \propto \frac{1}{\sqrt{M_r}} \tag{1.31}$$

The law also applies to the process of diffusion, i.e. the rate at which gases, initially held separately from each other, mix (see Figure 1.3). Table 1.6 gives the rates of effusion of several gases; the rates were measured under the same experimental conditions. As an exercise, you should confirm the validity of Graham's Law by plotting a graph of rate of effusion against $1/\sqrt{M_r}$; the plot will be linear.
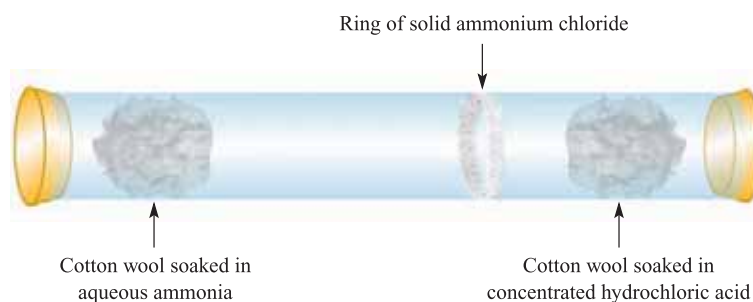
A classic experiment to illustrate Graham's Law is shown in Figure 1.8. Gaseous NH_3 and HCl react to produce ammonium chloride as a fine, white solid (equation 1.32).

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s) \tag{1.32}$$

Values of M_r for NH_3 and HCl are 17.03 and 36.46 respectively, and therefore molecules of HCl diffuse along the tube more slowly than do molecules of NH_3. As a result, NH_4Cl forms at a point that is closer to the end of the tube containing the cotton wool soaked in concentrated hydrochloric acid (Figure 1.8). This result can be quantified as shown in equation 1.33.

$$\frac{\text{Rate of diffusion of } NH_3}{\text{Rate of diffusion of HCl}} = \sqrt{\frac{36.46}{17.03}} = 1.463 \tag{1.33}$$

Fig. 1.8 A glass tube containing two cotton wool plugs soaked in aqueous NH_3 and HCl; the ends of the tube are sealed with stoppers. Solid NH_4Cl is deposited on the inner surface of the glass tube, nearer to the end at which the HCl originates.

Ring of solid ammonium chloride

Cotton wool soaked in aqueous ammonia

Cotton wool soaked in concentrated hydrochloric acid

Worked example 1.16	Applying Graham's Law of Effusion

If V cm^3 of NH$_3$ effuse at a rate of 2.25 cm^3 s^{-1}, and V cm^3 of an unknown gas X effuse at a rate of 1.40 cm^3 s^{-1} under the same experimental conditions, what is M_r for X? Suggest a possible identity for X.

By applying Graham's Law, and using values of A_r from the periodic table facing the inside front cover of this book:

$$\frac{\text{Rate of diffusion of NH}_3}{\text{Rate of diffusion of X}} = \sqrt{\frac{(M_r)_X}{(M_r)_{NH_3}}}$$

$$\frac{2.25}{1.40} = \sqrt{\frac{(M_r)_X}{17.03}}$$

$$(M_r)_X = \left(\frac{(2.25\,\text{cm}^3\,\text{s}^{-1})}{(1.40\,\text{cm}^3\,\text{s}^{-1})}\right)^2 \times 17.03 = 44.0$$

The molar mass of X is therefore 44.0, and possible gases include CO$_2$ and C$_3$H$_8$.

1.10 The periodic table

The arrangement of elements in the periodic table

The elements are arranged in the periodic table (Figure 1.9) in numerical order according to the number of protons possessed by each element. The division into *groups* places elements with the same number of valence electrons into vertical columns within the table. Under IUPAC recommendations, the

Fig. 1.9 The periodic table showing *s*-, *p*- and *d*-block elements and the lanthanoids and actinoids (*f*-block). A complete periodic table with more detailed information is given facing the inside front cover of the book. Strictly, the series of lanthanoid and actinoid metals each consist of 14 elements. However, La (lanthanum) and Ac (actinium) are usually classed with the *f*-block elements.

Table 1.7 IUPAC-recommended names for sections and groups in the periodic table.

Group number	Recommended name
1 (except H)	Alkali metals
2	Alkaline earth metals
15	Pnictogens
16	Chalcogens
17	Halogens
18	Noble gases
1 (except H), 2, 13, 14, 15, 16, 17, 18	Main group elements

groups are labelled from 1 to 18 (Arabic numbers) and blocks of elements are named as in Figure 1.9.

The *d*-block elements are also referred to as the *transition elements*, although the elements zinc, cadmium and mercury (group 12) are not always included. The vertical groups of three *d*-block elements are called *triads*. The names lanthanoid and actinoid are preferred over the names lanthanide and actinide because the ending '-ide' usually implies a negatively charged ion. However, the terms lanthanide and actinide are still in common use. The lanthanoids and actinoids are collectively termed the *f*-block elements. IUPAC-recommended names for some of the groups are given in Table 1.7.

The last row of elements that are coloured purple in Figure 1.9 consists of artificially produced elements: rutherfordium (Rf), dubrium (Db), seaborgium (Sg), bohrium (Bh), hassium (Hs), meitnerium (Mt), darmstadtium (Ds) and roentgenium (Rg). At the beginning of 2009, the number of elements in the periodic table stood at 117. Elements with atomic numbers 112–116 and 118 have been produced artificially in nuclear reactions, but the IUPAC has yet to assign symbols and names to these elements. Element 112 is currently known as ununbium ('one-one-two'), and similarly, elements 113, 114, 115, 116 and 118 are called ununtrium, ununquadium, ununpentium, ununhexium and ununoctium, respectively. This is the usual method of naming newly discovered elements until final names have been approved by the IUPAC.

Valence electrons

It is important to know the positions of elements in the periodic table. A fundamental property of an element is the *ground state valence electron configuration* (discussed further in Chapter 3) and this can usually be determined for any element by considering its position in the periodic table. For example, elements in groups 1 or 2 have one or two electrons in the outer (valence) shell, respectively. After the *d*-block (which contains 10 groups), the number of valence electrons can be calculated by subtracting 10 from the group number. Nitrogen (N) is in group 15 and has five valence electrons; tellurium (Te) is in group 16 and has six valence electrons. Trends in the behaviour of the elements follow periodic patterns (*periodicity*).

Learning the periodic table by heart is not usually necessary, but it is extremely useful to develop a feeling for the groupings of elements. To know that selenium is in the same group as oxygen will immediately tell you that there will be some similarity between the chemistries of these two elements. Care is needed though – there is a significant change in properties on descending a group as we shall discover in Chapters 21 and 22.

Worked example 1.17	Relationship between periodic group number and number of valence electrons

Find the positions of the following elements in the periodic table: N, K, Si, S, F, Al, Mg. For an atom of each element, determine the number of valence electrons.

Use the periodic table in Figure 1.9 to find the group in which each element lies:

Element	N	K	Si	S	F	Al	Mg
Group number	15	1	14	16	17	13	2

For elements in groups 1 and 2:

   Number of valence electrons = Group number

K has one valence electron.
Mg has two valence electrons.
For elements in groups 13 to 18:

   Number of valence electrons = Group number − 10

Si has four valence electrons.
S has six valence electrons.
F has seven valence electrons.
Al has three valence electrons.

1.11   Radicals and ions

Radicals, anions and cations

The presence of one or more unpaired electrons in an atom or molecule imparts upon it the property of a *radical*. A superscript $^{\bullet}$ may be used to signify that a species has an unpaired electron and is a radical. The neutral atom $^{19}_{9}F$, with one unpaired electron, is a radical (Figure 1.10).

The fluorine atom readily accepts one electron (Figure 1.10 and equation 1.34) to give an ion with a *noble gas configuration*.

$$F^{\bullet}(g) + e^{-} \longrightarrow F^{-}(g) \tag{1.34}$$

There is now a charge imbalance between the positive charge of the fluorine nucleus which has nine protons and the negative charge of the 10 electrons. On gaining an electron, the neutral fluorine radical becomes a negatively

Octet rule: see Section 3.20

A *radical* possesses at least one unpaired electron.

Fig. 1.10 The fluorine atom (a radical) becomes a negatively charged fluoride ion when it gains one electron. Only the valence electrons are shown. The fluoride ion has a noble gas configuration.

Gain an electron

Fluorine atom
(radical)

Fluoride ion
(non-radical)
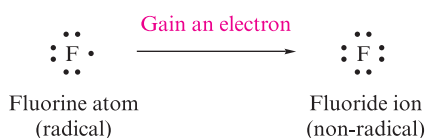
charged *fluoride ion*. The change in name from fluor*ine* to fluor*ide* is significant – the ending '-*ide*' signifies the presence of a negatively charged species. A negatively charged ion is called an *anion*.

The loss of one electron from a neutral atom generates a positively charged ion – a *cation*. A sodium atom may lose an electron to give a sodium cation (equation 1.35) and the positive charge arises from the imbalance between the number of protons in the nucleus and the electrons.

$$\text{Na}^{\bullet}(g) \longrightarrow \text{Na}^+(g) + e^- \tag{1.35}$$

Although in equations 1.34 and 1.35 we have been careful to indicate that the neutral atom is a radical, it is usually the case that *atoms* of an element are written without specific reference to the radical property. For example, equation 1.36 means exactly the same as equation 1.35.

$$\text{Na}(g) \longrightarrow \text{Na}^+(g) + e^- \tag{1.36}$$
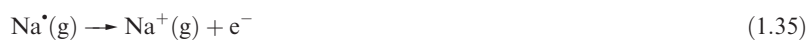
> An *anion* is a negatively charged ion, and a *cation* is a positively charged ion.

Elements with fewer than four valence electrons *tend to lose electrons and form cations with a noble gas configuration*, for example:

- Na forms Na^+ which has the same electronic configuration as Ne;
- Mg forms Mg^{2+} which has the same electronic configuration as Ne;
- Al forms Al^{3+} which has the same electronic configuration as Ne.

Elements with more than four valence electrons *tend to gain electrons and form anions with a noble gas configuration*, for example:

- N forms N^{3-} which has the same electronic configuration as Ne;
- O forms O^{2-} which has the same electronic configuration as Ne;
- F forms F^- which has the same electronic configuration as Ne.

The terms *dication*, *dianion*, *trication* and *trianion*, etc. are used to indicate that an ion carries a specific charge. A dication carries a 2+ charge (e.g. Mg^{2+}, Co^{2+}), a dianion has a 2− charge (e.g. O^{2-}, Se^{2-}), a trication bears a 3+ charge (e.g. Al^{3+}, Fe^{3+}) and a trianion has a 3− charge (e.g. N^{3-}, $[\text{PO}_4]^{3-}$).

As we discuss in the next section, ion formation is not the only option for an atom. Electrons may be shared rather than completely gained or lost. For example, in the chemistry of nitrogen and phosphorus, the gain of three electrons by an N or P atom to form N^{3-} or P^{3-} is not as common as the sharing of three electrons to form *covalent compounds*.

Worked example 1.18	Ion formation

With reference to the periodic table (Figure 1.9), predict the most likely ions to be formed by the following elements: Na, Ca, Br.

Firstly, find the position of each element in the periodic table. Elements with fewer than four valence electrons will tend to *lose* electrons, and elements with more than four valence electrons will tend to *gain* electrons so as to form a noble gas configuration.

Na is in group 1.
Na has one valence electron.
Na will easily lose one electron to form an [Ne] configuration.
Na will form an Na^+ ion.

Ca is in group 2.
Ca has two valence electrons.
Ca will lose two electrons to form an [Ar] configuration.
Ca will form a Ca^{2+} ion.

Br is in group 17.
Br has seven valence electrons.
Br will tend to gain one electron to give a [Kr] configuration.
Br will form a Br^- ion.

1.12 Molecules and compounds: bond formation

Covalent bond formation

A *molecule* is a discrete
neutral species containing a
covalent bond or bonds
between two or more
atoms.

A *molecule* is a discrete neutral species resulting from *covalent* bond formation between two or more atoms.

When two radicals combine, *pairing of the two electrons* may result in the formation of a covalent bond, and the species produced is molecular. Equation 1.37 shows the formation of molecular dihydrogen from two hydrogen atoms (i.e. radicals).

$$2H^{\bullet} \longrightarrow H_2 \qquad\qquad (1.37)$$

Homonuclear and heteronuclear molecules

The molecule H_2 is a *homonuclear diatomic* molecule. *Diatomic* refers to the fact that H_2 consists of two atoms, and *homonuclear* indicates that the molecule consists of identical atoms. Molecular hydrogen, H_2, should be referred to as *dihydrogen* to distinguish it from atomic hydrogen, H. Other homonuclear molecules include dioxygen (O_2), dinitrogen (N_2), difluorine (F_2), trioxygen (O_3) and octasulfur (S_8).

**Homonuclear diatomics:
see Chapter 4**

A *heteronuclear* molecule consists of more than one type of element. Carbon monoxide, CO, is a *heteronuclear diatomic* molecule. When a molecule contains three or more atoms, it is called a *polyatomic* molecule; carbon dioxide, CO_2, methane, CH_4, and ethanol, C_2H_5OH, are polyatomic, although CO_2 may also be called a *triatomic* molecule:

O$_3$ S$_8$ CO$_2$ C$_2$H$_5$OH
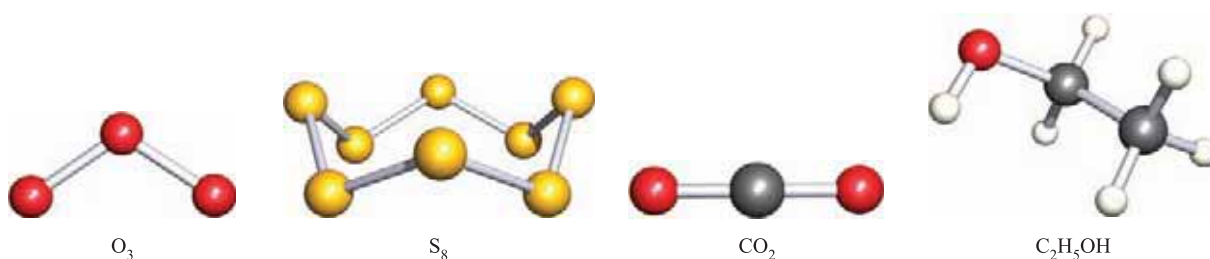
Covalent versus ionic bonding

The important difference between covalent and ionic bonding is the average distribution of the bonding electrons between the nuclei. The electrons that form a covalent bond are 'shared' *between* nuclei. This is represented in

(a)   (b)
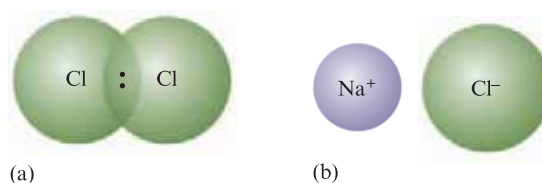
In a *covalent bond*, electrons are shared between atoms. When the transfer of one or more electrons from one atom to another occurs, *ions* are formed.
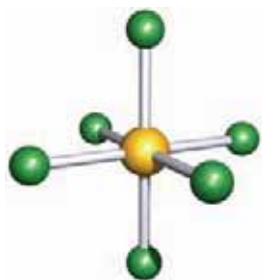
(1.2)

Figure 1.11a for the Cl_2 molecule which contains a Cl–Cl single bond. Since the two atoms are identical, the two bonding electrons are located symmetrically between the two chlorine nuclei.

The complete transfer of the bonding pair of electrons to one of the nuclei results in the formation of *ions*. Figure 1.11b schematically shows the situation for a single pair of ions in a sodium chloride lattice; there is a region between the ions in which the electron density approaches zero. Although Figure 1.11b shows an isolated pair of Na^+ and Cl^- ions, this is not a real situation for solid sodium chloride. Positive and negative ions attract one another and the net result is the formation of a 3-dimensional *ionic lattice*.

Molecules and compounds

We must make a careful distinction between the use of the terms *molecule* and *compound*. Compounds are *neutral* and include both covalent and ionic species – NaF (composed of Na^+ and F^- ions), CO (a covalent diatomic molecule) and SF_6 (**1.2**, a covalent polyatomic molecule) are all compounds. Since a molecule is a *discrete neutral species*, of these three compounds, only CO and SF_6 are molecules.

1.13 Molecules and compounds: relative molecular mass and moles

Relative molecular mass

M_r is also referred to as the molecular weight of a compound

The relative molecular mass (M_r) of a compound is found by summing the relative atomic masses of the constituent atoms. For example, a mole of carbon monoxide CO has a relative molecular mass of 28.01 (since the relative atomic masses of C and O are 12.01 and 16.00), and M_r for carbon dioxide CO_2 is 44.01.

Moles of compound

The relative molecular mass gives the mass (in g) of *one mole of a compound* and equation 1.38 gives the relationship between the mass (in g) and the number of moles.

$$\text{Amount in moles} = \frac{(\text{Mass in g})}{(M_r \text{ in g mol}^{-1})} \tag{1.38}$$

You should note that the dimensions for M_r in equation 1.38 are not strictly correct. Here, and throughout the book, we implicitly multiply by a standard state M^o of $1\,g\,mol^{-1}$ to adjust M_r to a quantity with units of $g\,mol^{-1}$. We do not distinguish further between M_r and $(M_r \times M^o)$; the usage will be clear, e.g. if we write '$M_r\ (g\,mol^{-1})$' then we really refer to $(M_r \times M^o)$.

The *molar mass*, M_r, is the mass in grams that contains 6.022×10^{23} particles and has units of $g\,mol^{-1}$.

Worked example 1.19   Relative molecular mass and moles

How many moles of molecules are present in 3.48 g of acetone, CH_3COCH_3?

First, write down the formula of acetone: C_3H_6O.

$$M_r = (3 \times 12.01) + (1 \times 16.00) + (6 \times 1.008) = 58.08$$

$$\text{Amount in moles} = \frac{(\text{Mass g})}{(M_r\,g\,mol^{-1})} = \frac{(3.48\,g)}{(58.08\,g\,mol^{-1})} = 0.0599\,\text{moles}$$

Note that in the first line of the calculation, the answer is rounded to two decimal places, but in the second line, it is rounded to three significant figures. For further help with decimal places and significant figures, see the accompanying *Mathematics Tutor* (www.pearsoned.co.uk/housecroft).

1.14 Concentrations of solutions

Molarity and molality

A solution of volume $1\,dm^3$ containing one mole of solute is called a one molar (1 M) solution.

Reactions in the laboratory are often carried out in solution, and the *concentration* of the solution tells us how much of a compound or ion is present in a given solution. Two common methods are used for describing the concentration of a solution. The first is to give the amount (in moles) of dissolved substance (the *solute*) per unit volume of solution. The *molarity* of a solution is the amount (in moles) of solute per dm^3 of solution and has units of $mol\,dm^{-3}$.

A solution made up of $1\,kg$ of solvent in which one mole of solute is dissolved is called a one molal (1 m) solution.

The second method is to give the amount (in moles) of dissolved substance per mass of *solvent* (not solution). The *molality* of a solution is the amount (in moles) of solute per kg of solvent and has units of $mol\,kg^{-1}$.

Although we will usually use molarities in this book, in practice, molality has the significant advantage of being independent of temperature.

Concentrations and amount of solute

In practice, we do not always work with one molar (1 M) solutions, and the moles of solute in a given solution can be found using equation 1.39 or, if the volume is in cm^3 as is often the case in the laboratory, a conversion from cm^3 to dm^3 must be made (equation 1.40).

$$\text{Amount in moles} = (\text{Volume in dm}^3) \times (\text{Concentration in mol\,dm}^{-3}) \quad (1.39)$$

$$x\,cm^3 = \left(\frac{x}{1000}\right) dm^3 \quad \text{or} \quad x\,cm^3 = (x \times 10^{-3})\,dm^3 \quad (1.40)$$

Worked example 1.20	Solution concentrations

If 1.17 g of sodium chloride (NaCl) is dissolved in water and made up to $100\,cm^3$ of aqueous solution, what is the concentration of the solution?

First, we need to find the number of moles of NaCl in 1.17 g:

$$M_r = 22.99 + 35.45 = 58.44\,g\,mol^{-1}$$

$$\text{Amount of NaCl} = \frac{1.17\,g}{58.44\,g\,mol^{-1}} = 0.0200\,\text{moles (to 3 sig. fig.)}$$

Next, we must ensure that the units for the next part of the calculation are consistent. The volume is given as $100\,cm^3$ and this must be converted to dm^3 so that the units of concentration are in $mol\,dm^{-3}$.

$$100\,cm^3 = \frac{100}{1000}\,dm^3 = 0.1\,dm^3$$

$$\text{Concentration in }mol\,dm^{-3} = \frac{\text{Amount in moles}}{\text{Volume in }dm^3}$$

$$= \frac{0.0200\,mol}{0.1\,dm^3}$$

$$= 0.200\,mol\,dm^{-3} \quad \text{(to 3 sig. fig.)}$$

Worked example 1.21	Solution concentrations

What mass of potassium iodide (KI) must be dissolved in water and made up to $50.0\,cm^3$ to give a solution of concentration 0.0500 M?

First, find the amount of KI in $50.0\,cm^3$ $0.0500\,mol\,dm^{-3}$ solution:

Units conversion for the volume: $50.0\,cm^3 = 50.0 \times 10^{-3}\,dm^3$

$$\text{Amount in moles} = (\text{Volume in }dm^3) \times (\text{Concentration in }mol\,dm^{-3})$$

$$\text{Amount of KI} = (50.0 \times 10^{-3}\,dm^3) \times (0.0500\,mol\,dm^{-3})$$

$$= 2.50 \times 10^{-3}\,mol \quad \text{(to 3 sig. fig.)}$$

Now convert moles to mass:

$$\text{Amount in moles} = \frac{\text{Mass in g}}{M_r\text{ in }g\,mol^{-1}}$$

or

$$\text{Mass in g} = (\text{Amount in moles}) \times (M_r\text{ in }g\,mol^{-1})$$

For KI, $M_r = 39.10 + 126.90 = 166.00$

$$\text{Mass of KI} = (2.50 \times 10^{-3}\,mol) \times (166.00\,g\,mol^{-1}) = 0.415\,g \quad \text{(to 3 sig. fig.)}$$

Worked example 1.22	Dilution of a solution

The concentration of an aqueous solution of sodium hydroxide, NaOH, is $0.500\,mol\,dm^{-3}$. What volume of this solution must be added to $250\,cm^3$ of water to give a solution of concentration $0.0200\,mol\,dm^{-3}$?

Let the volume to be added $= x\,\text{cm}^3 = x \times 10^{-3}\,\text{dm}^3$

Moles of NaOH in $x\,\text{cm}^3$ of $0.500\,\text{mol}\,\text{dm}^{-3}$ solution

$$= (x \times 10^{-3}\,\text{dm}^3) \times (0.500\,\text{mol}\,\text{dm}^{-3})$$

$$= 0.500x \times 10^{-3}\,\text{mol}$$

$0.500x \times 10^{-3}$ moles of NaOH are added to $250\,\text{cm}^3$ water, and the new volume of the solution is $(250 + x)\,\text{cm}^3$.

Unit conversion: $(250 + x)\,\text{cm}^3 = (250 + x) \times 10^{-3}\,\text{dm}^3$

Concentration of the new solution $= 0.0200\,\text{mol}\,\text{dm}^{-3}$

Amount in moles $= (\text{Volume in dm}^3) \times (\text{Concentration in mol}\,\text{dm}^{-3})$

$0.500x \times 10^{-3}\,\text{mol} = \{(250 + x) \times 10^{-3}\,\text{dm}^3\} \times (0.0200\,\text{mol}\,\text{dm}^{-3})$

Solving for x:

$$0.500x \times 10^{-3} = \{(250 \times 0.0200) + 0.0200x\} \times 10^{-3}$$

$$0.500x = (250 \times 0.0200) + 0.0200x$$

$$(0.500 - 0.0200)x = (250 \times 0.0200)$$

$$x = \frac{(250 \times 0.0200)}{(0.500 - 0.0200)}$$

$$= \frac{5.00}{0.480} = 10.4 \quad (\text{to 3 sig. fig.})$$

Therefore the volume to be added is $10.4\,\text{cm}^3$.

An ***aliquot*** is a measured fraction of a larger sample, usually a fluid.

In a calculation of this type, it is important not to forget that the addition of an aqueous sample (an *aliquot*) to a larger amount of solution causes the volume of the solution to increase. Ignoring this factor introduces an error into the calculation; the significance of the error depends on the relative magnitudes of the two volumes.

Worked example 1.23   Making up a solution to a given volume

A stock solution of potassium hydroxide, KOH, is 1.00 M. An $x\,\text{cm}^3$ aliquot of this solution is added to approximately $200\,\text{cm}^3$ of water in a volumetric flask and the volume of the solution is made up with water to $250\,\text{cm}^3$. What is the value of x if the concentration of the final solution is $0.0500\,\text{mol}\,\text{dm}^{-3}$?

Unit conversion for the volumes:

$$x\,\text{cm}^3 = x \times 10^{-3}\,\text{dm}^3$$

$$250\,\text{cm}^3 = 250 \times 10^{-3}\,\text{dm}^3$$

In the aliquot, amount of KOH

$$= (\text{Volume in dm}^3) \times (\text{Concentration in mol}\,\text{dm}^{-3})$$

$$= (x \times 10^{-3}\,\text{dm}^3) \times (1.00\,\text{mol}\,\text{dm}^{-3})$$

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

In $250\,\text{cm}^3$ of the final $0.0500\,\text{mol}\,\text{dm}^{-3}$ solution there are $x \times 10^{-3}$ moles of KOH.

$$x \times 10^{-3}\,\text{mol} = (250 \times 10^{-3}\,\text{dm}^3) \times (0.0500\,\text{mol}\,\text{dm}^{-3})$$

$$x = 250 \times 0.0500 = 12.5 \quad \text{(to 3 sig. fig.)}$$

Therefore the aliquot needed is of volume $12.5\,\text{cm}^3$.

1.15 Reaction stoichiometry

When we write a balanced or *stoichiometric* equation, we state the ratio in which the reactants combine and the corresponding ratios of products. In reaction 1.41, one molecule of pentane reacts with eight molecules of dioxygen to give five molecules of carbon dioxide and six molecules of water. This also corresponds to the ratio of *moles* of reactants and products.

$$C_5H_{12}(g) + 8O_2(g) \longrightarrow 5CO_2(g) + 6H_2O(l) \tag{1.41}$$
Pentane
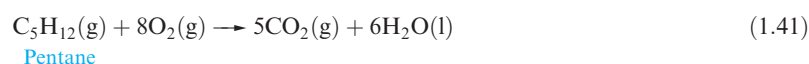
A ***balanced*** or ***stoichiometric*** equation for a chemical reaction shows the molecular or the molar ratio in which the reactants combine and in which the products form.

Worked example 1.24   **Amounts of reactants for complete reaction**

Zinc reacts with hydrochloric acid according to the equation:

$$\mathbf{Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)}$$

What mass of zinc is required to react completely with $30.0\,\text{cm}^3$ $1.00\,\text{M}$ hydrochloric acid?

This is the reaction of a metal with acid to give a salt and H_2. First write the stoichiometric equation:

$$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

Now find the amount (in moles) of HCl in the solution:

Unit conversion for the volume: $30.0\,\text{cm}^3 = 30.0 \times 10^{-3}\,\text{dm}^3$

Amount in moles $= (\text{Volume in dm}^3) \times (\text{Concentration in mol}\,\text{dm}^{-3})$

Amount of HCl $= (30.0 \times 10^{-3}\,\text{dm}^3) \times (1.00\,\text{mol}\,\text{dm}^{-3})$

$$= 3.00 \times 10^{-2}\,\text{mol}$$

Now look at the balanced equation. Two moles of HCl react with one mole of Zn, and therefore 3.00×10^{-2} moles of HCl react with 1.50×10^{-2} moles of Zn.

We can now determine the mass of zinc needed:

$$\text{Mass of Zn} = (\text{Amount in mol}) \times (A_r \text{ in g mol}^{-1})$$
$$= (1.50 \times 10^{-2} \text{ mol}) \times (65.41 \text{ g mol}^{-1})$$
$$= 0.981 \text{ g} \quad \text{(to 3 sig. fig.)}$$

We use A_r in the equation because we are dealing with atoms of an element.

Worked example 1.25   Amount of products formed

Carbon burns completely in dioxygen according to the equation:

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$
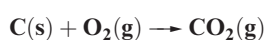
What volume of CO_2 can be formed under conditions of standard temperature and pressure when 0.300 g of carbon is burnt? (Volume of one mole of gas at 1.00×10^5 Pa and 273 K $= 22.7$ dm^3)

First, write the balanced equation:

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$
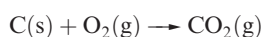
One mole of carbon atoms gives one mole of CO_2 (assuming complete combustion).
Determine the amount (in moles) of carbon:

$$\text{Amount of carbon} = \frac{\text{Mass}}{A_r} = \frac{0.300 \text{ g}}{12.01 \text{ g mol}^{-1}} = 0.0250 \text{ moles}$$

At standard temperature (273 K) and pressure (1.00×10^5 Pa), one mole of CO_2 occupies 22.7 dm^3.

$$\text{Volume occupied by 0.0250 moles of CO}_2 = (0.0250 \text{ mol}) \times (22.7 \text{ dm}^3 \text{ mol}^{-1})$$
$$= 0.568 \text{ dm}^3 \quad \text{(to 3 sig. fig.)}$$

Worked example 1.26   Amount of precipitate formed

When aqueous solutions of silver nitrate and sodium iodide react, solid silver iodide is formed according to the equation:

$$AgNO_3(aq) + NaI(aq) \longrightarrow AgI(s) + NaNO_3(aq)$$
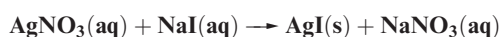
If 50.0 cm^3 0.200 mol dm^{-3} of aqueous $AgNO_3$ is added to 25 cm^3 0.400 mol dm^{-3} of aqueous NaI, what mass of AgI is formed?

The stoichiometric equation:

$$AgNO_3(aq) + NaI(aq) \longrightarrow AgI(s) + NaNO_3(aq)$$
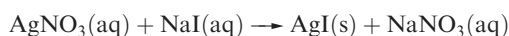
shows that $AgNO_3$ and NaI react in a 1:1 molar ratio.

Unit conversion for volumes: for $AgNO_3$, 50.0 cm$^3 = 50.0 \times 10^{-3}$ dm^3

for NaI, 25.0 cm$^3 = 25.0 \times 10^{-3}$ dm^3

The amount of $AgNO_3$ = (Volume in dm^3) × (Concentration in $mol\,dm^{-3}$)

$$= (50.0 \times 10^{-3}\,dm^3) \times (0.200\,mol\,dm^{-3})$$

$$= 0.0100\,mol \quad \text{(to 3 sig. fig.)}$$

The amount of NaI = (Volume in dm^3) × (Concentration in $mol\,dm^{-3}$)

$$= (25.0 \times 10^{-3}\,dm^3) \times (0.400\,mol\,dm^{-3})$$

$$= 0.0100\,mol \quad \text{(to 3 sig. fig.)}$$

From the stoichiometric equation, 0.0100 moles of $AgNO_3$ react completely with 0.0100 moles of NaI to give 0.0100 moles of solid AgI. For the mass of AgI, we need to find M_r.

M_r for $AgI = 107.87 + 126.90 = 234.77$

Mass of AgI = (Amount in mol) × (M_r in $g\,mol^{-1}$)

$$= (0.0100\,mol) \times (234.77\,g\,mol^{-1})$$

$$= 2.35\,g \quad \text{(to 3 sig. fig.)}$$

> ▶ A_r **values are given inside the front cover of the book**

Worked example 1.27   Excess reagents

The reaction of aqueous hydrochloric acid and potassium hydroxide takes place according to the equation:

$$HCl(aq) + KOH(aq) \longrightarrow KCl(aq) + H_2O(l)$$
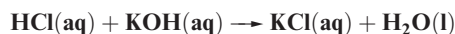
$25.0\,cm^3$ $0.0500\,mol\,dm^{-3}$ aqueous HCl is added to $30\,cm^3$ $0.0400\,mol\,dm^{-3}$ aqueous KOH. The reaction goes to completion. Which reagent was in excess? How many moles of this reagent are left at the end of the reaction?

From the stoichiometric equation:

$$HCl(aq) + KOH(aq) \longrightarrow KCl(aq) + H_2O(l)$$
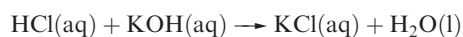
we see that HCl reacts with KOH in a molar ratio $1:1$.

Unit conversion for volumes: for HCl, $25.0\,cm^3 = 25.0 \times 10^{-3}\,dm^3$

for KOH, $30.0\,cm^3 = 30.0 \times 10^{-3}\,dm^3$

Amount of HCl = (Volume in dm^3) × (Concentration in $mol\,dm^{-3}$)

$$= (25.0 \times 10^{-3}\,dm^3) \times (0.0500\,mol\,dm^{-3})$$

$$= 1.25 \times 10^{-3}\,mol \quad \text{(to 3 sig. fig.)}$$

Amount of KOH = (Volume in dm^3) × (Concentration in $mol\,dm^{-3}$)

$$= (30.0 \times 10^{-3}\,dm^3) \times (0.0400\,mol\,dm^{-3})$$

$$= 1.20 \times 10^{-3}\,mol \quad \text{(to 3 sig. fig.)}$$

Since there are more moles of HCl in solution than KOH, the HCl is in excess.

Excess of HCl $= (1.25 \times 10^{-3}) - (1.20 \times 10^{-3}) = 0.05 \times 10^{-3}$ moles

Balancing equations

In this section, we provide practice in balancing equations. In any *balanced* equation, the number of moles of an element (alone or in a compound) must be the same on the left- and right-hand sides of the equation. An equation such as:

$$HCl + Zn \longrightarrow ZnCl_2 + H_2$$

is unbalanced. By inspection, we can see that two HCl are required on the left-hand side to give the correct number of H and Cl atoms for product formation on the right-hand side, i.e.:

$$2HCl + Zn \longrightarrow ZnCl_2 + H_2$$

If you know the reactants and products of a reaction, you can write an unbalanced equation. However, such an equation is not chemically meaningful until it is balanced. When balancing an equation, it is very important to remember that you must not alter the chemical formulae of the compounds. *The only change that can be made is the addition of coefficients in front of the compound formulae*.

Worked example 1.28   **Equation for the combustion of propane**

Balance the following equation for the complete combustion of propane:

$$C_3H_8 + O_2 \longrightarrow CO_2 + H_2O$$

It is probably best to start with the fact that there are three C atoms and eight H atoms on the left-hand side. Therefore, one mole of propane must produce three moles of CO_2 and four moles of H_2O:

$$C_3H_8 + O_2 \longrightarrow 3CO_2 + 4H_2O$$
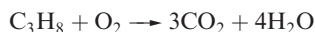
This leaves the O atoms unbalanced. On the right-hand side we have 10 O atoms, and therefore we need five O_2 on the left-hand side. This gives:

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

Give this a final check through:

Left-hand side:	3 C	8 H	10 O
Right-hand side:	3 C	8 H	10 O

Worked example 1.29   **The reaction of Zn with mineral acids**

Zinc reacts with HNO_3 and H_2SO_4 to give metal salts. Balance each of the following equations:

$$Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + H_2$$
$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

For the reaction:

$$Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + H_2$$
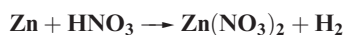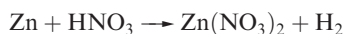
the product $Zn(NO_3)_2$ contains two NO_3 groups per Zn. Therefore, the ratio of $Zn : HNO_3$ on the left-hand side must be $1 : 2$. Thus, the initial

equation can be rewritten as follows:

$$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + H_2$$

This balances the Zn, N and O atoms on each side of the equation. Now check the numbers of H atoms on the left and right sides of the equation: these are equal and therefore the equation is balanced. Final check:

Left-hand side:	1 Zn	2 H	2 N	6 O
Right-hand side:	1 Zn	2 H	2 N	6 O

For the reaction:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

the product $ZnSO_4$ contains one SO_4 group per Zn. Therefore, the ratio of $Zn : H_2SO_4$ on the left-hand side is $1 : 1$:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$
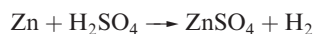
Now check to see if the H atoms on the left and right sides of the equation are equal; there are two H atoms on each side of the equation, and therefore the equation is balanced. Final check:

Left-hand side:	1 Zn	2 H	1 S	4 O
Right-hand side:	1 Zn	2 H	1 S	4 O

Worked example 1.30   Reactions between acids and bases

A reaction of the general type:

$$\textbf{Acid} + \textbf{Base} \longrightarrow \textbf{Salt} + \textbf{Water}$$

is a *neutralization reaction*. Balance each of the following equations for neutralization reactions:

$$\textbf{H}_2\textbf{SO}_4 + \textbf{KOH} \longrightarrow \textbf{K}_2\textbf{SO}_4 + \textbf{H}_2\textbf{O}$$

$$\textbf{HNO}_3 + \textbf{Al(OH)}_3 \longrightarrow \textbf{Al(NO}_3)_3 + \textbf{H}_2\textbf{O}$$

For the reaction:

$$H_2SO_4 + KOH \longrightarrow K_2SO_4 + H_2O$$
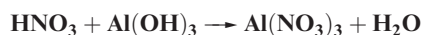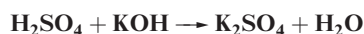
the product K_2SO_4 contains two K per SO_4 group. Therefore, the ratio of $KOH : H_2SO_4$ on the left-hand side must be $2 : 1$. The initial equation can be rewritten as follows:

$$H_2SO_4 + 2KOH \longrightarrow K_2SO_4 + H_2O$$
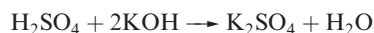
Now look at the formation of H_2O. On the left-hand side there are two H (in H_2SO_4) and two OH (in 2KOH) and these combine to give two H_2O. The balanced equation is:
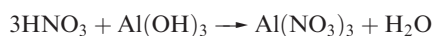
$$H_2SO_4 + 2KOH \longrightarrow K_2SO_4 + 2H_2O$$

Final check:

Left-hand side:	1 S	2 K	4 H	6 O
Right-hand side:	1 S	2 K	4 H	6 O

For the reaction:

$$HNO_3 + Al(OH)_3 \longrightarrow Al(NO_3)_3 + H_2O$$
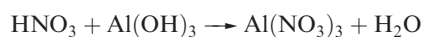
the product $Al(NO_3)_3$ contains three NO_3 groups per Al. Therefore, the ratio of $HNO_3 : Al(OH)_3$ on the left-hand side of the equation must be $3 : 1$:

$$3HNO_3 + Al(OH)_3 \longrightarrow Al(NO_3)_3 + H_2O$$

Finally look at the formation of H_2O. On the left-hand side there are three H (in $3HNO_3$) and three OH (in $Al(OH)_3$) and these combine to give three H_2O. The balanced equation is:

$$3HNO_3 + Al(OH)_3 \longrightarrow Al(NO_3)_3 + 3H_2O$$
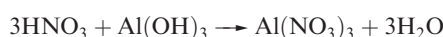
Final check:

Left-hand side:	3 N	1 Al	6 H	12 O
Right-hand side:	3 N	1 Al	6 H	12 O

A *precipitation reaction* is one in which a *sparingly soluble salt* (see Section 17.11) forms from a reaction that occurs in solution. The sparingly soluble salt comes out of solution as a *solid precipitate*.

When aqueous solutions of $AgNO_3$ and NaBr are mixed, a pale yellow *precipitate* of AgBr forms. The reaction is:

$$AgNO_3(aq) + NaBr(aq) \longrightarrow AgBr(s) + NaNO_3(aq)$$
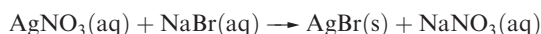
The precipitation reaction could also be represented by the equation:

$$Ag^+(aq) + Br^-(aq) \longrightarrow AgBr(s)$$
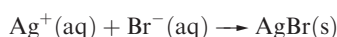
Here, the ions that remain in solution and are not involved in the formation of the precipitate are ignored; these ions are called *spectator ions*. When balancing an equation such as the one above, you must make sure that:

- the numbers of atoms of each element on the left- and right-hand sides of the equation balance, *and*
- the positive and negative charges balance.

Consider the following equation for the formation of PbI_2:

$$Pb^{2+}(aq) + 2I^-(aq) \longrightarrow PbI_2(s)$$
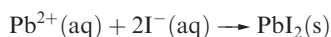
First check the numbers of atoms:

Left-hand side:	1 Pb	2 I
Right-hand side:	1 Pb	2 I

Now check the charges:
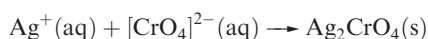
Left-hand side:	overall charge $= +2 - 2 = 0$
Right-hand side:	no charge

In the next three worked examples, we look at other examples of reactions involving ions.

Worked example 1.31   **The precipitation of silver chromate**

Aqueous Ag^+ ions react with $[CrO_4]^{2-}$ ions to give a red precipitate of Ag_2CrO_4. Write a balanced equation for the precipitation reaction.

First write down an equation that shows the reactants and product:

$$Ag^+(aq) + [CrO_4]^{2-}(aq) \longrightarrow Ag_2CrO_4(s)$$

Since the product contains two Ag, there must be two Ag^+ on the left-hand side:

$$2Ag^+(aq) + [CrO_4]^{2-}(aq) \longrightarrow Ag_2CrO_4(s)$$
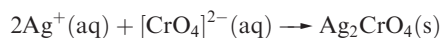
This equation is now balanced in terms of the numbers of Ag, Cr and O atoms on each side. Check that the charges balance:

Left-hand side: overall charge $= +2 - 2 = 0$

Right-hand side: no charge

Therefore, the equation is balanced.

Worked example 1.32   **The reaction of Zn with Ag⁺**

Zn reacts with Ag^+ to give solid silver:

$$Zn(s) + Ag^+(aq) \longrightarrow Zn^{2+}(aq) + Ag(s)$$

Balance this equation.

In terms of the number of Ag and Zn atoms on the left- and right-hand sides of the equation, the equation is already balanced, *but the charges do not balance*:

Left-hand side: overall charge $= +1$

Right-hand side: overall charge $= +2$

We can balance the charges by having two Ag^+ on the right-hand side:

$$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + Ag(s)$$
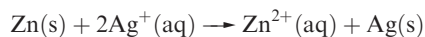
But, now there are two Ag on the left-hand side and only one Ag on the right-hand side. The final, balanced equation is therefore:

$$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$$

Worked example 1.33   **The reaction of Fe²⁺ and [MnO₄]⁻ ions in acidic aqueous solution**

Balance the following equation:

$$Fe^{2+} + [MnO_4]^- + H^+ \longrightarrow Fe^{3+} + Mn^{2+} + H_2O$$
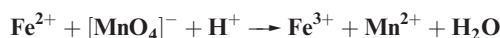
The best place to start is with the O atoms: there are four O atoms in $[MnO_4]^-$ on the left-hand side, but only one O on the right-hand side. Therefore, to balance the O atoms, we need four H_2O on the right-hand side:

$$Fe^{2+} + [MnO_4]^- + H^+ \longrightarrow Fe^{3+} + Mn^{2+} + 4H_2O$$

This change means that there are now eight H on the right-hand side, but only one H on the left-hand side. Therefore, to balance the H atoms, we need eight H^+ on the left-hand side:

$$Fe^{2+} + [MnO_4]^- + 8H^+ \longrightarrow Fe^{3+} + Mn^{2+} + 4H_2O$$
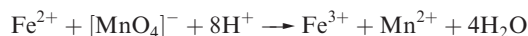
In terms of the *atoms*, the equation looks balanced, but if you check the *charges*, you find that the equation is not balanced:

Overall charge on left-hand side: $+2 - 1 + 8 = +9$

Overall charge on right-hand side: $+3 + 2 = +5$

The charges can be balanced without upsetting the balancing of the atoms if we have n Fe^{2+} on the left-hand side and n Fe^{3+} on the right-hand side, where n can be found as follows:

$$n Fe^{2+} + [MnO_4]^- + 8H^+ \longrightarrow n Fe^{3+} + Mn^{2+} + 4H_2O$$

Overall charge on left-hand side: $+2n - 1 + 8 = 2n + 7$

Overall charge on right-hand side: $+3n + 2$

The charges on each side of the equation will balance if:

$$2n + 7 = 3n + 2$$
$$3n - 2n = 7 - 2$$
$$n = 5$$

The balanced equation is therefore:

$$5Fe^{2+} + [MnO_4]^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$
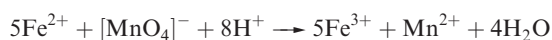
Check the charges again:

Left-hand side: $+10 - 1 + 8 = +17$

Right-hand side: $+15 + 2 = +17$

In reality, there are spectator ions in solution which make the whole system neutral.

For further practice in balancing equations, try problems 1.24–1.36 at the end of the chapter.

1.16 Oxidation and reduction, and oxidation states

Oxidation and reduction

When an element or compound burns in dioxygen to give an oxide, it is *oxidized* (equation 1.42).

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s) \tag{1.42}$$

Conversely, if a metal oxide reacts with dihydrogen and is converted to the metal, then the oxide is reduced (equation 1.43).

$$CuO(s) + H_2(g) \xrightarrow{\text{heat}} Cu(s) + H_2O(g) \tag{1.43}$$
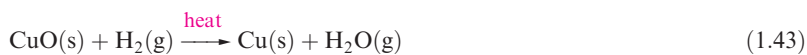
In reaction 1.42, O_2 is the *oxidizing agent* and in reaction 1.43, H_2 is the *reducing agent*.

Although we often think of oxidation in terms of *gaining oxygen* and reduction in terms of *losing oxygen*, we should consider other definitions of these processes. A *reduction* may involve *gaining hydrogen*; in equation 1.44, chlorine is reduced and hydrogen is oxidized.

$$Cl_2(g) + H_2(g) \longrightarrow 2HCl(g) \tag{1.44}$$

Loss of hydrogen may correspond to *oxidation* – for example, chlorine is oxidized when HCl is converted to Cl_2.

Oxidation and reduction may also be defined in terms of electron transfer – *electrons are gained in reduction* processes and are *lost in oxidation* reactions (equations 1.45 and 1.46):

$$S + 2e^- \longrightarrow S^{2-} \qquad\qquad \textit{Reduction} \qquad (1.45)$$

$$Zn \longrightarrow Zn^{2+} + 2e^- \qquad\qquad \textit{Oxidation} \qquad (1.46)$$

It is, however, sometimes difficult to apply these simple definitions to a reaction. In order to gain insight into reduction and oxidation processes, it is useful to use the concept of *oxidation states*.

Oxidation states

The concept of *oxidation states* and the changes in oxidation states that occur during a reaction provide a way of recognizing oxidation and reduction processes. Oxidation states are assigned to each atom of an element in a compound and *are a formalism*, although for ions such as Na^+, we can associate the charge of $1+$ with an oxidation state of $+1$.

The oxidation state of an *element* is zero. This applies to both atomic (e.g. He) and molecular elements (e.g. H_2, P_4, S_8).

In order to assign oxidation states to atoms in a *compound*, we must follow a set of rules, but be careful! The basic rules are as follows:

- The sum of the oxidation states of the atoms in a neutral compound is zero.
- The sum of the oxidation states of the atoms in an ion is equal to the charge on the ion, e.g. in the sulfate ion $[SO_4]^{2-}$, the sum of the oxidation states of S and O must be -2.
- Bonds between two atoms of the same element (e.g. $O-O$ or $S-S$) have no influence on the oxidation state of the element (see worked example 1.38).
- The oxidation state of hydrogen is usually $+1$ when it combines with a non-metal and -1 if it combines with a metal.
- The oxidation state of fluorine in a compound is always -1.
- The oxidation state of chlorine, bromine and iodine is *usually* -1 (exceptions are interhalogen compounds and oxides – see Chapter 22).
- The oxidation state of oxygen in a compound is usually -2.
- The oxidation state of a group 1 metal in a compound is usually $+1$; exceptions are a relatively small number of compounds which contain M^-, with the group 1 metal in a -1 oxidation state (see Figure 20.6).
- The oxidation state of a group 2 metal in a compound is $+2$.
- Metals from the *d*-block will usually have positive oxidation states (exceptions are some low oxidation state compounds – see Section 23.14).

Added to these rules are the facts that most elements in groups 13, 14, 15 and 16 can have variable oxidation states. In reality, it is essential to have a full picture of the structure of a compound before oxidation states can be assigned.

Worked example 1.34   Working out oxidation states

What are the oxidation states of each element in the following: KI, FeCl$_3$, Na$_2$SO$_4$?

KI: The group 1 metal is typically in oxidation state $+1$. This is consistent with the iodine being in oxidation state -1, and the sum of the oxidation states is 0.

FeCl$_3$: Chlorine is usually in oxidation state -1, and since there are 3 Cl atoms, the oxidation state of the iron must be $+3$ to give a neutral compound.

Na$_2$SO$_4$: Of the three elements, S can have a variable oxidation state and so we should deal with this element *last*. Na is in group 1 and usually has an oxidation state of $+1$. Oxygen is usually in an oxidation state of -2. The oxidation state of the sulfur atom is determined by ensuring that the sum of the oxidation states is 0:

$$(2 \times \text{Oxidation state of Na}) + (\text{Oxidation state of S})$$
$$+ (4 \times \text{Oxidation state of O}) = 0$$
$$(+2) + (\text{Oxidation state of S}) + (-8) = 0$$
$$\text{Oxidation state of S} = 0 + 8 - 2 = +6$$

Worked example 1.35   Variable oxidation states of nitrogen

Determine the oxidation state of N in each of the following species: NO, [NO$_2$]$^-$, [NO]$^+$, [NO$_3$]$^-$.

Each of the compounds or ions contains oxygen; O is usually in oxidation state -2.

NO: This is a neutral compound, therefore:

$$(\text{Oxidation state of N}) + (\text{Oxidation state of O}) = 0$$
$$(\text{Oxidation state of N}) + (-2) = 0$$
$$\text{Oxidation state of N} = +2$$

[NO$_2$]$^-$: The overall charge is -1, therefore:

$$(\text{Oxidation state of N}) + (2 \times \text{Oxidation state of O}) = -1$$
$$(\text{Oxidation state of N}) + (-4) = -1$$
$$\text{Oxidation state of N} = -1 + 4 = +3$$

[NO]$^+$: The overall charge is $+1$, therefore:

$$(\text{Oxidation state of N}) + (\text{Oxidation state of O}) = +1$$
$$(\text{Oxidation state of N}) + (-2) = +1$$
$$\text{Oxidation state of N} = +1 + 2 = +3$$

[NO$_3$]$^-$: The overall charge is -1, therefore:

$$(\text{Oxidation state of N}) + (3 \times \text{Oxidation state of O}) = -1$$
$$(\text{Oxidation state of N}) + (-6) = -1$$
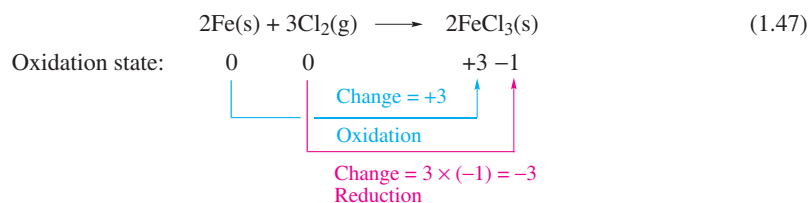$$\text{Oxidation state of N} = -1 + 6 = +5$$

Changes in oxidation states

> An *increase in the oxidation state* of an atom of an element corresponds to an *oxidation process*; a *decrease in the oxidation state* of an atom of an element corresponds to a *reduction process*.
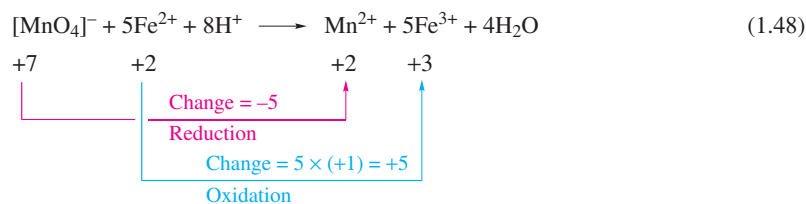
In equation 1.45, the change in oxidation state of the sulfur from 0 to -2 is reduction, and in reaction 1.46, the change in oxidation state of the zinc from 0 to $+2$ is oxidation.

In a reduction–oxidation (*redox*) reaction, the change in oxidation number for the oxidation and reduction steps *must balance*. In reaction 1.47, iron is oxidized to iron(III) and chlorine is reduced to chloride ion. The net increase in oxidation state of the iron *for the stoichiometric reaction* must balance the net decrease in oxidation state for the chlorine.

$$2Fe(s) + 3Cl_2(g) \longrightarrow 2FeCl_3(s) \qquad (1.47)$$

Oxidation state: 0   0   +3 −1

Change = +3
Oxidation
Change = $3 \times (-1) = -3$
Reduction

In equation 1.48, Fe^{2+} ions are oxidized by $[MnO_4]^-$; at the same time, $[MnO_4]^-$ is reduced by Fe^{2+} ions. The $[MnO_4]^-$ ion is the *oxidizing agent*, and Fe^{2+} is the *reducing agent*. In the reaction, the oxidation states of H and O remain as $+1$ and -2, respectively. The oxidation state of Mn decreases from $+7$ to $+2$, and the oxidation state of Fe increases from $+2$ to $+3$. The balanced equation shows that five Fe^{2+} ions are involved in the reaction and therefore the overall changes in oxidation states balance as shown in equation 1.48.

$$[MnO_4]^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O \qquad (1.48)$$

+7   +2   +2   +3

Change = −5
Reduction
Change = $5 \times (+1) = +5$
Oxidation

Worked example 1.36   Reduction of iron(III) oxide

When heated with carbon, Fe_2O_3 is reduced to Fe metal:

$$Fe_2O_3(s) + 3C(s) \xrightarrow{\text{heat}} 2Fe(s) + 3CO(g)$$
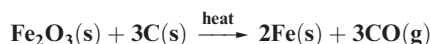
Identify the oxidation and reduction processes. Show that the oxidation state changes in the reaction balance.

The oxidation state of O is -2.
C(s) and Fe(s) are elements in oxidation state 0.
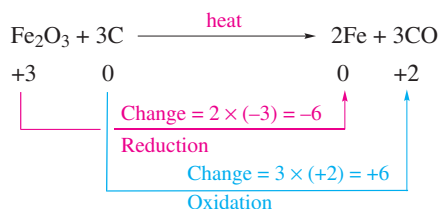Fe_2O_3 is a neutral compound:

(2 × Oxidation state of Fe) + (3 × Oxidation state of O) = 0

(2 × Oxidation state of Fe) − 6 = 0
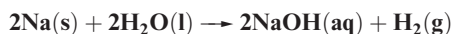
$$\text{Oxidation state of Fe} = \frac{+6}{2} = +3$$

In CO, the oxidation state of C $= +2$.

The oxidation process is C going to CO; the reduction process is Fe_2O_3 going to Fe. The oxidation state changes balance as shown below:

$$Fe_2O_3 + 3C \xrightarrow{\text{heat}} 2Fe + 3CO$$

$$\quad +3 \quad\quad 0 \quad\quad\quad\quad\quad\quad 0 \quad +2$$

Change $= 2 \times (-3) = -6$

Reduction

Change $= 3 \times (+2) = +6$

Oxidation

Worked example 1.37   Reaction of sodium with water

When sodium metal is added to water, the following reaction occurs:

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

State which species is being oxidized and which is being reduced. Show that the oxidation state changes balance.

In Na(s), Na is in oxidation state 0.

In $H_2(g)$, H is in oxidation state 0.

H_2O is a neutral compound:

$$(2 \times \text{Oxidation state of H}) + (\text{Oxidation state of O}) = 0$$

$$(2 \times \text{Oxidation state of H}) + (-2) = 0$$

$$\text{Oxidation state of H} = \frac{+2}{2} = +1$$

NaOH is a neutral compound; the usual oxidation states of Na and O are $+1$ and -2, respectively:

$$(\text{Oxidation state of Na}) + (\text{Oxidation state of O}) + (\text{Oxidation state of H}) = 0$$

$$(+1) + (-2) + (\text{Oxidation state of H}) = 0$$

$$\text{Oxidation state of H} = 2 - 1 = +1$$

Using these oxidation states, we can write the following equation and changes in oxidation states:

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

$$\quad 0 \quad\quad +1 \quad\quad\quad\quad\quad\quad +1 \ \ +1 \quad 0$$

Change $= 2 \times (+1) = +2$

Oxidation

No change

Change $= 2 \times (-1) = -2$

Reduction
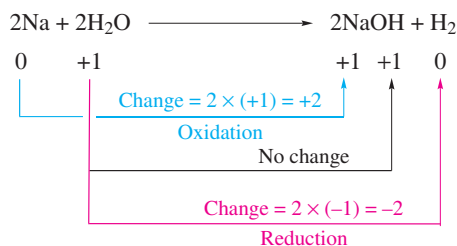
The equation shows that Na is oxidized; H is reduced on going from H_2O to H_2, but remains in oxidation state $+1$ on going from H_2O to NaOH. The changes in oxidation state balance.

Worked example 1.38	Hydrogen peroxide as an oxidizing agent

Hydrogen peroxide reacts with iodide ions in the presence of acid according to the following equation:

$$2I^- + H_2O_2 + 2H^+ \longrightarrow I_2 + 2H_2O$$

Show that the changes in oxidation states in the equation balance. Confirm that H_2O_2 acts as an oxidizing agent.
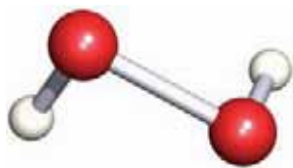
The structure of H_2O_2 is shown in the margin. The molecule contains an $O-O$ bond (i.e. a bond between like atoms – a *homonuclear bond*). This bond has no influence on the oxidation state of O. H_2O_2 is a neutral compound, therefore:

$(2 \times \text{Oxidation state of O}) + (2 \times \text{Oxidation state of H}) = 0$

$(2 \times \text{Oxidation state of O}) + 2(+1) = 0$

$\text{Oxidation state of O} = \dfrac{-2}{2} = -1$

In H_2O, the oxidation states of H and O are $+1$ and -2, respectively.
In H^+, hydrogen is in oxidation state $+1$.
In I^- and I_2, iodine is in oxidation states -1 and 0, respectively.
The oxidation state changes in the reaction are shown below; H remains in oxidation state $+1$ and does not undergo a redox reaction.
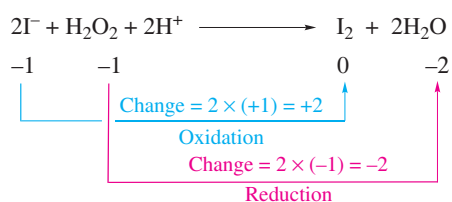
The equation shows that I^- is oxidized by H_2O_2, and therefore H_2O_2 acts as an oxidizing agent.

1.17 Empirical, molecular and structural formulae

Empirical and molecular formulae

The empirical formula of a compound gives the ratio of atoms of elements that combine to make the compound. However, this is not necessarily the same as the molecular formula, which tells you the number of atoms of the constituent elements in line with the relative molar mass of the compound. The relationship between the *empirical and molecular formulae of a compound* is illustrated using ethane, in which the ratio of carbon:hydrogen atoms is 1:3. This means that the *empirical formula* of ethane is CH_3. The relative molecular mass of ethane is 30, corresponding to two CH_3 units per molecule – the molecular formula is C_2H_6. In methane, the empirical formula is CH_4 and this corresponds directly to the molecular formula.

The *empirical formula* of a compound is the simplest possible formula (with integer subscripts) that gives the composition of the compound.
The *molecular formula* of a compound is the formula consistent with the relative molecular mass.

Worked example 1.39	Empirical and molecular formulae

A compound has the general formula C_nH_{2n+2}. This compound belongs to the family of *alkanes*. It contains 83.7% carbon by mass. Suggest the molecular formula of this compound.

Let the formula of the compound be C_xH_y. The percentage composition of the compound is 83.7% C and 16.3% H.

$$\% \text{ of C by mass} = \frac{\text{Mass of C in g}}{\text{Total mass in g}} \times 100$$

$$\% \text{ of H by mass} = \frac{\text{Mass of H in g}}{\text{Total mass in g}} \times 100$$

▶ ▶

A_r values are given inside the front cover of the book

For a mole of the compound, the total mass in g = relative molecular mass = M_r.

$$\% \text{ C} = 83.7 = \frac{(12.01 \times x)}{M_r} \times 100$$

$$\% \text{ H} = 16.3 = \frac{(1.008 \times y)}{M_r} \times 100$$

We do not know M_r, but we can write down the *ratio* of moles of C : H atoms in the compound – this is the empirical formula. From above:

$$M_r = \frac{12.01x}{83.7} \times 100 = \frac{1.008y}{16.3} \times 100$$

$$\frac{y}{x} = \frac{100 \times 16.3 \times 12.01}{100 \times 83.7 \times 1.008} = 2.32$$

The *empirical formula* of the compound is $CH_{2.32}$ or C_3H_7.
The compound must fit into a family of compounds of general formula C_nH_{2n+2}, and this suggests that the *molecular formula* is C_6H_{14}.

The working above sets the problem out in full; in practice, the empirical formula can be found as follows:

$$\% \text{ C} = 83.7 \qquad A_r \text{ C} = 12.01$$

$$\% \text{ H} = 16.3 \qquad A_r \text{ H} = 1.008$$

$$\text{Ratio C:H} = \frac{83.7}{12.01} : \frac{16.3}{1.008} \approx 6.97 : 16.2 \approx 1 : 2.32 = 3 : 7$$

Worked example 1.40	Determining the molecular formula of a chromium oxide

A binary oxide of chromium with $M_r = 152.02$ contains 68.43% Cr. Determine the empirical formula and the molecular formula. [Data: A_r Cr $= 52.01$; O $= 16.00$]

The binary chromium oxide contains only Cr and O. The composition by mass of the compound is:

68.43% Cr

$(100 - 68.43)\%$ O $= 31.57\%$ O

The ratio of moles of $\mathrm{Cr:O} = \dfrac{\%\mathrm{Cr}}{A_\mathrm{r}(\mathrm{Cr})} : \dfrac{\%\mathrm{O}}{A_\mathrm{r}(\mathrm{O})}$

$$= \dfrac{68.43}{52.01} : \dfrac{31.57}{16.00}$$

$$= 1.316 : 1.973$$

$$= 1 : \dfrac{1.973}{1.316}$$

$$= 1 : 1.5 \text{ or } 2 : 3$$

The empirical formula of the chromium oxide is therefore Cr_2O_3.
To find the molecular formula, we need the molecular mass, M_r:

$$M_\mathrm{r} = 152.02$$

For the empirical formula Cr_2O_3:

$$[2 \times A_\mathrm{r}(\mathrm{Cr})] + [3 \times A_\mathrm{r}(\mathrm{O})] = (2 \times 52.01) + (3 \times 16.00) = 152.02$$

This value matches the value of M_r. Therefore, the molecular formula is the same as the empirical formula, Cr_2O_3.

Worked example 1.41   **Determining the molecular formula of a sulfur chloride**

A binary chloride of sulfur with $M_\mathrm{r} = 135.02$ contains 52.51% Cl. What are the empirical and molecular formulae of the compound? [Data: A_r S$=32.06$; Cl$=35.45$]

The binary sulfur chloride contains only S and Cl. The composition by mass of the compound is:

52.51% Cl

$(100 - 52.51)\%$ S $= 47.49\%$ S

The ratio of moles of $\mathrm{S:Cl} = \dfrac{\%\mathrm{S}}{A_\mathrm{r}(\mathrm{S})} : \dfrac{\%\mathrm{Cl}}{A_\mathrm{r}(\mathrm{Cl})}$

$$= \dfrac{47.49}{32.06} : \dfrac{52.51}{35.45}$$

$$= 1.481 : 1.481$$

$$= 1 : 1$$

The empirical formula of the sulfur chloride is therefore SCl.
The molecular mass, M_r, of the compound is 135.02.
For the empirical formula SCl: $A_\mathrm{r}(\mathrm{S}) + A_\mathrm{r}(\mathrm{Cl}) = 32.06 + 35.45 = 67.51$.
This mass must be doubled to obtain the value of M_r. Therefore, the molecular formula is S_2Cl_2.

Formulae of solvates

Before we leave the topic of molecular formulae, we must highlight the particular case of *solvates* . When a compound crystallizes from a solution of the compound, the crystals that form may contain *solvent of crystallization*.

The compound is then called a *solvate*, and if the solvent is water, the compound is a *hydrate*. The formula of the solvated compound shows the molar ratio in which the solvent of crystallization is present. For example, blue crystals of copper(II) sulfate are actually copper(II) sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$. A 'centred-dot' is placed between the molecular formula of the unsolvated compound and the solvate. The use of the dot has no implication for structure, but conveys only the stoichiometry of the solvate.

Structural formulae and 'ball-and-stick' models

Neither the empirical nor the molecular formula provides information about the way in which the atoms in a molecule are connected. The molecular formula H_2S does not indicate the arrangement of the three atoms in a molecule of hydrogen sulfide, but structure **1.3** *is* informative. We could also have arrived at this structure by considering the number of valence electrons available for bonding.

Covalent bonding and structure: see Chapters 4–7

For some molecular formulae, it is possible to connect the atoms in more than one reasonable way and the molecule is said to possess *isomers*. An example is C_4H_{10} for which two structural formulae **1.4** and **1.5** can be drawn. More detailed structural information can be obtained from 'ball-and-stick' or 'tube' models. Models **1.6–1.8** ('ball-and-stick') and **1.9–1.11** ('tube') correspond to formulae **1.3–1.5**. We expand the discussion of drawing structural formulae for organic molecules in Section 24.3.

Isomers: see Sections 6.11, 23.5 and 24.6–24.8
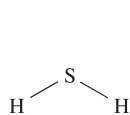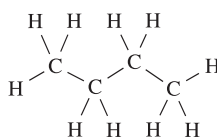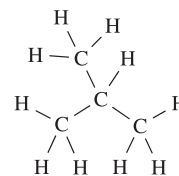
(1.3) (1.4) (1.5)
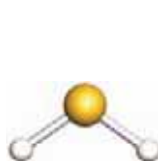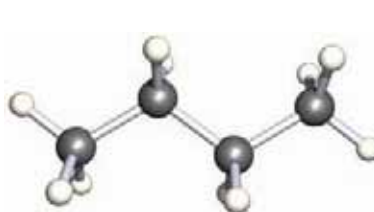
(1.6) (1.7) (1.8)

(1.9) (1.10) (1.11)

1.18 Basic nomenclature

In this section we outline some fundamental nomenclature and set out some important IUPAC ground rules for organic and inorganic compounds. We summarize some widely used 'trivial' names of compounds and you should become familiar with these as well as with their IUPAC counterparts. Detailed nomenclature rules and the specifics of organic chain numbering are found in Chapters 24–35.

Basic organic classifications: straight chain alkanes

The general formula for an alkane with a straight chain backbone is C_nH_{2n+2}; the molecule is *saturated* and contains only C–C and C–H bonds. The simplest member of the family is *methane* CH_4, **1.12**. The name methane carries with it two pieces of information:

- *meth-* is the prefix that tells us there is one C atom in the carbon chain;
- the ending *-ane* denotes that the compound is an alkane.

The names of organic compounds are composite with the *stem* telling us the number of carbon atoms in the main chain of the molecule. These are listed in the middle column of Table 1.8. For a straight chain *alkane*, the name is completed by adding *-ane* to the prefix in the table. Compounds **1.13** (C_3H_8) and **1.14** (C_7H_{16}) are both alkanes. Using the stems from Table 1.8, **1.13** with a 3-carbon chain is called propane, and **1.14** with a 7-carbon chain is called heptane.

Basic organic classifications: functional groups

A *functional group* in a molecule imparts a characteristic reactivity to the compound. The functional group in an alkene is the C=C double bond and, in an alcohol, the functional group is the −OH unit. The organic functional groups that we will describe in this book are listed in Table 1.9. The presence of most of these groups is recognized by using an instrumental technique such as infrared, electronic or nuclear magnetic resonance spectroscopy – see Chapters 12–14.

(1.13)   **(1.14)**

Basic inorganic nomenclature

The aim of the IUPAC nomenclature is to provide a compound or an ion with a name that is unambiguous. One problem that we face when dealing with some inorganic elements is the possibility of a variable oxidation state. A simple example is that of distinguishing between the two common oxides of carbon, i.e. carbon monoxide and carbon dioxide. The use of 'mono-' and 'di-' indicates that the compounds are CO and CO_2 respectively.

(1.12)

Table 1.8 Numerical descriptors.

Number	Stem used to give the number of C atoms in an organic carbon chain	Prefix used to describe the number of groups or substituents
1	meth-	mono-
2	eth-	di-
3	prop-	tri-
4	but-	tetra-
5	pent-	penta-
6	hex-	hexa-
7	hept-	hepta-
8	oct-	octa-
9	non-	nona-
10	dec-	deca-
11	undec-	undeca-
12	dodec-	dodeca-
13	tridec-	trideca-
14	tetradec-	tetradeca-
15	pentadec-	pentadeca-
16	hexadec-	hexadeca-
17	heptadec-	heptadeca-
18	octadec-	octadeca-
19	nonadec-	nonadeca-
20	icos-	icosa-

The accepted numerical prefixes are listed in Table 1.8. Note that 'di-' should be used in preference to 'bi-'.

Binary compounds 1   A binary compound is composed of only *two* types of elements. We deal first with cases where there is no ambiguity over oxidation states of the elements present, e.g. *s*-block metal. Examples of such binary compounds include NaCl, CaO, HCl, Na_2S and $MgBr_2$. The formula should be written with the more electropositive element (often a metal) placed first. The names follow directly:

NaCl   sodium chloride
Na_2S sodium sulfide
CaO   calcium oxide
$MgBr_2$ magnesium bromide
HCl   hydrogen chloride

A ***binary compound*** is composed of two types of elements.

Table 1.9 Selected functional groups for organic molecules.

Name of functional group	Functional group	Example; where it is in common use, a trivial name is given in **pink**
Alcohol	—OH	Ethanol (CH_3CH_2OH)
Aldehyde	—C with =O and —H	Ethanal (CH_3CHO) Acetaldehyde
Ketone	—C with =O and —R $R \neq H$	Propanone (CH_3COCH_3) Acetone
Carboxylic acid	—C with =O and —O—H	Ethanoic acid (CH_3CO_2H) Acetic acid
Ester	—C with =O and —O—R e.g. R = alkyl	Ethyl ethanoate ($CH_3CO_2C_2H_5$) Ethyl acetate
Ether	R'—O with R R = R' or R $\neq$ R'	Diethyl ether ($C_2H_5OC_2H_5$)
Amine	—NH_2	Ethylamine ($CH_3CH_2NH_2$)
Amide	—C with =O and —NH_2	Ethanamide (CH_3CONH_2) Acetamide
Halogenoalkane	—X X = F, Cl, Br, I	Bromoethane (CH_3CH_2Br)
Acid chloride	—C with =O and —Cl	Ethanoyl chloride (CH_3COCl) Acetyl chloride
Nitrile	—C≡N	Ethanenitrile (CH_3CN) Acetonitrile
Nitro	—NO_2	Nitromethane (CH_3NO_2)
Thiol	—SH	Ethanethiol (CH_3CH_2SH)

Anions   The endings '*-ide*', '*-ite*' and '*-ate*' generally signify an anionic species. Some examples are listed in Table 1.10. The endings '-ate' and '-ite' *tend* to indicate the presence of oxygen in the anion (i.e. an oxoanion) and are used for anions that are derived from oxoacids; e.g. the oxoanion derived from sulfuric acid is a sulfate.

There is more than one accepted method of distinguishing between the different oxoanions of elements such as sulfur, nitrogen and phosphorus

Table 1.10 Names of some common anions. In some cases, more than one name is accepted by the IUPAC.

Formula of anion	Name of anion
H^-	Hydride
$[OH]^-$	Hydroxide
F^-	Fluoride
Cl^-	Chloride
Br^-	Bromide
I^-	Iodide
O^{2-}	Oxide
S^{2-}	Sulfide
Se^{2-}	Selenide
N^{3-}	Nitride
$[N_3]^-$	Azide *or* trinitride(1−)
P^{3-}	Phosphide
$[CN]^-$	Cyanide *or* nitridocarbonate (1−)
$[NH_2]^-$	Amide *or* azanide
$[OCN]^-$	Cyanate *or* nitridooxidocarbonate (1−)
$[SCN]^-$	Thiocyanate *or* nitridosulfidocarbonate (1−)
$[SO_4]^{2-}$	Sulfate *or* tetraoxidosulfate (2−)
$[SO_3]^{2-}$	Sulfite *or* trioxidosulfate (2−)
$[NO_3]^-$	Nitrate *or* trioxidonitrate (1−)
$[NO_2]^-$	Nitrite *or* dioxidonitrate (1−)
$[PO_4]^{3-}$	Phosphate *or* tetraoxidophosphate (3−)
$[PO_3]^{3-}$	Phosphite *or* trioxidophosphate (3−)
$[ClO_4]^-$	Perchlorate *or* tetraoxidochlorate (1−)
$[CO_3]^{2-}$	Carbonate *or* trioxidocarbonate (2−)

(Table 1.10). Older names such as sulfate, sulfite, nitrate and nitrite are still accepted within the IUPAC guidelines.[§] In *Chemistry*, we have made every effort to stay within the IUPAC recommendations while retaining the most common alternatives, e.g. sulfate.

Oxidation states The oxidation state is very often indicated by using the Stock system of Roman numerals. The numeral is always an integer and is placed after the name of the element to which it refers. The oxidation number can be zero, positive or negative.[†] An oxidation state is assumed to be positive unless otherwise indicated by the use of a negative sign. Thus, (III) is taken to read '(+III)'; but for the negative state, write (−III).

In a formula, the oxidation state is written as a superscript (e.g. $[Mn^{VII}O_4]^-$) but in a name, it is written on the line (e.g. iron(II) bromide). Its use is important when the name could be ambiguous (see below).

Binary compounds 2 We look now at binary compounds where there could be an ambiguity over the oxidation state of the more electropositive element (often a metal). Examples of such compounds include $FeCl_3$, SO_2, SO_3, ClF, ClF_3 and $SnCl_2$. Simply writing 'iron chloride' does not distinguish between the chlorides of iron(II) and iron(III), and for $FeCl_3$ it is necessary to write iron(III) chloride. Another accepted name is iron trichloride.

The oxidation state of sulfur in SO_2 can be seen immediately in the name sulfur(IV) oxide, but also acceptable is the name sulfur dioxide. Similarly, SO_3 can be named sulfur(VI) oxide or sulfur trioxide.

Accepted names for ClF, ClF_3 and $SnCl_2$ are:

ClF   chlorine(I) fluoride or chlorine monofluoride
ClF_3 chlorine(III) fluoride or chlorine trifluoride
$SnCl_2$ tin(II) chloride or tin dichloride

Cations Cations of metals where the oxidation state does not usually vary, notably the *s*-block elements, may be named by using the name of the metal itself (e.g. sodium ion, barium ion), although the charge may be indicated (e.g. sodium(1+) ion, barium(2+) ion).

Where there may be an ambiguity, the charge must be shown (e.g. iron(II) or iron(2+) ion, copper(II) or copper(2+) ion, thallium(I) or thallium(1+) ion).[‡]

The names of polyatomic cations are introduced as they appear in the textbook. Look for the ending '-ium'; this often signifies the presence of a cation, although remember that '-ium' is a common ending in the name of elemental metals (see Section 1.5).

Three of the most common cations that you will encounter are:
- H^+ hydrogen ion, hydrogen(1+), hydron;
- $[H_3O]^+$ oxonium ion, oxidanium ion;
- $[NH_4]^+$ ammonium ion, azanium ion.

[§] *Nomenclature of inorganic chemistry*, IUPAC *Recommendations 2005*, senior eds N.G. Connelly and T. Dambus, RSC Publishing, Cambridge, 2005.

[†] A zero oxidation state is signified by 0, although this is not a Roman numeral.

[‡] An older form of nomenclature which is sometimes encountered uses the suffix '-ous' to describe the lower oxidation state and '-ic' for the higher one. Thus, copper(I) is cuprous and copper(II) is cupric.

1.19 Final comments

The aim of this first chapter is to provide a point of reference for basic chemical definitions, ones that you have probably encountered before beginning a first year university chemistry course. If you find later in the book that a concept appears to be 'assumed', you should find some revision material to help you in Chapter 1. Section 1.18 gives some basic guidelines for naming organic and inorganic compounds, and more detailed nomenclature appears as the book progresses.

We have deliberately *not* called Chapter 1 'Introduction'. There is often a tendency to pass through chapters so-labelled without paying attention to them. In this text, Chapter 1 is designed to help you and to remind you of basic issues.

PROBLEMS

Use values of A_r from the front inside cover of the book.

1.1 What is 0.0006 m in (a) mm, (b) pm, (c) cm, (d) nm?

1.2 A typical C=O bond distance in an aldehyde is 122 pm. What is this in nm?

1.3 The relative molecular mass of NaCl is 58.44 and its density is $2.16 \, \text{g cm}^{-3}$. What is the volume of 1 mole of NaCl in m^3?

1.4 The equation $E = h\nu$ relates the Planck constant (h) to energy and frequency. Determine the SI units of the Planck constant.

1.5 Kinetic energy is given by the equation: $E = \frac{1}{2}mv^2$. By going back to the base SI units, show that the units on the left- and right-hand sides of this equation are compatible.

1.6 Calculate the relative atomic mass of a sample of naturally occurring boron which contains 19.9% $^{10}_{5}\text{B}$ and 80.1% $^{11}_{5}\text{B}$. Accurate masses of the isotopes to 3 sig. fig. are 10.0 and 11.0.

1.7 The mass spectrum of molecular bromine shows three lines for the parent ion, Br_2^+. The isotopes for bromine are $^{79}_{35}\text{Br}$ (50%) and $^{81}_{35}\text{Br}$ (50%). Explain why there are three lines and predict their mass values and relative intensities. Predict what the mass spectrum of HBr would look like; isotopes of hydrogen are given in Section 1.7. (Ignore fragmentation; see Chapter 10.)

1.8 Convert the volume of each of the following to conditions of standard temperature (273 K) and pressure (1 bar = 1.00×10^5 Pa) and give your answer in m^3 in each case:
(a) $30.0 \, \text{cm}^3$ of CO_2 at 290 K and 101 325 Pa (1 atm)
(b) $5.30 \, \text{dm}^3$ of H_2 at 298 K and 100 kPa (1 bar)
(c) $0.300 \, \text{m}^3$ of N_2 at 263 K and 102 kPa
(d) $222 \, \text{m}^3$ of CH_4 at 298 K and 200 000 Pa (2 bar)

1.9 The partial pressure of helium in a $50.0 \, \text{dm}^3$ gas mixture at 285 K and 10^5 Pa is 4.0×10^4 Pa. How many moles of helium are present?

1.10 A $20.0 \, \text{dm}^3$ sample of gas at 273 K and 2.0 bar pressure contains 0.50 moles N_2 and 0.70 moles Ar. What is the partial pressure of each gas, and are there any other gases in the sample? (Volume of one mole of ideal gas at 273 K, 1.00×10^5 Pa (1 bar) = $22.7 \, \text{dm}^3$.)

1.11 Determine the amount (in moles) present in each of the following: (a) 0.44 g PF_3, (b) $1.00 \, \text{dm}^3$ gaseous PF_3 at 293 K and 2.00×10^5 Pa, (c) 3.480 g MnO_2, (d) 0.0420 g $MgCO_3$. (Volume of 1 mole of ideal gas at 273 K, 10^5 Pa = $22.7 \, \text{dm}^3$.)

1.12 What mass of solid is required to prepare $100.0 \, \text{cm}^3$ of each of the following solutions:
(a) $0.0100 \, \text{mol dm}^{-3}$ KI; (b) $0.200 \, \text{mol dm}^{-3}$ NaCl;
(c) $0.0500 \, \text{mol dm}^{-3}$ Na_2SO_4?

1.13 With reference to the periodic table, write down the likely formulae of compounds formed between:
(a) sodium and iodine, (b) magnesium and chlorine, (c) magnesium and oxygen, (d) calcium and fluorine, (e) lithium and nitrogen, (f) calcium and phosphorus, (g) sodium and sulfur and (h) hydrogen and sulfur.

1.14 Use the information in the periodic table to predict the likely formulae of the oxide, chloride, fluoride and hydride formed by aluminium.

1.15 Give balanced equations for the formation of each of the compounds in problems 1.13 and 1.14 from their constituent elements.

1.16 What do you understand by each of the following terms: proton, electron, neutron, nucleus, atom, radical, ion, cation, anion, molecule, covalent bond, compound, isotope, allotrope?

1.17 Suggest whether you think each of the following species will exhibit covalent or ionic bonding. Which of the species are compounds and which are molecular: (a) NaCl; (b) N_2; (c) SO_3; (d) KI; (e) NO_2; (f) Na_2SO_4; (g) $[MnO_4]^-$; (h) CH_3OH; (i) CO_2; (j) C_2H_6; (k) HCl; (l) $[SO_4]^{2-}$?

1.18 Determine the oxidation state of nitrogen in each of the following oxides: (a) NO; (b) NO_2, (c) N_2O_3; (d) N_2O_4; (e) N_2O_5.

1.19 In each reaction below, assign the oxidation and reduction steps, and, for (b)–(g), show that the changes in oxidation states for the oxidation and reduction processes balance:
(a) $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
(b) $Mg(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + H_2(g)$
(c) $2Ca(s) + O_2(g) \longrightarrow 2CaO(s)$
(d) $2Fe(s) + 3Cl_2(g) \longrightarrow 2FeCl_3(s)$
(e) $Cu(s) + 2AgNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2Ag(s)$
(f) $CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(g)$
(g) $[MnO_4]^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \longrightarrow$
$\qquad\qquad Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$

1.20 (a) In a compound, oxygen is usually assigned an oxidation state of -2. What is the formal oxidation state in the allotropes O_2 and O_3, in the compound H_2O_2, and in the ions $[O_2]^{2-}$ and $[O_2]^+$?
(b) Determine the oxidation and reduction steps during the decomposition of hydrogen peroxide which occurs by the following reaction:

$$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$$

1.21 Give a systematic name for each of the following compounds: (a) Na_2CO_3; (b) $FeBr_3$; (c) $CoSO_4$; (d) $BaCl_2$; (e) Fe_2O_3; (f) $Fe(OH)_2$; (g) LiI; (h) KCN; (i) KSCN; (j) Ca_3P_2.

1.22 Write down the formula of each of the following compounds: (a) nickel(II) iodide; (b) ammonium nitrate; (c) barium hydroxide; (d) iron(III) sulfate; (e) iron(II) sulfite; (f) aluminium hydride; (g) lead(IV) oxide; (h) tin(II) sulfide.

1.23 How many atoms make up the carbon chain in (a) octane, (b) hexane, (c) propane, (d) decane, (e) butane?

1.24 Balance the following equations:
(a) $C_4H_{10} + O_2 \longrightarrow CO_2 + H_2O$
(b) $SO_2 + O_2 \longrightarrow SO_3$
(c) $HCl + Ca \longrightarrow H_2 + CaCl_2$
(d) $Na_2CO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O$
(e) $HNO_3 + Mg \longrightarrow Mg(NO_3)_2 + H_2$
(f) $H_3PO_4 + NaOH \longrightarrow Na_2HPO_4 + H_2O$

1.25 Find x, y and z in the following reactions:
(a) $2CO + O_2 \longrightarrow 2CO_x$
(b) $N_2 + xH_2 \longrightarrow yNH_3$
(c) $Mg + 2HNO_3 \longrightarrow Mg(NO_3)_x + H_2$
(d) $xH_2O_2 \longrightarrow yH_2O + zO_2$

(e) $xHCl + CaCO_3 \longrightarrow CaCl_y + CO_2 + H_2O$
(f) $xNaOH + H_2SO_4 \longrightarrow Na_ySO_4 + zH_2O$
(g) $MnO_2 + xHCl \longrightarrow MnCl_2 + Cl_2 + yH_2O$
(h) $xNa_2S_2O_3 + I_2 \longrightarrow yNaI + zNa_2S_4O_6$

1.26 Balance the following equations.
(a) $Fe + Cl_2 \longrightarrow FeCl_3$
(b) $SiCl_4 + H_2O \longrightarrow SiO_2 + HCl$
(c) $Al_2O_3 + NaOH + H_2O \longrightarrow Na_3Al(OH)_6$
(d) $K_2CO_3 + HNO_3 \longrightarrow KNO_3 + H_2O + CO_2$
(e) $Fe_2O_3 + CO \xrightarrow{\text{heat}} Fe + CO_2$
(f) $H_2C_2O_4 + KOH \longrightarrow K_2C_2O_4 + H_2O$

1.27 Balance the following equations.
(a) $AgNO_3 + MgCl_2 \longrightarrow AgCl + Mg(NO_3)_2$
(b) $Pb(O_2CCH_3)_2 + H_2S \longrightarrow PbS + CH_3CO_2H$
(c) $BaCl_2 + K_2SO_4 \longrightarrow BaSO_4 + KCl$
(d) $Pb(NO_3)_2 + KI \longrightarrow PbI_2 + KNO_3$
(e) $Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$

1.28 Balance the following equations.
(a) $C_3H_8 + Cl_2 \longrightarrow C_3H_5Cl_3 + HCl$
(b) $C_6H_{14} + O_2 \longrightarrow CO_2 + H_2O$
(c) $C_2H_5OH + Na \longrightarrow C_2H_5ONa + H_2$
(d) $C_2H_2 + Br_2 \longrightarrow C_2H_2Br_4$
(e) $CaC_2 + H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

1.29 In each of the following, mixing the aqueous ions shown will produce a precipitate. Write the formula of the neutral product, and then balance the equation.
(a) $Ag^+(aq) + Cl^-(aq) \longrightarrow$
(b) $Mg^{2+}(aq) + [OH]^-(aq) \longrightarrow$
(c) $Pb^{2+}(aq) + S^{2-}(aq) \longrightarrow$
(d) $Fe^{3+}(aq) + [OH]^-(aq) \longrightarrow$
(e) $Ca^{2+}(aq) + [PO_4]^{3-}(aq) \longrightarrow$
(f) $Ag^+(aq) + [SO_4]^{2-}(aq) \longrightarrow$

1.30 Balance each of the following equations:
(a) $Fe^{3+} + H_2 \longrightarrow Fe^{2+} + H^+$
(b) $Cl_2 + Br^- \longrightarrow Cl^- + Br_2$
(c) $Fe^{2+} + [Cr_2O_7]^{2-} + H^+ \longrightarrow$
$\qquad\qquad Fe^{3+} + Cr^{3+} + H_2O$
(d) $NH_2OH + Fe^{3+} \longrightarrow N_2O + Fe^{2+} + H_2O + H^+$
(e) $[S_2O_3]^{2-} + I_2 \longrightarrow [S_4O_6]^{2-} + I^-$
(f) $[MoO_4]^{2-} + [PO_4]^{3-} + H^+ \longrightarrow$
$\qquad\qquad [PMo_{12}O_{40}]^{3-} + H_2O$
(g) $HNO_3 + H_2SO_4 \longrightarrow$
$\qquad\qquad [H_3O]^+ + [NO_2]^+ + [HSO_4]^-$

1.31 Balance the following equation for the reaction of magnesium with dilute nitric acid:

$$Mg(s) + HNO_3(aq) \longrightarrow Mg(NO_3)_2(aq) + H_2(g)$$

Use the balanced equation to determine the mass of Mg that will completely react with $100.0\,cm^3$ $0.50\,M$ nitric acid.

**1.32** Balance the following equation for the reaction of aqueous phosphoric acid with sodium hydroxide:

$$H_3PO_4(aq) + NaOH(aq) \longrightarrow$$
$$Na_3PO_4(aq) + H_2O(l)$$
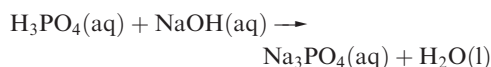
$15.0\,cm^3$ aqueous phosphoric acid of concentration $0.200\,mol\,dm^{-3}$ is added to $50.0\,cm^3$ aqueous NaOH of concentration $2.00\,mol\,dm^{-3}$. Which reagent is in excess, and how many moles of this reagent remain unreacted?

1.33 Balance the following equation for the precipitation of silver chromate:

$$AgNO_3(aq) + K_2CrO_4(aq) \longrightarrow$$
$$Ag_2CrO_4(s) + KNO_3(aq)$$
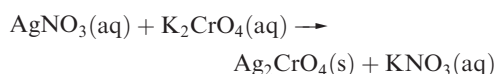
$5.00\,g$ of K_2CrO_4 is dissolved in water and the volume of the solution is made up to $100.0\,cm^3$. $25.0\,cm^3$ of a $0.100\,mol\,dm^{-3}$ solution of $AgNO_3$ is added to the solution of K_2CrO_4. Determine the mass of Ag_2CrO_4 that is formed.

**1.34** Balance the following equation:

$$[C_2O_4]^{2-}(aq) + [MnO_4]^-(aq) + H^+(aq) \longrightarrow$$
$$Mn^{2+}(aq) + CO_2(g) + H_2O(l)$$
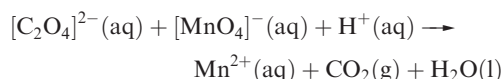
What volume of $0.200\,M$ aqueous $KMnO_4$ will react completely with $25.0\,cm^3$ $0.200\,M$ aqueous $K_2C_2O_4$ in the presence of excess acid?

1.35 $5.00\,g$ of solid $CaCO_3$ is thermally decomposed in the following reaction:

$$CaCO_3(s) \xrightarrow{\text{heat}} CaO(s) + CO_2(g)$$

What mass of CaO is formed? This oxide reacts with water to give $Ca(OH)_2$. Write a balanced equation for this process.

1.36 Balance the following equation for the reaction of sodium thiosulfate with diiodine:

$$Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + NaI$$
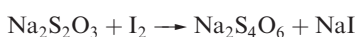
Diiodine is insoluble in water, but dissolves in aqueous potassium iodide solution. $0.0250\,dm^3$ of a solution of I_2 in aqueous KI reacts exactly with $0.0213\,dm^3$ $0.120\,M$ sodium thiosulfate solution. What is the concentration of the diiodine solution?

1.37 An organic compound **A** contains 40.66% C, 23.72% N and 8.53% H. The compound also contains oxygen. Determine the empirical formula of the compound. The molecular mass of **A** is 59.07. What is its molecular formula?

1.38 (a) A chloride of platinum, $PtCl_x$, contains 26.6% Cl. What is the oxidation state of the platinum in this compound?

(b) Two oxides of iron, **A** and **B**, contain 69.94 and 72.36% Fe, respectively. For **A**, $M_r = 159.70$; for **B**, $M_r = 231.55$. What are the empirical formulae of **A** and **B**?

1.39 Crystalline copper(II) sulfate contains water. The formula of the crystalline solid is $CuSO_4 \cdot xH_2O$. Determine x if the crystals contain 12.84% S and 4.04% H.

1.40 (a) Glucose, $C_xH_yO_z$, contains 40.00% C and 6.71% H. What is the empirical formula of glucose? If the molecular mass of glucose is 180.16, determine its molecular formula.

(b) A fluoride of tungsten, WF_x, contains 38.27% F. What is the oxidation state of tungsten in this compound?

CHEMISTRY IN DAILY USE

1.41 The Avogadro Project aims to define the kilogram with respect to a precise value of the Avogadro constant, L. For this task, spheres of ultrapure silicon are being made. Let the mass of a sphere be M, and its volume be V. (a) Write down an expression for the density of silicon. (b) What is the mass of one atom of silicon if the molar mass is M_r? (c) The structure of elemental silicon is described in terms of a repeating unit called the *unit cell*. If the volume of the unit cell is V_c and it contains n atoms, how many atoms are present in the entire sphere? (d) What is the mass of the sphere of silicon in terms of M_r, L, V, V_c and n? (e) Rearrange the equation from part (d) to show how a value of the Avogadro constant can be determined.

1.42 Atmospheric pressure, P_{atm}, decreases with altitude. The composition of the atmospheric air is the same at sea level as it is on Mount Everest (8850 m), and comprises 20.9% O_2. The partial pressure of O_2 in air taken into the lungs is given by the equation:

$$P(O_2) = 0.209\,(P_{atm} - P_{vap})$$

where P_{vap} is the saturated water vapour pressure in the lungs.

(a) If $P_{vap} = 6300\,Pa$, determine $P(O_2)$ at sea level, with $P_{atm} = 101\,kPa$.

(b) The summit of the Matterhorn is at 4480 m. What is the atmospheric pressure at this altitude if $P(O_2) = 10\,700\,Pa$? Comment on any assumptions that you have made.

1.43 Although it is not common to administer anaesthetics at very high altitudes, the Kunde Hospital in Nepal is at 3900 m. Isoflurane is a
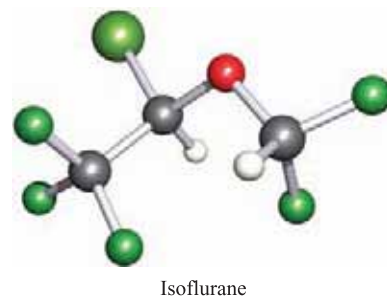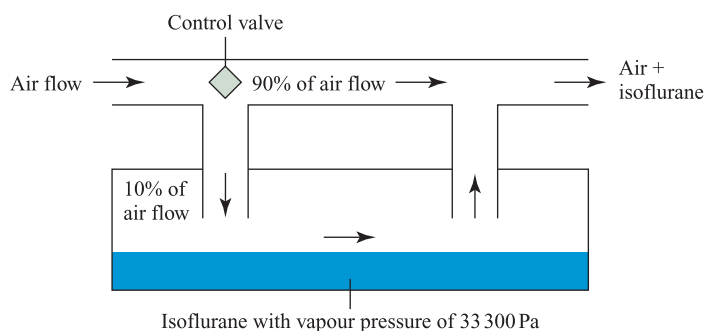
Fig. 1.12 A schematic representation of an isoflurane vaporizer, and the structure of isoflurane. Colour code: C, grey; O, red; F, green; H, white; Cl, large green. [The left-hand scheme is based on Figure 2 in M. Eales and R. Cooper (2007), *Anaesthesia and Intensive Care Medicine*, vol. 8, p. 111.]

general anaesthetic that is administered by inhalation. Figure 1.12 shows a typical isoflurane vaporizer. (a) At sea level, where atmospheric pressure (P_{atm}) is 101 kPa, what percentage of isoflurane will the vaporizer deliver in the outgoing air stream shown in Figure 1.12? (b) In Kunde Hospital, $P_{atm} = 59$ kPa. If the same vaporizer is used to administer a general anaesthetic, how does the reduction in atmospheric pressure at high altitude affect the delivery of isoflurane?

1.44 UF_6 is a colourless, volatile solid with a vapour pressure of 1 bar at 329 K. Uranium possesses several isotopes, and during the reprocessing of uranium fuel in the nuclear power industry, it is necessary to separate $^{235}_{92}UF_6$ and $^{238}_{92}UF_6$ in order to produce $^{235}_{92}U$-enriched UF6. Why can a centrifuge be used for the separation of $^{235}_{92}UF_6$ and $^{238}_{92}UF_6$?

1.45 Mount Etna in Italy is a continuously degassing volcano. It releases about 1.5 Tg of SO_2 per year. (a) How many moles of SO_2 are emitted per year by Mount Etna? (b) Determine the approximate daily emission rate of SO_2. (c) Among the techniques used to sample for SO_2 emissions is a Giggenbach bottle in which the gas stream is passed through aqueous NaOH. The products of the reaction of SO_2 with hydroxide ions are $[SO_4]^{2-}$, $[HS]^-$ and H_2O. Write a balanced equation for this reaction.

1.46 The structure of aspirin is shown below. Aspirin is hydrolysed in the body to give salicylic acid or salicylate ion. For an average adult human, concentrations of salicylate in body plasma exceeding 5.1 mmol dm^{-3} are likely to be fatal. (a) What mass of salicylic acid corresponds to 5.1 mmol dm^{-3}? (b) Prophylactic aspirin therapy may involve a dose of 160 mg day^{-1}. If complete

hydrolysis of the aspirin occurs, how many mmol of salicylic acid are produced per dose?

Aspirin ($C_9H_8O_4$)   Salicylic acid ($C_7H_6O_3$)

1.47 Ammonium nitrate, NH_4NO_3, is an important agricultural fertilizer. What mass of NH_4NO_3 would you need to dissolve in water to produce a 2.00 dm^3 solution that contained 200.0 mg dm^{-3} of nitrogen-content by weight?

1.48 Current interest in hydrogen as a 'clean fuel' leads to active research in hydrogen storage materials. Metal hydrides such as $NaBH_4$, MgH_2 and $LiAlH_4$ release H_2 when they react with water, and have relatively high hydrogen storage capacities because hydrogen is released both from the metal hydride and from the water.
  (a) Balance the following equations:

$$NaBH_4 + H_2O \longrightarrow NaOH + H_3BO_3 + H_2$$

$$MgH_4 + H_2O \longrightarrow Mg(OH)_2 + H_2$$

$$LiAlH_4 + H_2O \longrightarrow LiOH + Al(OH)_3 + H_2$$

  (b) Use the balanced equations to determine the hydrogen storage capacity of each system in terms of a percentage weight.