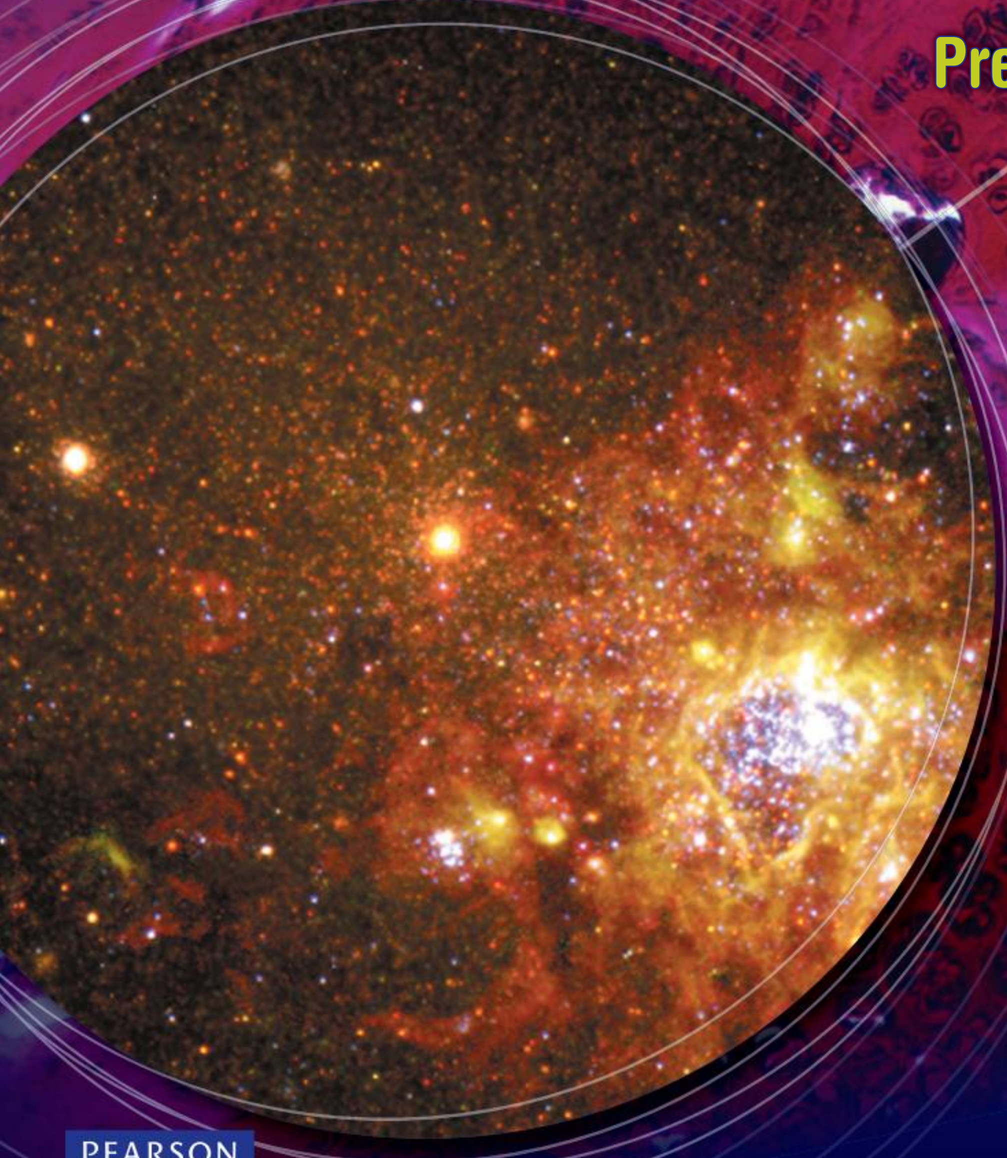
Chemistry Contexts 1

SECOND EDITION

Preliminary



Debbie Irwin

Ross Farrelly

Patrick Garnett

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Periodic Table

Alternative group numbers →

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 Hydrogen **H** 1.008																	2 Helium **He** 4.003
3 Lithium **Li** 6.941	4 Beryllium **Be** 9.012											5 Boron **B** 10.81	6 Carbon **C** 12.01	7 Nitrogen **N** 14.01	8 Oxygen **O** 16.00	9 Fluorine **F** 19.00	10 Neon **Ne** 20.18
11 Sodium **Na** 22.99	12 Magnesium **Mg** 24.31											13 Aluminium **Al** 26.98	14 Silicon **Si** 28.09	15 Phosphorus **P** 30.97	16 Sulfur **S** 32.07	17 Chlorine **Cl** 35.45	18 Argon **Ar** 39.95
19 Potassium **K** 39.10	20 Calcium **Ca** 40.08	21 Scandium **Sc** 44.96	22 Titanium **Ti** 47.87	23 Vanadium **V** 50.94	24 Chromium **Cr** 52.00	25 Manganese **Mn** 54.94	26 Iron **Fe** 55.85	27 Cobalt **Co** 58.93	28 Nickel **Ni** 58.69	29 Copper **Cu** 63.55	30 Zinc **Zn** 65.41	31 Gallium **Ga** 69.72	32 Germanium **Ge** 72.64	33 Arsenic **As** 74.92	34 Selenium **Se** 79.96	35 Bromine **Br** 79.90	36 Krypton **Kr** 83.80
37 Rubidium **Rb** 85.47	38 Strontium **Sr** 87.62	39 Yttrium **Y** 88.91	40 Zirconium **Zr** 91.22	41 Niobium **Nb** 92.91	42 Molybdenum **Mo** 95.94	43 Technetium **Tc** [97.91]	44 Ruthenium **Ru** 101.1	45 Rhodium **Rh** 102.9	46 Palladium **Pd** 106.4	47 Silver **Ag** 107.9	48 Cadmium **Cd** 112.4	49 Indium **In** 114.8	50 Tin **Sn** 118.7	51 Antimony **Sb** 121.8	52 Tellurium **Te** 127.6	53 Iodine **I** 126.9	54 Xenon **Xe** 131.3
55 Cesium **Cs** 132.9	56 Barium **Ba** 137.3	57-71 Lanthanides	72 Hafnium **Hf** 178.5	73 Tantalum **Ta** 180.9	74 Tungsten **W** 183.8	75 Rhenium **Re** 186.2	76 Osmium **Os** 190.2	77 Iridium **Ir** 192.2	78 Platinum **Pt** 195.1	79 Gold **Au** 197.0	80 Mercury **Hg** 200.6	81 Thallium **Tl** 204.4	82 Lead **Pb** 207.2	83 Bismuth **Bi** 209.0	84 Polonium **Po** [209.0]	85 Astatine **At** [210.0]	86 Radon **Rn** [222.0]
87 Francium **Fr** [223.0]	88 Radium **Ra** [226.0]	89-103 Actinides	104 Rutherfordium **Rf** [261.1]	105 Dubnium **Db** [262.1]	106 Seaborgium **Sg** [266.1]	107 Bohrium **Bh** [264.1]	108 Hassium **Hs** [277]	109 Meitnerium **Mt** [268]	110 Darmstadtium **Ds** [271]	111 Roentgenium **Rg** [272]							

Lanthanides	57 Lanthanum **La** 138.9	58 Cerium **Ce** 140.1	59 Praseodymium **Pr** 140.9	60 Neodymium **Nd** 144.2	61 Promethium **Pm** [144.9]	62 Samarium **Sm** 150.4	63 Europium **Eu** 152.0	64 Gadolinium **Gd** 157.3	65 Terbium **Tb** 158.9	66 Dysprosium **Dy** 162.5	67 Holmium **Ho** 164.9	68 Ersium **Er** 167.3	69 Thulium **Tm** 168.9	70 Ytterbium **Yb** 173.0	71 Lutetium **Lu** 175.0
Actinides	89 Actinium **Ac** [227.0]	90 Thorium **Th** 232.0	91 Protactinium **Pa** 231.0	92 Uranium **U** 238.0	93 Neptunium **Np** [237.0]	94 Plutonium **Pu** [244.1]	95 Americium **Am** [243.1]	96 Curium **Cm** [247.1]	97 Berkelium **Bk** [247.1]	98 Californium **Cf** [251.1]	99 Einsteinium **Es** [252.1]	100 Fermium **Fm** [257.1]	101 Mendelevium **Md** [258.1]	102 Nobelium **No** [259.1]	103 Lawrencium **Lr** [262.1]

KEY

3	→ Atomic number
Lithium	→ Name of element
Li	→ Symbol of element
6.94	→ Atomic mass

Where the atomic weight is not known, the relative atomic mass of the most common radioactive isotope is shown in brackets. The atomic weights of Np and Tc are given for the isotopes ^{237}Np and ^{99}Tc.

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- Click on the Companion Website—live button to go to the live Companion Website. An Internet connection is required. ➤ Companion Website—live
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- 700 MB of available hard disk space
- Internet Explorer 5.01, 5.5, 6.0 or 6.1

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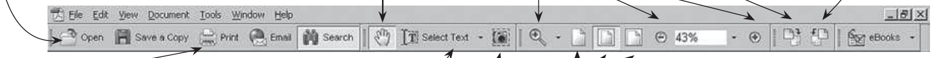

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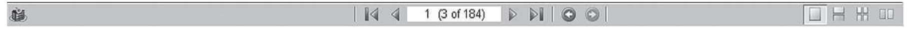

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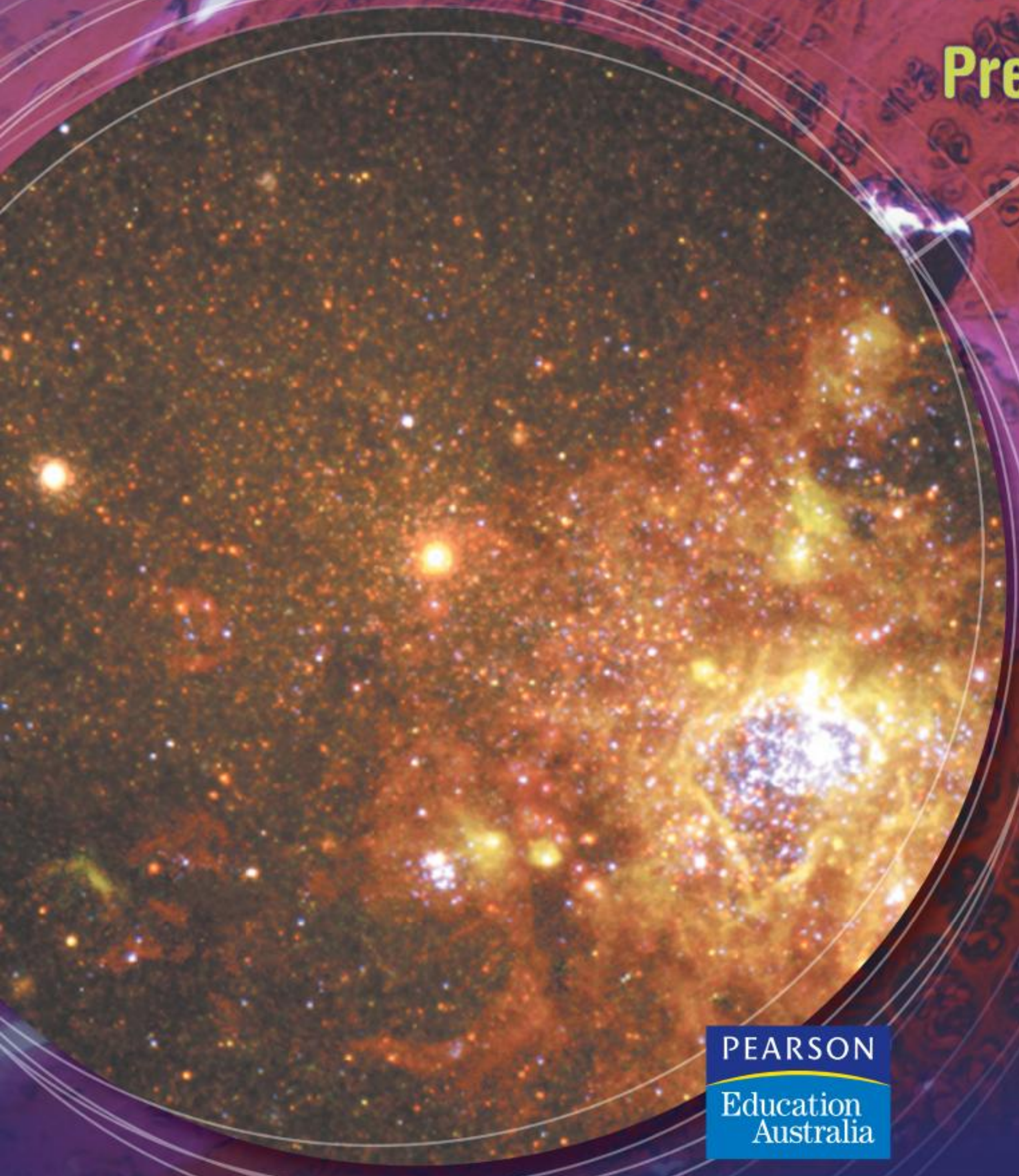

Debbie Irwin
Ross Farrelly
Patrick Garnett

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Education Australia

Sydney, Melbourne, Brisbane, Perth and
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MODULE 1

the chemical earth

This module will cover the following material:

- the kinetic theory of matter
- origin of the elements and the chemical composition of the Earth
- separation of mixtures
- the periodic table
- Dalton's atomic theory
- chemical formulas and equations
- properties of elements
- atomic structure and isotopes
- ions and ionic bonding
- molecules and covalent bonding
- electron dot formulas
- chemical decomposition and synthesis
- metallic, ionic, covalent molecular and covalent network substances
- extraction of elements.

CHAPTER 1

THE EARTH: A MIXTURE OF CHEMICALS

1.1 The scope of chemistry

Chemistry deals with the composition, structure, properties and reactions of matter. Our planet Earth provides us with a vast array of chemical substances to study and use. Metals such as gold and aluminium, non-metals such as carbon, sulfur, oxygen and hydrogen, chemical compounds such as sodium chloride, carbon dioxide, methane and water, and mixtures including crude oil, granite and concrete are used by us every day. The extraction and purification of these substances from the Earth can be understood and improved using our increasing knowledge of chemistry.

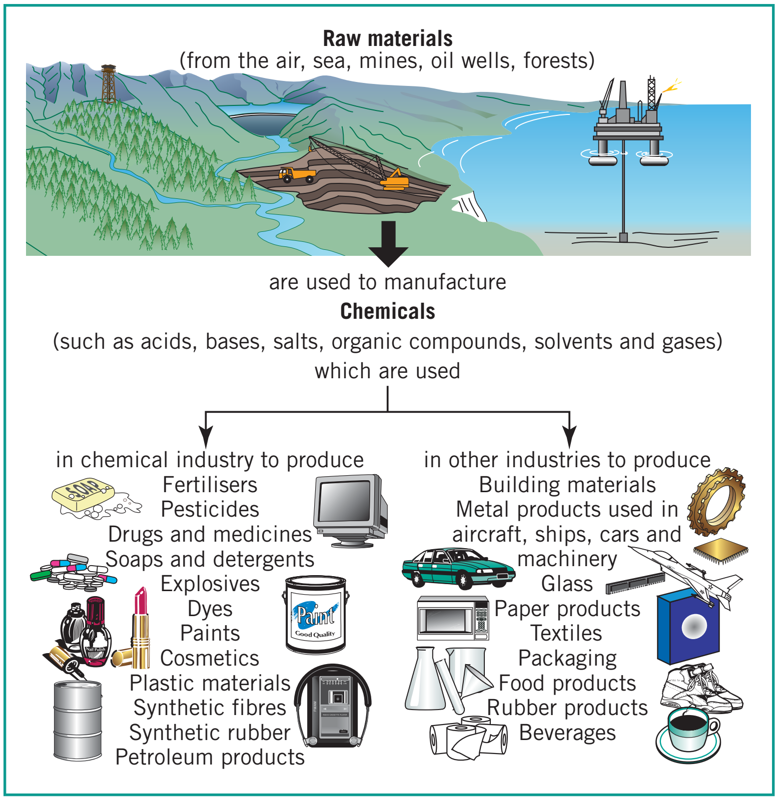


Figure 1.1 The Earth provides the raw materials of the chemical industry.

An understanding of chemistry is fundamental to all biological systems including human biology. This relationship exists partly because the biosphere (containing all living things) and the environment in which organisms live are made up of chemical substances. Life itself is a very complicated system of interrelated chemical processes.

Chemistry also finds applications in many other scientific disciplines. These include agricultural science, engineering, pharmacy, medicine, space science, oceanography and environmental science. The overlap of chemistry with other sciences has led to the development of 'new' sciences that have become disciplines in their own right. Examples of these newer disciplines are biochemistry, geochemistry, astrochemistry and chemical engineering. Because of its application in many sciences, chemistry is often referred to as the 'central science'.

Today, chemists continue to extend our chemical knowledge. Universities, the CSIRO (Commonwealth Scientific and Industrial Research Organisation), various government instrumentalities and many industries employ chemists to work on a wide range of activities. The extent and importance of chemical industries can be gauged by considering the range of products that are manufactured by these industries. This includes fertilisers, pesticides, food preservatives, petroleum, metals, paper, paint, cosmetics, rubber, plastics, pharmaceuticals, textiles, and many others.

Figure 1.2 Epoxy fibreglass, Kevlar, Mylar, carbon fibre, polyester and stainless steel are just some of the materials used in state-of-the-art yachting.

Chemistry has made a significant contribution to the quality of life in our society. The efficiency of the food production industry today is largely due to the use of fertilisers and pesticides. The polymer and plastics industry has had an enormous impact in many areas such as furniture, clothing, children's toys and food packaging. The pharmaceutical industry, with its development of vaccines, antibiotics and pain relievers, has also had a substantial impact on the quality of life we enjoy.

However, side-effects of the chemical industry and the occasional irresponsible use of chemicals have had damaging environmental consequences. The agricultural insecticide DDT has become notorious because it weakens the eggshells of certain birds and has led some species to the verge of extinction. At the beginning of the Second World War, however, DDT was viewed more favourably as it was used extensively in the control of malarial mosquitoes and saved millions of human lives.

Another example of the beneficial and detrimental aspects of the application of chemicals is the use of fertilisers. While fertilisers have enabled our agricultural producers to become highly efficient, their indiscriminate overuse, resulting in them being washed into streams and lakes, has contributed to the excessive growth of algae, to the detriment of other aquatic life.

These experiences illustrate the need to carefully monitor and control the use of chemicals in all aspects of life. Clearly, the chemical industry makes an important contribution to present-day living standards but it is equally important to ensure that these benefits are not obtained at an unacceptably high cost to the environment.

❇ Review exercise 1.1

1 **Identify** one chemical used for each of the following: food preservative, analgesic (pain killer), cleaning agent, fuel, fertiliser, pesticide, building material, antibiotic, textile, plastic.

2 **Define** each of the following fields of science: biochemistry, geochemistry, astrochemistry and chemical engineering.

1.2 States and properties of matter: the kinetic theory

Chemistry is the study of the composition, structure, properties and reactions of matter. Matter is defined as anything that has mass and occupies space, such as wood, water, steel and air. Light, sound and magnetic fields are examples of phenomena that are not matter.

States of matter

Matter commonly exists in three states—gas, liquid and solid. Water, for example, exists as steam, liquid water and ice. The characteristics of solids, liquids and gases are summarised in Table 1.1. These characteristics reveal some information about the arrangement of particles in solids, liquids and gases.

Table 1.1 Characteristics of solids, liquids and gases

	Solid	Liquid	Gas
Shape	definite	variable	variable
Volume	definite	definite	variable
Compressibility	almost incompressible	very slightly compressible	highly compressible
Diffusion	negligible	slow	fast
Thermal expansion	slightly expandable	moderately expandable	highly expandable

A model for the arrangement of particles in solids, liquids and gases is illustrated in Figure 1.3.

Gases

The *kinetic theory* uses a model of a gas that assumes gases are made up of particles of matter in a state of constant motion. The term 'kinetic' indicates that it is the motion of these gas particles that plays a key role in their physical properties. The kinetic theory is based on the following assumptions:

1 Gases consist of tiny particles called molecules.

2 The average distance between the molecules of a gas is very large compared with the size of each gas molecule, i.e. in gases the particles are widely spaced.

3 The molecules of a gas move in rapid, random, straight-line motion. These movements result in collisions with each other and with the sides of any container.

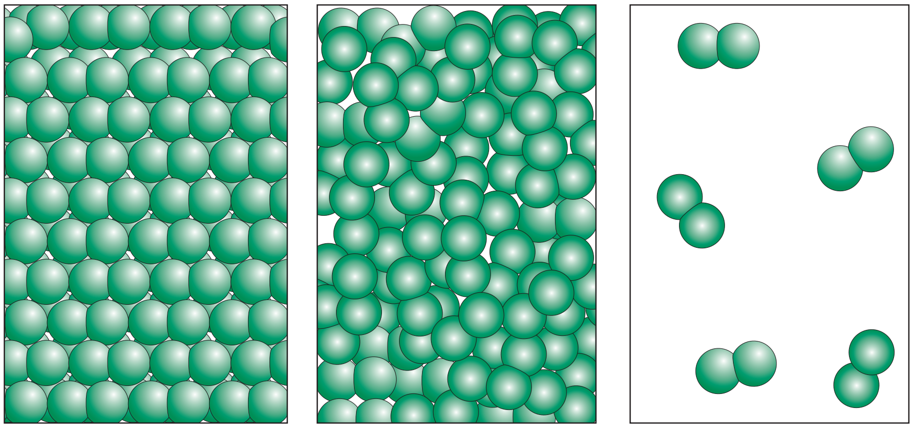


Figure 1.3 Arrangement of particles in solids, liquids and gases

4 The molecules of a gas exert negligible attractive or repulsive forces on one another, so the molecules move virtually independently.

5 All collisions of gas molecules are perfectly elastic. This means that there is no net energy loss during these collisions.

6 The average kinetic energy of the molecules increases as the temperature of the gas increases.

The kinetic theory is used to explain the physical properties of gases. Gas pressure is explained in terms of collisions of the gas molecules with the walls of the container. For example, an inflated balloon maintains its shape due to collisions of the gas molecules with the inside surface of the balloon.

The diffusion of gases can be explained in terms of the constant motion of gas molecules. If a bottle of perfume is spilt, the scent quickly becomes apparent throughout the room. This is because gas particles are in constant motion and will continue to move in all directions until stopped by the walls of a container. Gases always spread to occupy all the available space. This is called *diffusion*.

The compressibility of gases can be explained by the large spacing between the molecules compared with the size of each molecule. Most of the volume occupied by a gas is empty space. As a result, gases can be compressed, as happens in car and bicycle tyres and in gas cylinders. The kinetic theory can be extended to explain the behaviour of solids and liquids. In the gaseous state, the particles are widely spaced and exhibit random straight-line movement. Intermolecular forces are so small that they can be ignored. However, in solids and liquids ('the condensed states') the particles are much closer together and are restricted in their movement. Attractive forces exist between the particles. As a result, the properties of solids and liquids are quite different from those of gases.

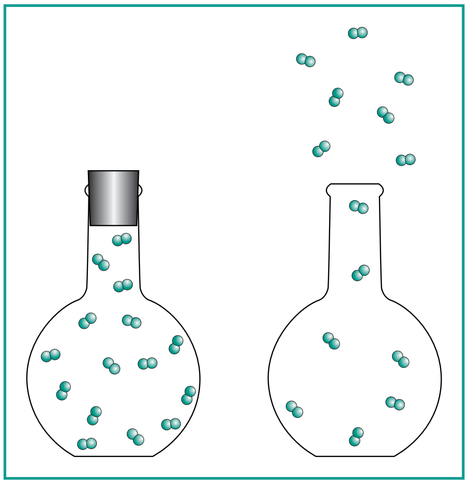


Figure 1.4 Gases spread to occupy the available space. The spacing between molecules is very large compared with the size of the molecules.

Liquids

Although the particles are much closer in liquids than in gases, they still constantly change their positions. The particles can slip past each other but, because of their close proximity, a particle cannot travel far before colliding with a

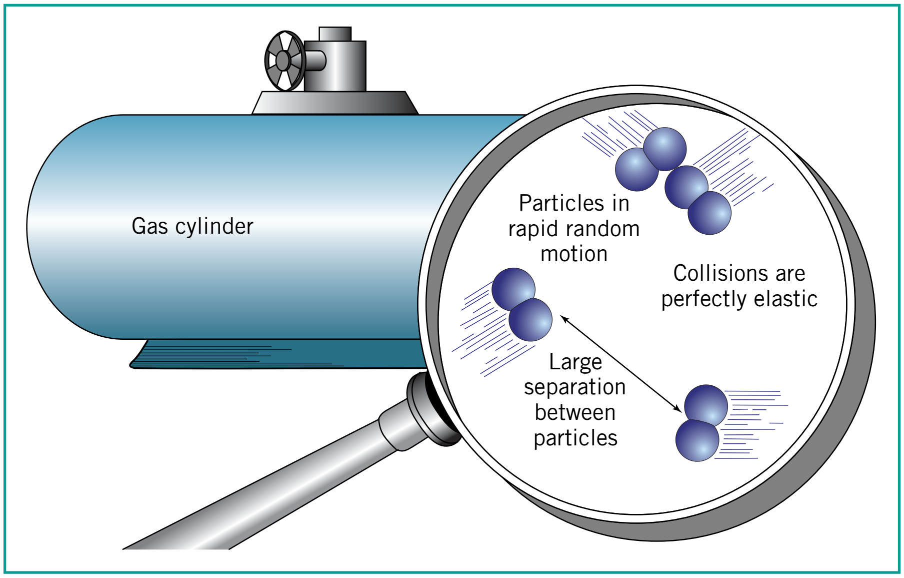


Figure 1.5 The kinetic theory accounts for the behaviour of gases.

neighbouring particle. This allows the particles to move relative to one another and is why liquids have a variable shape. The fact that the particles of a liquid do not occupy fixed positions allows the liquid to flow and hence take on the shape of its container. It is also the reason that diffusion occurs in liquids. The lack of space between particles is the reason that liquids are virtually incompressible and have a definite volume.

Solids

In solids the particles are closely packed and held fairly rigidly in position. The movement of particles in solids is therefore more restricted than in liquids, and much more restricted than in gases. Each particle in a solid occupies a fixed position in relation to its neighbours and the particles vibrate about these fixed positions in the limited space available to them. As a result, solids have a definite shape as well as a definite volume.

Figure 1.6 There is a fourth state of matter, plasma, which makes up most of the matter in the universe. This is composed of rapidly moving charged particles such as electrons and positive ions and is found in stars.

Review exercise 1.2

1 **Outline** how the models of gases, liquids and solids presented in Figure 1.3 can account for each of the observed characteristics of these states of matter given in Table 1.1.

2 **Explain** how a smell produced from cooking in the kitchen can quickly travel around a whole house.

3 **Analyse** how the kinetic theory explains the fact that the pressure of a gas in a sealed container remains constant indefinitely, provided the volume and temperature are kept constant.

4 **Account** for the observation that gases are easily compressed.

5 **Explain** why gases spread to occupy the available space.

6 Use the kinetic theory to **describe** the different arrangement of particles in solids and liquids, and **explain** the properties that result.

1.3 Classification of matter

The matter that makes up the Earth includes naturally occurring matter such as rocks, air and water, and matter modified by human activity such as most metals, glass and plastics. A classification scheme for different kinds of matter found on Earth is shown in Figure 1.7. In this scheme, matter is classified into pure substances and mixtures.

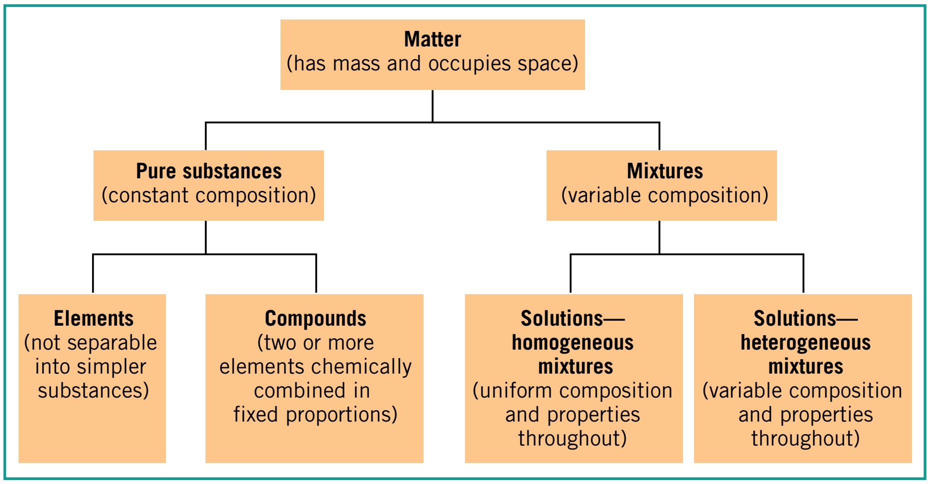


Figure 1.7 Classification of matter

Pure substances consist of matter that is homogeneous—that is, it has the same type and distribution of particles throughout, and a definite, fixed composition. Pure substances include elements and compounds. *Elements* are substances that cannot be separated by chemical change into simpler substances, such as carbon, oxygen and copper. They also consist of only one type of atom. *Compounds* are substances composed of two or more elements combined in fixed proportions. Water and carbon dioxide are examples of compounds. Water consists of hydrogen and oxygen, which are chemically combined; carbon dioxide contains combined carbon and oxygen. Compounds have quite different properties from those of the elements they contain. Water, for example, has very different properties from the elements hydrogen and oxygen which, as elements, exist as gases at normal temperatures. Iron(II) sulfide is a compound that contains chemically combined iron and sulfur. Like most compounds, iron(II) sulfide has vastly different properties from those of the elements from which it is formed (see Table 1.2).

Table 1.2 Properties of iron, sulfur and iron(II) sulfide

	Iron	Sulfur	Iron(II) sulfide
State at 25°C	solid	solid	solid
Colour	grey	yellow	black
Melting point (°C)	1535	113	1195
Boiling point (°C)	2750	445	decomposes
Density (g/cm^3)	7.9	2.1	4.8
Magnetic	yes	no	no

Matter that contains two or more pure substances is described as a *mixture*. Mixtures can contain different proportions of the same component substances. Pure substances, on the other hand, always have the same composition.

Mixtures can be homogeneous or heterogeneous. *Homogeneous* mixtures have uniform composition and properties throughout. For example, when sugar is dissolved in water, it forms a solution in which the sugar and water are uniformly mixed, and is therefore homogeneous. A container of air is another homogeneous mixture, this time of gases.

Heterogeneous mixtures are those that are not uniform in composition and properties throughout. For example, granite is a heterogeneous mixture that consists of the minerals quartz, feldspar, mica and usually hornblende. It is often possible to identify these separate components in a granite sample by visual observation. Concrete, which consists of cement, sand and rock aggregate, is another example of a heterogeneous mixture.

In Figure 1.8, atoms are represented as shaded circles. Figures **a, b** and **c** are representations of three different elements, X, Y and Z. As they illustrate elements, each contains only one type of atom. Note that in **a** and **b** the atoms are combined into pairs (diatomic molecules) and the element is represented as X_2 and Y_2. In **c** the atoms exist separately (as monatomic molecules) and the element is represented as Z. Compounds are combinations of different elements, as illustrated in **d** and **e**. In **d** one atom of Y is combined with one atom of X and is represented as XY. In **e** two atoms of Z are combined with each atom of X and the compound is represented as XZ_2.

Mixtures are not pure substances. For example, **f** illustrates a mixture of elements X_2 and Z, while **g** represents a mixture of element Y_2 and compound XZ_2.

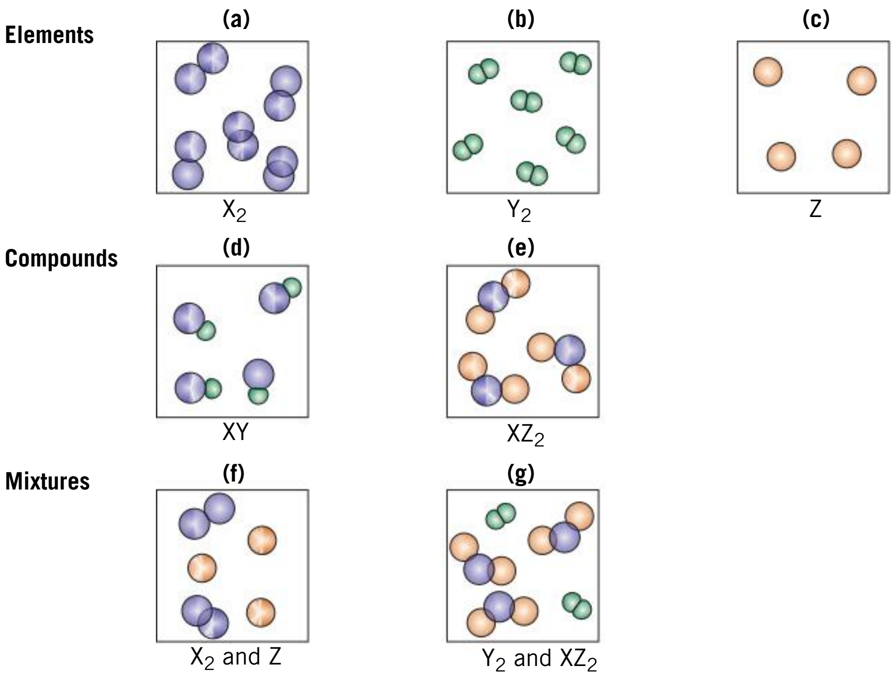


Figure 1.8 The classification of matter using three imaginary elements, X, Y and Z

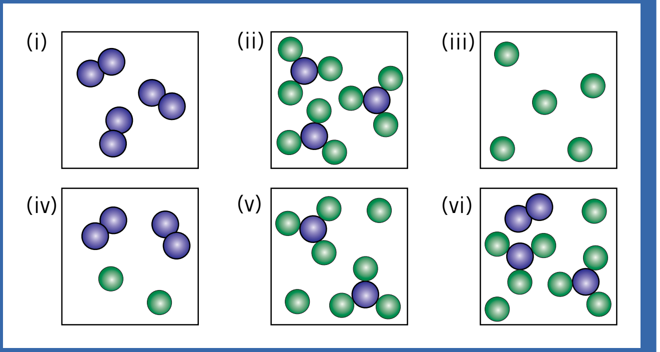
Review exercise 1.3

1 **Distinguish** between the following terms:

- **a** element and compound
- **b** homogeneous mixture and heterogeneous mixture
- **c** compound and homogeneous mixture.

2 If 🟣 represents an atom of P and 🟢 an atom of Q, **identify** for each of the diagrams below:

- **a** whether an element, compound or mixture is present
- **b** the symbolic representations of the substances present.



3 **Classify** the following as elements, compounds, homogeneous mixtures or heterogeneous mixtures:

- **a** molten iron
- **b** salt
- **c** carbon dioxide
- **d** sugar
- **e** lemonade
- **f** nitrogen
- **g** water
- **h** concrete
- **i** air
- **j** wine.

1.4 Chemicals of the Earth

About 4.5 billion years ago, large amounts of material from exploded stars came together under the influence of gravity to form the sun and planets in our solar system. Initially the Earth may have been a cold, relatively homogeneous body. Some time in the first billion years, the Earth's temperature rose significantly. This was probably a result of the release of heat due to gravitational contraction, the impact of meteors on the Earth's surface and the radioactive decay of some elements. The increase in temperature caused the Earth to melt and allowed some separation of the substances making up the Earth. This process is known as *differentiation* or *fractionation*. The more dense elements such as iron and nickel sank to form a core, while in the outer regions, oxygen combined with other elements to form a variety of compounds.

A layered structure

Today the Earth is believed to have a layered structure (see Figure 1.9) consisting of:

1. a dense core of mostly iron and nickel
2. a thick, relatively homogeneous mantle composed mainly of magnesium and silicon oxides, and magnesium and iron silicates
3. a thin, heterogeneous crust, consisting of oxygen, silicon, aluminium, iron, calcium, sodium, potassium, magnesium and less than 1% of the many other elements.

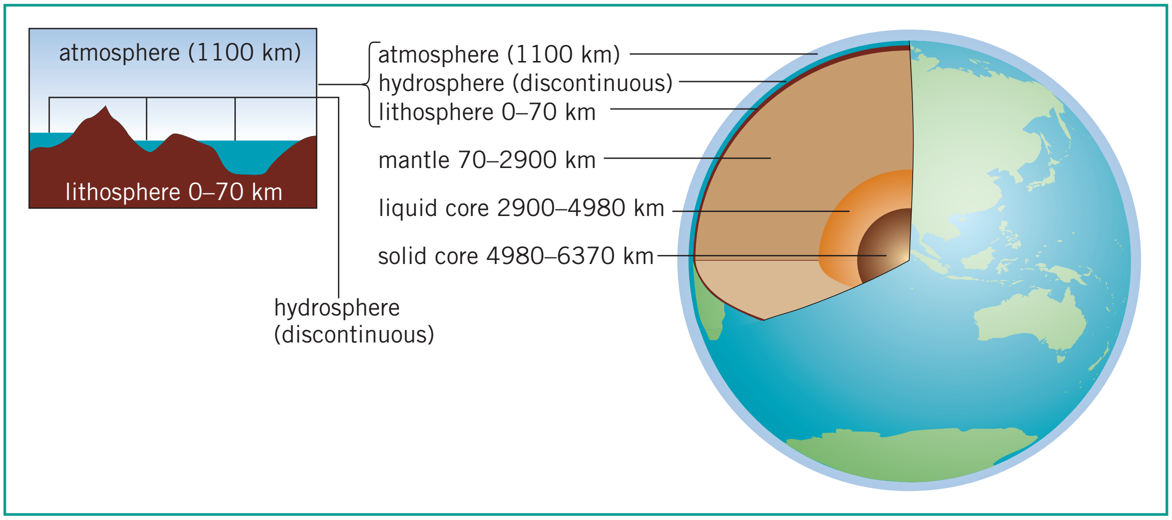


Figure 1.9 Layered structure of the Earth

Evidence for this layered structure comes from observations of the Earth's density and seismology (the study of how shock waves, generated by earthquakes, travel through the Earth).

The Earth's crust includes a solid lithosphere, liquid hydrosphere and gaseous atmosphere, together with a living biosphere that overlaps the other three components. These are the parts of the Earth with which we interact the most and therefore of which our chemical knowledge is greatest. Their composition includes combinations of many elements, compounds and mixtures.

The lithosphere

The *lithosphere* is composed mostly of rocks and soil, which are mixtures of minerals. Minerals are naturally occurring solid elements or compounds with a definite composition or range of compositions. Examples of minerals include: quartz, a compound of silicon and oxygen; feldspars, which are a group of compounds containing various combinations of sodium, potassium, calcium, aluminium, silicon and oxygen; calcite, containing calcium, carbon and oxygen; and many other minerals such as pyroxene, biotite, iron oxides and kaolinite, a clay mineral. Few elements are found uncombined in the lithosphere, with gold, sulfur and carbon being notable exceptions.

Figure 1.10 Quartz (silicon dioxide) can sometimes be found as well-developed six-sided crystals.

The atmosphere

The atmosphere is a mixture composed mostly of uncombined lighter elements such as nitrogen, oxygen and argon with small percentages of compounds such as carbon dioxide, methane and water. The composition of the atmosphere is shown in Table 1.3 but varies somewhat according to location and climate.

Table 1.3 Composition (by volume) of unpolluted dry* air

Substance	Percentage
Nitrogen	78.1
Oxygen	20.9
Argon	0.93
Carbon dioxide	0.035
Others	Each < 0.01

*Water vapour is also present, somewhere in the range 0–5%.

The hydrosphere

The *hydrosphere* includes the Earth's oceans, seas, lakes, rivers and underground water. By far its major constituent is water, with varying quantities of compounds containing chlorine, sodium, magnesium, potassium, calcium, sulfur, bromine and many other elements. The hydrosphere also has a variable composition, with differences in the composition between fresh and sea water being particularly marked.

The biosphere

The *biosphere* is that part of the Earth in which living organisms live out their life cycles. The biosphere contains a vast array of living things with many chemical characteristics in common. All living things on Earth are composed of compounds based on the element carbon. Other elements essential to living things include oxygen, hydrogen, nitrogen, sulfur and phosphorus. These elements are provided from the surrounding lithosphere, atmosphere and hydrosphere in the form of compounds such as water and carbon dioxide, and elements such as the oxygen we breathe.

Elemental cycles

The continuous flow of elements, such as carbon, oxygen, nitrogen and phosphorus, in various forms between the biosphere, lithosphere, hydrosphere and atmosphere is essential to maintaining life on earth. The carbon cycle is illustrated in Figure 1.11.

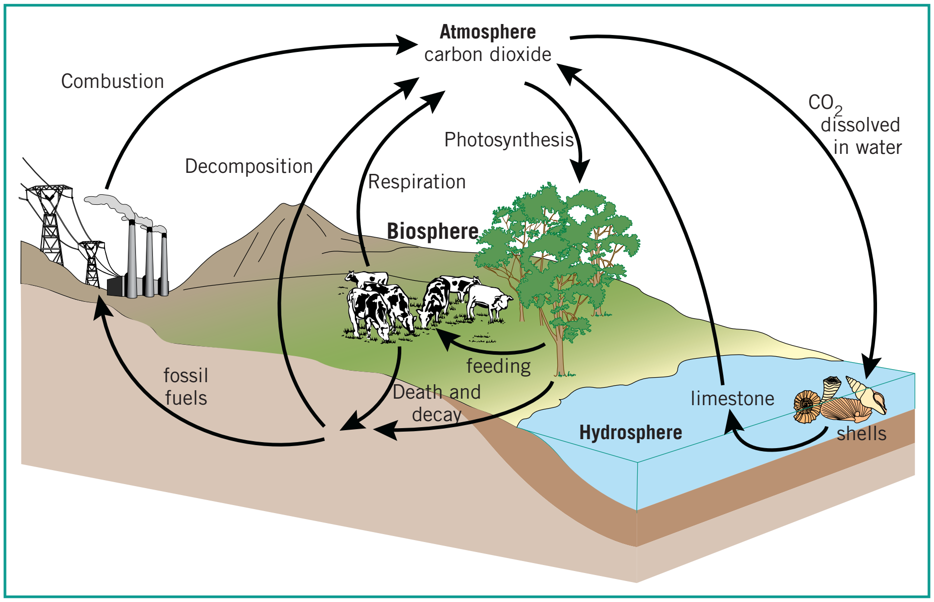


Figure 1.11 Carbon and other elements are continuously being recycled throughout the various components of the environment.

CHEMISTRY CONTEXT

❇ ORIGIN OF CHEMICAL ELEMENTS

Scientists now believe that the universe began with the ‘Big Bang’ probably about 15 billion years ago. According to the Big Bang Theory, the universe began with a massive explosion. In this explosion a mixture of protons, neutrons, electrons and other subatomic particles collectively known as plasma was created. All the elements found in the universe are believed to have been formed from this original material.

During the first few minutes of the universe’s existence, hydrogen and helium formed. This material continued to expand until, millions of years later, gravitational forces caused it to contract into massive clouds where stars could be created.

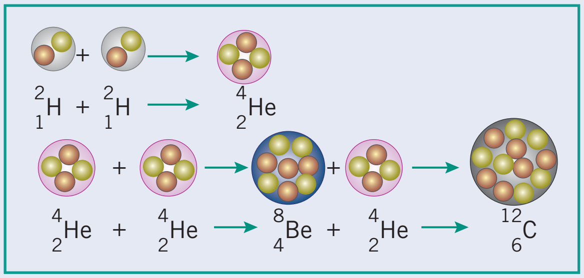


Figure 1.12 **Fusion equations illustrating the formation of helium from hydrogen and carbon from helium**

Within these stars, conditions existed that allowed the formation of heavier elements through the processes of nuclear fusion. Fusion processes in stars are believed to take place in a series of stages, which depend upon the mass and therefore temperature of the star.

The fusion processes within stars lead to the formation of elements as heavy as iron. Heavier elements are formed by neutron capture processes that occur during a supernova, when large stars explode, blasting large amounts of material into space. The subsequent condensation of material from previous supernovas can lead to the formation of new stars, known as second- or third-generation stars. In these stars the proportion of heavier elements is higher than that found in first-generation stars. This is the case for our own sun, which is believed to have formed about 4.5 billion years ago. This means that most of the elements on the Earth and in other planets in the solar system are in fact older than the solar system itself.

This process of formation of chemical elements suggests that the abundance of elements on Earth is essentially fixed and will not change significantly. The various chemical reactions that occur on Earth may change the way in which these elements are combined, but do not change the overall abundance of each element.

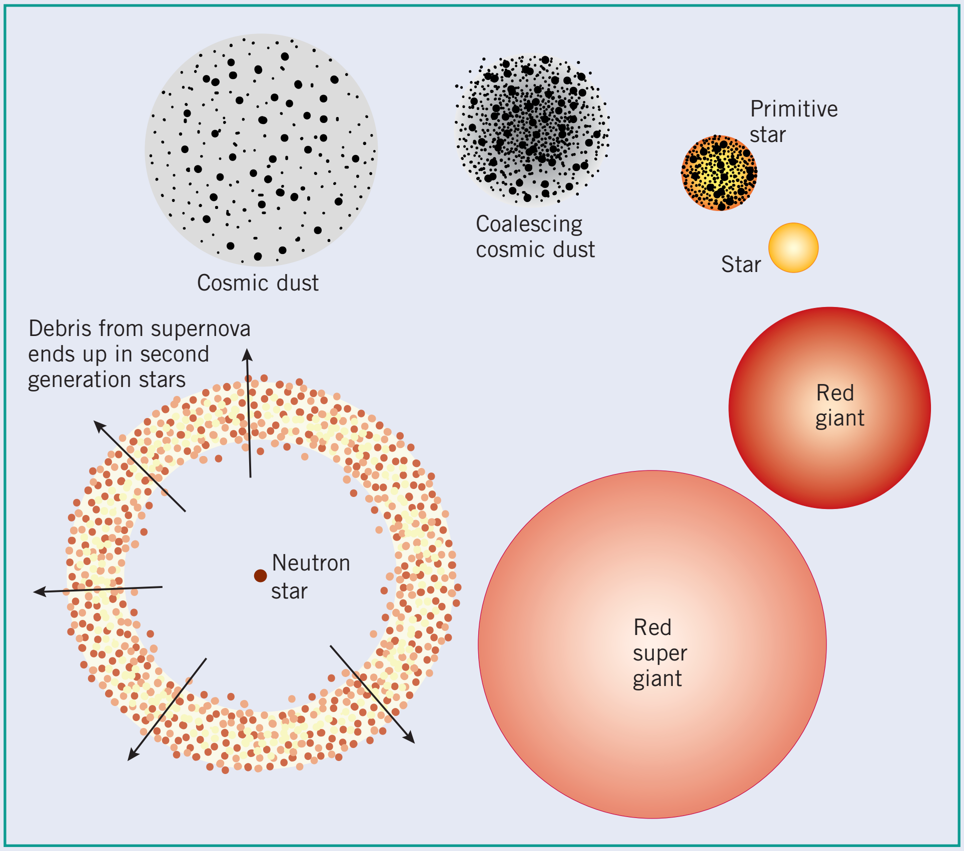


Figure 1.13 **The life cycle of a star (light chemical elements form in the early stages and the heavier elements form in the later stages)**

❄ Review exercise 1.4

1 **Define** in your own words the terms:
  - **a** biosphere
  - **b** lithosphere
  - **c** atmosphere
  - **d** hydrosphere.

2 **Identify** two examples of:
  - **a** elements essential for animal life
  - **b** elements essential for plant life
  - **c** compounds essential for plant life
  - **d** compounds essential for animal life.

3 What are minerals? **Identify** two examples.

1.5 Useful mixtures

Humans have been able to use many of the natural mixtures found on Earth. The lithosphere provides us with building materials such as granite and sandstone, pottery utensils made from clays, sand, which is the major constituent of glass, and fuels such as coal and natural gas.

The hydrosphere provides us with water, a mixture containing variable quantities of dissolved salts. These natural minerals present in water are useful sources of essential elements required to sustain life. The presence of varying levels of sodium, potassium, magnesium and calcium in the form of their chloride or bicarbonate salts is used as a marketing tool in the sale of spring and mineral water.

Our increasing knowledge of the biosphere has provided humans with many useful mixtures. Plant extracts, including sugar syrup, dyes and drugs such as aspirin from the willow tree, and animal products such as milk and sheepskins, are examples of naturally occurring mixtures we have found to be beneficial.

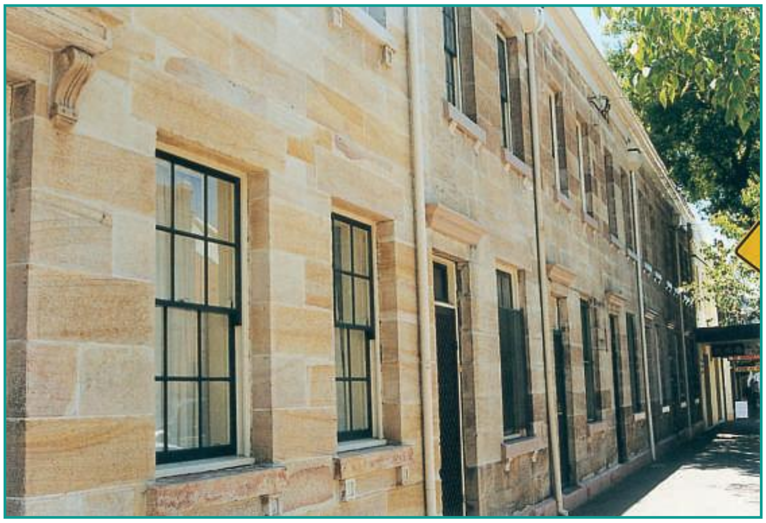


Figure 1.14 Many historic buildings in Sydney are made from locally available mixtures such as sandstone.

In particular, the Australian environment has provided firstly Aborigines and later settlers from Europe and Asia with many materials. The history of Aboriginal land use contains many examples, from ochre dyes to baskets woven from plant fibres and an extensive range of bush medicines. Early European settlers found the sandstone rock of Sydney a particularly useful building material, as can be seen in the historic buildings around Circular Quay.

With increased skill levels and technology we have used many of the rocks of New South Wales, including granite, shale and marble as well as sandstone. Limestone is still used as a major constituent of concrete.

❇ Review exercise 1.5

1 For the following naturally occurring mixtures **identify** the main:

- **a** element in the mixture we describe as coal
- **b** compound in the mixture we describe as sand
- **c** compound in the solution we describe as tap water.

2 Many of the dyes and drugs used by humans were initially obtained from plants or animals but are now produced synthetically. **Explain** why you think this may be so.

3 Humans also use naturally occurring mixtures to extract or separate useful substances. **Identify** an example of:

- **a** a construction metal obtained from a naturally occurring metal ore
- **b** two liquid fuels obtained from oil
- **c** a compound used in cooking obtained from sea water
- **d** an element or compound obtained from the atmosphere used to cool medical samples to low temperatures.

1.6 Separation of mixtures

Very few elements or compounds occur naturally in the pure state. Mostly they are found as mixtures. Many useful substances in the biosphere, lithosphere, atmosphere and hydrosphere were not available to early humans because they could not isolate these substances from the mixtures in which they occur naturally. The great variety of useful substances available to us today is the result of improvements in our ability to separate and extract substances. Aluminium, which is the most abundant metal in the lithosphere, only became cheaply available after an economical method of extraction, the Hall-Heroult process, was developed in the late nineteenth century.

Scientists are constantly developing more efficient and economical means of separating and extracting useful substances. For example, many goldfields that were abandoned earlier this century because they were considered uneconomical to mine are now being reworked using a new method of extraction (cyanidation).

Common techniques for separating the components of mixtures are filtration, solution, evaporation, crystallisation, sedimentation, centrifugation, decantation, sieving, distillation, fractional distillation, chromatography and magnetic separation.

Figure 1.15 Filters for a car engine

Filtration

In the *filtration* process, undissolved solid particles are separated from a liquid (or a gas) by passing the mixture through a screen such as a filter paper that is fine enough to collect the particles of the solid. Filtration is used in the purification of our water supply and is also used to remove solids from petrol in car engines. A vacuum cleaner separates solid particles from air, and car engines include an air filter to remove solid particles from the air.

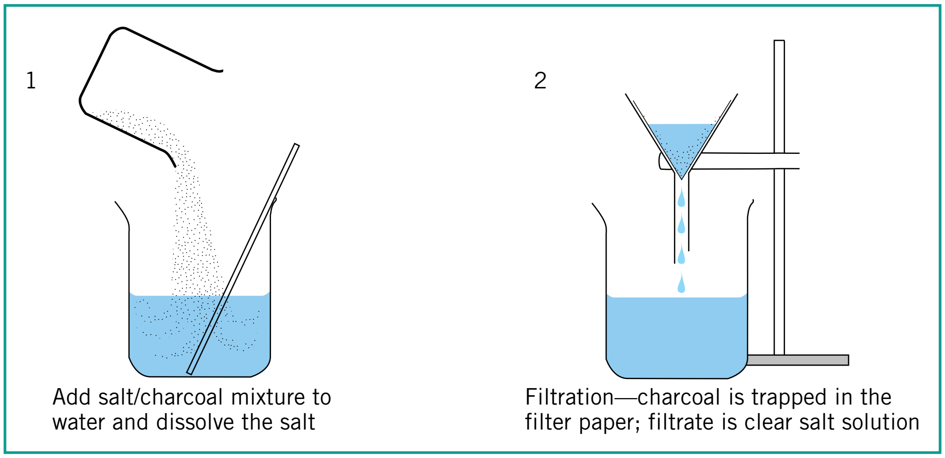
Solution

Solution can be used as a separation process because of the fact that some constituents of a mixture dissolve in a solvent such as water more readily than others. Solution is usually used in combination with filtration, evaporation or crystallisation.

Evaporation

This method of separation relies upon the substances in the mixture having different volatilities. One of the substances evaporates far more readily, leaving the other behind. In a laboratory we often use an evaporating basin and Bunsen burner to speed up the process. *Evaporation* is used in many countries, including Australia, to collect common salt, mostly sodium chloride, from sea water. Sea water is allowed to fill large shallow ponds and the heat from the sun is used to evaporate the water. As the water evaporates, the salt forms as small crystals, which are collected and later refined.

A mixture of charcoal and salt can easily be separated by combining the three methods of solution, filtration and evaporation. Salt is soluble in water but charcoal is insoluble. If water is added to the mixture, the salt will dissolve. The charcoal can then be filtered from the solution using a filter paper, as shown in Figure 1.16. The salt can be recovered by evaporating the filtrate to dryness.



Add salt/charcoal mixture to water and dissolve the salt

Filtration—charcoal is trapped in the filter paper; filtrate is clear salt solution

Figure 1.16 Solution and filtration to separate two solids of different solubilities

Figure 1.17 Salt evaporation lagoons at Dampier, Western Australia (CRA Ltd)

Crystallisation

Crystallisation depends on the components of the mixture having different solubilities in a selected liquid, usually water. Crystallisation is used in the production of sugar from sugar cane and sugar beet. Mixtures containing two or more soluble components can also often be separated by solution, filtration and fractional crystallisation, provided the components have different solubilities at different temperatures. For example, a mixture of salt and baking soda can be separated by dissolving it in hot water and then cooling the resultant solution. While both substances are soluble in hot water, the baking soda is much less soluble in cold water and most of it will crystallise from the solution when it is cooled. This can then be filtered, leaving all the salt and only a small amount of baking soda in solution.

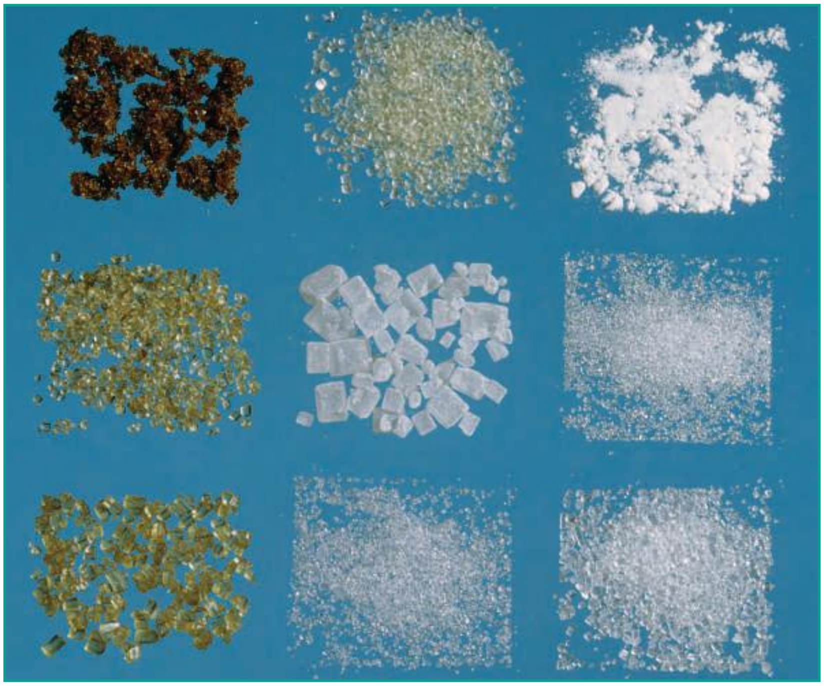


Figure 1.18 A selection of different types of sugar crystals including brown, Demerara, caster and others

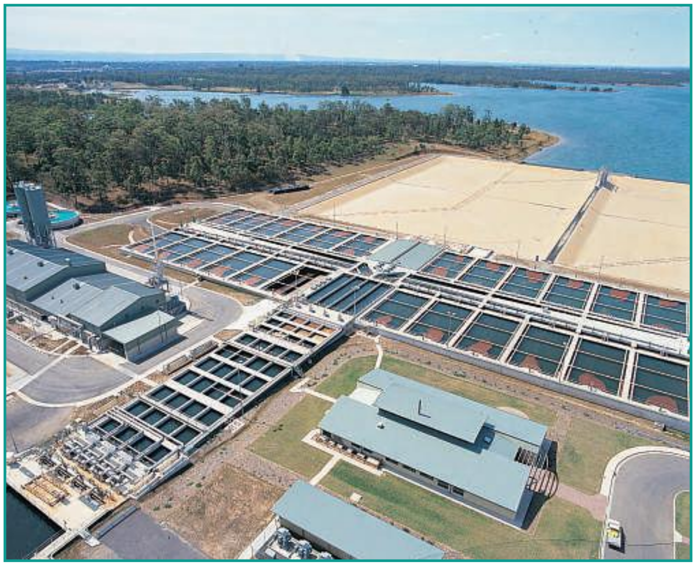


Figure 1.19 Sedimentation tanks at a Sydney water purification plant

Figure 1.20 A flour sieve being used to remove any large particles

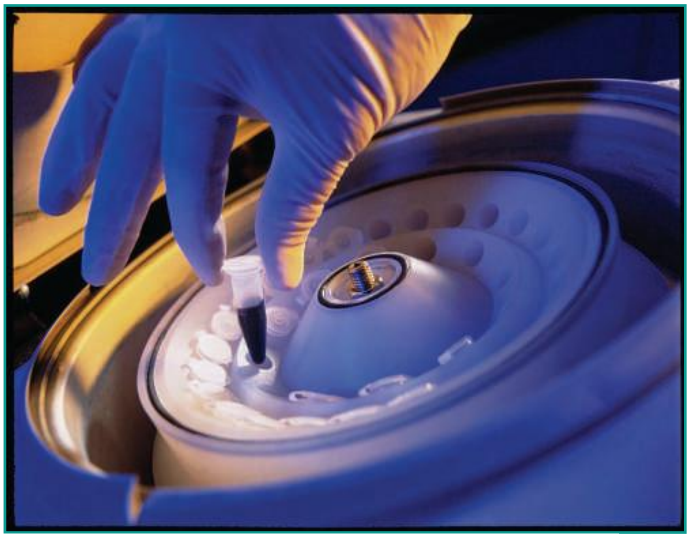


Figure 1.21 Medical centrifuge

Sedimentation

Sedimentation occurs when solid particles are allowed to settle from water (or other liquids) or air. This occurs most readily if the water or air is not moving. It can easily be demonstrated when water is mixed with some soil or mud and then left to settle. Sedimentation is an essential process in the purification of water supplies and in waste water treatment.

Decantation

Decantation is the process of pouring off a liquid from above a solid that has been allowed to settle by sedimentation. Most people would be familiar with this process in the kitchen, when water is poured off vegetables that have been boiled in water.

Sieving

Sieving is the process of separating solid particles of various sizes. You may have seen sieves being used in a bank to separate coins of different denominations. This process is used to sort foodstuffs and is commonly employed in the mining industry to separate mineral particles of different sizes.

Centrifugation

Centrifugation separates mixtures of chemicals using a spinning motion in a machine called a centrifuge. It is commonly used to separate liquids from solids in a manner similar to, but faster than, sedimentation. A common example is the spin dryer in a washing machine. The method may also be used to separate finely divided solid particles present in a liquid mixture. Centrifuges are used widely in industry, for example, to separate cream from milk and plasma from blood.

Distillation

Distillation is often used in the purification of liquids. Distillation involves boiling a liquid and cooling the gas produced to condense it back to the liquid state. Distillation is effective where the components in a mixture have very different boiling points. The component with the lowest boiling point boils off first, is cooled in a condenser and collected as a pure liquid, as shown in Figure 1.22. The components with higher boiling points remain in the distilling flask.

Pure water can be obtained from sea water using the process of distillation. Water boils at a much lower temperature than salt and can be separated in this way, leaving the salt in the distilling flask. It is likely that with future developments in solar energy, Australia will obtain substantial amounts of pure water from the distillation of salt water using solar stills. Distillation is also used in the manufacture of spirits such as brandy, whisky and rum. These spirits are obtained by the distillation of wines, fermented grains and sugar cane respectively.

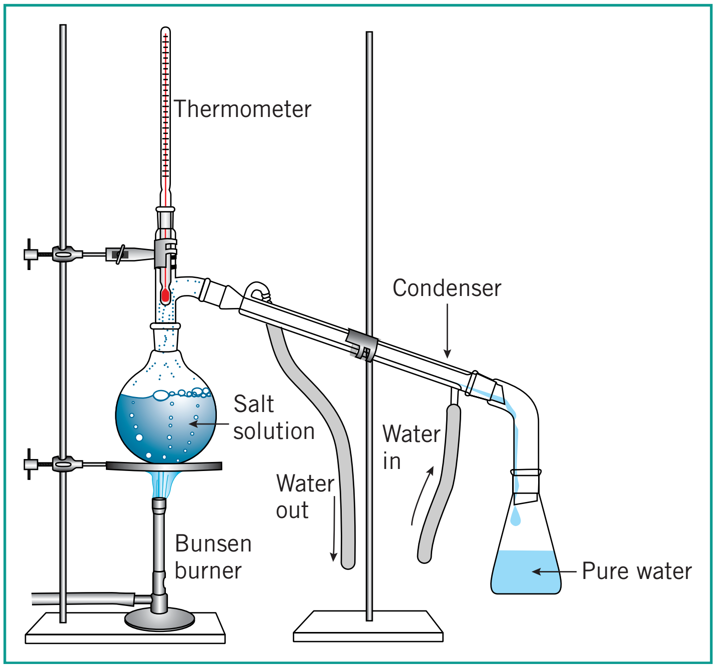


Figure 1.22 A simple distillation procedure to obtain pure water from a salt solution

Fractional distillation

Fractional distillation is the separation of a mixture of several different liquids with similar boiling points. The process involves numerous vaporisation–condensation steps through which the components are gradually separated. In the petroleum industry, repeated fractional distillation is used to separate the components of crude oil into aviation spirit, petroleum, kerosene, lubricants, waxes and asphalt.

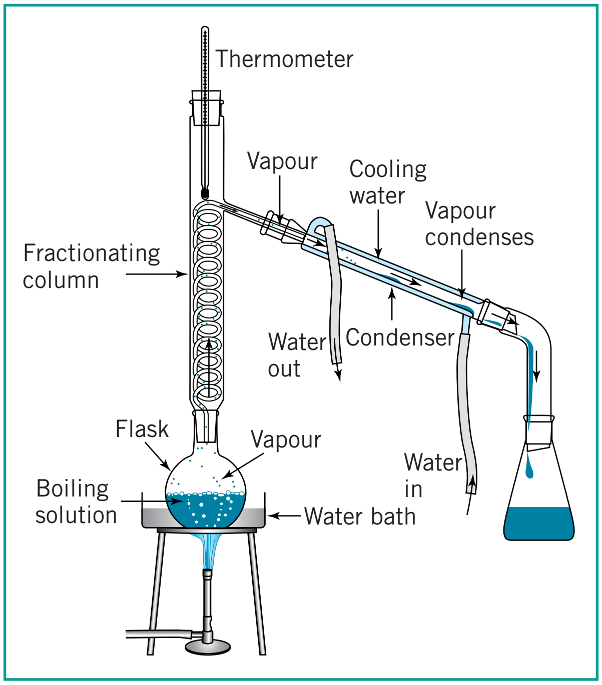


Figure 1.23 Fractional distillation in a laboratory

Figure 1.24 Drug distillation—chemotherapy drug fractions being separated

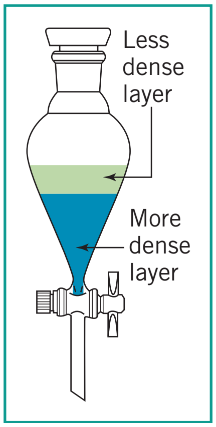


Figure 1.25 A separating funnel is used to separate immiscible liquids.

Separating gases in the air

To separate oxygen and nitrogen, the two major components of air, the air must first be treated to remove carbon dioxide, water and solid particles, then liquefied and finally separated by fractional distillation. The liquefication of the air is quite difficult and requires cooling using some cold liquid nitrogen, combined with expansion of the air, which causes it to cool and condense. The liquid air enters a fractionating column and separates due to the different boiling points of nitrogen (–183°C) and oxygen (–196°C). The nitrogen boils and is removed from the top of the fractionating column. The nitrogen can be re-liquefied by expansion. The separated gases must then be stored in strong-walled or insulated containers such as Dewar flasks.

Separating two immiscible liquids

Liquids that do not mix with each other are said to be *immiscible*. They form separate layers, with the less dense liquid floating on top of the denser liquid. A separating funnel (Figure 1.25) is a simple piece of laboratory equipment that allows these liquids to be separated efficiently. The denser liquid is run off through a tap at the bottom of the flask, leaving the less dense liquid in the funnel.

Chromatography

Chromatography is a relatively recent development but is particularly useful for separating components that are represented in small quantities of mixtures. There are several different chromatographic techniques including column chromatography, paper chromatography, thin layer chromatography and gas chromatography. In each of these techniques the mixture is passed over the surface of an inert substance such as alumina, silica or special paper. The separation of the components in the mixture occurs because the components adsorb, or cling, to the surface of the inert substance with different strengths.

Column chromatography can be used, for example, to separate the various pigments found in plant matter. A solution of the pigments is passed through a column packed with alumina, as shown in Figure 1.26. The different pigments will pass through the column at different speeds, depending on the strength with which they adhere to the alumina. The less strongly adsorbed components pass more quickly through the column than those that are adsorbed more strongly. The pigments can be collected as they wash out of the column.

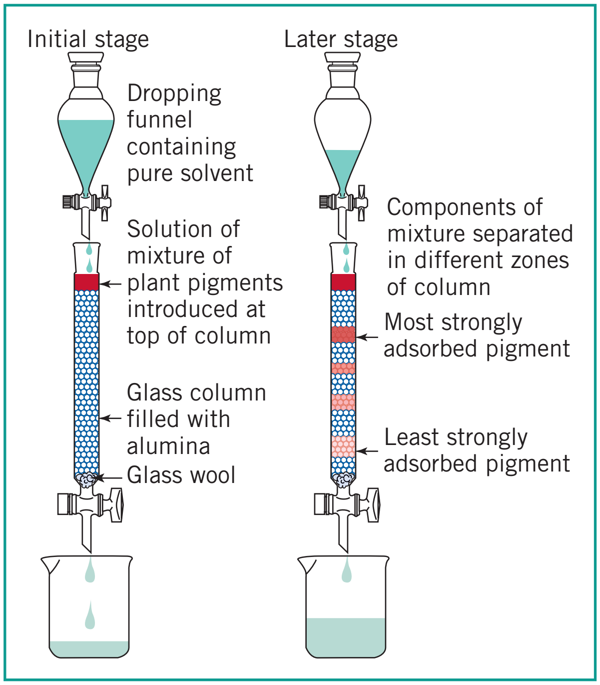


Figure 1.26 Separation of plant pigments by column chromatography

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

Thin layer chromatography is very similar to paper chromatography. The mixture moves up a plate made from glass or plastic and coated with a thin layer of a fine powder such as aluminium oxide. It is a more expensive process than paper chromatography but is faster and capable of detecting smaller quantities of substances.

Gas chromatography is used to detect the components present in a gas or vaporised mixture. The gas mixture is passed through a tube containing a particular solid such as carbon or silica. The different components present pass through the tube at different rates and can be detected as they emerge from the tube. The components of natural gas can be analysed in this way.

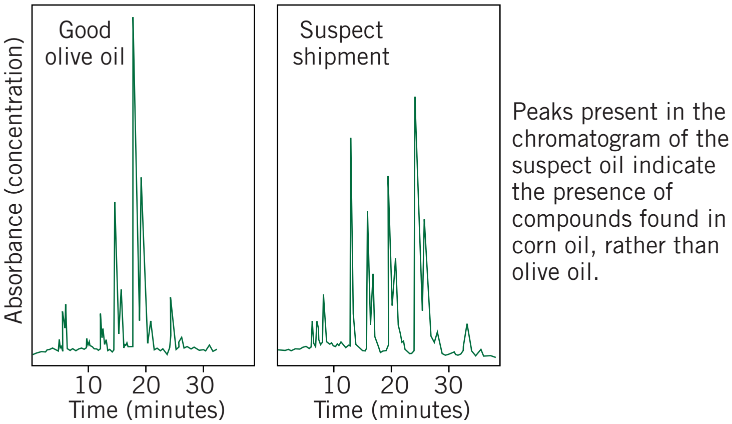


Figure 1.27 Gas chromatogram

Figure 1.28 Large electromagnets are used in waste recycling to separate iron-based objects.

Magnetic separation

Some components of a mixture can be separated from the mixture because they are magnetic. Iron-containing minerals such as magnetite are separated from iron ore in this way. The crushed ore sample is passed between the poles of a strong electromagnet, thus separating out the magnetic material and allowing the crushed rock particles to be removed. Magnetic separation is also used to separate some of the components of mineral sands.

❄ Review exercise 1.6

1 **Identify** which methods of separation work because of the different boiling points of the components of the mixture.

2 **Outline** how the following separations could be achieved:

  a sand from a sand–water mixture

  b water from a salt solution

  c alcohol from wine

  d salt from a sand–salt–water mixture

  e potassium dichromate from a potassium dichromate–ammonium chloride mixture. The solubilities of potassium dichromate and ammonium chloride are roughly the same in hot water but potassium dichromate is much less soluble than ammonium chloride in cold water.

  f drugs from prepared medicines.

1.7 Chemical analysis

The process of finding out what is present in a particular chemical sample is called *chemical analysis*. Chemical analysis can be qualitative or quantitative. Qualitative analysis involves determining what substances are present in a sample. Quantitative analysis is about determining how much of each substance is present in a sample. Two common methods of quantitative analysis are gravimetric analysis and volumetric analysis. *Volumetric analysis* is concerned with the measurement of solution volumes. *Gravimetric analysis* is a method of analysis that involves the measurement of masses.

Percentage composition

The percentage composition of a chemical compound specifies the percentage by mass of each of the different elements present in the compound. For example, water consists of 11.1% hydrogen and 88.9% oxygen by mass. A 100 g sample of water therefore contains 11.1 g of hydrogen and 88.9 g of oxygen.

The percentage composition of a compound can be determined experimentally using gravimetric analysis. For example, information about chemical composition can be determined by decomposing the compound and weighing one or more of the products.

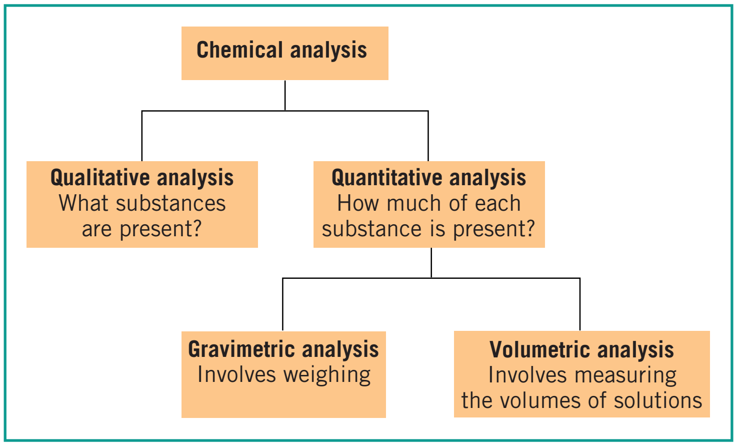


Figure 1.29 Chemical analysis

Figure 1.30 Volumetric analysis being used in quality control of a pharmaceutical

➜ Example 1.1

A 12.60 g sample of hydrated sodium carbonate ($Na_2CO_3.10H_2O$) is heated in a drying oven to constant mass (that is, it is heated and reweighed until no further change in mass occurs due to removal of water of crystallisation). The final mass of the sample is 5.81 g. Determine the percentage of water in the sample.

initial mass = 12.60 g

final mass = 5.81 g

mass change = 2.60 – 5.81 = 6.79 g

% water = 6.79/12.60 × 100 = 53.9%

A knowledge of the composition of compounds can be quite useful. From the data in Table 1.4 it is apparent that haematite and magnetite contain higher percentages of iron than iron pyrites. Such considerations can be important in the economics of the mining and metal extraction industries.

Depending on mining and transportation costs, the mining company will then decide whether it is economically feasible to mine these ore deposits.

Table 1.4 Percentage of iron in three iron compounds

Iron compound	Formula	Percentage of iron
Haematite	Fe_2O_3	70
Magnetite	Fe_3O_4	72
Iron pyrites	FeS_2	46

❇ Review exercise 1.7

1 **Explain** how volumetric and gravimetric analysis differ.

2 **Calculate** the percentage of carbon in a sample of brown coal that had an initial mass of 247.5 g, and after intense heating to remove all water and other impurities, finally had a mass of 203.4 g (assumed to be pure carbon).

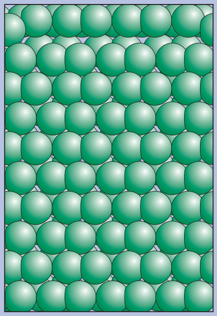
3 **Explain** why mining companies carefully analyse samples of ores before they choose to mine a particular location.

*KEY POINTS

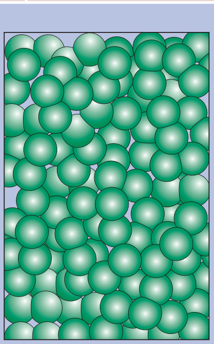
- Chemistry deals with the composition, structure, properties and reactions of matter.
- Chemistry is concerned with:
  - the study of substances that occur in the natural world
  - the extraction and separation of useful substances from naturally occurring materials and the synthesis of new substances
  - the analysis of substances to determine their composition.
- When chemicals are used, careful consideration needs to be given to both the benefits and possible undesirable effects of their manufacture and use.
- Matter is anything that has mass and occupies space.
- Matter can exist in the solid, liquid and gaseous states.
- The characteristics of solids, liquids and gases are shown in the table and diagram.

Characteristics of solids, liquids and gases

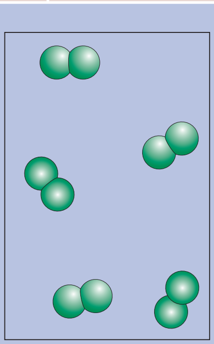
	Solid	Liquid	Gas
Shape	definite	variable	variable
Volume	definite	definite	variable
Compressibility	almost incompressible	very slightly compressible	highly compressible
Diffusion	negligible	slow	fast
Particle arrangement	closely packed, fixed positions	fairly closely packed, not fixed positions	widely spaced, move independently
Thermal expansion	small	moderate	large



Solid
Particles closely packed and held in position.



Liquid
Particles close to one another but free to move.



Gas
Particles far apart and move independently of one another.

- The kinetic theory of gases explains the physical properties of gases. The main ideas are as follows.
  - Gases are composed of molecules.
  - The molecules are widely spaced.
  - The molecules move rapidly.
  - The forces of attraction between molecules are negligible.

  - Collisions between molecules are perfectly elastic.
  - The average kinetic energy of the molecules increases with temperature.
- Kinetic energy is energy due to motion.
- The kinetic theory can be extended to solids and liquids.
- In solids the particles are closely packed and vibrate about fixed positions.
- In liquids the particles are fairly closely packed but can move past each other.
- Intermolecular forces are important in solids and liquids.
- Matter can be classified into the two categories of pure substances (elements and compounds) and mixtures.
  - *Elements* are pure substances that cannot be separated by chemical change into simpler substances.
  - *Compounds* are pure substances composed of two or more elements chemically combined in fixed proportions.
  - *Mixtures* are two or more substances mixed together in variable proportions.
- Homogeneous mixtures or solutions have uniform composition and properties throughout.
- Heterogeneous mixtures are not uniform in composition and properties throughout.
- The Earth has a layered structure consisting of the crust, mantle and core.
- The Earth's crust includes a solid lithosphere, liquid hydrosphere and gaseous atmosphere, and a living biosphere which overlaps the other three components of the crust.
- The abundance of elements on the earth is essentially fixed; chemical reactions that occur on the Earth change the way these elements are combined.
- The biosphere, lithosphere, hydrosphere and atmosphere consist of mixtures of elements and compounds.
- Mixtures that occur naturally and are used by humans include granite, sand, sandstone, coal, water and natural dyes.
- Mixtures can be separated by the following processes:
  - *Filtration*—undissolved solid particles are separated from a liquid or gas by passing the mixture through a filter.
  - *Solution*—one or more component(s) of a mixture dissolve more readily in a solvent (often water).
  - *Evaporation*—one of the components of a mixture evaporates more readily.
  - *Crystallisation*—components in a mixture have different solubilities in water (or other liquid solvents) and crystallise separately from solution.
  - *Sedimentation*—solid particles settle out from a liquid or gas mixture in which they occur.
  - *Centrifugation*—a spinning motion is used to separate components of a mixture that have different densities or exist in different states.
  - *Decantation*—liquid is separated from a solid by pouring off the liquid.
  - *Sieving*—solid particles are separated according to their sizes by passing them through a perforated barrier.

  - *Distillation* (and fractional distillation)—components with different boiling points in a liquid mixture are separated by boiling and condensing the mixture.
  - *Chromatography*—components in a liquid or gas mixture are separated by passing the mixture over the surface of a substance to which the components of the mixture adsorb with different strengths.
  - *Magnetic separation*—components with different magnetic properties are separated by passing the mixture through a magnetic field.
- Qualitative analysis is the identification of substances present in a sample.
- Quantitative analysis is the determination of how much of each substance is present in a sample.
- Gravimetric analysis is a method of analysis that involves the measurement of masses.
- Volumetric analysis is a method of analysis that involves the measurement of solution volumes.
- The percentage composition of a chemical compound specifies the percentage mass of each of the different elements in the compound.

∗ APPLICATION AND INVESTIGATION

1 Choose one chemical substance familiar to you and **investigate** the advantages and disadvantages of its use. **Investigation**

2 a **Recall** the essential differences between solids and liquids and between liquids and gases.

  b **Identify** three examples of substances for each of the solid, liquid and gaseous states.

3 **Explain** why the incompressibility of liquids is important in the functioning of car brakes. **Investigation**

4 **Explain** the following observations.

  a Gases are compressible, whereas solids and liquids are essentially incompressible.

  b Solids have a definite shape, whereas liquids and gases take the shape of their container.

  c There is usually a small increase in volume when a solid changes to a liquid and a large increase when a liquid changes to a gas.

5 **Identify** which of the assumptions of the kinetic theory of gases cannot be applied to liquids and solids.

6 **Investigate** the fourth state of matter, plasma. How is it formed? Does it occur anywhere on Earth? **Investigation**

7 **Outline** the essential difference between a pure substance and a mixture.

8 Using diagrams (such as those shown in Figure 1.8, for example) **construct** representations of:

- **a** an element **a** in which the atoms are combined as diatomic molecules
- **b** a compound in which one atom of **a** is combined with three atoms of **b**
- **c** a mixture of the element and compound in **a** and **b** above.

9 When magnesium, a grey metal, is burnt in oxygen it burns with a brilliant flame to form a white powder, magnesium oxide.

- **a** **Classify** magnesium, oxygen and magnesium oxide as elements, compounds or mixtures.
- **b** **Explain** why the properties of magnesium oxide are quite different from those of magnesium and oxygen.

10 **Classify** each of the following as either an element or a compound:

N_2, He, C_2H_5OH, KI, C, NH_4NO_2 and Cl_2.

➲ **Investigation** 11 Briefly **describe** the composition of the Earth's crust, mantle and core and **explain** how the separation of these layers is thought to have occurred.

12 **Identify** an example of an element, a compound and a heterogeneous mixture found naturally in the lithosphere.

13 **Discuss** how the atmosphere could be considered as both a homogeneous mixture and a heterogeneous mixture.

➲ **Investigation** 14 **Investigate** our current understanding of how the element iron is formed in stars and why it is relatively abundant in the universe.

15 **Explain** why it is difficult to totally separate two or more soluble solids by filtration and crystallisation.

16 **Propose** how the following separations could be achieved:

- **a** iron filings from an iron filings–charcoal mixture
- **b** sugar from a sugar solution
- **c** small amounts of insecticide from fruit
- **d** oxygen from air
- **e** red blood cells from blood plasma
- **f** water from sea water.

17 **Identify** eight common but useful materials and **classify** these as elements, compounds, homogeneous mixtures or heterogeneous mixtures. **Identify** which of these materials are used in a naturally occurring form and which have been processed in some way.

➲ **Investigation** 18 **Identify** the substances that are used to make glass. **Explain** how glasses of different colours are produced.

➲ **Investigation** 19 **Investigate** and **summarise** the synthesis of either aspirin or paracetamol.

20 **Calculate** the percentage of salt in a 50 g packet of potato crisps if the crisps are crushed and mixed with water, then filtered and the solution evaporated, leaving 2.13 g of solid salt.

CHAPTER 2

ELEMENTS OF THE EARTH

2.1 Abundance of elements on Earth

The abundance of the most common elements in all their various forms in the universe and Earth are compared in Figure 2.1.

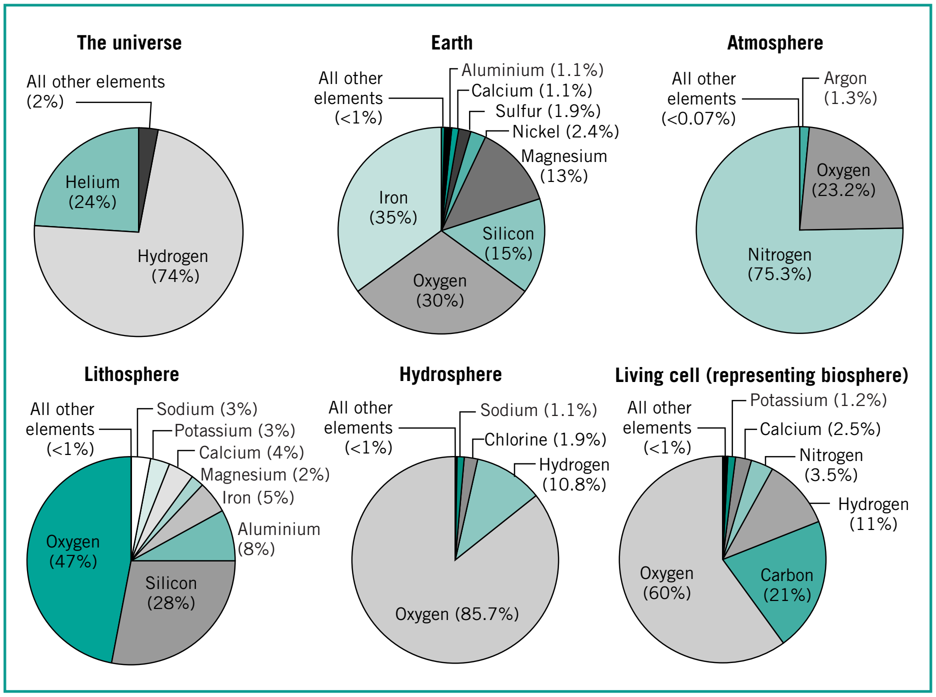
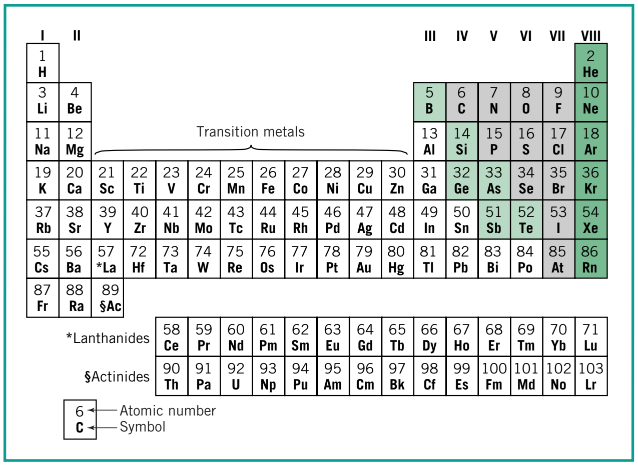


Figure 2.1 The distribution, as mass percentages, of the most abundant elements in the universe and Earth

All the substances found on Earth, whether occurring naturally or created by humans, are made from only about 115 elements. The different combinations of these elements give rise to the millions of compounds that have been isolated or synthesised. Of the 115 elements only 89 are known to occur naturally on Earth. The others do not occur naturally or exist only for very short times as a result of radioactive decay. A periodic table including symbols for the first 111 elements is presented in Figure 2.2.



I	II											III	IV	V	VI	VII	VIII
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 §Ac															

*Lanthanides	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
§Actinides	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Figure 2.2 The periodic table of elements: white indicates metals (except H), pale green semi-metals, grey non-metals and dark green noble gases.

Forms of elements on Earth

Figure 2.1 compares, by mass, the most common elements found in both the universe and Earth. In the universe the overwhelming majority of matter is found as uncombined elements, mainly hydrogen and helium. On Earth the situation is different, and it is interesting to consider the forms these elements take in their different locations. The most abundant element on Earth is iron, followed by oxygen, silicon and magnesium. The most abundant element in the biosphere, lithosphere and hydrosphere is oxygen and it is the second most abundant in the atmosphere. The reactivities of elements usually result in them combining with other elements to form a great variety of compounds. Chemical reactivity is discussed in greater detail in Unit 2.3. The biosphere, lithosphere, atmosphere and hydrosphere therefore consist of a vast number of mixtures containing various combinations of elements and compounds.

The lithosphere is composed mostly of rocks, which are mixtures of various minerals. A *mineral* is a naturally occurring solid element or compound with a definite composition or range of compositions that has a specific arrangement of atoms. Table 2.1 identifies some common minerals that occur on Earth, together with their chemical compositions. Only very small amounts of some elements such as copper, gold and sulfur occur uncombined as the free element in the lithosphere.

Table 2.1 Common classes of minerals

Mineral	Chemical formula
Silicates	
quartz plagioclase feldspar biotite mica kaolinite olivine	SiO_2 $(Ca,Na)(Al,Si)_4O_8$ $K(Fe,Mg)_3(OH)_2AlSi_3O_{10}$ $Al_2S_2O_5(OH)_5$ $(Mg,Fe)_2SiO_4$
Oxides	
corundum haematite ilmenite gibbsite	Al_2O_3 Fe_2O_3 $FeTiO_3$ $Al_2O_3.3H_2O$
Carbonates	
calcite	$CaCO_3$
Sulfides	
pyrite galena	FeS_2 PbS
Sulfates	
gypsum	$CaSO_4.2H_2O$
Halides	
halite fluorite	$NaCl$ CaF_2
Native elements	
copper gold sulfur	Cu Au S

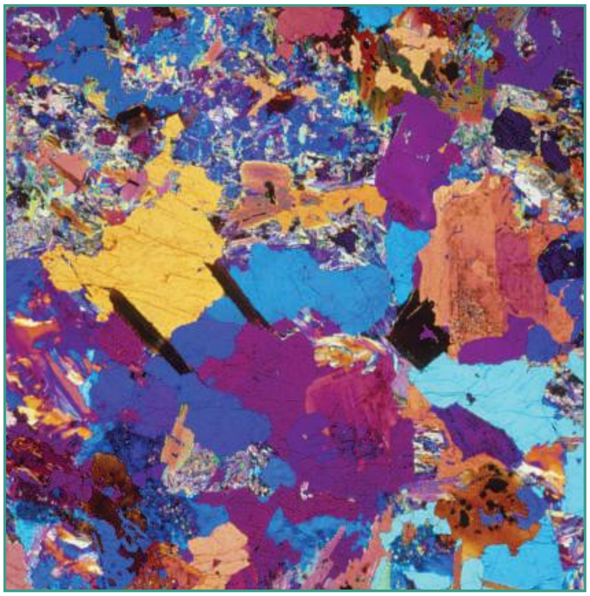


Figure 2.3 Photomicrograph of a thin section of granite in polarised light. Crystals of various minerals can be identified.

❋ Review exercise 2.1

1 **Identify** at least four different forms or combinations in which the element oxygen may be found on Earth.

2 The Earth's crust consists of the outer portion of the Earth, which is about 40 km thick. The most abundant element in the crust is oxygen, with iron coming fourth at about 5%. If the whole planet is considered, the most abundant element is thought to be iron, which makes up about 35% of the Earth's mass. **Account** for the difference in the abundance of iron in the Earth's crust compared with the entire planet. (Review Unit 1.4.)

2.2 Formulae of elements

Elements consist of atoms of the same type. Each element is given a one-letter or two-letter symbol, which is used as a shorthand way of writing the element. For example, hydrogen has the symbol H and helium the symbol He.

Metals

In metals the elemental symbol is used as the formula. The formulae of iron and copper, for example, are written as Fe and Cu respectively.

Molecules

Many elements exist in nature as simple molecules. Molecules are particles that can move independently of each other. Molecules may contain one atom or more. The noble gases, e.g. helium, argon and krypton, exist in their natural state as molecules formed from only one atom, sometimes called *monatomic molecules*. Their formulae are the same as their chemical symbol, i.e. He, Ar, Kr. Most molecules consist of a group of two or more atoms held together by chemical bonds. Hydrogen gas (H_2), for example, consists of molecules in which two hydrogen atoms are bonded together. The numerical subscript in the formula H_2, '2' in this case, indicates the number of atoms of hydrogen present in the molecule. Similarly, the gases oxygen (O_2) and fluorine (F_2), the liquid bromine (Br_2) and the solid iodine (I_2) all exist as molecules in which two atoms are bonded together. Such molecules are described as *diatomic molecules*.

Some elements exist as *polyatomic molecules*. One form of phosphorus, white phosphorus, consists of molecules in which four atoms of phosphorus are bonded together (P_4), while one form of sulfur consists of molecules that contain eight sulfur atoms (S_8). The molecular structures of some common elements are shown in Figure 2.4.

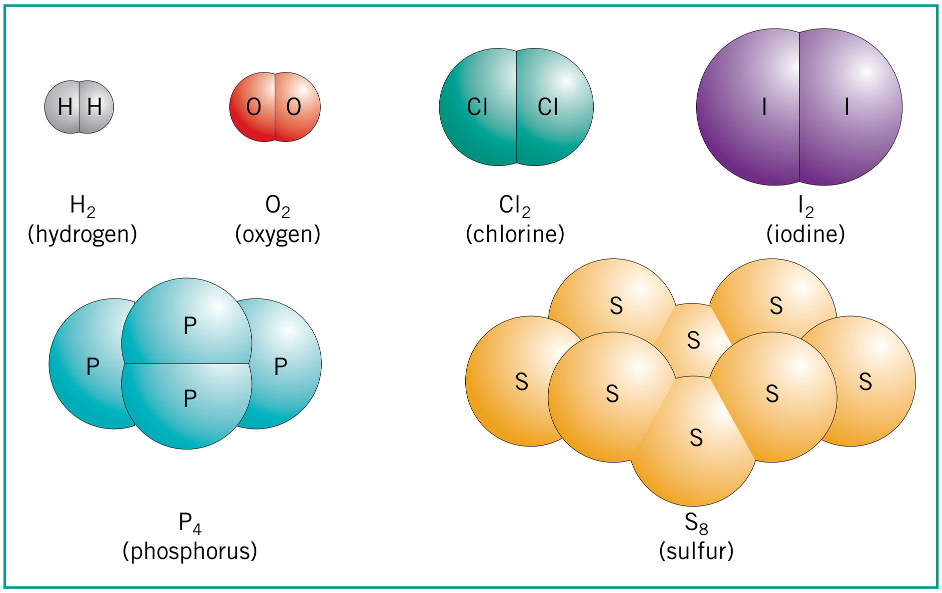


Figure 2.4 The molecular structures of some common elements

Table 2.2 contains the formulae of some common molecular elements. Each formula indicates the composition of the molecule by using the symbol of the element and a subscript, to the right of the symbol, which indicates the number of atoms in each molecule of the element.

Table 2.2 The molecular formulae of some common elements

Name	Formula	Name	Formula
Argon	Ar	Krypton	Kr
Bromine	Br_2	Neon	Ne
Chlorine	Cl_2	Nitrogen	N_2
Fluorine	F_2	Oxygen	O_2
Helium	He	Ozone	O_3
Hydrogen	H_2	Phosphorus	P_4
Iodine	I_2	Sulfur	S_8

Many compounds also exist as molecules. In fact, covalent molecular compounds are one group of a common method of classifying compounds which will be discussed in Unit 5.3. In these compounds the formula represents the number of atoms of each element in one molecule of the compound. Water molecules (H_2O) contain two hydrogen atoms and one oxygen atom bonded together. Similarly, an ammonia molecule (NH_3) consists of one nitrogen and three hydrogen atoms. The molecular structures of some common compounds are shown in Figure 2.5.

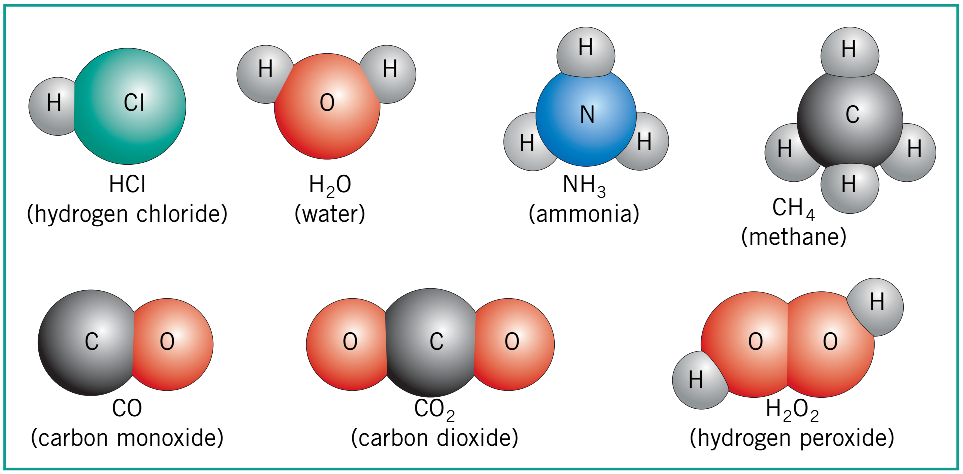


Figure 2.5 Molecular structures of some common compounds

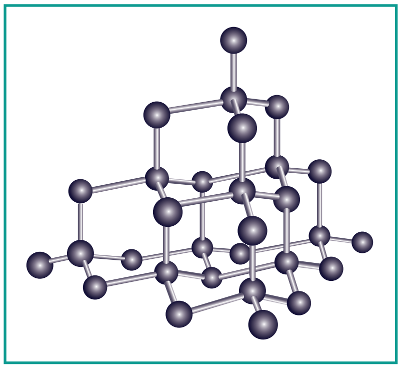


Figure 2.6 The network structure of carbon (diamond)

Network elements

A small number of elements exist as neither simple molecules nor metals, but as rather complicated network structures. For these elements, notably carbon and silicon, the simple elemental symbols are also the formulae C and Si.

❄ Review exercise 2.2

1 **Distinguish** between a hydrogen atom and a hydrogen molecule.

2 **Identify** the correct formula to represent each of the following elements: carbon, iron, bromine, calcium, fluorine, copper, silicon.

3 **Identify** two elements that exist as each of the following types of molecule:
   a monoatomic
   b diatomic
   c polyatomic.

2.3 Reactivity of elements

Chemical elements vary in their *reactivity*, that is, their tendency to react. Some metals such as calcium react readily and so are usually found combined with other elements, for example, as calcium carbonate and calcium sulfate. Sodium metal is so reactive that it is never found naturally in its pure form. Sodium will react readily with the oxygen present in air or with water found in the atmosphere or hydrosphere (Figure 2.7). Other metals such as gold have a very low reactivity and so gold is mostly found in its pure form, uncombined with other elements. The history of the discovery of metals is related to their reactivity. The least reactive metals, gold, silver and copper, were found much earlier in human history than the more reactive metals iron, aluminium and calcium. Metal reactivity is discussed in detail in Module 2. The elements in the second column from the right in the periodic table (group VII) include fluorine, chlorine, bromine and iodine. These non-metal elements are also highly reactive and are not found in nature as the free elements. Instead they occur in combined form as compounds. For example, chlorine occurs commonly as sodium chloride, common salt, either in salt deposits or dissolved in the ocean.


Figure 2.7 Sodium burning in air

The *noble gases* are the elements in the extreme right-hand column of the periodic table. Members of this group include helium, neon, argon, krypton and xenon. All the noble gases are extremely unreactive and because of this are sometimes referred to as the *inert gases*. The marked differences in the reactivity of different elements are now known to be related to the arrangement of the electrons within atoms of the elements.

❄ Review exercise 2.3

1 **Describe**, with examples, how the reactivity of different elements is related to their occurrence in nature as free elements or as compounds.

2 **Identify** three reactive and three non-reactive elements, including examples of metals and non-metals in both categories.

2.4 Metals, non-metals and semi-metals

Physical properties are those that can be determined without changing the chemical composition of the substance. Physical properties include odour, colour, taste, lustre, hardness, density, mechanical strength, malleability (ability to be beaten into sheets), ductility (ability to be drawn into wires), electrical conductivity, thermal conductivity, melting point, boiling point and solubility. The physical properties of the elements vary widely, as illustrated in Table 2.3.

Table 2.3 Physical properties of a selection of elements

	Density (g cm^{-3})	Thermal conductivity (J s^{-1} m^{-1} K^{-1})	Electrical conductivity (MS m^{-1})	Melting point (°C)
Aluminium	2.70	237	37	660
Boron	2.34	27	10^{-10}	2300
Bromine	3.12	0.12	10^{-16}	–7
Carbon (graphite)	2.26	10	0.07	3974
Copper	8.96	401	58.4	1085
Germanium	5.32	6160	10^{-4}	937
Gold	19.3	317	44	1064
Hydrogen	8.2×10^{-5}	0.18	–	–259
Iodine	4.94	0.45	10^{-13}	114
Iron	7.86	80	10.3	1535
Mercury	13.53	8.3	1.0	–39
Oxygen	1.3×10^{-3}	0.026	–	–219
Platinum	21.4	72	9.3	1772
Silicon	2.33	142	10^{-3}	1410
Silver	10.5	429	63	962
Sodium	0.97	141	21	98
Sulfur	2.07	0.27	10^{-21}	113
Tungsten	19.3	174	19	3410

Using physical properties such as those in Table 2.3, elements may be classified into three groups: metals, non-metals and semi-metals.

It is usually fairly easy to experimentally distinguish between members of these three groups, although it is not always clear-cut. Semi-metals, not surprisingly, exhibit some properties characteristic of metals and other properties that are more like those of non-metals.

Metals

Because the physical properties of metals can vary greatly, it is difficult to give a single definition that can be used to distinguish metals from non-metals. However, by examining a range of properties typical of most metals, it is possible to make a list of their characteristics. Typically, *metals* share the following physical properties:

- relatively high densities (although lithium, sodium and potassium are less dense than water)
- good conductors of heat and electricity
- malleable (can be beaten into sheets) and ductile (can be drawn into wires)
- have a shiny surface when freshly cut or cleaned (lustrous)
- relatively high melting points (although mercury and gallium have quite low melting points).

Figure 2.8 Aluminium products

The uses of metals in modern society are often related to their physical properties. For example, aluminium is widely used in domestic utensils, drink cans, saucepans, cooking foil, building construction as roofing and window frames, and in boat construction. These uses relate to aluminium's thermal conductivity, malleability and attractive lustre. More details about the uses and properties of metals are discussed in the next module.

Figure 2.9 Silver and gold are often used in jewellery and ornaments.

Non-metals

Non-metal elements, which occur as solids, liquids and gases, display a very broad range of physical properties. Typically, *non-metals* share the following physical properties:

- state and form is variable, for example, oxygen is a gas, bromine a liquid and sulfur a solid
- usually not lustrous
- poor conductors of heat and electricity (except carbon in the form of graphite)
- not malleable or ductile, often brittle
- variable melting points as shown in Table 2.3.

Because non-metals display a very wide range of physical properties, they find many different applications. Of those that are used as pure elements, the most commonly known are:

- *carbon (graphite)*—used in 'lead' pencils and as a lubricant because of its softness and layer structure, which allows layers of atoms to slide over each other. It is also used in electrodes in batteries and electrolytic processes because of its electrical conductivity.

Figure 2.10 A selection of non-metals: sulfur, bromine, phosphorous, iodine and carbon

Figure 2.11 Silicon: a semi-metallic element

- *carbon (diamond)*—used in jewellery because it is transparent and has a high refractive index and dispersive power, and in drill tips because of its high melting point and hardness
- *sulfur*—used in vulcanising rubber, and in the manufacture of sulfuric acid, fungicides, insecticides and hydrogen sulfite bleaches due to its abundance and reactivity
- *phosphorus*—used in smoke bombs and the manufacture of match heads because of its reactivity
- *helium*—used in airships due to its very low density and lack of reactivity
- *neon*—used in 'neon lights' because of its ability to glow red and give out a great deal of light when excited by an electric discharge
- *chlorine*—used in water treatment because it is a bactericide and algicide, and as a bleaching agent because of its reactivity in decolourising other chemicals.

Semi-metals

Semi-metals are also known as metalloids. The physical properties of semi-metals, as the name suggests, are a combination of some of the properties of metals and non-metals. Semi-metals have a wide range of properties. Their conductivities vary considerably with temperature and can be increased dramatically if the semi-metal is mixed with very small amounts of other elements such as arsenic and boron. This property is exploited in the use of silicon and germanium as semi-conductors in transistors, silicon chips for integrated circuits and photocells.

Table 2.4 summarises the properties of these three groups of elements: metals, non-metals and semi-metals.

Table 2.4 Properties of metals, non-metals and semi-metals

Property	Metals	Non-metals	Semi-metals
Melting point	usually high	usually low	high
Boiling point	usually high	usually low	usually high
Electrical conductivity	high	very low	low
Heat conductivity	high	very low	low
Appearance	lustrous	usually not lustrous	variable
Examples	aluminium, lithium	chlorine, carbon	silicon, arsenic

Elements and the periodic table

In the periodic table, which was introduced in Unit 2.1, the metals, non-metals and semi-metals are grouped together. On the periodic table shown in Figure 2.2, a diagonal line is marked from the top of the third column or group to the lower right corner. This diagonal separates metals from non-metals. Elements to the left and below the diagonal are metals, with the exception of hydrogen. Metals make up the majority of the known elements. Thus, potassium (K), chromium (Cr), silver (Ag) and aluminium (Al) are all metals. Elements to the right and above the diagonal are non-metals. These include carbon (C), chlorine (Cl) and xenon (Xe).

The semi-metals, notably boron (B), silicon (Si), germanium (Ge), arsenic (As), antimony (Sb) and tellurium (Te), are grouped along the diagonal. As noted above, these elements display some properties characteristic of metals and some characteristic of non-metals. These elements are also known as metalloids.

❇ Review exercise 2.4

1 **Propose** which of the physical properties given in Table 2.3 you think best identifies an element as a metal. **Justify** your choice.

2 The table below gives physical properties of a number of metals. Use this table to answer the questions that follow.

Metal	**Density ($g\ cm^{-3}$)**	**Melting temperature (°C)**	**Electrical conductivity ($MS\ m^{-1}$)**	**Thermal conductivity ($J\ s^{-1}\ m^{-1}\ K^{-1}$)**	**Tensile strength**
V	8.96	1085	57.9	401	high
W	11.4	327	4.8	37	low
X	1.74	650	23	156	low
Y	2.7	660	38	237	moderate
Z	7.86	1535	10.3	80	very high

a Based on nothing more than the information in this table, **identify** which metal would be most suitable for the following purposes:

i electrical wiring in a house

ii building a bridge

iii constructing the frame of an ultralight aircraft

iv producing saucepans.

b **Outline** other information that would be needed before deciding whether the metal could actually be used for that purpose.

3 **Construct** a table to summarise which characteristics of germanium make it like a metal and which characteristics make it like a non-metal.

4 **Identify** three everyday items that contain integrated circuits (silicon chips).

5 From the periodic table (Figure 2.2), **classify** as metals, non-metals or semi-metals the elements Li, Zn, Se, Ce, Br, Sb and Xe.

6 **Explain** why the location of the semi-metals on the periodic table is appropriate.

*KEY POINTS

- A total of approximately 115 elements have been identified, each of which has a unique name and symbol.
- All of the millions of compounds and mixtures found on the Earth are made from various combinations of these elements.
- In the universe, hydrogen and helium are by far the most abundant elements.
- In the whole Earth, iron (35%), oxygen (30%), silicon (15%) and magnesium (13%) are the most abundant elements.
- Chemical elements occur throughout the biosphere, lithosphere, hydrosphere and atmosphere in the form of pure elements, compounds and mixtures.
- Many elements and compounds exist in nature as simple molecules.
- A molecule is the smallest particle of an element or compound that can exist by itself. Most molecules consist of a group of two or more atoms held together by chemical bonds.
- The formulas of elements:
  - for metals and network elements are the elements' symbols
  - for molecular elements indicate the composition of the molecules in terms of the types and numbers of atoms present.
- Chemical elements vary in their reactivity.
- The reactivity of an element is linked to the nature of its occurrence. Less reactive elements are more likely to be found in nature as the uncombined element; more reactive elements are more likely to occur combined with other elements in compounds.
- Physical properties are those properties of a substance that can be determined without changing the chemical composition of the substance.
- The physical properties of elements can be used to classify them as metals, non-metals or semi-metals.
- The physical properties typical of most metals are:
  - high density
  - good conductor of heat
  - good conductor of electricity
  - malleable and ductile
  - lustrous
  - high melting point and solid at room temperature.
- Each metal is unique and may have properties that are not typical.
- In the periodic table:
  - metals occur to the bottom and left
  - non-metals occur to the top and right
  - semi-metals occur along a diagonal separating metals from non-metals.

- The physical properties typical of metals, non-metals and semi-metals are summarised in the table below.

Physical properties of metals, non-metals and semi-metals

Property	Metals	Non-metals	Semi-metals
Melting point	usually high	usually low	high
Boiling point	usually high	usually low	usually high
Electrical conductivity	high	very low	low
Heat conductivity	high	very low	low
Appearance	lustrous	usually not lustrous	variable
Examples	aluminium, lithium	chlorine, carbon	silicon, arsenic

- The physical properties of elements often determine their uses.

∗ APPLICATION AND INVESTIGATION

1 **Explain** how it is possible to form millions of different compounds when only approximately 115 different elements have been identified.

2 Oxygen is the most abundant element in the Earth's crust (47% by mass). However, it makes up only 30% by mass of the whole Earth and a mere 0.057% of the mass of the universe. **Account** for these differences in percentage composition.

3 The formulas C and N_2 are used to represent carbon and nitrogen respectively. **Deduce** what these formulas indicate about these two elements.

4 **Construct** diagrams such as those shown in Figure 2.5 to represent the following:

a argon
b oxygen
c sulfur trioxide.

5 **Identify** the elements that are chemically combined in the following molecules of compounds:

a	water	H_2O
b	sugar	$C_{12}H_{22}O_{11}$
c	ammonia	NH_3

6 Use their relative reactivities to **explain** why:

a copper is sometimes found as a free element on the Earth but potassium is not
b sulfur is sometimes found as a free element on the Earth but bromine is not.

7 **Identify** the particular physical properties that make the following elements suitable for the use identified:

- **a** tungsten in electric light filaments
- **b** lead in roof flashing
- **c** steel in car bodies
- **d** graphite in 'lead' pencils
- **e** aluminium in saucepans
- **f** helium in weather balloons
- **g** mercury in thermometers.

8 An element does not conduct electricity, is shiny and melts at 114ºC. Is the element likely to be a metal, non-metal or semi-metal? **Justify** your choice.

9 Find in the periodic table the elements represented by the following symbols and **identify** them as metals, non-metals or semi-metals:

Sr, Ge, Xe, Mo, H, Se

➲ **Investigation**

10 **Investigate**, using secondary sources, how 'doping' silicon with small amounts of boron or arsenic can radically alter its semi-conductor properties.

ATOMS COMBINE TO FORM COMPOUNDS

CHAPTER 3

3.1 Atomic theory

Elements have so far been described as the basic substances from which all matter is composed. In addition, compounds have been defined as combinations of elements chemically bonded to each other. There are, however, some fundamental questions that have not been answered. For instance, how is one element different from another? How do compounds form? How is a compound different from a mixture? To answer these questions it is necessary to have a theory that provides a mental picture or model of matter and can be used to explain the properties of matter. This theory is called the *atomic theory*.

As long ago as 460 BC, the Greek philosopher Democritus suggested that matter consists of large numbers of small particles. He called these particles 'atomos' meaning indivisible. Other philosophers, notably Aristotle and Plato, opposed this view and maintained that matter did not consist of small particles but instead was continuous. Although the atomic view of matter was resurrected periodically, there was very little experimental evidence that could be used to test the validity of the theory.

Figure 3.1 Democritus is honoured on Greece's 10-drachma coin for his introduction of the term 'atom'.

Early in the nineteenth century, John Dalton proposed that a particular element consists of identical atoms, and that different elements are made up of different types of atoms. At the time he formulated his theory, atoms were thought of as hard, indivisible spheres which were the smallest particles capable of existence. Today it is accepted that the atom has a structure of its own, and is made up of three fundamental particles known as protons, electrons and neutrons. The masses and charges of these particles are summarised in Table 3.1.

Table 3.1 Properties of protons, electrons and neutrons

Particle	Symbol	Mass (kg)	Relative mass	Charge (C)	Relative charge
Proton	p	1.673×10^{-27}	1	1.60×10^{-19}	+1
Neutron	n	1.675×10^{-27}	1	0	0
Electron	e	9.110×10^{-31}	~1/1840	1.60×10^{-19}	–1

Protons and neutrons have approximately the same mass, about 1.67×10^{-27} kg. Electrons have a much smaller mass, about 1/1840th the mass of protons and neutrons. The mass of an electron is therefore almost negligible for most purposes when compared with the masses of protons and neutrons.

Protons and electrons have equal and opposite charges of 1.60×10^{-19} coulombs.

It is conventional to describe protons as having a positive charge and electrons as being negatively charged. Because 1.60×10^{-19} coulomb (C) is a fundamental

Figure 3.2 Aerial view of the Fermi National Accelerator Laboratory at Batavia, Illinois. Particles are accelerated to very high energies using strong electric and magnetic fields. (Fermilab Photo Department)

CHEMISTRY CONTEXT

❇ DALTON'S ATOMIC THEORY

Figure 3.3 John Dalton (1766–1844), the father of the modern atomic theory

Early in the nineteenth century, an English school teacher, John Dalton, revived the concept of atoms and proposed an atomic theory based on the experimental evidence available at that time. In this theory, Dalton proposed a different kind of atom for each element.

The main ideas or postulates of Dalton's theory can be stated as follows.

1. Elements consist of extremely small, indivisible particles called atoms. In chemical reactions, atoms are conserved; that is, they are not created, destroyed or changed into different kinds of atoms.
2. All atoms of the same element are identical and therefore have the same properties, such as mass and size.
3. Atoms of different elements have different properties.
4. Compounds are formed when atoms of more than one element combine.
5. In a given compound, the relative numbers of atoms of each kind are definite and constant. In general, these relative numbers are simple integers.
6. Atoms of two or more elements may combine in different ratios to form more than one compound.

Although Dalton's theory is still largely accepted, his first two postulates have since been modified. Dalton proposed that atoms were small, indivisible particles. It is now known that atoms can be split if they are bombarded by high-energy particles, and some atoms spontaneously disintegrate by radioactive decay. However, under normal conditions most atoms are essentially indivisible.

Dalton's second postulate, that all atoms of the same element are identical, has also been modified. It has been found that different atoms of the same element are not necessarily all the same. An element may exist in different atomic forms with slightly different masses. These different forms are called *isotopes* and are discussed in Unit 3.1.

quantity of charge, the proton and electron are usually described as having charges of +1 and –1 respectively. Neutrons are uncharged (neutral).

Since as early as the 1950s, physicists have known of the existence of subatomic particles other than protons, electrons and neutrons. They have discovered that protons are made of even smaller particles called *quarks*. The number and types of particles continue to increase with improvements in the quality of linear and cyclic accelerators, which cause high-energy beams of charged particles to collide. Knowledge of these other subatomic particles is beyond the scope of this course.

A model of the atom

The atom can be visualised in terms of two main regions. These regions are the nucleus and the surrounding space occupied by the electrons.

The structure of the nucleus is as follows:

- It is the central part of the atom, and contains the protons and neutrons.
- It has a positive charge equal to the number of protons.
- It is exceedingly small compared with an atom. The diameter of an average nucleus is 10^{-15} m, compared with an average atomic diameter of 10^{-10} m. Thus, the atomic diameter is about 100 000 times the diameter of the nucleus. (This is the size of a golf ball compared with the Sydney Football Stadium.)
- It contains over 99.9% of the mass of an atom. This is due to the relatively large masses of the proton and neutron compared with the mass of the electron.
- It is exceptionally dense. This is due to its large mass and small volume. (A matchbox full of nuclear material would have a mass of the order of billions of tonnes.)

The arrangement of the electrons around the nucleus is as follows:

- The electrons move through a relatively large space outside the nucleus.
- They are kept moving around the nucleus by various forces.
- In an uncharged atom, the number of electrons equals the number of protons in the nucleus.

A diagrammatic representation of the structure of an atom is shown in Figure 3.4.

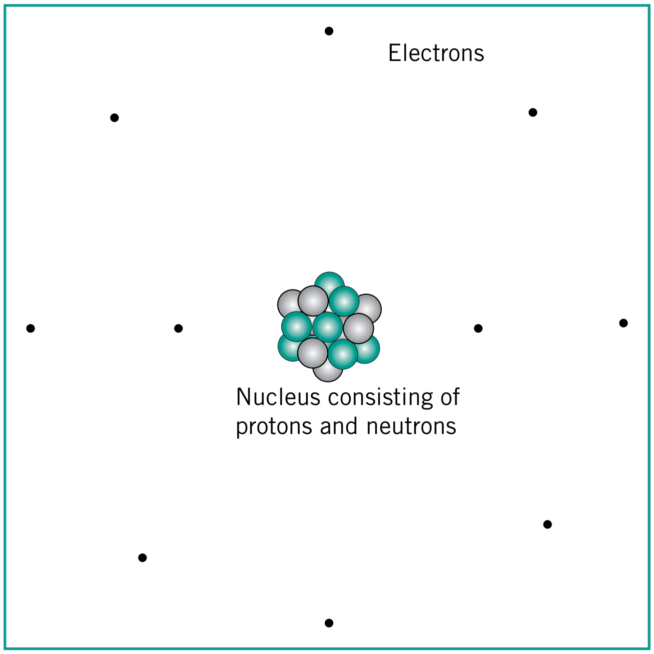


Figure 3.4 A model for the structure of an atom

How atoms differ

The composition of a particular atom is conveniently described in terms of two numbers: the atomic number and the mass number.

The *atomic number*, Z, is the number of protons in the nucleus of an atom. This has a fixed value for atoms of any one element. Carbon, for example, has an atomic number of six. Every carbon atom contains six protons in the nucleus. In an electrically neutral atom, the numbers of electrons and protons are equal.

Therefore, if an atom has no net charge, the atomic number determines the number of electrons in the atom as well as the number of protons in the nucleus.

The *mass number*, A, is the sum of the numbers of protons and neutrons in the nucleus of an atom. The mass number, the atomic number and the number of neutrons in a nucleus are related in the following way:

$$A = Z + \text{number of neutrons}$$

If the mass number and atomic number are known, it is possible to work out the number of neutrons in a nucleus. For example, fluorine has an atomic number of nine and a mass number of nineteen, so a fluorine nucleus must contain nine protons and ten neutrons.

It is sometimes convenient to identify the structure of an atom using the following convention:

$${}^{A}_{Z}\mathrm{X}$$

where
X is the element symbol
Z is the atomic number
A is the mass number.

From this shorthand representation it is possible to identify the element, the numbers of protons and neutrons in the nucleus, and the number of electrons in an electrically neutral atom. For example, a neutral phosphorus atom contains 15 protons and 16 neutrons in the nucleus, and 15 electrons. The elemental symbol for phosphorus is P, Z = the number of protons = 15, and A = the number of protons and neutrons = 31. Therefore the atom is represented as ${}^{31}_{15}\mathrm{P}$.

Isotopes

All atoms of the same element have the same number of protons in the nucleus. However, all atoms of the same element do not necessarily have the same mass. Atoms of the same element with different masses have different numbers of neutrons in the nucleus. For example, oxygen atoms can exhibit one of three different masses. Over 99% of oxygen atoms have a mass number of 16, while 0.20% have a mass number of 18, and 0.04% have a mass number of 17. All oxygen atoms have eight protons in the nucleus, so the three types of atoms can be represented as ${}^{16}_{8}\mathrm{O}$, ${}^{17}_{8}\mathrm{O}$ and ${}^{18}_{8}\mathrm{O}$.

The difference between these three types of atoms is that ${}^{16}_{8}\mathrm{O}$ atoms have eight neutrons in the nucleus, ${}^{17}_{8}\mathrm{O}$ have nine and ${}^{18}_{8}\mathrm{O}$ have ten. These different types of oxygen atoms are called *isotopes* and are often written as oxygen-16, oxygen-17 and oxygen-18.

Isotopes are defined as different atoms of an element that have the same number of protons but different numbers of neutrons in the nucleus. Table 3.2 gives a list of some well-known isotopes. The three isotopes of hydrogen are given special names because of their particular importance. Although the isotopes of an element have different masses, they have the same chemical properties.

Table 3.2 Some well-known isotopes

Name	Symbol	Number of protons in nucleus	Number of neutrons in nucleus	Number of electrons in neutral atom
Hydrogen	H	1	0	1
Deuterium	H	1	1	1
Tritium	H	1	2	1
Carbon-12	C	6	6	6
Carbon-13	C	6	7	6
Carbon-14	C	6	8	6
Oxygen-16	O	8	8	8
Oxygen-17	O	8	9	8
Oxygen-18	O	8	10	8
Uranium-235	U	92	143	92
Uranium-238	U	92	146	92

❇ Review exercise 3.1

1 **a** The idea that matter consists of large numbers of small particles was proposed by Democritus in about 460 BC. **Identify** the ideas in Dalton's theory that were unique.

b **Identify** which of Dalton's postulates have been revised as a result of more modern experimental evidence. **Outline** how they have changed.

2 **Describe** how protons, neutrons and electrons are arranged in atoms, using ${}^{11}_{5}\mathrm{B}$ as an example.

3 **Distinguish** between the atomic number and the mass number of an atom.

4 **Calculate** the number of protons, neutrons and electrons in the following electrically neutral atoms:

a ${}^{7}_{3}\mathrm{Li}$

b ${}^{20}_{10}\mathrm{Ne}$

c ${}^{35}_{17}\mathrm{Cl}$

d ${}^{107}_{47}\mathrm{Ag}$

e ${}^{208}_{82}\mathrm{Pb}$

f ${}^{14}_{7}\mathrm{N}$

5 Using ${}^{A}_{Z}\mathrm{X}$ notation, write the symbols for atoms of the following elements:

a iron, with 26 protons and 30 neutrons

b silicon, with 14 protons and 14 neutrons

c silicon, with 14 protons and 16 neutrons

d potassium, with 19 protons and 20 neutrons.

3.2 The arrangement of electrons in atoms

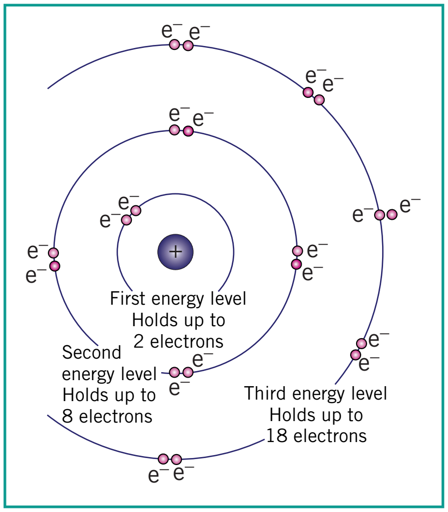


Figure 3.5 The three lowest energy levels in the Bohr model of the atom

At the beginning of the twentieth century, one of the major challenges in science was to understand the nature of electrons and their location within atoms. Famous physicists including Thomson, Millikan, Rutherford, Bohr and many others contributed to these ideas. Dalton's model of atoms as extremely small indivisible particles was replaced by the nuclear model, in which the atom was viewed as consisting of a small, dense, positively charged nucleus surrounded by electrons. Our understanding of the location of electrons changed through a series of models including Thomson's 'plum pudding' model, Rutherford's 'planetary model', the Bohr model and eventually the quantum mechanical model.

In the Bohr model and subsequent models, the electrons are considered to exist in energy levels or shells. These energy levels or shells can be thought of in terms of defined energies associated with particular average distances from the nucleus. The first energy level or shell is the one closest to the nucleus, and can hold a maximum of two electrons. The second energy level or shell is further from the nucleus, and can accommodate up to eight electrons. The third energy level can hold up to 18 electrons, the fourth up to 32 electrons, and so on.

The following principles are used to determine the electron configuration of an atom.

1. Place the electrons into energy levels or shells, starting with the energy level or shell closest to the nucleus (which has the lowest energy) first.
2. As each energy level is filled, start filling the next energy level.

As an example, consider the sodium atom. The atomic number of sodium is 11, so there are 11 electrons in a sodium atom. The first two electrons are located in the first energy level or shell. The next eight electrons are located in the second energy level. The eleventh electron is located in the third energy level. The electron configuration of sodium can therefore be written as 2, 8, 1. Other examples of electron configurations are as follows:

Oxygen ($Z = 8$)	2, 6
Magnesium ($Z = 12$)	2, 8, 2
Argon ($Z = 18$)	2, 8, 8

The electron configurations of the first 20 elements are shown in Table 3.3.

Note from Table 3.3 that the electron configurations of potassium and calcium indicate that in these elements, electrons exist in the fourth energy level despite the fact that the third energy level has not been filled to its capacity of 18 electrons. This apparent anomaly is addressed in Module 8, The chemistry of art.

From Table 3.3 note also that hydrogen, lithium and sodium have one electron in their highest or valence energy level (or outermost shell). Similarly, oxygen and sulfur have six electrons in their valence energy level. In the periodic table, elements with the same number of valence electrons occur in the same column or group. Thus group I elements have one valence electron, group IV elements have four valence electrons and group VII elements have seven valence electrons. The only exception to this generalisation is helium, in group VIII, which has two valence electrons. This represents a filled energy level, however, as the first energy level can hold only two electrons.

Table 3.3 Electron configurations of the first twenty elements

Hydrogen	1	Sodium	2, 8, 1
Helium	2	Magnesium	2, 8, 2
Lithium	2, 1	Aluminium	2, 8, 3
Beryllium	2, 2	Silicon	2, 8, 4
Boron	2, 3	Phosphorus	2, 8, 5
Carbon	2, 4	Sulfur	2, 8, 6
Nitrogen	2, 5	Chlorine	2, 8, 7
Oxygen	2, 6	Argon	2, 8, 8
Fluorine	2, 7	Potassium	2, 8, 8, 1
Neon	2, 8	Calcium	2, 8, 8, 2

The lack of reactivity of the noble gases suggests that a noble gas electron configuration is particularly stable. For helium, this represents two electrons in the first energy level, but for the other noble gases it represents eight electrons in the valence energy level. A valence electron configuration of eight electrons is referred to as a *stable electron octet*. Most atoms attain an octet electron configuration when they form bonds with other atoms.

Review exercise 3.2

1 **Identify** the electron configurations for the following elements:

lithium (Z = 3), sulfur (Z = 16), chlorine (Z = 17), calcium (Z = 20).

2 **Identify** the valence (outermost shell) electron configurations for elements in:

a Group III
b Group VI.

3 **Summarise** the evidence that suggests that an electron octet is a particularly stable valence electron configuration.

3.3 Ions

Simple ions

Positively charged ions, or *cations*, are formed when one or more electrons are removed from an atom. The resultant ion therefore has more protons than electrons. For example, when a sodium atom loses an electron, the sodium ion formed has 11 protons and 10 electrons and has a relative charge of +1. The sodium ion is represented as Na^+.

Negatively charged ions, or *anions*, are formed when an atom gains one or more electrons. An oxygen atom can gain two electrons to form an oxide ion, O^{2-}. An oxide ion contains eight protons in the nucleus and 10 electrons outside the nucleus, and has a relative charge of –2.

A list of common simple ions is included in Table 3.4. Cations are named after the element from which they were derived. Anions are named by adding the suffix 'ide' to the stem of the element's name.

Table 3.4 Common simple ions

+1	+2	+3	+4	–1	–2	–3
hydrogen H^+	magnesium Mg^{2+}	aluminium Al^{3+}	tin(IV) Sn^{4+}	hydride H^-	oxide O^{2-}	nitride N^{3-}
lithium Li^+	calcium Ca^{2+}	iron(III) Fe^{3+}	lead(IV) Pb^{4+}	fluoride F^-	sulfide S^{2-}	phosphide P^{3-}
sodium Na^+	strontium Sr^{2+}	chromium(III) Cr^{3+}		chloride Cl^-		
potassium K^+	barium Ba^{2+}	gold(III) Au^{3+}		bromide Br^-		
silver Ag^+	manganese(II) Mn^{2+}			iodide I^-		
gold(I) Au^+	iron(II) Fe^{2+}					
copper(I) Cu^+	cobalt(II) Co^{2+}					
	nickel(II) Ni^{2+}					
	copper(II) Cu^{2+}					
	zinc Zn^{2+}					
	mercury(II) Hg^{2+}					
	tin(II) Sn^{2+}					
	lead(II) Pb^{2+}					

The cations in Table 3.4 are, with the exception of the hydrogen ion, all derived from metallic elements. The anions are derived from non-metals, which occur on the right-hand side of the periodic table.

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

Ions and the periodic table

The periodic table can be used to predict the charges on simple ions formed by many elements. The elements in the first column (group I elements), with lithium at the top, all form ions with a charge of +1. The elements in group II form ions with a charge of +2, such as Mg^{2+} and Ca^{2+}. Elements in group III usually form ions with a charge of +3. In group IV the elements carbon and silicon tend not to form ions; however, tin and lead do form +4 ions, although these elements also form +2 ions. The elements in group V, with nitrogen at the top, usually form ions with a charge of –3. The elements in group VI form –2 ions such as O^{2-} and S^{2-}, and those in group VII –1 ions such as F^-, Cl^- and Br^-. As described previously, the elements in group VIII are inert and do not tend to form ions at all.

The elements in the middle of the periodic table, from scandium across to zinc and going down the table, form positive ions, often with a charge of +2, although there are numerous exceptions. Many of these elements form ions with different charges, such as Fe^{2+} and Fe^{3+}.

From the discussion above, it can be seen that metals form positive ions and non-metals form negative ions. The oppositely charged ions can form ionic compounds through the formation of ionic bonds. These are discussed in detail in Chapter 5.

Polyatomic ions

Simple cations and anions can be thought of as atoms that have lost or gained electrons. *Polyatomic ions* are groups of atoms bonded to one another that have a net positive or negative charge. The carbonate ion, CO_3^{2-}, is an example of a polyatomic ion. The carbon atom and three oxygen atoms are joined together by covalent bonds similar to those involved in molecules. The superscript 2– represents the electrical charge on the ion. This indicates that there are two more electrons in the carbonate ion than the total number of protons possessed by the four atoms, and therefore this ion is negatively charged.

A list of common polyatomic ions is included in Table 3.5. Note that there are many more polyatomic anions than cations.

Table 3.5 Common polyatomic ions

–1	–2	–3	+1	+2
hydroxide OH^-	carbonate CO_3^{2-}	phosphate PO_4^{3-}	ammonium NH_4^+	mercury(I) Hg_2^{2+}
nitrate NO_3^-	sulfate SO_4^{2-}			
nitrite NO_2^-	sulfite SO_3^{2-}			
hydrogencarbonate HCO_3^-	peroxide O_2^{2-}			
hydrogensulfate HSO_4^-	hydrogen phosphate HPO_4^{2-}			
dihydrogenphosphate $H_2PO_4^-$	dichromate $Cr_2O_7^{2-}$			
ethanoate(acetate) CH_3COO^-	chromate CrO_4^{2-}			
hypochlorite ClO^-	oxalate $C_2O_4^{2-}$			
cyanide CN^-				
permanganate MnO_4^-				

Review exercise 3.3

1 **Describe**, with examples, how cations and anions are formed from atoms.

2 **Identify** what would have to happen to an oxygen atom for it to become an O^{2-} ion.

3 **Identify** the type of ions formed by
   - **a** metals
   - **b** non-metals.

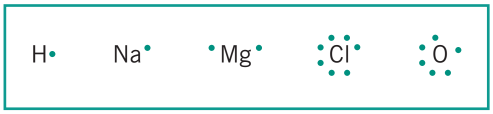
   Give examples.

4 Use the periodic table to **predict** the probable charge on each of the following ions: potassium, phosphide, calcium, aluminium, iodide.

5 **Recall** the correct formulae and charges for the following polyatomic ions: sulfate, hydroxide, nitrate, ammonium.

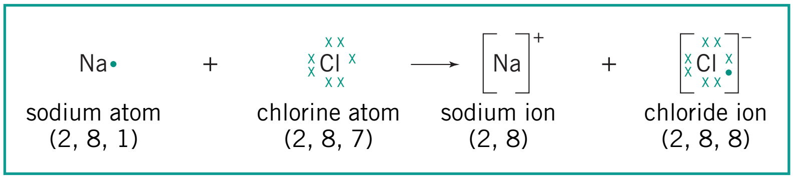
3.4 Electron dot diagrams

Electron dot diagrams, or Lewis dot diagrams, are a simple way of showing the arrangement of valence electrons in atoms and the formation of bonds between atoms. The formation of ionic and covalent bonds that hold ions and atoms together involves a rearrangement of valence electrons between atoms. Electron dot diagrams for an atom use a dot or other marker (such as an x or o) for each valence electron. For example, the electron dot diagrams for hydrogen, sodium, magnesium, chlorine and oxygen atoms are as follows.

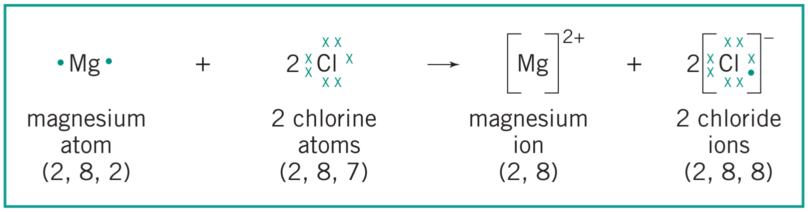


Formation of ions

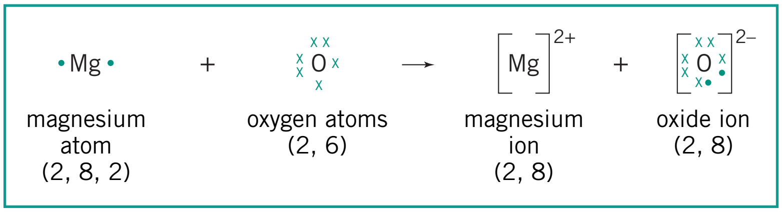
Electron dot diagrams can be used to represent the formation of positive and negative ions from neutral atoms, by the loss or gain of one or more electrons. For example, in the formation of sodium and chloride ions from their neutral atoms:



Note that the sodium atom has lost a valence electron and the chlorine atom has gained an electron. Also both ions, the sodium ion and the chloride ion, have achieved a valence electron octet, having the same electron configurations as neon and argon respectively. Although the sodium and chlorine electrons are identical, they are shown differently in the diagram so that the transfer can be followed easily. Remember that dots are only a means of counting electrons; they do not show the location of the electrons. Magnesium also forms an ionic compound with chlorine. In this instance, the magnesium atom loses two electrons to achieve a noble gas electron configuration or stable octet. For each magnesium atom that loses two electrons, two chlorine atoms gain one electron to form chloride ions.

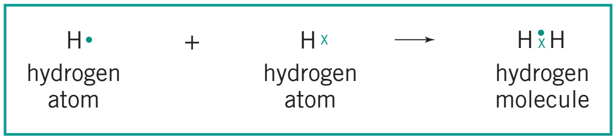


Similarly, magnesium also forms an ionic compound with oxygen.



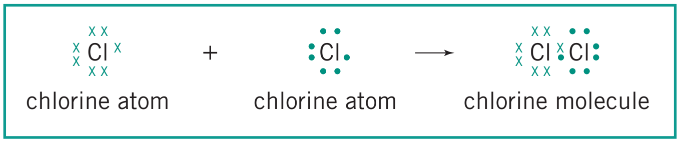
Simple molecules

As discussed in Unit 2.2, most molecules consist of a group of two or more atoms held together by covalent bonds. Table 2.2 listed the names and formulas of many elements that exist as molecules, including the noble gases, which are sometimes described as monatomic molecules. The bonds in polyatomic molecules are covalent bonds, in which electrons are shared between adjacent atoms. Electron dot diagrams can be used to illustrate the formation of covalent bonds between atoms. For example, the formation of a hydrogen molecule from two hydrogen atoms can be represented as follows:



In the hydrogen molecule, both hydrogen atoms share two valence electrons, one contributed by each of the two hydrogen atoms. Bonds in which two electrons are shared are called *single covalent bonds* and can be represented by a line drawn between the atoms. Hence the molecule is represented as H–H.

When two chlorine atoms combine to form a chlorine molecule, the chlorine atoms share a pair of electrons. In this way, each chlorine atom obtains a share in eight valence electrons and acquires the electron configuration of the noble gas argon. As in the formation of ions, the octet rule is obeyed in most covalent molecular substances.



The number of covalent bonds formed by an atom depends on the number of electrons in its valence or outer energy level. The electron dot diagrams for the elements from lithium to neon in the periodic table are shown as follows:

Fluorine will tend to form one single covalent bond in molecules, as it will then have a share in eight valence electrons. Oxygen with six valence electrons requires two more electrons to achieve a complete octet. Oxygen will therefore tend to form two covalent bonds when it forms molecules. Similarly, nitrogen and carbon will form three and four covalent bonds respectively. Figure 3.6 shows electron dot diagrams for some simple molecules.

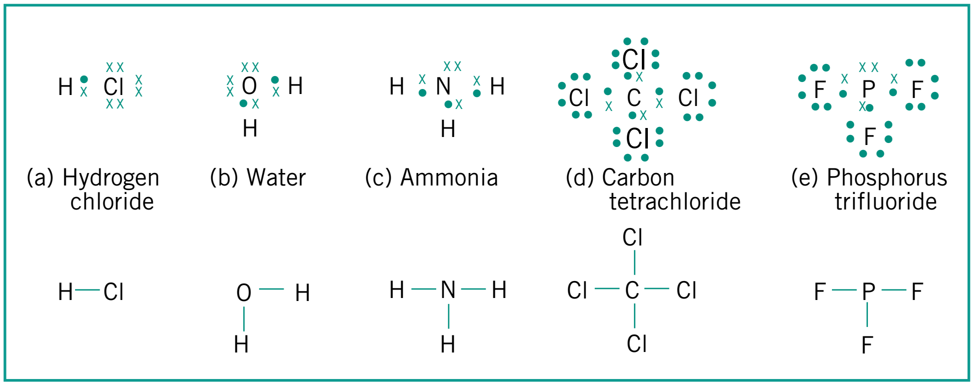
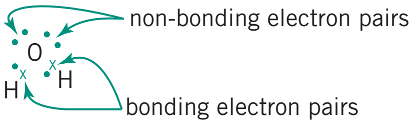


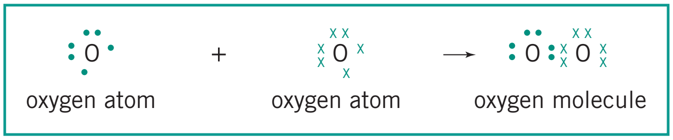
Figure 3.6 Electron dot diagrams for some simple molecules

The electron pairs forming covalent bonds in molecules are called *bonding electron pairs*. The remaining electron pairs, if any, are called *non-bonding electron pairs* or *lone pairs*. In the water molecule, for example, there are two bonding electron pairs and two non-bonding electron pairs.



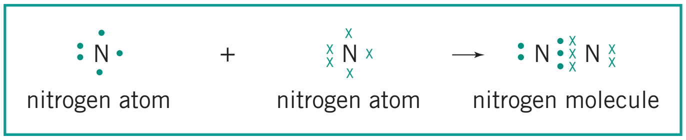
Molecules with multiple covalent bonds

The oxygen atom with six valence electrons is two electrons short of an electron octet. In forming the molecule O_2, each oxygen accepts a share of two electrons belonging to the other atom. Hence four electrons are shared by the two oxygen atoms.



A covalent bond in which there are two shared pairs of electrons is called a *double covalent bond* and can be represented by two parallel lines joining the atoms. An oxygen molecule may be shown as O=O.

The nitrogen atom has five valence electrons and is three electrons short of a stable octet. By sharing three pairs of electrons, a nitrogen molecule is formed.



This arrangement in which three electrons are shared is called a *triple covalent bond*. Figure 3.7 shows some other molecules containing multiple covalent bonds.

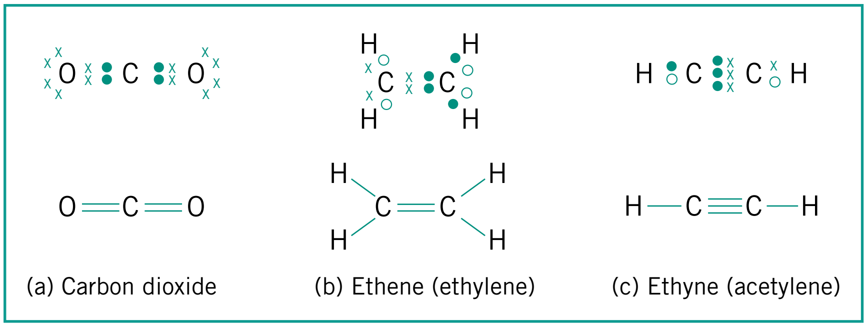


Figure 3.7 Simple molecules containing multiple covalent bonds

❄ Review exercise 3.4

1 **Construct** electron dot diagrams illustrating the valence electrons in the following:
  - **a** potassium atoms and iodine atoms
  - **b** potassium ions and iodide ions in potassium iodide.

2 **Construct** electron dot diagrams for the following ionic compounds:
  - **a** calcium oxide
  - **b** sodium oxide
  - **c** magnesium fluoride
  - **d** lithium chloride.

3 **Construct** electron dot diagrams for the following covalent molecules:
  - **a** HF
  - **b** Br_2
  - **c** Cl_2O
  - **d** CH_3OH

4 **Deduce** the number of electrons shared in the formation of each of the following bonds:
  - **a** a single covalent bond
  - **b** a double covalent bond
  - **c** a triple covalent bond.

5 **Demonstrate** the bonding in the molecules in **a** to **d** below, using:
    - **i** the electron dot notation
    - **ii** the straight-line bond notation.
  - **a** HCN
  - **b** CS_2
  - **c** C_2H_2
  - **d** HCHO

3.5 Chemical formulae and naming of compounds

Compounds consist of two or more elements that are chemically combined. The formulas of compounds contain the symbols of the elements involved, and the subscripts indicate the relative numbers of atoms of each element in the compound. Like elements, compounds can be classified into groups. According to the arrangement of atoms, their bonding and structure, compounds may be classified as covalent molecular, covalent network or ionic. These groups are discussed in detail in Unit 5.3.

Covalent molecular compounds

In *covalent molecular compounds* the formula represents the number of atoms of each element in one molecule of the compound. Water molecules (H_2O) contain two hydrogen atoms and one oxygen atom covalently bonded together. Similarly, an ammonia molecule (NH_3) consists of one nitrogen and three hydrogen atoms. The molecular structures of some common compounds are shown in Figure 3.8.

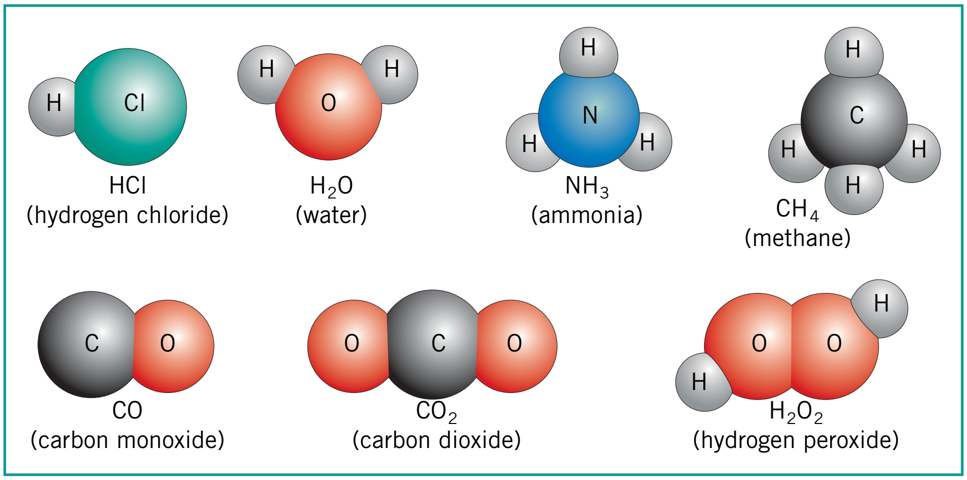


Figure 3.8 The molecular structures of some common compounds

There is a systematic procedure for naming molecular compounds formed between non-metallic elements. However, several well-known substances are known by their common names. These include ammonia (NH_3), water (H_2O), hydrogen peroxide (H_2O_2), hydrogen sulfide (H_2S) and nitrous oxide (N_2O). Unfortunately, these names do not provide enough information about the composition of these substances. However, the substances are so well known that these names continue to be used.

The procedure for systematically naming molecular compounds is described in Example 3.1.

➜ Example 3.1

Step	For N_2O_4
1 The name of the element closer to the bottom or left-hand side of the periodic table is written first.	Nitrogen
2 The second part of the name is obtained by adding the suffix '-ide' to the stem of the name of the second element.	Nitrogen oxide (as the oxygen becomes ox-ide)
3 Where a molecule contains more than one atom of one type, the number of atoms is indicated by the prefix 'mono-', 'di-', 'tri-', 'tetra-', 'penta-' or 'hexa-', which stand for 1, 2, 3, 4, 5 and 6 respectively. The prefix 'mono-' is not used for the first-named element.	Dinitrogen tetroxide (as there are two nitrogen atoms and four oxygen atoms)

The formulae and names of some commonly encountered molecular compounds are shown in Table 3.6. The common names are provided for compounds known by these names.

Table 3.6 The molecular formulae of some common compounds

Molecular formula	Systematic name	Common name
CO	carbon monoxide	–
CO_2	carbon dioxide	–
N_2O	dinitrogen monoxide	nitrous oxide
NO	nitrogen monoxide	nitric oxide
NO_2	nitrogen dioxide	–
N_2O_4	dinitrogen tetroxide	–
SO_2	sulfur dioxide	–
SO_3	sulfur trioxide	–
H_2O	dihydrogen oxide	water
H_2O_2	dihydrogen dioxide	hydrogen peroxide
H_2S	dihydrogen sulfide	hydrogen sulfide
HF	hydrogen fluoride	hydrogen fluoride
HCl	hydrogen chloride	hydrogen chloride
NH_3	–	ammonia
CH_4	methane or carbon tetrahydride	methane
CCl_4	tetrachloromethane	carbon tetrachloride

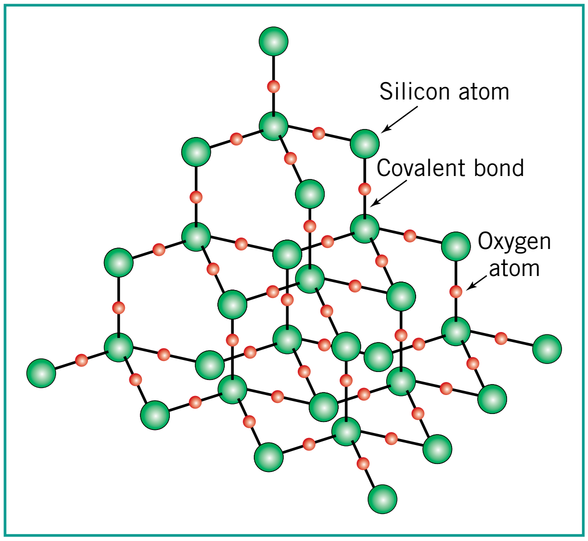


Figure 3.9 SiO_2 crystal lattice in quartz

Covalent network compounds

Covalent network compounds do not occur as simple molecules. For example, silicon dioxide contains silicon and oxygen atoms covalently bonded together in an extended three-dimensional network structure (Figure 3.9). For every one silicon atom there are two oxygen atoms, so the formula SiO_2 represents the relative numbers of atoms of each element in the compound. This formula represents the simplest or empirical formula of the compound. Silicon dioxide (SiO_2) and silicon carbide (SiC) are compounds of this type.

Ionic compounds

Ionic compounds such as sodium chloride consist of oppositely charged ions held together by electrostatic attraction to form a crystal lattice. The electrostatic attraction between the oppositely charged ions is called *ionic bonding*. Ionic bonds are strong, so ionic solids like sodium chloride and potassium fluoride are hard, brittle and difficult to cut.

X-ray diffraction evidence suggests that the ions in an ionic solid are arranged in a regular three-dimensional lattice. The structure of sodium chloride is shown in Figure 3.10. In the lattice, each positive sodium ion is surrounded by six negative chloride ions and each negative chloride ion is surrounded by six positive sodium ions. In the solid compound, the position of the ions is fixed, and apart from vibration about these fixed positions no other movement of the ion occurs.

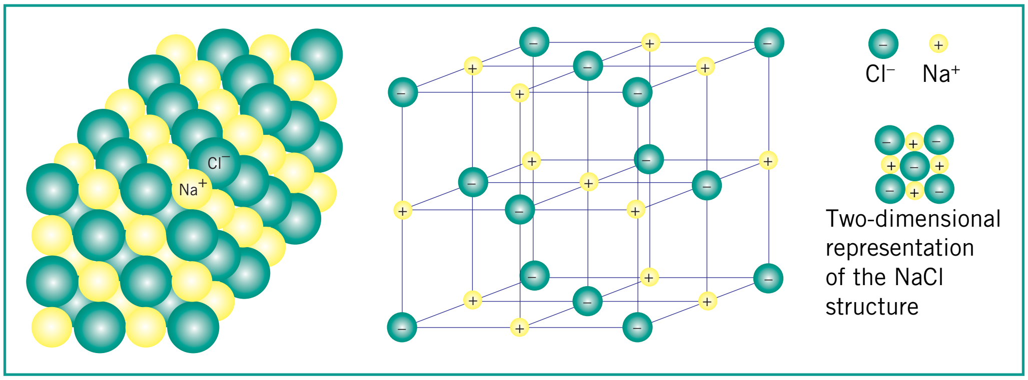


Figure 3.10 Ways of representing the structure of ionic sodium chloride

In ionic compounds, the basic particles that make up the compounds are ions. Because ionic compounds are electrically neutral, the number of positive charges must equal the number of negative charges. In sodium chloride the numbers of sodium and chloride ions are equal, and the formula is therefore represented as NaCl. This is also called an *empirical formula* as it specifies the simplest whole-number ratio of the number of ions of each element in the compound.

If the charges on the ions in an ionic compound are not equal in magnitude, then to preserve electrical neutrality there will be more ions with the smaller charge. For example, the formula of the compound formed between calcium (Ca^{2+}) and chloride (Cl^-) ions is $CaCl_2$. This formula indicates that in calcium chloride there are two chloride ions for every calcium ion. The formula of an ionic compound therefore indicates the relative numbers of ions of each type in the compound.

➜ Example 3.2

Write formulae for the compounds formed between:

1 sodium ions (Na^+) and oxide ions (O^{2-})

2 calcium ions (Ca^{2+}) and phosphate ions PO_4^{3-}

1 Ions: Na^+O^{2-} $2 \times Na^+ + 1 \times O^{2-} = Na_2O$

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

For the compound to be electrically neutral, there must be two sodium ions for every oxide ion. The formula will therefore be Na_2O.

2 Ions: $Ca^{2+}PO_4^{3-}$ $3 \times Ca^{2+} + 2 \times PO_4^{3-} = Ca_3(PO_4)_2$

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

For the compound to be electrically neutral, there must be two phosphate ions for every three calcium ions. The formula is written $Ca_3(PO_4)_2$.

Note that where there are two or more units of a polyatomic ion in a formula, the polyatomic ion is enclosed in brackets to show that the subscript applies to the entire ion.

Naming ionic compounds

When naming ionic compounds, the procedure described below is followed.

➜ Example 3.3

Naming of $Fe_2(SO_4)_3.9H_2O$:

1 The name of the positive ion is written first.	iron(III)
2 The name of the negative ion is written after the positive ion.	iron(III) sulfate
3 Where the ionic compound has water molecules of crystallisation, the number of water molecules is indicated.	iron(III) sulfate-9-water

Note that in naming ionic compounds, prefixes are not used to identify the relative numbers of ions in the compound.

❇ Review exercise 3.5

1 The formulae N_2 and O_2 are used to represent nitrogen and oxygen respectively. **Outline** what these formulae indicate about these two elements.

2 **Construct** molecular formulae for the following:

- **a** ammonia
- **b** nitrogen dioxide
- **c** hydrogen sulfide
- **d** hydrogen peroxide
- **e** sulfur tetrafluoride
- **f** sulfur hexafluoride

g dinitrogen pentoxide
h nitrogen triiodide.

3 **Identify** the names of the compounds represented by the following molecular formulas:
a CO
b CO_2
c HF
d CH_4
e SO_3
f PCl_3
g N_2O_3
h BrF_5

4 **Identify** the formulas for the ionic compounds that form between the following ions:
a Na^+ and NO_3^-
b K^+ and I^-
c Hg^{2+} and CN^-
d Al^{3+} and OH^-
e Ca^{2+} and MnO_4^-
f NH_4^+ and SO_4^{2-}
g Fe^{3+} and O^{2-}
h Mg^{2+} and PO_4^{3-}

5 **Identify** the names of the following ionic compounds (refer to Table 3.5):
a $KMnO_4$
b $Ca(HCO_3)_2$
c $Mg(HSO_4)_2$
d $Na_2CO_3.10H_2O$
e PbO
f $NaHSO_3$
g Cu_2O
h $Fe(OH)_3$

6 **Identify** the formulas of the following ionic compounds:
a ammonium sulfide
b potassium nitrite
c calcium sulfate-2-water
d lead(II) fluoride
e copper(II) nitrate
f tin(II) carbonate
g magnesium nitride
h aluminium sulfate.

*KEY POINTS

- Atoms consist of a nucleus surrounded by electrons. The nucleus of an atom has the following characteristics:
    - It contains positively charged protons and uncharged neutrons, which have about the same mass.
    - It is very small compared with the total size of the atom.
    - It contains most of the atom's mass.
    - It is very dense.
    - It has a positive charge equal to the number of protons.
- The electrons in an atom have the following characteristics:
    - They move through the space around the nucleus.
    - They have almost negligible mass compared with the mass of protons and neutrons.
    - They have negative charge.
- In an electrically neutral atom, the number of protons equals the number of electrons.
- The atomic number, Z, of an element is the number of protons in the nucleus of an atom of that element.
- The mass number, A, of an atom of an element is the sum of the numbers of protons and neutrons in the nucleus of that atom.
- The structure of an atom can be represented as ${}^{A}_{Z}X$ where X is the element's symbol, Z is the atomic number and A is the mass number.
- Each of the elements that have been identified has a unique name and symbol.
- Isotopes are atoms of the same element that have different numbers of neutrons in the nucleus.
- The electrons in an atom can exist in only certain allowed energy levels or shells.
- The electron configurations of atoms can be represented in terms of the numbers of electrons in each energy level, for example, phosphorus 2, 8, 5.
- The valence electrons of an atom are the electrons in the outermost energy level.
- Elements in the same group in the periodic table have the same valence or outer energy level electron configuration.
- Simple ions are electrically charged species formed when atoms gain or lose electrons.
- Polyatomic ions are electrically charged groups of atoms.
- Cations are positive ions, anions are negative ions.
- The periodic table of the elements can be used to predict the charges on simple ions.
- Electron dot diagrams show the arrangement of valence electrons in atoms, molecules and ions.

- In simple ionic compounds there is a transfer of one or more electrons from one atom to another to form positive and negative ions.
- When diatomic or polyatomic molecules form, the atoms share electrons.
- When atoms form ions or molecules, they usually achieve a noble gas electron configuration, frequently an electron octet.
- The formula of a substance indicates the composition of the substance.
- The formulas of elements:
  - For a metal or a covalent network element, the formula is the element's symbol.
  - For a molecular element, the formula indicates the actual number of atoms in the molecule.
- The formulae of compounds:
  - For a molecular compound, the formula indicates the actual number and type of atoms in the molecule.
  - For a covalent network compound, the formula indicates the relative numbers of atoms of each element.
  - For an ionic compound, the formula indicates the relative numbers of each type of ion.

* APPLICATION AND INVESTIGATION

1 From the information in the table below,

a **Identify** those species that are:

i isotopes

ii neutral atoms

iii positive ions

iv negative ions.

b Use the periodic table to **identify** each of the elements.

c Write the actual symbol, and charge if appropriate, of each of the species.

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

2 Complete the table below.

Symbol	$^{16}_{8}O$	$^{17}_{8}O^{2-}$	$_{11}Na$		$_{4}Be^{2+}$
Protons				17	
Neutrons			12	20	5
Electrons				18	
Net charge	0		+1		
Atomic number			11		
Mass number			23		

3 **Construct** the electron configurations for atoms of the following elements:

- **a** helium
- **b** aluminium
- **c** neon
- **d** nitrogen
- **e** carbon
- **f** potassium.

4 For atoms of the elements Ne, F, C and O **identify** the following:

- **a** the group of the periodic table to which they belong
- **b** the electron configuration
- **c** the number of valence electrons
- **d** the charge of the simple ion the element is most likely to form.

5 **Construct** electron dot diagrams for the following ionic compounds:

- **a** sodium fluoride
- **b** potassium oxide
- **c** calcium sulfide
- **d** magnesium chloride.

6 **Construct** electron dot diagrams for the following molecules:

a	iodine	I_2
b	nitrogen	N_2
c	ammonia	NH_3
d	carbon tetrachloride	CCl_4
e	nitrogen trifluoride	NF_3
f	carbon dioxide	CO_2

7 **Investigate** the important differences between the following models of the atom: Thomson's, Rutherford's, Bohr's and the quantum mechanical model.

Investigation

8 **a** **Distinguish** between the terms 'symbol' and 'formula'.

b **Explain** the difference between Co and CO.

9 **Distinguish** between:

- **a** atoms, molecules, simple ions and polyatomic ions
- **b** elements and compounds.

10 Aspirin and sucrose are two important compounds. Aspirin contains 9 carbon atoms, 8 hydrogen atoms and 4 oxygen atoms per molecule. In sucrose there are 12 carbon atoms, 22 hydrogen atoms and 11 oxygen atoms per molecule. **Construct** molecular formulas for aspirin and sucrose.

11 **Identify** how many atoms of hydrogen are present in each of the following formulae:

- **a** H_2O_2
- **b** $(NH_4)_2SO_4$
- **c** $C_2H_5CO_2H$
- **d** $(NH_4)_2HPO_4$

12 **Classify** the following molecular substances as consisting of monatomic, diatomic or polyatomic molecules.

CO, Cl_2, NH_3, CH_4, HCl, HNO_3, Ne, F_2

13 **Identify** the formulae of the following:

- **a** iodine
- **b** phosphorus
- **c** methane
- **d** hydrogen bromide
- **e** phosphorus trichloride
- **f** phosphorus pentachloride
- **g** carbon tetrachloride
- **h** chlorine trifluoride.

14 **Deduce** names for the following molecules:

- **a** F_2
- **b** SO_2
- **c** HI
- **d** I_2
- **e** HCl
- **f** P_2O_5
- **g** NF_3
- **h** CF_4

15 **Deduce** names for the following ionic compounds:

- **a** $MgCl_2$
- **b** $KHSO_4$
- **c** $Fe_2O_3.3H_2O$
- **d** $(NH_4)_2SO_3$
- **e** $Ca(HCO_3)_2$
- **f** PbO_2

16 **Construct** formulae for the following compounds:

- **a** mercury(I) chloride
- **b** mercury(II) nitrate-1-water
- **c** aluminium phosphate
- **d** ammonium carbonate
- **e** potassium permanganate
- **f** copper(II) carbonate.

17 Some of the polymer molecules that form plastics or proteins contain hundreds or thousands of atoms. **Investigate** how the formulas of these polymers are represented.

Investigation

CHAPTER 4

CHEMICAL CHANGE

4.1 Physical and chemical changes

Matter can undergo two types of changes, physical and chemical.

Physical changes are changes in physical properties such as volume or density, or changes in state such as changes from solid to liquid or from liquid to gas. Physical changes occur without a change in the composition of the particular substance. The change in volume of mercury or alcohol when it is heated is an example of a physical change that has common application in thermometers. Another example of physical change is the boiling of water, in which water is changed from the liquid to the gaseous state. Physical changes generally involve relatively small amounts of energy being absorbed or released.

Chemical changes are those in which new substances with different compositions and properties are formed. The combustion of petrol in car engines and methane in gas ovens are examples of chemical changes. In both cases, new substances (carbon dioxide and water) are produced, and heat and light energy are released. Another example of chemical change is the electrolysis of water. When an electric current is passed through water, two new substances, hydrogen gas and oxygen gas, are produced. Chemical changes usually involve large quantities of energy being absorbed or released, generally in the form of heat, light or electricity.

Energy changes associated with physical and chemical change

In general, the energy changes associated with physical processes such as boiling, melting and dissolving are much smaller than those associated with chemical changes. The information in Table 4.1 illustrates the scale of the differences involved.

Table 4.1 Energy changes associated with some physical and chemical changes

Process	Type of change	Energy involved (kJ mol^{-1})
$H_2O(l) \rightarrow H_2O(g)$	physical (boiling)	+44
$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$	chemical (decomposition)	+286
$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$	physical (dissolving)	–45
$NaOH(s) \rightarrow Na(s) + \frac{1}{2}O_2(g) + \frac{1}{2}H_2(g)$	chemical (decomposition)	+425

The energy values in the table are a measure of the energy absorbed or released in these processes. A negative value indicates that energy is released, and a positive value means that energy is absorbed.

The first process in Table 4.1 represents the boiling of water. When liquid water boils to form gaseous water, a physical change, 44 kJ of heat is absorbed for each mole (18 grams) of water that changes from liquid to gas. The second process represents the electrolysis of liquid water to produce hydrogen gas and oxygen gas. In this process, a chemical change, 286 kJ of energy is absorbed in the form of electrical energy. Both these processes are changes made to liquid water. However, the physical process of boiling involves a much smaller quantity of energy than the chemical decomposition reaction that produces hydrogen and oxygen.

The difference between these values can be explained in terms of the changes in the bonding involved. In liquid water there are strong covalent bonds between hydrogen and oxygen atoms. In addition to these strong bonding forces within the water molecules, there are relatively weak intermolecular forces between the water molecules.

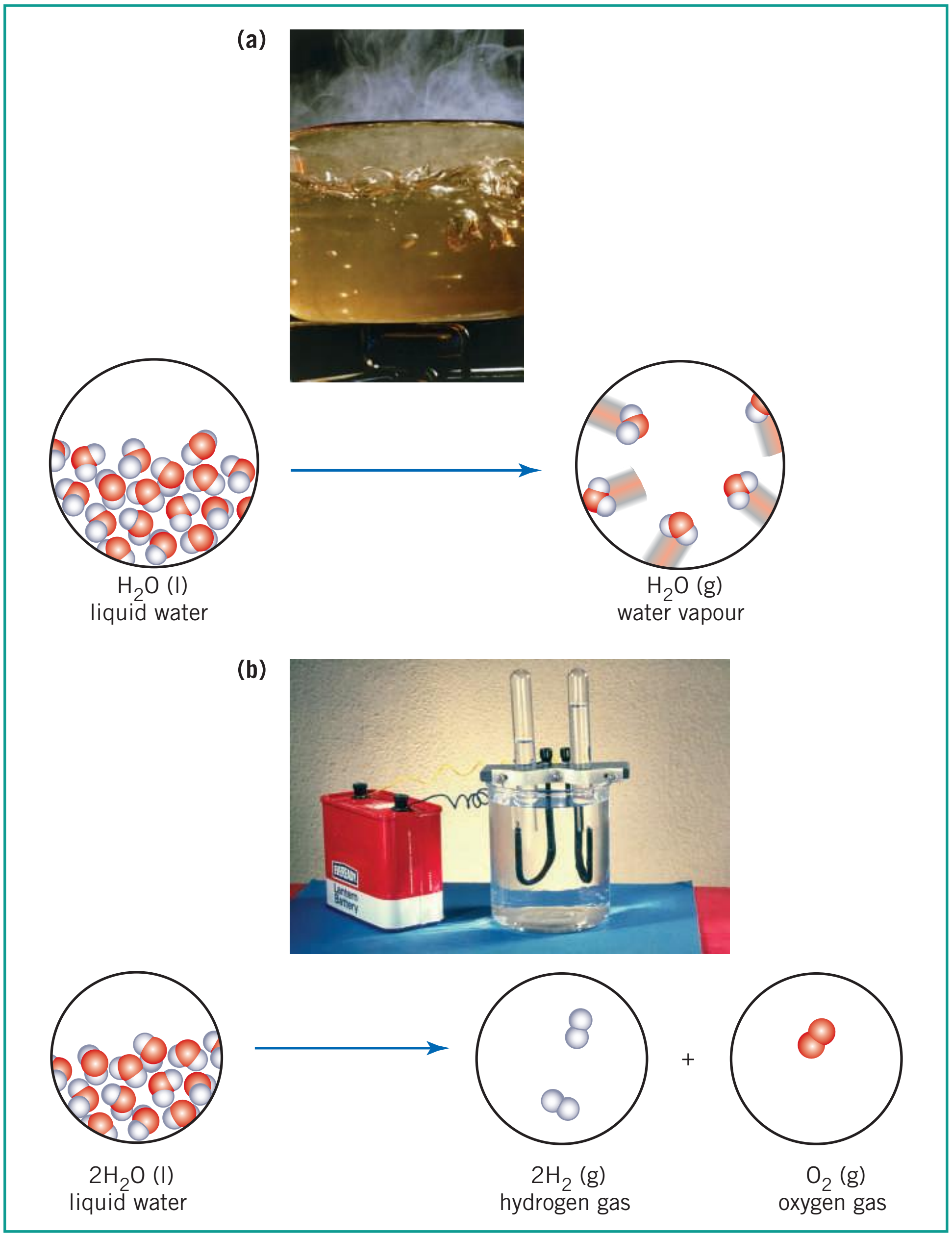


Figure 4.1 A model of the processes occurring at a molecular level when **(a)** water boils from liquid to gas, and **(b)** water is decomposed to form hydrogen and oxygen

When liquid water is heated, it absorbs energy. Its temperature increases as the molecules move with greater speed. Eventually the water molecules have sufficient kinetic energy to overcome the intermolecular forces between water molecules in the liquid and escape into the gaseous state. The breaking of these intermolecular forces when water boils from liquid to gas requires an input of energy, in this case, heat.

The chemical process in which electricity is used to decompose liquid water into hydrogen and oxygen involves the breaking of strong covalent bonds between hydrogen and oxygen within water molecules and the formation of covalent bonds between hydrogen atoms in H_2 and oxygen atoms in O_2. Much larger amounts of energy are involved than in breaking the weaker intermolecular forces. These two processes are illustrated, at a molecular level, in Figure 4.1.

Table 4.1 also compares the energy change associated with dissolving sodium hydroxide in water with that accompanying the decomposition of sodium hydroxide into its elements. Again the chemical process is associated with a much greater energy change.

The generalisation that physical changes involve smaller quantities of energy than chemical changes needs to be used with some caution, as it is not universally true. For example, the energy required to vaporise (change from liquid to gas) silicon and iron are 410 $kJ\ mol^{-1}$ and 402 $kJ\ mol^{-1}$ respectively. Although these represent physical changes, the high energies involved reflect the strength of the bonding between the atoms in the liquid states of these substances.

❄ Review exercise 4.1

1 **Classify** the following as physical or chemical changes:

- **a** chopping wood
- **b** burning wood
- **c** melting candle wax
- **d** burning candle wax
- **e** rusting iron
- **f** dissolving sugar in tea
- **g** forming an iron nail from an iron block
- **h** boiling an egg.

2 **Explain** in your own words the difference between a physical change and a chemical change. Give examples.

3 Consider the following processes:

- **i** the condensation of water vapour from the gas to the liquid state, as occurs in the formation of dew
- **ii** the explosive reaction between hydrogen gas and oxygen gas to form liquid water.

For these two processes:

- **a** **identify** the processes as physical or chemical changes
- **b** **explain**, at a molecular level, the changes occurring in terms of the arrangement of particles
- **c** **predict** whether energy is released or absorbed in the process, and the relative amounts of energy involved.

4.2 Chemical equations

Chemical reactions are processes in which chemical change occurs and are characterised by the formation of new substances. For example, when magnesium is burnt in air, a new substance, magnesium oxide, is produced. In chemical reactions, the arrangement of atoms is changed to produce new substances but atoms are neither created nor destroyed. Thus a characteristic of chemical reactions is that mass is conserved—that is, the mass of the reacting substances equals the mass of the product substances.

Chemical reactions can be represented by equations. The burning of magnesium can be represented by the following 'word equation':

magnesium + oxygen → magnesium oxide

By substituting chemical formulas into the 'word equation', chemical equations can be obtained which indicate what is taking place at an atomic/molecular/ionic level. The chemical equation for the burning of magnesium is as follows:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

When writing chemical equations, the following conventions are adopted:

1. The formulas of the reactant species are written on the left-hand side of the arrow and the formulas of the product species on the right-hand side.
2. The coefficients (numbers) written in front of formulas indicate the number of particles—that is, atoms, molecules or formula units—of that substance relative to all the other substances in the reaction.
3. The physical states of the reactants and products under the reaction conditions may be denoted by writing, to the right of each formula, (g), (l) or (s) to represent gas, liquid and solid respectively. If the reaction occurs in aqueous solution (that is, the substance is dissolved in water), the symbol (aq) can be used to denote 'in aqueous solution'.
4. The number of atoms of each element on the left-hand and right-hand sides of the equation must be equal.
5. The sum of the electrical charges on the left-hand and right-hand sides of the equation must be equal.

Interpreting chemical equations

The chemical equation for the burning of magnesium can be interpreted in the following ways.

1. Magnesium metal reacts with oxygen gas to produce solid magnesium oxide.
2. For every two magnesium atoms that react, one molecule of oxygen is needed and two formula units of magnesium oxide are produced.

The relative numbers of reactant and product particles are illustrated in Figure 4.2.

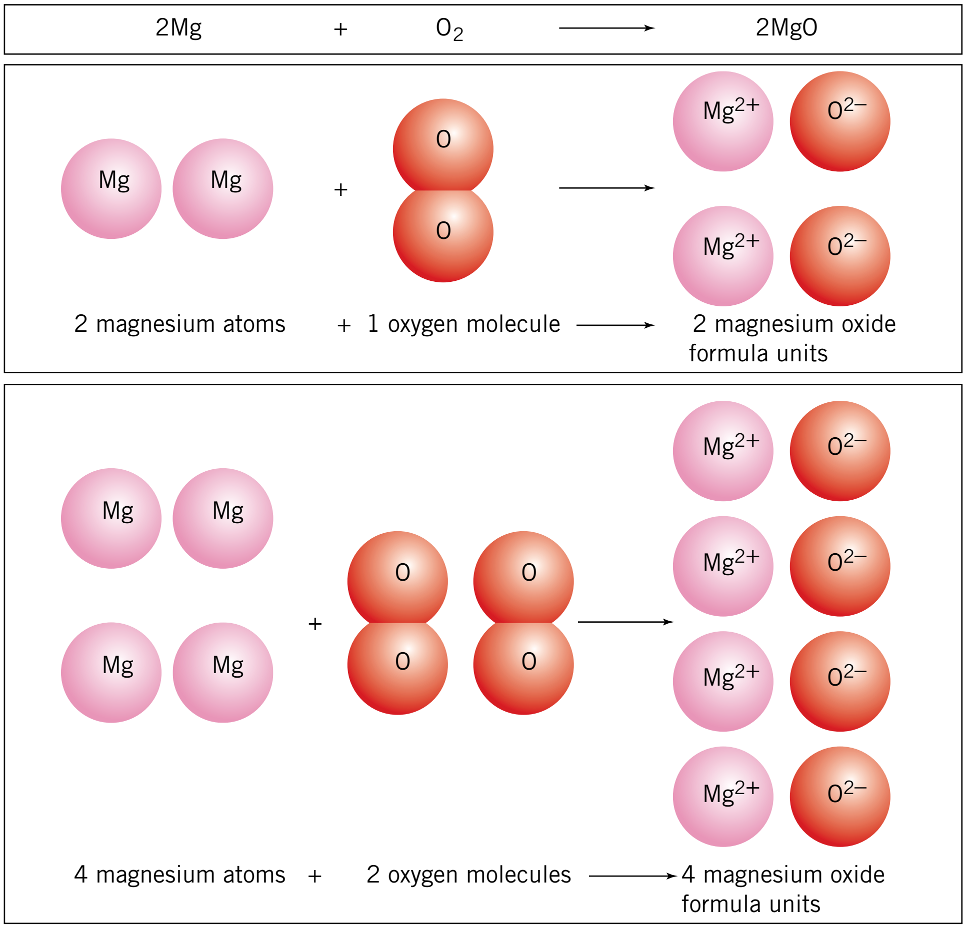


Figure 4.2 Interpreting a chemical equation

✻ Review exercise 4.2

1 One of the rules concerning balanced chemical equations is that the number of atoms of each element on the left-hand and right-hand sides of the equation must be equal. If this were not true, **identify** which fundamental chemical law would be violated.

2 The chemical equation for the burning of methane, the major constituent in natural gas, is:

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

Summarise in your own words what this equation means.

3 **Construct** balanced chemical equations for the following reactions:

a the reaction of ammonia gas with hydrogen chloride gas to form solid ammonium chloride

b the decomposition of solid calcium carbonate when it is heated into solid calcium oxide and carbon dioxide gas.

c the reaction of aqueous solutions of silver nitrate and sodium chloride to form solid silver chloride and aqueous sodium nitrate.

4.3 Balancing chemical equations

To represent a chemical reaction correctly, the equation must be 'balanced'. To be balanced, the number of atoms of each element on the left-hand and right-hand sides of the equation must be equal. Balancing equations is achieved by changing the coefficients in front of the formulas in the equation.

The general procedure for writing balanced chemical equations is as follows.

1 Write a word equation for the reaction which includes all the reactants and products.
2 Under each of the reactants and products in the word equation, write the correct formula of the species concerned.
3 Alter the coefficients in front of each formula to balance the number of atoms of each element on both sides of the equation.
4 Check that the number of atoms of each element is the same on both sides of the equation.
5 Write in the physical states for each species.

→ Example 4.1

Construct balanced chemical equations for the following reactions.

1 The burning of hydrogen in oxygen to form water

a Write the word equation.

hydrogen + oxygen → water

b Write the formulae for the reactants and products.

$H_2 + O_2 \rightarrow H_2O$

c Balance each atom separately.

$H_2 + O_2 \rightarrow 2H_2O$

(balances O atoms)

$2H_2 + O_2 \rightarrow 2H_2O$

(balances H atoms)

d Mark in the physical states for each species.

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

2 The reaction between solid aluminium hydroxide and aqueous sulfuric acid to form aqueous aluminium sulfate and water

a aluminium hydroxide + sulfuric acid → aluminium sulfate + water

b $Al(OH)_3 + H_2SO_4 \rightarrow Al_2(SO_4)_3 + H_2O$

c $\mathbf{2}Al(OH)_3 + H_2SO_4 \rightarrow Al_2(SO_4)_3 + H_2O$ (balances Al atoms)

$2Al(OH)_3 + \mathbf{3}H_2SO_4 \rightarrow Al_2(SO_4)_3 + H_2O$ (balances sulfate ions)

$2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + \mathbf{6}H_2O$ (balances H, O atoms)

d $2Al(OH)_3(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 6H_2O(l)$

3 The burning of butane in oxygen to form carbon dioxide and water

a butane + oxygen → carbon dioxide + water

b $C_4H_{10} + O_2 \rightarrow CO_2 + H_2O$

c $C_4H_{10} + O_2 \rightarrow CO_2 + \mathbf{5}H_2O$ (balances H atoms)

$C_4H_{10} + O_2 \rightarrow \mathbf{4}CO_2 + 5H_2O$ (balances C atoms)

$C_2H_{10} + \frac{\mathbf{13}}{\mathbf{2}} O_2 \rightarrow 4CO_2 + 5H_2O$ (balances O atoms)

$\mathbf{2}C_4H_{10} + \mathbf{13}O_2 \rightarrow \mathbf{8}CO_2 + \mathbf{10}H_2O$ (removes fractional coefficient)

d $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$

✻ Review exercise 4.3

1 Balance the following equations:

- **a** $Cl_2(g) + H_2(g) \rightarrow HCl(g)$
- **b** $Cl_2(g) + O_2(g) \rightarrow Cl_2O(g)$
- **c** $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$
- **d** $Mg(s) + HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$
- **e** $Fe(s) + O_2(g) \rightarrow Fe_2O_3(s)$
- **f** $C_2H_6(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$

2 **Construct** balanced chemical equations for the following reactions:

- **a** burning carbon in oxygen to form carbon dioxide
- **b** burning carbon in a limited supply of oxygen to form carbon monoxide
- **c** burning aluminium in chlorine gas to form aluminium chloride
- **d** heating solid potassium chlorate, $KClO_3$, to form solid potassium chloride and oxygen gas
- **e** reacting aluminium with aqueous hydrochloric acid, HCl, to produce aqueous aluminium chloride and hydrogen gas
- **f** burning hydrogen sulfide gas in oxygen to form gaseous sulfur dioxide and gaseous water.

4.4 Decomposition of compounds

We can differentiate between pure substances, elements and compounds, according to how easily they can be decomposed. Elements, such as zinc, cannot be decomposed into simpler substances. If solid zinc is heated, it will melt to form liquid zinc and, at sufficiently high temperatures, will boil to form gaseous zinc.

$$Zn(s) \rightarrow Zn(l) \rightarrow Zn(g)$$

These changes are physical changes. The zinc atoms have moved relative to each other but they are still the same unaltered zinc atoms.

However, under certain conditions, compounds can be decomposed into their constituent elements or simpler compounds. This decomposition can be brought about by adding energy as heat, light or electricity.

Thermal decomposition

The process by which heat breaks compounds down into simpler substances is known as *thermal decomposition*. In this process, which is a type of chemical change, the arrangement of particles in the compounds changes. The particles are rearranged to form different compounds or elements.

The compound mercury(II) oxide, when heated strongly, decomposes into the elements mercury and oxygen (Figure 4.3).

$$2HgO(s) \rightarrow 2Hg(l) + O_2(g)$$

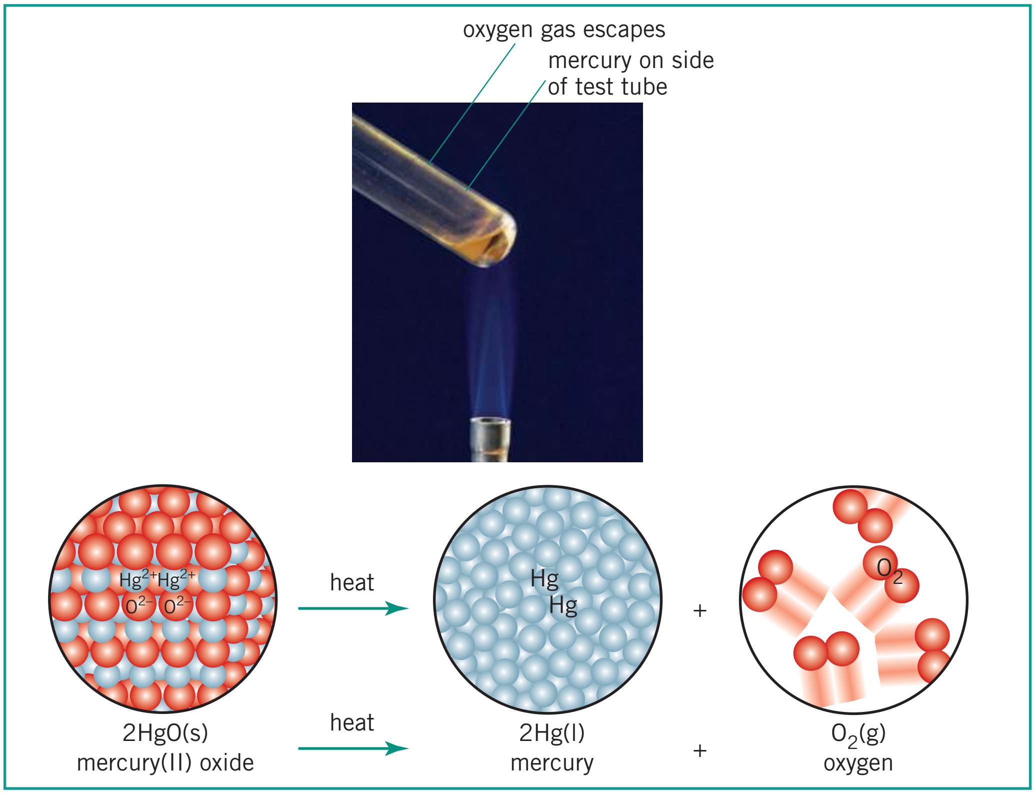


Figure 4.3 Mercury(II) oxide decomposes when heated to form mercury metal and oxygen gas.

This reaction is a chemical change in which the actual substances present have been altered. The reaction has changed the nature and arrangement of the particles involved. The Hg^{2+} ions that were arranged with O^{2-} ions in the solid HgO have changed to Hg atoms in liquid mercury. Similarly, the O^{2-} ions that were in the HgO solid have changed to oxygen atoms covalently bonded in O_2 molecules. It should be noted, however, that no atoms have been formed or destroyed in this process. The form of the atoms, such as Hg atoms or Hg^{2+} ions, have changed but the atoms have been conserved.

Another compound, copper(II) carbonate, decomposes when strongly heated to form different compounds—copper(II) oxide and carbon dioxide.

$$CuCO_3(s) \rightarrow CuO(s) + CO_2(g)$$

Again in this process the nature and arrangement of particles has changed. Solid $CuCO_3$ contains Cu^{2+} ions and CO_3^{2-} ions. After the reaction, the Cu^{2+} ions remain but are now arranged with O^{2-} ions in solid CuO, and CO_2 gas molecules have been produced.

Our knowledge of compounds and the ease with which they can be decomposed by heat is used every day. In baking, the thermal decomposition of bicarb soda (sodium hydrogencarbonate) to produce carbon dioxide gas is used to make cakes rise when they cook.

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

Similarly, lime (calcium oxide), which is used as a treatment for acidic soils, is produced by the thermal decomposition of limestone (calcium carbonate).

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Figure 4.4 Thermal decomposition of bicarb soda causes a cake to rise while cooking.

Decomposition by electrical energy and light energy

Other forms of energy such as electricity and light may also bring about the decomposition of compounds. As discussed in Unit 4.1, water can be decomposed into the elements hydrogen and oxygen if an electric current is passed through it (see Figure 4.5). This is called *electrolysis*. The reaction is:

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

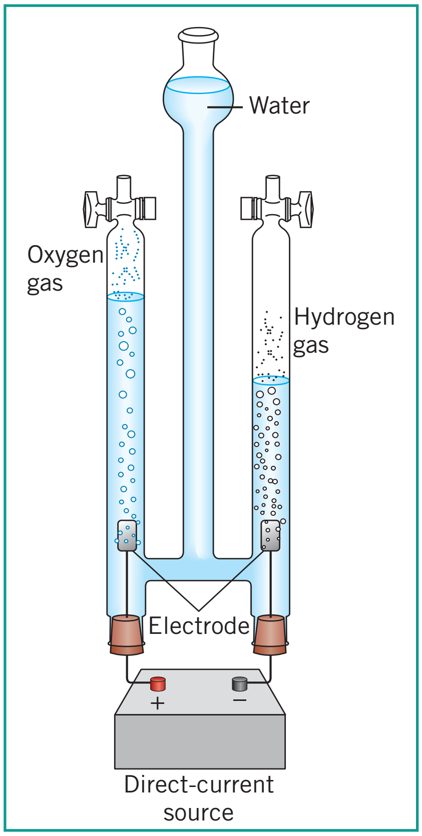


Figure 4.5 The decomposition of water by electrolysis, a chemical change

Many other substances can be decomposed in this way. In fact, it was the process of electrolysis that greatly increased our ability to extract metals from their ores. Metals such as aluminium and sodium can only be extracted from their ores in this way.

Light energy can also cause the decomposition of some compounds. For example, silver salts such as silver chloride decompose when exposed to light, to produce silver metal. The use of silver bromide in black and white photographic film depends on this decomposition reaction. In this process, light causes the following decomposition reaction to occur:

$$AgBr(s) \rightarrow Ag(s) + \frac{1}{2} Br_2(g)$$

The Ag^+ ions are converted to Ag atoms. These form a 'latent' image, which is enhanced when the photographic film is developed.

Many dyes and pharmaceutical products are also 'light sensitive' and will undergo decomposition if exposed to light. It is for this reason that many of these substances are stored in dark glass or opaque containers.

❇ Review exercise 4.4

1 **Describe** what is meant by the term 'chemical decomposition'. **Identify** whether this an example of a physical or chemical change.

2 a **Compare** the boiling and electrolysis of water in terms of the substances present 'before' and 'after'.
  b **Identify** the processes in part **a** as physical change or chemical change, and **explain** your choice.

3 **Explain** how sodium hydrogencarbonate can make a cake rise.

4 **Identify** the following processes as physical change or chemical decomposition:
  a the gradual reaction of hydrogen peroxide to form water and oxygen
  b the melting of ice
  c the evaporation of kerosene
  d the electrolysis of zinc iodide to form zinc and iodine.

4.5 Synthesis of chemical substances

Many of the products we use, some of the foods we eat and most of the medicines we take are products of chemical synthesis. *Synthesis* is the process of forming a compound from elements or from other compounds. This process involves chemical change and usually leads to the formation of a more complex substance. Elements cannot be synthesised in chemical processes. They are extracted from naturally occurring ores.

Initially many of the compounds synthesised by humans were produced because a previous naturally occurring source was diminishing or limited. An example of this is the synthesis of ammonia. In the nineteenth and early twentieth centuries, farmers depended on animal manure and naturally occurring sodium nitrate deposits as sources of nitrogenous fertilisers. The need for fertiliser increased, and this led to the development of the Haber process, in which hydrogen gas and nitrogen gas are combined to form ammonia.

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

While the overall reaction in the Haber process releases energy, fairly high temperatures are required to break the chemical bonds in nitrogen and hydrogen so the reaction can take place.

The ammonia is often reacted with sulfuric acid or nitric acid to form ammonium sulfate or ammonium nitrate, which can be used as fertilisers.

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

Another example in which chemical synthesis has replaced natural sources is the dyeing industry. Initially all dyestuffs were natural products obtained primarily from vegetable sources. Indigo, for example, was derived from plants and Tyrian purple from a particular mollusc. Work by chemists in the nineteenth century, notably Henry Perkins, developed methods of synthesising a wide range of coloured dyestuffs using chemicals isolated from coal. This greatly increased the availability of coloured dyes for fabrics and clothing.

The plastics industry is another major industry that synthesises an extraordinary array of useful chemical substances starting with chemicals derived from petroleum. These include polyethylene, polystyrene, PVC, PET, perspex, Teflon, nylon, Kevlar and many others.

In these various synthesis processes, energy often has to be provided in order to allow for the rearrangement of atoms in the reacting compounds. Whether a particular reaction absorbs or releases energy depends on the relative bonding strengths within the reactants and products. However, even if energy is released in a reaction, the reactants often need to have energy supplied, usually in the form of heat or light, in order for the initial bond rearrangement to take place.

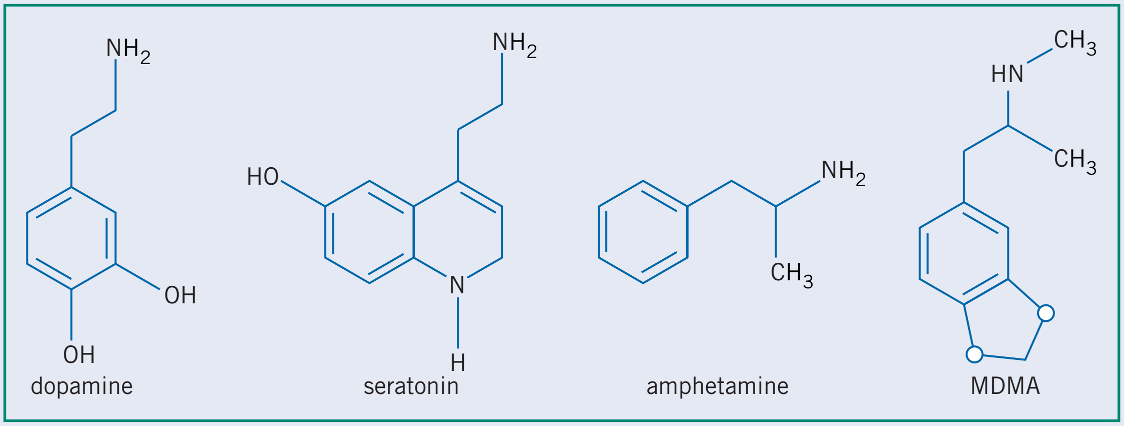
CHEMISTRY CONTEXT

CHEMICAL SYNTHESIS OF ECSTASY (3,4-METHYLENEDIOXYMETHAMPHETAMINE OR MDMA)

Ecstasy belongs to the group of drugs called amphetamines. Amphetamines are also known as pep pills and act as artificial stimulants to the human nervous system in a similar way to the natural substance adrenaline. When we are stressed or under threat, the central nervous system gets us ready for action by changing our body's physiology through the release of adrenaline and other hormones, and neurotransmitters. This causes heart rate and blood pressure to increase and a redirection of blood flow into the muscles. Ecstasy works on the brain to initiate a similar response and the user feels refreshed by a burst of energy. It also results in the release of serotonin, dopamine and noradrenaline in the brain, giving the user an enhanced feeling of wellbeing. Ecstasy may also cause some hallucinogenic effects.

Ecstasy was first made from methylenedioxyamphetamine (MDA) in Germany in 1912 by chemists working for Merck Pharmaceuticals and was patented in May 1914. The US Army experimented with it throughout the 1950s, and later doctors treating various mental illnesses began using it with their patients. It wasn't until the 1970s that it was used for recreational purposes and soon after became illegal. Ecstasy has been approved by the US government for use by war veterans suffering from post-traumatic stress disorder.

Today, ecstasy can be synthesised through a variety of chemical reaction pathways, including steps such as oxidation and amination (adding an NH_2 group). These processes often result in a mixture of chemical products.



dopamine seratonin amphetamine MDMA

Figure 4.6 Molecular structures of the synthetic drug ecstasy (MDMA), amphetamine, and the natural substances dopamine and serotonin

❇ Review exercise 4.5

1 **Explain** the difference between extraction, synthesis and decomposition.

2 **Explain** why elements can't be synthesised chemically.

3 **Identify** one example of a chemical change that involves each of the following types of energy: heat, light and electricity.

4 **Identify** the type of energy involved in the following chemical processes and whether the energy is absorbed or released:
   a photosynthesis, in which carbon dioxide and water are converted by plants into glucose and oxygen
   b the burning of methane to form carbon dioxide and water
   c the chemical reactions occurring in a torch battery
   d the chemical reactions occurring when a glow worm 'glows'.

4.6 Bond energy

In Unit 4.1 the energy changes accompanying physical and chemical change were discussed. In general terms it was suggested that chemical change is often accompanied by the absorption or release of greater quantities of energy than physical change because chemical change involves the breaking (and making) of chemical bonds.

In chemical compounds, atoms of two or more elements are chemically combined. The atoms are held together by chemical bonds, which are either covalent or ionic. Chemical compounds are often classified into three general types—ionic compounds, covalent molecular compounds and covalent network compounds. The detailed structures of these types of compounds will be described in Chapter 5 but the strength of ionic and covalent bonds within these compounds will be considered in this section.

Covalent bonding is the sharing of electrons between atoms. By sharing electrons, atoms usually achieve a share in a noble gas electron configuration, that is, a valence electron octet. In covalent bonds the shared bonding electrons are simultaneously attracted to the nuclei of both bonded atoms. It is this simultaneous electrostatic attraction of both nuclei for the shared electrons that constitutes the covalent bond. To separate the atoms joined by a covalent bond requires a considerable quantity of energy. This is sometimes referred to as the *bond energy*. The bond energies for covalent bonds vary in the approximate range 150–1100 kJ mol^{-1}. Several examples of covalent bond energies are listed in Table 4.2.

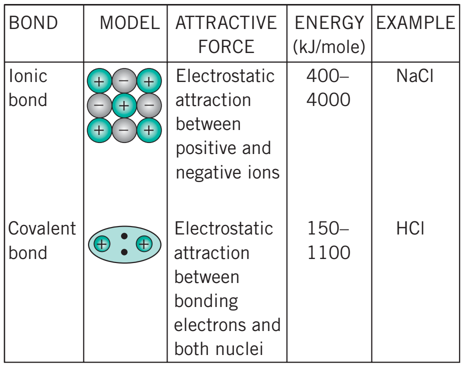
Table 4.2 Bond energy for several covalent bonds

Covalent bond	Bond energy (kJ mol^{-1})
H–H	436
H–Cl	431
Cl–Cl	242
O–H	463
C–C	346
C–O	358

Simple *covalent molecular substances* consist of molecules in which the atoms are held together by covalent bonds. The bond energy indicates the strength of the forces holding the atoms together in the molecule. For example, to decompose an HCl molecule into separate H and Cl atoms requires 431 kJ mol^{-1} of energy. These large bond energies explain the observation that chemical change is usually accompanied by the absorption or release of considerable quantities of energy.

Covalent network substances consist of a three-dimensional arrangement of atoms joined by covalent bonds. For example, in silicon dioxide (Figure 3.9) every silicon atom is covalently bonded to four oxygen atoms and each oxygen atom is covalently bonded to two silicon atoms. Each Si–O bond has a bond energy of 163 kJ mol^{-1}, which makes the disruption of the entire lattice very difficult indeed. For this reason silicon dioxide has a very high melting point.

Unit 3.5 describes ionic bonding as the electrostatic attraction of oppositely charged ions within a three-dimensional lattice of positive and negative ions (Figure 3.10). In sodium chloride the lattice consists of Na$^+$ and Cl$^-$ ions. The separation of the Na$^+$ and Cl$^-$ ions requires a large amount of energy, called the *lattice energy*, which is a measure of the strength of the ionic bond. The ionic lattice energies for several compounds are shown in Table 4.3.



BOND	MODEL	ATTRACTIVE FORCE	ENERGY (kJ/mole)	EXAMPLE
Ionic bond	⊕⊖⊕ ⊖⊕⊖ ⊕⊖⊕	Electrostatic attraction between positive and negative ions	400–4000	NaCl
Covalent bond	⊕ : ⊕	Electrostatic attraction between bonding electrons and both nuclei	150–1100	HCl

Figure 4.7 Chemical bonds and bond energies

Table 4.3 Ionic lattice energies for several ionic compounds

Ionic compound	Ionic lattice energy (kJ mol^{-1})
NaCl	788
KCl	718
$MgCl_2$	2523
$CaCl_2$	2255
MgO	3800
CaO	3419

For NaCl the energy required to separate the Na$^+$ and Cl$^-$ ions is 788 kJ mol^{-1}, which indicates the considerable strength of ionic bonds. Similarly, the quantity of energy needed to separate Mg^{2+} and O^{2-} ions in magnesium oxide is 3800 kJ mol^{-1}. The range of ionic lattice energies is approximately 400–4000 kJ mol^{-1}.

When compounds are decomposed into their constituent elements, large quantities of energy are usually required. This is because the decomposition reaction involves breaking strong covalent or ionic bonds within these substances. On the other hand, changes of state such as liquid water to steam require much smaller quantities of energy. This process only involves breaking weak intermolecular forces between molecules. These intermolecular forces, which will be described in more detail in Chapter 5, range up to about 40 kJ mol^{-1} in strength. They are therefore much weaker than either covalent or ionic bonding forces.

❇ Review exercise 4.6

1 **Describe** the two major types of chemical bonds in compounds.

2 **Explain** why the energy needed to separate different elements within a compound is an indication of the strength of the bonding within the compound.

*KEY POINTS

- Chemical changes are those in which new substances with different compositions and properties are formed.
- Chemical changes are often accompanied by the absorption or release of large quantities of energy, generally in the form of heat, light or electricity.
- Chemical changes involve changes in the nature and arrangement of atomic particles so that different combinations of atoms are produced.
- Physical changes are those in which substances undergo changes in physical properties such as volume or density, or changes in state such as changes from solid to liquid or from liquid to gas.
- Physical changes occur without a change in the composition of the particular substance involved.
- Physical changes are often accompanied by the absorption or release of small quantities of energy.
- When water boils, it changes state from liquid to gas; however, the two states both consist of water (H_2O) molecules.
- When water is electrolysed, it decomposes into two new substances, hydrogen gas (H_2) and oxygen gas (O_2).
- Elements cannot be decomposed by chemical change into simpler substances.
- Compounds can be chemically decomposed into elements or simpler compounds using heat, light or electricity.
- Chemical reactions are represented by chemical equations.
- Chemical equations show the relationships between the numbers of particles of reactants and products in a chemical reaction.
- In balanced chemical equations:
  - the numbers of atoms of each element on both sides of the equation are equal
  - the sums of the electrical charges on each side of the equation are equal
  - the symbols (g), (l), (s) and (aq) are used to represent gas, liquid, solid and aqueous solution respectively.
- In balanced chemical equations, the coefficients in front of the formulas are altered so that the number of atoms of each element are equal on both sides of the equation.
- The law of conservation of mass states that in chemical reactions there is no gain or loss in mass.
- The extraction of metals involves separating metals from their ores and involves chemical change.
- Chemical synthesis is the process of forming compounds from elements or other compounds.
- Chemical synthesis produces many of the products, foods and medicines we use today.

- Covalent bonds and ionic bonds are strong chemical bonds.
- Large quantities of energy are needed to separate the different elements within a compound—this energy is an indication of the strength of the chemical bonds in compounds.

✱ APPLICATION AND INVESTIGATION

1 **Classify** each of the following as a physical or chemical change:
   - **a** evaporation of petrol
   - **b** tarnishing of silver
   - **c** ripening of fruit
   - **d** dissolving salt in water
   - **e** digestion of food
   - **f** formation of snowflakes.

2 Three substances undergo changes when treated as described in the following table.

Substance	Treatment	Observations
Lead	Strongly heated to 500°C	Grey-silver solid melts to form a grey-silver liquid at 327°C
Zinc iodide	Strongly heated to 700°C	White crystalline solid changes to a grey liquid and a purple vapour
Lead(II) bromide	Electrolysed at 500°C	Pale yellow liquid which forms a brown gas at one electrode and a silver liquid at the other electrode

Identify the three changes as physical changes or chemical changes. **Justify** your answers.

3 A white crystalline solid seems unable to be separated into simpler components using physical methods. However, if the white solid is melted and an electric current is passed through it, a grey solid and brown liquid are produced. **Identify**, with reasons, whether the white solid is an element, a compound or a mixture.

4 For processes **i** to **iv** below:
   - **a** **identify** whether the process would absorb or release energy
   - **b** **predict** whether the process would involve the exchange of a relatively small or large quantity of energy
   - **c** **classify** the process as a physical change or chemical change.
     - **i** burning magnesium
     - **ii** sublimation of carbon dioxide (dry ice)
     - **iii** condensation of water
     - **iv** burning a candle

5 For questions **4c i** and **4c ii** draw diagrammatic representations to illustrate these processes at a molecular or atomic level.

6 **Summarise** in words what is meant by each of the following equations.

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

b $Cu(s) + 2AgNO_3(aq) \rightarrow 2Ag(s) + Cu(NO_3)_2(aq)$

7 Balance the following equations.

a $Al(s) + O_2(g) \rightarrow Al_2O_3(s)$

b $C_2H_2(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$

c $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + NaCl(aq)$

d $Ca(s) + H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$

e $NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$

f $C_7H_5N_3O_6(s) \rightarrow N_2(g) + H_2O(g) + CO(g) + C(s)$

8 **Construct** balanced chemical equations for the following reactions.

a Sodium when burnt in chlorine produces solid sodium chloride.

b When solid sodium oxide reacts with water, an aqueous solution of sodium hydroxide is formed.

c Magnesium carbonate when heated forms solid magnesium oxide and carbon dioxide.

d Iron(III) oxide when heated with carbon monoxide produces iron metal and carbon dioxide.

e Calcium carbonate treated with hydrochloric acid (aqueous hydrogen chloride) forms carbon dioxide, water and aqueous calcium chloride solution.

f Liquid benzene (C_6H_6) is burnt in oxygen to form carbon dioxide and gaseous water.

g Aluminium metal reacts with aqueous copper(II) sulfate to form copper metal and aluminium sulfate solution.

h Solid ammonium nitrate is heated to form nitrous oxide (dinitrogen monoxide) and gaseous water.

9 When wood is burned, the ash that remains weighs less than the wood did initially. **Explain** these observations in terms of the law of conservation of mass.

10 Nitrogen dioxide reacts with water according to the following equation:

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$

If nine molecules of nitrogen dioxide reacted, **calculate** the following:

a the number of molecules of nitric acid produced

b the number of molecules of nitric oxide produced.

11 When octane burns in oxygen, the reaction is as follows:

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

If 96 molecules of CO_2 were produced, **calculate** the following:

a the number of molecules of octane and oxygen that reacted

b the number of molecules of water produced.

12 **Identify** the following reactions as chemical decomposition or chemical synthesis.

a $PbO(s) + C(s) \rightarrow Pb(s) + CO(g)$

b $2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$

c $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

d $SO_2(g + \frac{1}{2}O_2(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

➲ Investigation

13 **Investigate** and write a brief outline of the synthesis of one of the following: saccharin, nylon or DDT.

14 Ethanol (CH_3CH_2OH), commonly called alcohol, melts at –114°C and boils at 78°C. However, to separate ethanol into its constituent elements, carbon, oxygen and hydrogen, requires a large amount of energy, 235 kJ mol^{-1}.

a **Identify** what the low melting and boiling points of ethanol indicate about the strength of its intermolecular forces.

b **Explain** what the large amount of energy required to decompose ethanol into its constituent elements indicates about the strength of the bonding within ethanol molecules. **Identify** the type of bonding.

BONDING AND STRUCTURE DETERMINE PROPERTIES

CHAPTER 5

5.1 Physical and chemical properties of matter

Chemical substances may be identified by careful observation of their properties. Although several substances may have similar properties, no two substances are alike in all respects. The use of properties to identify substances can be illustrated by comparing the properties of gold and fool's gold as shown in Table 5.1.

Table 5.1 Properties of gold and fool's gold

Property	Gold	Fool's gold (iron pyrites)
Colour	yellow/gold	yellow/gold
Lustre	metallic	metallic
Hardness	soft and malleable	hard and brittle
Density (g cm^{-3})	19.3	5.0
Melting point (°C)	1063	1171
Solubility in water	insoluble	insoluble

These substances share many similar properties, which accounts for the fact that iron pyrites has often been wrongly identified as gold. Despite the similarity of many of their properties, the substances can be readily distinguished by their differing hardnesses and densities.

Figure 5.1 Gold (left) and fool's gold (right) have outwardly similar appearances.

It is convenient to distinguish between the physical and chemical properties of substances. Examples of physical and chemical properties are shown in Table 5.2.

Table 5.2 Examples of physical and chemical properties

Physical properties
odour, colour, taste, lustre, hardness, density, mechanical strength, malleability (the ability to be beaten into sheets), ductility (the ability to be drawn into wires), electrical conductivity, thermal conductivity, melting point, boiling point, solubility
Chemical properties
reactions with oxygen, water, acids, bases; specific reactions with other substances

Physical properties are those that can be determined without changing the chemical composition of the substance. For example, the physical properties of iron include the following: grey solid, metallic lustre, fairly soft when pure, malleable, ductile, good electrical and thermal conductor, high melting point (1535°C). *Chemical properties* are those that relate to the ability of a substance to form new substances. Chemical properties include changes that occur when a substance breaks down or reacts with other substances during a chemical reaction.

The chemical properties of iron include the following:

- It reacts slowly with moist air to form rust.
- If finely divided, it will burn in oxygen when heated.
- It reacts with steam and dilute acids to form hydrogen.

❇ Review exercise 5.1

1 **Describe** one chemical and two physical properties of each of paper, petrol, water and natural gas.

2 Six bottles contain sodium chloride, oxygen, copper(II) sulfate, water, iron and sulfur. **Propose** which physical properties could be used to identify each of these substances.

5.2 Comparison of properties of compounds and their constituent elements

When elements combine to form a compound, they become chemically bonded to one another, not simply mixed together. In the chemical reaction that takes place when elements combine, the nature and arrangement of particles changes. For example, when magnesium burns in oxygen to form magnesium oxide according to the equation

$$2\text{Mg(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{MgO(s)}$$

- the magnesium atoms (Mg) change to magnesium ions (Mg^{2+})
- the oxygen atoms (in O_2 molecules) change to oxide ions (O^{2-}), and
- the Mg^{2+} and O^{2-} ions are arranged in a particular pattern within the magnesium oxide.

The composition of magnesium oxide is described as being definite and constant, because for every one Mg^{2+} ion there is one O^{2-} ion. On a mass basis this corresponds to 60.3% magnesium and 39.7% oxygen. The composition of magnesium oxide is always the same, in contrast to the variable compositions possible for mixtures. The fact that all pure samples of the same compound contain the same elements combined together in the same proportions by mass is known as the *Law of constant composition*. As its title suggests, this law indicates that the composition of a compound is the same regardless of its source or method of preparation, provided that the compound is pure.

Compounds have quite different properties from those of the elements that combined to form them. For example, magnesium oxide is a white powder, while magnesium is a silver-grey metal and oxygen is a colourless gas. Similarly, water has very different properties from those of the elements hydrogen and oxygen, which exist as gases at normal temperatures. Lead(II) sulfide is a compound that contains chemically combined lead and sulfur. Like most compounds, lead(II) sulfide has vastly different properties from those of the elements from which it is formed. Lead(II) sulfide commonly occurs as the mineral galena, which has a shiny metallic appearance and cubic crystal structure. A comparison of the properties of this mineral with those of its constituent elements is given in Table 5.3, and the substances are shown in Figure 5.2.

Table 5.3 Properties of lead, sulfur and lead(II) sulfide (galena)

	Lead	Sulfur	Lead(II) sulfide
State at 25°C	solid	solid	solid
Colour	grey	yellow	grey
Melting point (°C)	327	113	1114
Boiling point (°C)	1740	445	–
Density (g/cm^3)	11.3	2.1	7.5
Conducts electricity (solid)	yes	no	no
Conducts electricity (molten)	yes	no	yes

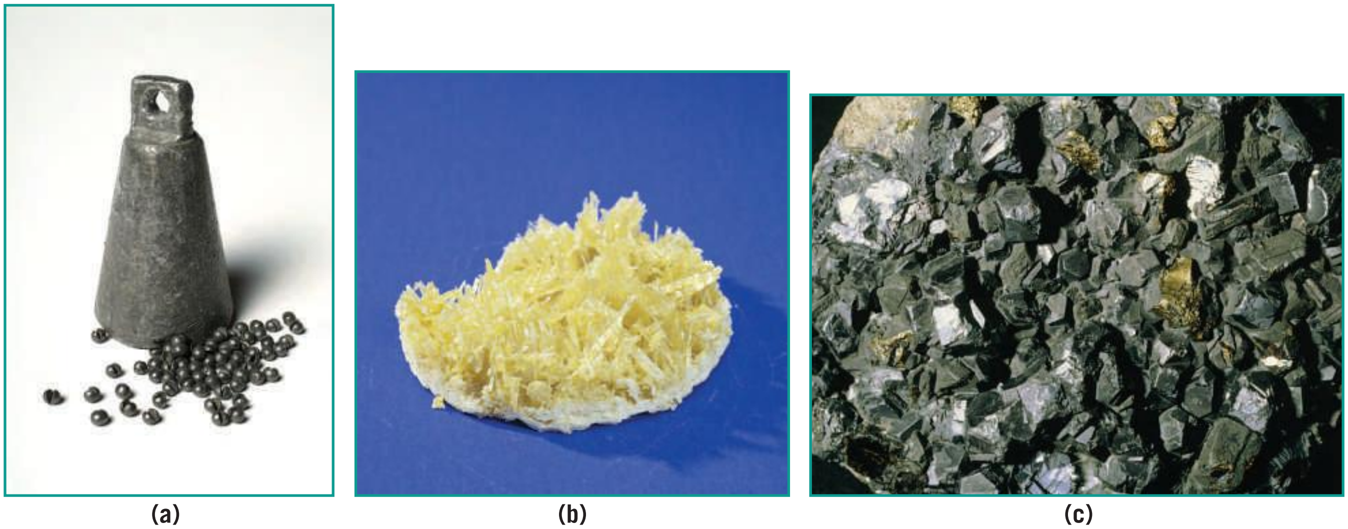

(a) (b) (c)

Figure 5.2 (a) Lead (b) Sulfur (c) Galena (lead sulfide)

❇ Review exercise 5.2

1. **Describe** the difference between water and a mixture of hydrogen and oxygen gas, by:
   - **a** drawing diagrammatic representations at a molecular level
   - **b** comparing their properties
   - **c** comparing their compositions.
2. A 10 g sample of the compound copper(II) oxide contains 2.0 g of oxygen. **Calculate** the mass of oxygen that a 30 g sample of the same compound would contain. **Identify** which law is applied in making this calculation.

5.3 Structure and bonding in substances

All substances are made up of atoms, molecules or ions. The way these particles are arranged in a substance is described as the *structure* of the substance. The structure of the substance depends on:

- the nature of the particles present
- the forces holding the particles together.

The strength of diamond, the relatively high boiling point of water and the solubility of salt in water are all related to their structures.

Many of the physical properties of a particular substance can provide evidence of the structure of that substance.

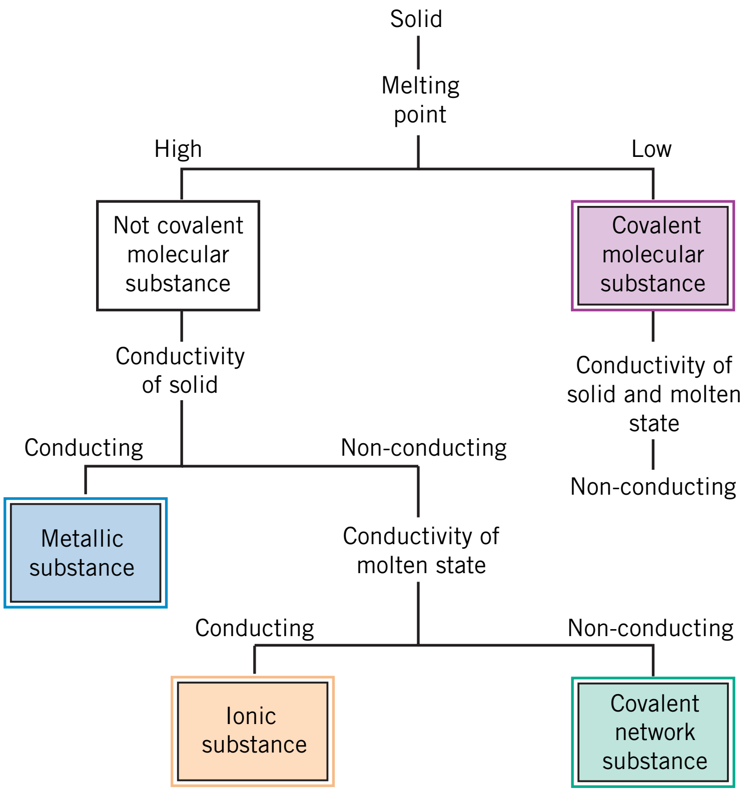


Figure 5.3 The classification of substances on the basis of their physical properties

The melting points of solids provide information regarding the forces of attraction between the particles in the solid. The electrical conductivity of a substance in its solid or liquid (molten) state reveals information about the nature of the particles within the substance. On the basis of their melting points and electrical conductivities, substances can be classified into four classes with the following properties:

- *covalent molecular substances*—low melting point, non-conducting in the solid and liquid states
- *covalent network substances*—high melting point, non-conducting in the solid and liquid states
- *ionic substances*—high melting point, non-conducting in the solid state but conductivity in the liquid state
- *metallic substances*—high melting point, high conductivity in the solid and liquid states.

Figure 5.3 illustrates this classification.

The similar physical properties shared by substances within each class can be explained in terms of the nature of the particles and the bonding present in these substances.

Covalent molecular substances

Both covalent molecular substances and covalent network substances are held together by *covalent bonds*, that is, atoms sharing pairs of electrons. In most cases the shared pair or pairs of electrons are provided by both of the atoms, but in some bonds, called *coordinate covalent bonds* or dative covalent bonds, the pair of electrons is provided by only one of the two atoms. An example of this is carbon monoxide. The third pair of shared electrons is supplied by the O atom.

Numerous commonly occurring pure substances on Earth, such as oxygen, carbon dioxide and water, consist of molecules and are known as covalent molecular substances. They have the following properties in common:

- They have low melting and boiling points; many are liquids or gases at room temperature.
- They are non-conductors of electricity in both the solid and liquid states.
- They form solids that are generally quite soft and often have a waxy appearance.

Experimental evidence indicates that all covalent molecular substances exist as groups of atoms called molecules. Substances like iodine, ammonia and naphthalene (in moth balls) are composed of molecules. The crystal structure of iodine is shown in Figure 5.4.

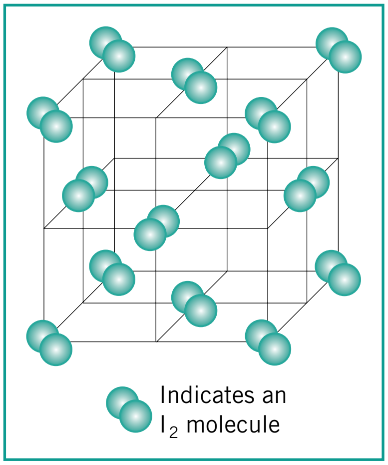


Figure 5.4 The crystal structure of iodine (the spacing between molecules is exaggerated in this diagram)

The effect of heat energy

The melting and boiling points of covalent molecular substances are much lower than those of covalent network, ionic and metallic substances, indicating that the forces between the molecules are relatively weak. The nature of the weak forces between molecules in covalent molecular solids and liquids will be discussed later.

In iodine, for example, the low melting point of 114°C indicates that the forces between the molecules are quite weak. However, a large amount of energy is required to separate iodine molecules into individual atoms. For the process $I_2(g) \rightarrow 2I(g)$ to occur to a significant extent, a temperature of 1000°C is required. This indicates that there must be strong bonding forces, in this case covalent bonds, between the iodine atoms within iodine molecules.

A similar argument can be applied to the difference in the melting and boiling points of water and the temperature required to actually separate the individual atoms in water molecules. Water melts at 0°C and boils at 100°C, which indicates that the forces between water molecules are relatively weak. Gaseous water has to be heated to very much higher temperatures before the covalent bonds within the water molecules are broken.

The non-conductivity of covalent molecular substances is due to the lack of mobile charged species in the solid and liquid states. There are no ions or free-moving electrons capable of conducting an electric current.

Most covalent molecular substances, such as iodine and candle wax, are described as soft. This property is also a result of the weak forces that exist between molecules in these substances.

Covalent network substances (covalent lattices)

Elements such as carbon and silicon (Group IV or 14), and compounds such as silicon dioxide and silicon carbide, exist as covalent lattices and are described as having a three-dimensional covalent network structure.

Covalent network substances have the following characteristic properties:

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

The key to their properties lies in the three-dimensional network of strong covalent bonds between the atoms that hold the lattice together. The high melting and boiling points and the extreme hardness of covalent network substances suggest that the atoms in these solids are joined by very strong covalent bonds. These strong covalent bonds produce rigid three-dimensional network structures, as seen in silicon carbide and silicon dioxide (Figures 5.5 and 3.9 respectively).

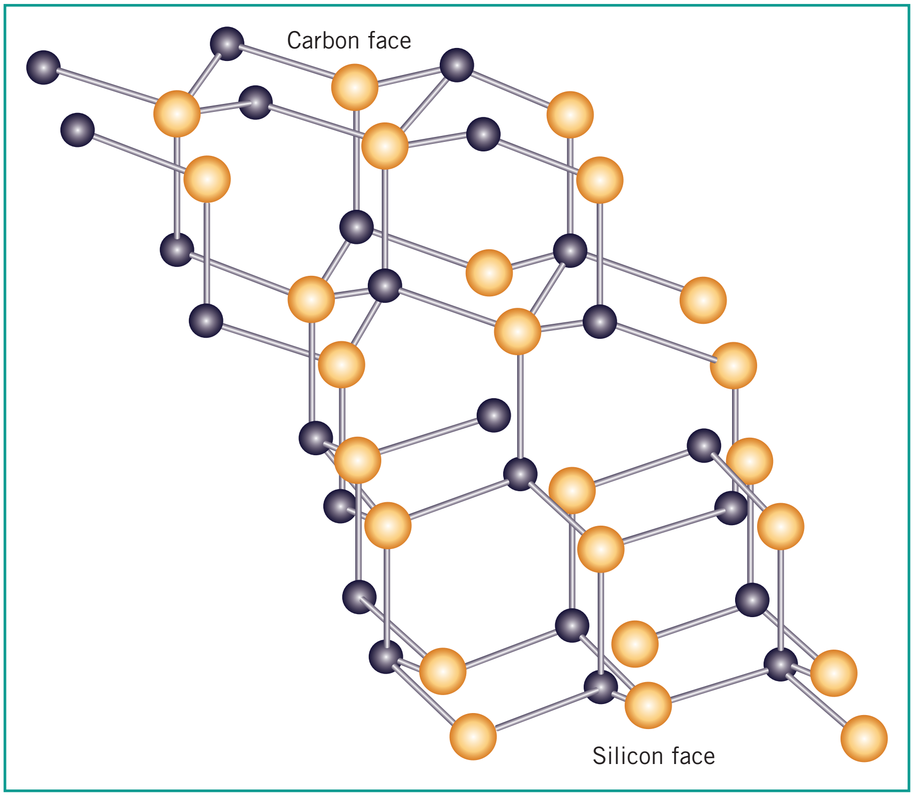


Figure 5.5 Crystal lattice of silicon carbide

The non-conductivity of covalent network substances is due to the lack of mobile charged species in the solid and liquid states. There are no free-moving electrons or charged ions capable of conducting an electric current (graphite is an exception).

Ionic compounds

As discussed in Unit 3.5, ionic compounds, such as sodium chloride, calcium fluoride and calcium oxide, contain oppositely charged ions held together by electrostatic attraction and arranged in regular three-dimensional lattices. Most ionic compounds are formed from a metal combined with a non-metal or negatively charged polyatomic ion (e.g. sulfate, carbonate).

The physical properties of ionic compounds are as follows:

- They are hard and brittle.
- They are non-conductors of electricity in the solid state, but good conductors when molten or in aqueous solution.
- They have high melting and boiling points.

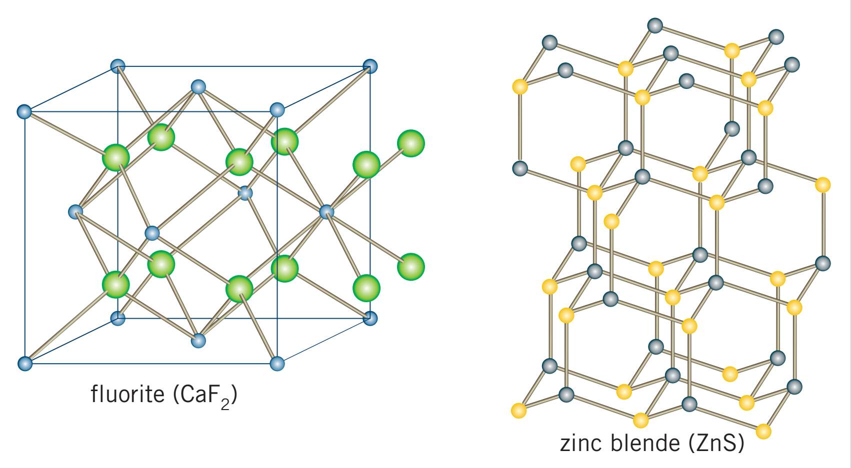


Figure 5.6 Crystal structure of ionic fluorite (CaF_2) and zinc bende (ZnS)

These properties suggest that ionic substances consist of oppositely charged ions arranged in a three-dimensional array. Ionic lattices are held together by electrostatic attractive forces between these oppositely charged ions. This is called *ionic bonding*.

The strong electrostatic attraction between oppositely charged ions results in ionic solids like sodium chloride being hard, brittle and difficult to cut. Their brittleness results from the fact that if a layer of ions in the crystal is forced to slide past another layer, the orderly arrangement of ions is disturbed. As a result of the displacement, ions of similar charge are forced closer to one another, with an increase in repulsive forces and a decrease in attractive forces. The crystal will therefore fracture.

The high melting and boiling points of ionic substances are also due to the strength of the electrostatic attractive forces between the oppositely charged ions.

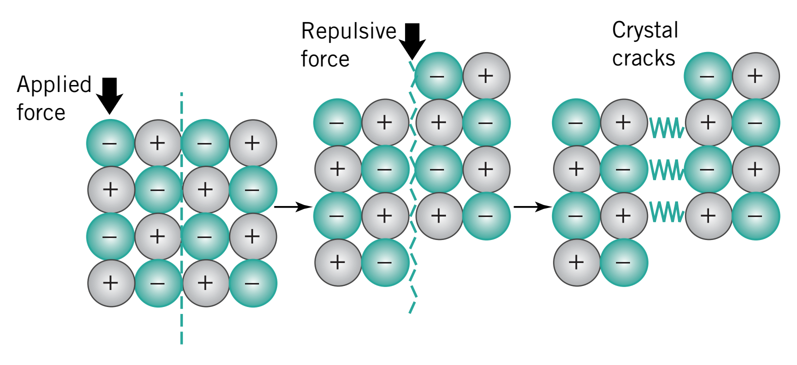


Figure 5.7 Ionic solids are brittle. An applied force causes the crystal to shatter.

Ionic solids do not conduct electricity because although they contain electrically charged particles, the ions occupy fixed positions and are not free to move. Molten (liquid) ionic compounds do conduct electricity because in the molten state the ions are able to move through the liquid. Although molten ionic compounds do conduct an electric current, they do not conduct as well as metals.

Aqueous solutions of ionic compounds also conduct electricity. It is therefore reasonable to conclude that in aqueous solution the ions are separated from each other and are free to move. Mobile ions are therefore responsible for the conduction of electric current in aqueous solution as well as in the molten state.

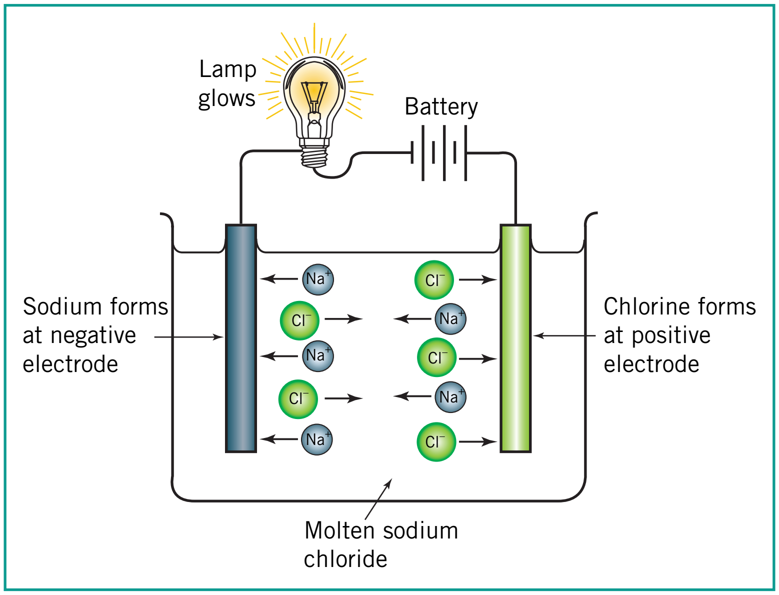


Figure 5.8 Movement of ions when a direct current is passed through molten sodium chloride

Metals

The properties of metals were described in Unit 2.4 and are included here again for convenience:

- They have relatively high densities (although lithium, sodium and potassium are less dense than water).
- They are good conductors of heat and electricity.
- They are malleable (can be beaten into sheets) and ductile (can be drawn into wires).
- They have a shiny surface when freshly cut or cleaned (lustrous).
- They have relatively high melting points (although mercury and gallium have quite low melting points).

Chemists have devised a model to explain the structure of and bonding in metals. In this model, it is believed that the outermost or valence electrons in metal atoms move about freely within a three-dimensional arrangement or lattice of positively charged metal ions. The metal consists of positive ions surrounded by a 'sea' of mobile electrons. The outer electrons are said to be *delocalised* as they are not associated with a particular metal ion and can move through the lattice of metal ions. The negatively charged electrons are attracted to the positively charged metal ions in the lattice and this electrostatic attraction holds the lattice together. This type of bonding is called *metallic bonding* and is illustrated in Figure 5.9.

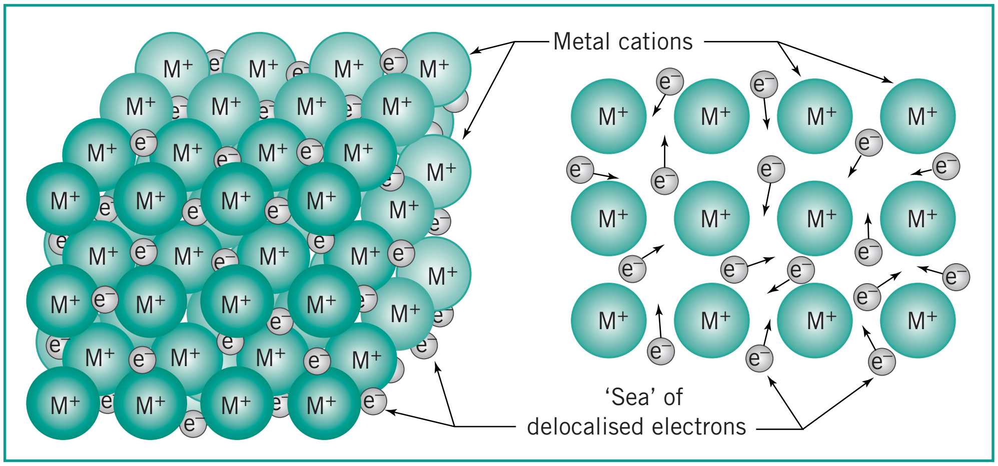


Figure 5.9 Metallic bonding (the spacing between ions is exaggerated in the right-hand diagram)

The high densities indicate that in metals the cations are packed tightly together. The malleability and ductility of metals indicate that there is only limited resistance to the movement of ions with respect to one another. In metallic bonding, the delocalised electrons do not belong to any particular ion, so the bonding is said to be non-directional. Therefore if sufficient force is applied to the metal, one layer of ions can slide over another without disrupting the metallic bonding. As a result, metals can be readily hammered into sheets or drawn into wires, as shown in Figure 5.10.

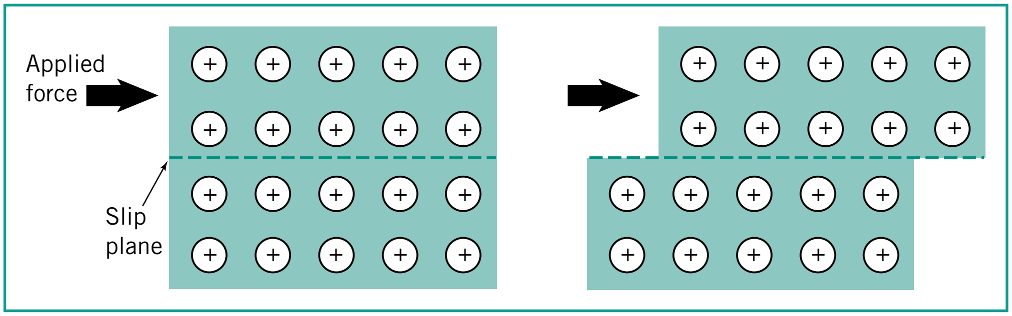


Figure 5.10 Metals are malleable and ductile. An applied force causes one layer of ions to slide over another.

From the high electrical conductivity in the solid state it can be inferred that metals contain mobile charged particles. Metals are good conductors of electricity because of the mobility of the delocalised electrons within the lattice. When a metal is used in an electrical circuit, electrons entering one end of the metal cause a similar number of electrons to be displaced from the other end, and the metal conducts.

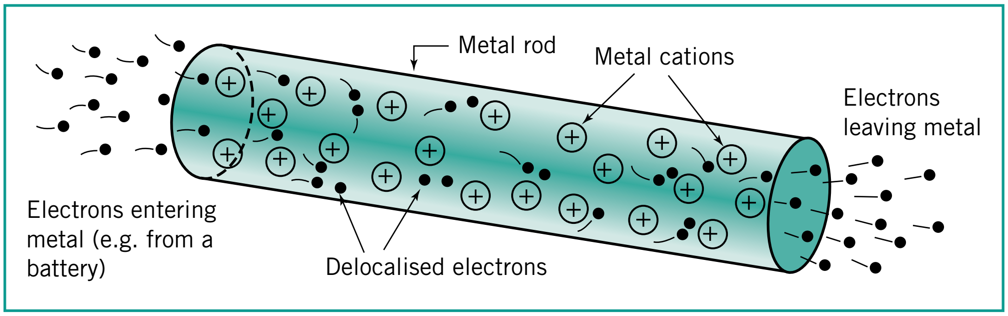


Figure 5.11 Electrical conduction by a metal

The delocalised electrons are also responsible for the transmission of heat energy in metals. The mobile electrons acquire heat energy from the heat source and begin to move more rapidly. As a result, the heat energy is transferred to cooler parts of the lattice.

The high melting and boiling points of most metals are due to the strong electrostatic attraction between the positive metal ions and the delocalised electrons. Beryllium, magnesium, calcium, strontium and barium form metals ions with a 2+ charge by releasing two electrons per atom. They tend to form stronger metallic bonds and consequently have higher melting points and boiling points than lithium, sodium, potassium and rubidium, which possess only one delocalised electron per atom.

The properties of these four classes of substances are summarised in Table 5.4.

Table 5.4 Comparing the four classes of substances

Class	Property	Melting point	Conductivity	
			Solid	Molten
Metallic	variable hardness	high	high	high
Ionic	very hard, very brittle	high	none	high
Covalent molecular	soft brittle solids; can be solids, liquids or gases at room temperature	low	none	none
Covalent network	very hard, brittle	very high	none	none

❄ Review exercise 5.3

1 The ability to conduct an electric current is one property that can help to determine the structure of a substance. **Outline** the necessary conditions for a substance to conduct an electric current.

2 **Summarise** what a substance's melting point indicates about the strength of the forces between particles within the substance.

3 **Classify** the following substances as metals, ionic, covalent molecular or covalent network substances.

Substance A: has a low melting point and negligible conductivity in both the solid and molten states.

Substance B: has a high melting point and a high conductivity in both the solid and liquid states.

Substance C: has a high melting point, does not conduct in the solid state but the molten state has high conductivity.

Substance D: has a very high melting point and negligible conductivity in both the solid and molten states.

4 **Classify** the following substances on the basis of their composition as metallic, ionic, covalent molecular or covalent network substances.

a	calcium oxide	CaO
b	carbon dioxide	CO_2
c	silver	Ag
d	copper(II) chloride	$CuCl_2$
e	nitrogen dioxide	NO_2
f	silicon dioxide	SiO_2
g	iodine	I_2
h	carbon	C

5 'In covalent molecular substances the forces within molecules are strong but the forces between molecules are weak.' **Explain** what is meant by this statement, supporting your answer using chlorine (Cl_2) as an example. Chlorine has a melting point of –101°C but does not break up into separate atoms except at very high temperatures.

6 Covalent molecular and covalent network substances both include atoms joined by strong covalent bonds. **Discuss**, with examples, why these different classes of substances have quite different physical properties.

7 **a** **Explain** why molten KCl conducts an electric current but solid KCl does not.

b **Explain** why ionic compounds have high melting and boiling points.

8 **Identify** four physical properties of metals and **explain** these properties in terms of the 'delocalised electron' model of metallic bonding.

9 Consider the following substances, all in the solid state:

N_2, Cu, NaF, SiC.

Match each of these solids with one of the following statements.

a This high melting point solid conducts electricity only in the molten state.

b This solid is a good electrical conductor.

c This hard crystalline substance has a very high melting point and does not conduct an electric current in the solid or molten state.

d This solid has a very low melting point.

*KEY POINTS

- Physical properties are those that can be determined without changing the chemical composition of the substance.
- Chemical properties are those that relate to the ability of a substance to form new substances.
- Chemical properties include changes that occur when a substance breaks down or reacts with other substances during a chemical reaction.
- Compounds have quite different properties from those of the elements that combined to form them.
- The law of constant composition states that all pure samples of the same compound contain the same elements combined together in the same proportions by mass.
- Substances are classified into four classes on the basis of their structure and bonding: covalent molecular substances, covalent network (covalent lattice) substances, ionic compounds, metals.
- Some of the properties of these four groups of substances are shown in Table 5.5.

Table 5.5

Class	Property	Melting point	Conductivity	
			Solid	Molten
Metallic	variable hardness	high	high	high
Ionic	very hard, very brittle	high	none	high
Covalent molecular	soft brittle solids; can be solids, liquids or gases at room temperature	low	none	none
Covalent network	very hard, brittle	very high	none	none

- Covalent molecular substances include most non-metal elements and compounds consisting of non-metals only.
- Within molecules, atoms are held together by the electrostatic attraction between shared electrons and the nuclei of adjacent atoms. This form of bonding is called covalent bonding.
- There are weak attractive forces between covalent molecules.

- The properties of covalent molecular substances are listed and explained in Table 5.6.

Table 5.6

Property	Explanation
Low melting and boiling points	Forces between molecules are weak
Non-conductors of electricity when solid or liquid	The molecules are uncharged and electrons are localised in covalent bonds or on the atoms
The solids are generally soft	Forces between molecules are weak

- Covalent network substances include non-metal elements such as carbon and silicon, and some compounds such as silicon carbide and silicon dioxide.
- In covalent network substances, every atom is covalently bonded to other atoms, forming a giant network. No separate molecules can be distinguished.
- The properties of covalent network substances are listed and explained in Table 5.7.

Table 5.7

Property	Explanation
Very high melting and boiling points	Strong covalent bonding extending throughout the lattice
Non-conductors of electricity in the solid or liquid state	Electrons localised (except in graphite) in covalent bonds or on the atoms
Hard and brittle	Atoms strongly bound, distortion breaks covalent bonds
Chemically inert	The bonding extends throughout the crystal and the non-polar nature of the bonding makes them resistant to chemical attack
Insoluble in water and most other solvents	The strong covalent bonding extending throughout the crystal lattice accounts for the insolubility of these substances

- Ionic substances consist of positive ions and negative ions arranged in a regular lattice.
- Ionic bonding is an electrostatic attraction between oppositely charged ions.

- The ionic bonding model can be used to explain the properties of ionic crystals (see Table 5.8).

Table 5.8

Property	Explanation
Hard and brittle	Ions are tightly bound by electrostatic forces in the crystal lattice
Non-conductivity of electricity when solid	Ions occupy fixed positions in the lattice. Electrons are strongly held by nuclei of individual ions
Conductivity of electricity when molten or in aqueous solution	Mobile ions can transfer electric charge
High melting and boiling points	Ions tightly bound by strong electrostatic forces

- A metal consists of a lattice of positively charged metallic ions surrounded by a ‘sea’ of mobile delocalised electrons.
- Metallic bonding is the electrostatic attraction between delocalised electrons and the positive metallic ions.
- The metallic bonding model can be used to explain the properties of metals as shown in Table 5.9.

Table 5.9

Property	Explanation
Relatively high density	Ions tightly packed in the lattice
Malleability and ductility	Metallic bonding is non-directional, therefore metal lattices can be deformed without disrupting the metallic bonding
Conductivity of electricity and heat	Mobile delocalised electrons transfer charge and heat energy
High melting and boiling points	Strong metallic bonding exists throughout the lattice

*APPLICATION AND INVESTIGATION

1 a **Describe** a physical property that makes each of the following useful: iron, copper, lead, alcohol, helium.

b **Describe** a chemical property that makes each of the following useful: petrol, oxygen, carbon dioxide.

➲ Investigation 2 **Explain**, using copper(II) oxide as an example, why the properties of a simple compound are quite different from those of the elements from which it was formed.

3 The gems, rubies and sapphires, are slightly impure forms of aluminium oxide. **Investigate** the structures of these gems and why they display such different colours.

⊂ **Investigation**

4 **a** Briefly **describe** the three major types of bonding—metallic, ionic and covalent—and **explain** how this can lead to four classes of solid substances.

b **Describe** why covalent molecular and covalent network substances have such different melting points.

5 It has been found that most substances that have an odour are covalent molecular substances. **Propose** a reason for this observation.

6 Consider the information below.

Compound	Boiling point (°C)
CH_4	–162
H_2O	100
NH_3	–33
SO_2	–10

Order the substances in terms of increasing strength of forces between their molecules.

7 A certain solid is a non-conductor of electricity and has a high melting point. **Identify** the type of structure possessed by this solid. **Describe** further tests that could be performed in order to make a definite decision about the type of solid.

8 Carbon and silicon both have four valence electrons and form compounds with formulas CO_2 and SiO_2, respectively. These oxides have very different properties: CO_2 sublimes at 78°C, whereas SiO_2 melts at 1713°C and boils at 2230°C. **Explain** the differences in these properties in terms of the structures of these substances.

9 Silicon carbide has a structure similar to diamond.

⊂ **Investigation**

a **Construct** a diagram representing the arrangement of atoms in a silicon carbide crystal.

b **Predict** the properties of silicon carbide in terms of its structure.

c **Investigate** the properties of silicon carbide and **compare** them with your predictions in **b**.

10 Neither solid sodium chloride nor water are electrical conductors. However, when sodium chloride dissolves in water it forms a conducting solution. **Explain** this observation.

11 **Explain** why metals are malleable while ionic solids are not.

12 Classify the substances listed below into three groups:

- **a** those in which the bonds are metallic
- **b** those in which the bonds are ionic
- **c** those in which the bonds are covalent.

SiH_4, Cu, sulfur dioxide, $MgBr_2$, P_4O_{10}, Na_2S, sterling silver, K_2O, F_2O, strontium chloride, MgH_2, SiC, Pb, AsH_3, CsCl, B_2O_3, bronze, diamond

13 Identify the types of particles present (molecules, atoms, ions) in crystal lattices of the following:

- **a** sodium
- **b** sodium chloride
- **c** diamond
- **d** carbon dioxide.

14 Identify which attractive forces must be overcome in the following processes:

- **a** $I_2(s) \rightarrow I_2(g)$
- **b** $I_2(g) \rightarrow 2I(g)$
- **c** shattering a sodium chloride crystal with a hammer
- **d** bending an iron nail until it breaks.

15 Identify the charged species that conduct the current in the following:

- **a** molten NaI
- **b** molten Cu
- **c** solid Al
- **d** molten $Mg(NO_3)_2$
- **e** a solution of $Al(NO_3)_3$.

16 Explain the following in terms of the structure of the substances involved.

- **a** In the solid state, copper is a good conductor of electricity and is malleable, whereas diamond is a non-conductor and extremely hard.
- **b** Naphthalene ($C_{10}H_8$) is a soft solid with a low melting point, whereas quartz (SiO_2) is a hard solid with a high melting point.

17 Classify the following solid substances as ionic, covalent molecular, covalent network or metallic:

- **a** a lattice consisting of atoms covalently bonded to neighbouring atoms
- **b** a solid only at extremely low temperatures
- **c** a good conductor of heat and electricity
- **d** a good conductor of electricity only in the molten state
- **e** a lattice consisting of positive ions sharing electrons with neighbouring positive ions.

18 Classify, with explanations, the following solids as covalent molecular, metallic, ionic or covalent network:

- **a** a soft solid that decomposes at 250°C; the solid does not conduct electricity
- **b** violet crystals that melt at 114°C; neither the solid nor the liquid conducts electricity

- **c** hard, colourless crystals that melt at 2045ºC; the solid is a non-conduct but the liquid conducts electricity
- **d** hard grey solid that melts at 3410ºC; both the solid and liquid conduct electricity.

19 Consider the substances potassium bromide, gold, silicon carbide and sulfur.

- **a** **Identify** which of these solid substances will conduct electricity.
- **b** **Identify** which of these substances will conduct electricity in the liquid state but not the solid state.
- **c** **Explain** how the ‘mode’ of electrical conduction in molten potassium bromide differs from that in solid gold.
- **d** **Predict** which of the four substances is the hardest. **Justify** your prediction.

20 Diamond is one form of carbon. **Investigate** the arrangement of the atoms and the bonding in two other forms of carbon: graphite and ‘bucky balls’. On the basis of their properties, how would you **classify** these substances?

Investigation

*MODULE 1 REVIEW

MULTIPLE-CHOICE QUESTIONS

1 The chemical formula for manganese(IV) oxide is

A MnO_4
B Mn_2O_4
C MnO_2
D Mn_2O

2 The name of the compound with chemical formula SO_2 is

A sodium dioxide.
B sodium(IV) oxide.
C sulfur dioxide.
D disulfur oxide.

3 $^{211}_{83}Bi$ is an isotope of bismuth. Each atom of this isotope contains

A 83 neutrons.
B 211 electrons.
C 83 protons and 128 electrons.
D 128 protons and 128 electrons.

4 The typical features of covalent molecular substances include:

A rigid solids, many conduct electricity in the aqueous solution or molten state.
B gases, liquids or soft, low melting point solids at room temperature.
C hard solids with high melting points, commonly non-conductors of electricity.
D conduct electricity in the solid, malleable and ductile.

5 The nitrate ion is represented as

A N^{3-}
B NO^{2-}
C NO_3^-
D NO_2^{2-}

6 In which one of the following changes are the particles involved moving further apart?

A solidification of wax as it cools
B condensation of steam
C crystallisation of copper(II) sulfate from solution
D heating water from 20°C to 50°C

7 Which of the following shows the correct formula for the chemical name given?

A sodium chloride NaCl
B sodium sulfite Na_2SO_4
C sodium sulfide NaS
D sodium sulfate $Na(SO_4)_2$

8 The name of the compound with chemical formula P_2O_3 is

A phosphorus oxide.
B diphosphorus trioxide.
C phosphorus(III) trioxide.
D phosphorus(II) trioxide.

9 Which of the following groups contain species that have the same number of electrons (are isoelectronic)?

A F^-, Cl^-, Br^-, I^-
B Rb^+, Kr, Sr^{2+}, Br^-
C F^-, O^{2-}, N^{3-}, Na^+
D Na, Mg, Al, Si

10 In order to separate two miscible liquids with differing boiling points, which method of separation would be used?

A thin layer chromatography
B distillation
C decantation
D centrifugation

11 Different isotopes of an element have atoms with identical:

A atomic weight.
B atomic number.
C neutron number.
D mass number.

SHORT-ANSWER QUESTIONS

12 An element has the symbol $^{15}_{7}X$

a In one atom of X, write down the number of:
  i protons
  ii neutrons.

b Write a similar symbol for an isotope of element X.

13 a In terms of the particle theory of matter, **explain** what is happening to the particles of ice as it is melting.

b **Identify** the types of particles present in ice.

14 Consider the melting points of the following oxides of three elements.

Compound	Melting point (°C)	Boiling point (°C)
CaO	2570	2850
SiO_2	1700	2230
H_2O	0	100

a **Identify** the state of each of the compounds at room temperature (25°C).

b For each compound, **identify** the type of bonding that is present.

15 **Describe** the steps you would take to separate a mixture of sodium chloride, silicon dioxide (sand) and sulfur. For each step, explain why your method would work.

16 The table below lists the properties of five substances known to be Mg, SiO_2, KCl, I_2 and HI (not in correct order).

Use the information in the table to **identify** A–E.

Property	A	B	C	D	E
Melting point (°C)	1700	–51	650	114	770
Solid conducts electricity	no	no	yes	no	no
Soluble in water	no	yes	no	no	yes
Aqueous solution conducts electricity	NA	yes	NA	NA	yes
NA = information not applicable, that is, substance does not form aqueous solution.					

17 Consider the following processes:

- **i** sublimation (solid to a gas) of iodine when heated
- **ii** $I_2(g) \rightarrow 2I(g)$
- **iii** breaking a 'black lead' (graphite) pencil in half
- **iv** shattering a copper sulfate crystal
- **v** stretching a piece of copper into a thin wire.

For each of the processes above, **identify**:

a the types of bonds or forces being broken

b the types of particles (molecules, atoms or ions) being separated.

18 Chemistry is involved in many processes associated with preparing and cooking food.

a **Identify** one physical change that commonly occurs when food is cooked and the energy change associated with this process.

b **Identify** one chemical reaction that occurs during the cooking of food. What type of reaction is this?

MODULE 2

Metals

- **Chapter 6** THE EXTRACTION AND USES OF METALS
- **Chapter 7** CHEMICAL REACTIONS OF METALS
- **Chapter 8** THE PERIODIC TABLE
- **Chapter 9** MEASURING THE AMOUNTS OF SUBSTANCES: THE MOLE
- **MODULE 2** REVIEW

This module will cover the following material:

- uses of metals from ancient times to the present
- the influence of metals on human cultural development
- properties and uses of metals
- minerals and ores
- extraction of metals from their ores
- factors affecting the current use of metals
- uses of metals in alloys
- the periodic table as a method of organising the elements based on repeating patterns of physical and chemical properties
- the historical development of the periodic table
- recycling of metals
- the mole—a method of measuring quantities of reacting substances.

CHAPTER 6

THE EXTRACTION AND USES OF METALS

The cultural development of humans has been closely associated with the discovery of new materials and their uses as tools, weapons and artefacts. To a large extent, cultural achievements have been defined in terms of the materials used during particular periods of human history such as the Stone Age, Copper Age (5000–3000 BC), Bronze Age (3000–1000 BC) and Iron Age (from 1000 BC). Archaeological evidence suggests that humans first used metals around 14 000 years ago. Until that time, the main materials used by humans were wood, stone, bone, shells and plant products.

6.1 The historical use of metals

The first metals used by humans were those that were found in their elemental form, that is, uncombined with other elements. Gold, silver and copper can be found as almost pure metals in various parts of the world and were initially used by humans to make jewellery, ornaments and tools. The ability of these metals to be beaten and bent into various shapes and their relative scarcity made them prized possessions.

Most metals, however, are chemically combined with other elements, forming naturally occurring compounds called *minerals*. To extract a metal from its mineral, a large input of energy is required. This energy is required to break and rearrange the strong chemical bonds within the compound. In general, the ease of extraction of a metal from a mineral is directly related to the strength of the bonds within the metal compound and to its position in the activity series (see Chapter 7). The first metal to be extracted from its ores was copper. In the Middle East around 5000 BC, humans discovered that heat could be used to extract copper from malachite, a green copper-containing mineral (see Chemistry Context on page 114). Iron is higher in the activity series than copper and is consequently somewhat more difficult to extract from its ores. The carbon reduction of iron minerals to produce iron metal requires higher temperatures than for copper and less reactive metals. It was not until improvements to furnaces allowed increased temperatures to be achieved that new metals such as lead, tin and iron could be extracted from their mineral ores. The earliest records of iron extraction occur 3500 years ago. Its early use in human history is due both to the abundance of high-grade iron ores and its relative ease of extraction. Aluminium, on the other hand, is a more reactive metal than iron and cannot be extracted by chemical reduction. The extraction of metals higher on the activity series, such as aluminium, did not take place until the nineteenth century. This is because more reactive metals can only be extracted by electrolysis. As a result of its reactivity, aluminium can only be extracted from its ores using the more difficult and expensive method of electrolytic reduction. Therefore the use of aluminium does not appear until quite recently in human history. Details of the extraction of some metals from minerals are discussed later in this chapter.

Another important discovery was that the properties of metals could be significantly altered by combining them with other elements to form alloys, such as bronze, brass and steel. This further extended the range of metallic materials available, the use of which has shaped the development of human civilisation.

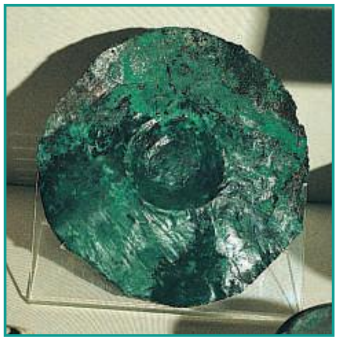


Figure 6.1 Copper dish. Copper was the first metal to be extracted from its ore. The copper age (5000–3000 BC) marked the beginning of the widespread use of metals.

Early uses of copper

Initially copper was used to make ornaments, tools, weapons and cooking implements. The Egyptians made and wore copper beads and used copper pipes to convey water. The excellent thermal conductivity of copper made it ideal as a cooking pot, a use that continues to the present day.

One of the disadvantages of copper, regarding its use in weapons and tools, is that it is a rather soft metal. The chance discovery that a small amount of tin added to the copper increased the hardness of the metal was a major breakthrough.

Figure 6.2 Bronze articles were made as early as 3000 BC.

Bronze: an alloy of copper

The deliberate addition of tin to copper to produce a much harder metal alloy, bronze, was of such importance that this stage of human cultural development is called the Bronze Age (3000–1000 BC). Bronze had many advantages over copper. Bronze cutting tools, such as axes and knives, maintain good cutting edges and are easily resharpened. Bronze shields and armour were much stronger than any other material available at the time. This was of strategic significance to nations waging war on their neighbours. Bronze also casts extremely well and is very durable. Statues many thousands of years old are evidence of the durability of bronze and the metallurgical skills of ancient civilisations.

Contemporary uses of copper

Contemporary uses of copper are mostly related to its excellent electrical and thermal conductivity, resistance to corrosion and ability to form a huge range of alloys. Copper is second only to silver as an electrical conductor and is used extensively in electrical cables and wiring, appliances, electrical generators and motors. Copper pipes, tanks and hot water systems are used for plumbing because copper does not corrode in hot water.

Copper piping is also used in air conditioning units and heat exchangers such as car radiators because it loses heat quickly. Copper's ability to form a wide range of alloys (more than one thousand different alloys have been formed) is one of the main reasons that copper remains one of the most important metals today. Some of these alloys are discussed later, in Unit 6.3.

Figure 6.3 Today copper is used extensively for electrical and plumbing applications.

The use of iron through history

Figure 6.4 Meteorites were an early source of elemental iron.

Iron has been known since ancient times. References in ancient writings to 'metal of heaven' probably refer to iron, which is a major constituent of many meteorites. This source of iron was of course quite limited and during the Bronze Age iron was up to eight times more valuable than gold.

The Iron Age began around 1000 BC when knowledge of the techniques used to extract iron from iron ores such as haematite spread throughout the Middle East, Asia and Europe (see Chemistry Context on page 114). During this period, iron replaced bronze in many applications, particularly the manufacture of tools and weapons. Pure iron is, however, susceptible to corrosion (rusting) and is relatively soft. It is likely that artisans discovered by accident that iron contaminated with carbon forms an alloy (steel) that is more corrosion resistant and harder than pure iron. The further discovery that the steel becomes even harder and keeps a better edge by heating it to a moderate temperature and then dunking it in cold water (see Unit 6.3) meant that bronze was eventually replaced by iron in many applications.

Although carbon steels (iron–carbon alloys) were probably first made about 1000 BC, the large-scale production of steel did not begin until the middle of the nineteenth century. Today there are many types of steel that have various uses, particularly in building construction and in the manufacture of cars, machinery and household appliances. The different types of steel and their uses are described in more detail in Unit 6.3. Iron remains the most abundant, useful and important of all metals.

Figure 6.5 The Eiffel Tower and the Sydney Harbour Bridge are famous landmarks made of steel, an alloy of iron.

❇ Review exercise 6.1

1 **Account** for the fact that copper, gold and silver were used long before any other metals.

2 **Explain** why heat or other forms of energy are required to extract a metal from the mineral in which it occurs naturally.

3 **Identify** the type of bonds found in:
  a copper(II) sulfide
  b aluminium oxide.

4 **Describe** two areas of discovery that have increased the range of metallic materials available for human use.

5 **Explain** why the Copper Age and the Bronze Age occurred before the Iron Age.

6 **Describe** three modern uses of copper and **identify** the property responsible for each use.

7 **Discuss** why the formation of the alloy bronze had such a significant impact on human civilisation.

8 **Identify** the mineral haematite (Fe_2O_3) by its chemical name.

9 **Explain** why iron (or iron alloys):
  a replaced bronze in many applications around 1000 BC
  b is the most extensively used metal
  c is rarely used in its pure form.

Figure 6.6 Some kitchen items made of aluminium.

Figure 6.7 Aluminium alloys are used when lightweight strength is required.

6.2 Contemporary uses of metals

Copper and iron are still widely used today. However, other metals such as aluminium and titanium are now also of considerable importance. The present-day uses of a range of metals are included in Table 6.1.

Aluminium

Despite being the most abundant metal in the Earth's crust and possessing some remarkably useful properties, aluminium was not used extensively until the beginning of the twentieth century. The reason for this is that aluminium was extremely difficult and expensive to extract from its ore, bauxite, which contains the mineral gibbsite, $Al_2O_3.3H_2O$, together with various impurities. In fact, a bar of aluminium was considered so rare and valuable in the mid-nineteenth century that it was placed on display next to the Crown Jewels at the Paris Exhibition in 1855. When a new, commercially viable method of extracting aluminium was developed in 1886, production costs dropped dramatically and the use of aluminium metal increased rapidly.

Table 6.1 Current uses of selected metals

Metal	Properties	Uses
Copper	Excellent thermal and electrical conductor, malleable and ductile, low reactivity, readily forms alloys	Electrical cables and wiring, radiators, refrigeration systems, water pipes, alloys including bronze (casting) and brass (fittings and fixtures)
Iron	Soft, malleable, magnetic, good thermal and electrical conductor, fairly reactive, readily forms alloys	Due to its susceptibility to corrosion it is usually converted to steel, which is used in buildings and bridges, automobiles, machinery and appliances
Aluminium	Low density, relatively soft when pure, excellent thermal and electrical conductor, malleable and ductile, good reflector of heat and light, readily forms alloys	Saucepans, frying pans, drink cans, cooking foil, food packaging, roofing, window frames, appliance trim, decorative furniture, electrical cables, aircraft and boat construction
Titanium	Great strength, high melting point, low density, low reactivity, readily forms alloys	In lightweight, high-strength alloys used in high-temperature environments, e.g. spacecraft and aircraft, pipes and linings for vats where acids are used
Chromium	Shiny silver appearance, resists corrosion, readily forms alloys	Plating other metals, as an additive in steel alloys, e.g. stainless steel
Cobalt	Magnetic, readily forms alloys	In alloys such as alnico to manufacture permanent magnets
Nickel	Magnetic, readily forms alloys	As an additive in steel alloys, invar (Fe, Ni) used in scientific instruments, as an alloy (Ni, Cu) in making coins, nichrome (Ni, Cr) used in electrical heating elements
Zinc	Fairly reactive but forms protective oxide layer, readily forms alloys	In galvanising iron, in the outer casing and negative electrode of dry cells, alloy (brass) used in fittings and fixtures
Gold	Shiny gold appearance, excellent thermal and electrical conductor, unreactive, readily forms alloys	Electrical connections, jewellery, monetary standard, dentistry

Due to its low density and its resistance to corrosion, aluminium has displaced steel in many commercial and industrial situations. For example, aluminium is used widely in building construction as roofing, window frames, appliance trim and decorative furniture. It is also used in the manufacture of a range of domestic utensils such as saucepans, frying pans, drink cans and cooking foil.

Aluminium is also an excellent electrical and thermal conductor and is highly reflective, making it useful in such diverse applications as electrical transmission lines, telescope reflectors, food packaging and saucepans.

Aluminium can be strengthened by the addition of small amounts of other metals such as titanium to produce many alloys that are valued for their low density and strength. As a result they are extensively used in spacecraft, aircraft and boat construction.

Titanium

Although titanium was discovered in 1791, it was not until 1910 that the pure metal was isolated.

Titanium is the ninth most abundant element in the earth's crust, occurring primarily in the minerals rutile and ilmenite. Pure titanium is a lustrous solid, similar in appearance to stainless steel. It melts at high temperatures, has a low density and great strength and is very resistant to corrosion. Alloys of titanium are very strong and are used in situations where lightweight strength and resistance to high temperatures are required, such as in jet engine components, aircraft, spacecraft and missiles.

Titanium alloys are biocompatible and therefore can be used for surgical implants such as artificial knee and hip joints.

Because titanium is so resistant to corrosion, it is used in marine environments as propellers and other ship parts and in chemical factories where corrosive acids are used. Titanium is also added to other metals such as aluminium, iron, manganese and molybdenum to improve their strength.

Figure 6.8 Titanium is used in jet engines where resistance to high temperatures is critical.

Figure 6.9 Titanium replacement hips.

❊ Review exercise 6.2

1 Aluminium is the most abundant metal in the Earth's crust and has many valuable properties. **Outline** why aluminium was not used extensively until the early twentieth century.

2 **Propose** why aluminium roofing might be preferred to steel roofing.

3 Titanium is used in desalination plants where sea water is converted into fresh water. **Identify** the properties of titanium that make it suited to this purpose.

6.3 Alloys

Most metals are not used in their pure form but have other elements added to modify their properties and thus extend their range of uses. The presence of a small proportion of other elements in a metal to form an alloy can alter some of its properties significantly. In general, alloys are harder than pure metals. Pure aluminium, copper and iron are too soft to be used for construction, but the addition of small quantities of other elements greatly increases their hardness. This is because the different-sized atoms of other elements interrupt the orderly arrangement of atoms in the lattice and prevent them from sliding over each other as easily—in other words, they can block slip planes. Thus bronze, an alloy of copper and tin, is harder than either pure copper or pure tin. The tin atoms prevent layers of copper atoms from being displaced as easily. This is illustrated in Figure 6.10.

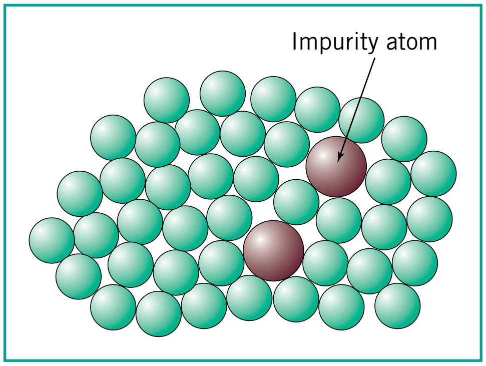


Figure 6.10 Impurity atoms can block slip planes and increase the hardness of a metal.

Another advantage of alloying is that it often increases the resistance of the metal to corrosion. Stainless steel, for example, is much more resistant to corrosion than pure iron. By carefully choosing the percentages of different elements to be added to a metal, the properties of the metal can be altered to meet specific needs. Consequently, new alloys can be ‘designed’ for a particular purpose where very specific properties are required. Table 6.2 includes examples of the properties and uses of some selected alloys. The compositions of some alloys often vary considerably, so the values in the table are mostly typical examples.

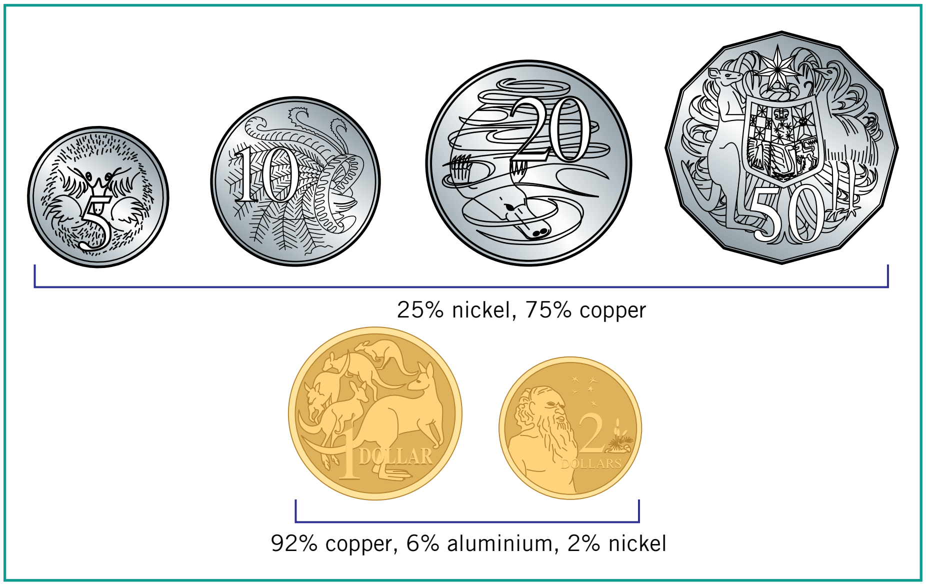


Figure 6.11 Australian coins are alloys of copper with other metals.

Figure 6.12 Dental amalgam is an alloy that expands as it solidifies to fill the cavity in the tooth.

Table 6.2 Alloys and their uses

Alloy	Composition	Properties	Some uses
Bronze	90% Cu, 10% Sn	Strong, resists wear and corrosion, easily cast, sonorous	Church bells, statues, bearings
Brass	65% Cu, 35% Zn	Resists corrosion, ductile, easy to machine, polishes well	Doorknobs, screws
Cupronickel	75% Cu, 25% Ni	Hard-wearing, attractive silver colour	'Silver' coins, for example, 10¢ piece
Stainless steel	74% Fe, 18% Cr, 8% Ni	Resists corrosion	Sinks, cutlery
Mild steel	99.8% Fe, 0.2% C	Hard but easily worked	Nails, cables and chains
Solder	33% Sn, 67% Pb	Low melting point	Joining pipes and wires
Duralium	96% Al, 4% Cu	Low density but very strong	Aircraft bodies
Pewter	Old: 70% Pb, 30% Sn. Modern: 91% Sn, 7.5% Sb, 1.5% Cu	Easily worked, durable. Modern pewter attractive silver colour	Drinking jugs, ornaments
Jewellery gold (14 carat)	58% Au, 42% other, for example, Ag, Cu, Pd, Pt	Easily worked, harder than pure gold, unreactive, attractive gold colour	Jewellery, ornaments
Sterling silver	92% Ag, 8% Cu	Easily worked, harder than pure silver, unreactive, attractive silver colour	Jewellery, ornaments
Dental amalgam	60% Ag, 28% Sn, 12% Cu, 0.05% Pt dissolved in Hg. Other metals: Hg ratio 1 : 0.73 (42% Hg)	Easily worked	Fillings for teeth

Steel

Iron, in various forms of steel, is used extensively in building construction and the manufacture of cars and other machinery. These steels usually contain small amounts of carbon alloyed with iron. The properties of carbon steels can be changed by altering the amounts of carbon added to the iron. As shown in Table 6.3, increasing the proportion of carbon increases the strength and hardness of the steel produced. They can be further changed by 'working' the steel in forging and rolling processes, and by heat treatment such as annealing, quenching and tempering.

Annealing involves heating the metal to a moderate temperature and then letting it cool down slowly. This makes the metal softer and more ductile by allowing larger crystals to form. *Quenching* also involves heating to moderate temperatures but is followed by rapid cooling, often by plunging in water. This produces a hard but brittle metal with small crystals. *Tempering* is when quenched metals are heated again but to lower temperatures and allowed to cool. This reduces brittleness without losing hardness.

Some specialist steels contain small amounts of other metals. For example, stainless steel used in cutlery and sinks consists of iron alloyed with chromium and nickel. Some steels have other metals added to form 'alloy steels' with special properties. Table 6.3 includes a selection of steels formed by adding other elements to iron, producing alloys with properties that make them suitable for particular purposes.

Figure 6.13 Drill bits are hardened by quenching.

Table 6.3 Types of steel

Type	Element alloying with iron	Major properties	Uses
Carbon steels			
mild steel	< 0.2% C	ductile and malleable	nails, chains, cables, machinery
structural steel	0.2–0.5% C	hard, strong	girders, vehicles, rails
tool steel	0.9–1.5% C	very hard, strong	tool blades, cutlery
Alloy steels			
stainless	10–25% Cr, 4–22% Ni	corrosion resistant	cutlery, sinks, hospital items
chrome	2–5% Cr	very hard, tough	armour plate, gears
chrome–vanadium	3–10% Cr, 1–5% V	great tensile strength	springs, car parts
manganese	10–15% Mn	very hard, abrasion resistant	safes, crushers, mechanical shovels
molybdenum	5% Mo	strong, heat resistant	drive shafts, gears
tungsten	12–20% W, 2–5% Cr, 1–3% V	hard at high temperatures	cutting and grinding tools
silicon	2–5% Si	easily magnetised and demagnetised	electromagnets, transformers
alnico	6–12% Al, 14–20% Ni, 2–35% Co	retains magnetism	permanent magnets
invar	36% Ni	low rate of expansion	pendulums, surveyors' tapes

Figure 6.14 Some of the many uses of steel.

Solder

Solder is an alloy of lead and tin. It has a melting point lower than either of these pure metals. Solder is a metal filler used to join two pieces of metal together. The solder is melted and allowed to fill the space between the pieces to be joined, and as it cools it solidifies, bonding the two pieces together. Soldering is used extensively in the electronics industry.

Brass

Brass is an alloy consisting mostly of copper and zinc, although small amounts of other elements such as lead, tin and aluminium may be present. Brass is resistant to corrosion and therefore brass fasteners (screws, bolts, nails and so on) may be used in situations where other metals would rust. Brass also has an attractive finish and is used for decorative elements such as doorknobs and knockers.

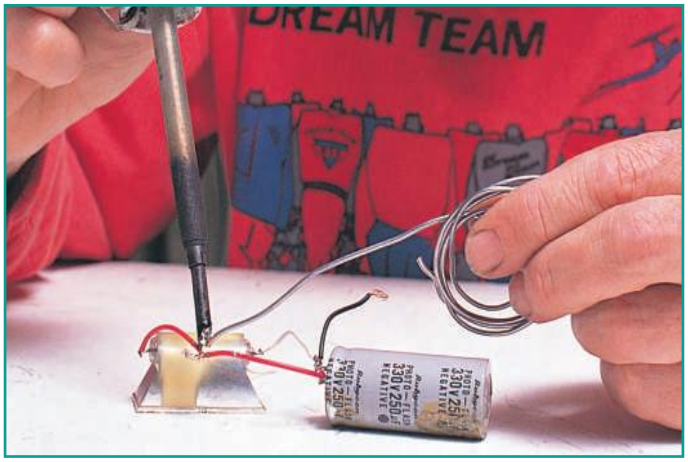


Figure 6.15 Solder is an alloy of lead and tin.

Figure 6.16 Brass has an attractive finish and polishes well.

❊ Review exercise 6.3

1. a **Define** the term ‘alloy’.
   b **Describe** how alloys are made.
   c **Explain** why they are so important in modern society.
2. **Explain** how the addition of small quantities of other elements can increase the hardness of a metal.
3. **Discuss** how the uses of iron can be greatly extended by:
   a manufacturing alloys with different compositions
   b different heat treatments of steels.
4. a **Identify** three alloys in which copper is the major component.
   b **Outline** a specific use for each alloy you listed in **a**.
   c **Identify** the property mainly responsible for that use.
5. **Identify** three examples of and two uses for:
   a carbon steel
   b a named alloy steel.

6.4 Minerals and ores

The reactivity of a given metal with substances in the atmosphere, lithosphere and hydrosphere determines the likelihood of finding that metal in the Earth’s crust in the uncombined elemental form. Most metals are reactive and are therefore usually found combined with other elements in naturally occurring compounds called *minerals*. Table 6.4 identifies, for some common metals, the likelihood of the metal being found in uncombined elemental form. Highly reactive metals such as potassium and sodium are never found as the free element but unreactive metals such as gold are much more likely to be found as the free element.

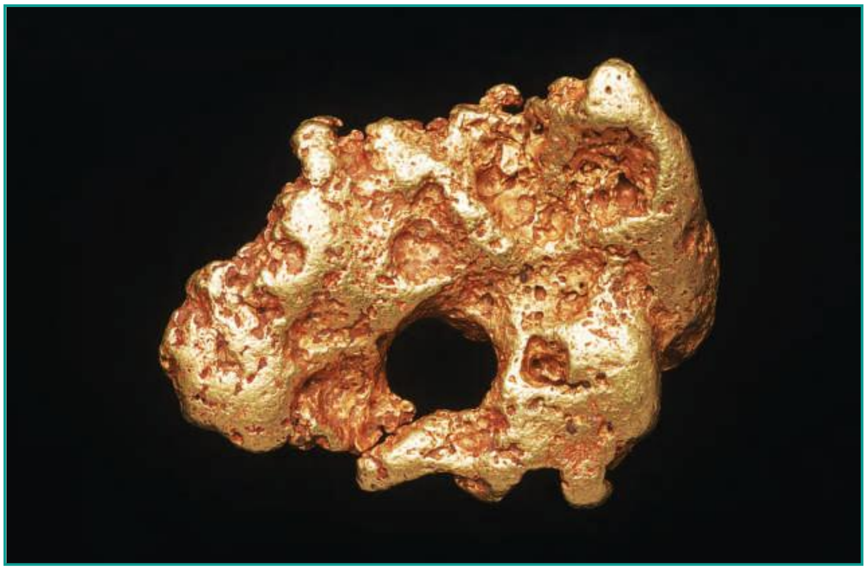


Figure 6.17 Gold is very unreactive and may be found in the uncombined elemental form. Usually gold occurs as tiny specks but occasionally a large nugget may be discovered.

Table 6.4 Occurrence of metals as elements in the earth's crust

Metal	Found in uncombined elemental form
Gold Platinum Silver	frequently
Mercury Copper Lead	occasionally
Tin Nickel Iron Zinc	rarely
Aluminium Magnesium Calcium Sodium Potassium	never

As described in Chapter 2, minerals are naturally occurring substances, usually compounds, with a definite composition or range of compositions and crystal structures. Minerals usually contain metals in the form of oxides, carbonates, silicates, sulfides and sulfates. Although metal silicates are the most common class of mineral, it is very difficult to extract metals from these compounds. The extraction of metals from oxide and sulfide minerals is much easier and these make up the most important minerals. Table 6.5 shows the principal mineral sources of some common metals.

Table 6.5 Principal mineral sources of some common metals

Metal	Mineral	Chemical composition
Aluminium	Bauxite	Al_2O_3
Chromium	Chromite	$FeO.Cr_2O_3$
Copper	Chalcocite	Cu_2S
	Chalcopyrite	$CuFeS_2$
	Malachite	$CuCO_3.Cu(OH)_2$
Iron	Haematite	Fe_2O_3
	Magnetite	Fe_3O_4

Table 6.5 *Continued*

Metal	Mineral	Chemical composition
Lead	Galena	PbS
Manganese	Pyrolusite	MnO_2
Mercury	Cinnabar	HgS
Molybdenum	Molybdenite	MoS_2
Tin	Cassiterite	SnO_2
Titanium	Rutile	TiO_2
	Ilmenite	$FeTiO_3$
Zinc	Sphalerite	ZnS
	Calamine	$ZnCO_3$

The Earth's lithosphere comprises about 47% oxygen, 28% silicon and much smaller percentages of the other elements. The most abundant metal in the lithosphere is aluminium (8%), followed by iron (5%), calcium (4%), sodium (3%), potassium (3%), magnesium (2%) and smaller percentages of the other metals. Even though these metals form a very small proportion of all the atoms in the crust, some highly concentrated mineral deposits exist.

To obtain metals in their elemental form they must be extracted from their minerals. Minerals usually occur in nature as mixtures with other minerals. If the mineral is present in sufficient quantity to make the mining and extraction of the metal economically viable, it is called an *ore*. For example, copper makes up only about 0.005% of the Earth's lithosphere but it can exist in ore deposits containing minerals such as malachite and chalcopyrite in sufficient concentration to make the mining and extraction of the copper an economic option. An ore is therefore defined as a naturally occurring deposit that is a mixture of minerals from which a substance, usually a metal, can be economically extracted. Another well-known example is bauxite, an aluminium ore containing hydrated aluminium oxide (known as gibbsite or boehmite) together with haematite, silica and clay minerals. Ores and their constituent minerals form as the result of a variety of geological processes, including crystallisation from molten rock, crystallisation from hot aqueous solutions, weathering of older rocks, sedimentation and biological processes.

❊ Review exercise 6.4

1 **Describe** the essential feature that allows a mineral deposit to be classed as an ore.

2 **Explain** why sulfide and oxide minerals are considered more important ores than the more abundant silicate minerals.

3 Nickel makes up only about 0.008% of the mass of the lithosphere. Given its relative scarcity, **explain** how it can be possible to extract nickel as a useful metal.

CHEMISTRY CONTEXT

❇ THE HISTORICAL EXTRACTION OF COPPER AND IRON

Extraction of copper

As stated in Unit 6.1, the archaeological records suggest that copper was the first metal to be extracted from its minerals and consequently was the first metal used extensively by humans. This period of human history is generally regarded as the transition from the Stone Age to the age of metals and is sometimes referred to as the Copper Age (5000–3000 BC). The ancient method of extraction of copper was probably a fortunate discovery. To extract copper from ores such as malachite ($CuCO_3.Cu(OH)_2$) and chalcopyrite ($CuFeS_2$), moderately high temperatures and an abundant supply of carbon are required. Both these conditions would have been present in campfires and the charcoal-fired pottery kilns that had been used for thousands of years. In regions where the blue-green rocks containing copper-bearing minerals were present, it was only a matter of time before someone made the connection between the droplets of copper found at the bottom of the campfire or kiln and the rocks containing these minerals.

The green-coloured malachite, which is a copper hydroxy carbonate, decomposes on heating to form copper(II) oxide according to the equation:

$$CuCO_3.Cu(OH)_2 \rightarrow 2CuO + CO_2 + H_2O$$

The black copper(II) oxide then reacts with carbon, in the form of charcoal, to form copper metal and carbon dioxide according to the equation:

$$2CuO + C \rightarrow 2Cu + CO_2$$

The extraction of copper from chalcopyrite probably took place later. In this process, silica (SiO_2) in the form of sand is added to remove the iron as slag ($FeSiO_3$). The modern extraction process occurs in several stages but can be represented by the equation:

$$2CuFeS_2(s) + 5O_2(g) + 2SiO_2(s) \rightarrow 2Cu(l) + 4SO_2(g) + 2FeSiO_3(l)$$

Extraction of iron

The extraction of iron from iron ores, particularly haematite, occurred several thousand years later in history than copper or lead, mainly as a result of the higher temperatures required for its extraction. Haematite (Fe_2O_3) was mixed with charcoal and heated to high temperatures in primitive furnaces by blowing air through the mixture with a bellows.

The overall reaction can be represented by the equation:

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$$

The resulting spongy lump of metal was repeatedly heated to red hot and hammered to expel the impurities (slag), leaving wrought iron. It is not known exactly when or where iron was first extracted, but the Hittites, who lived in what is now Turkey, perfected the technique around 1500 BC. By 1000 BC the knowledge of iron metallurgy had spread widely and the Iron Age had replaced the Bronze Age. In about 500 BC the Chinese developed the first blast furnaces, which reached much higher temperatures and were able to produce molten iron, which could be poured into casts to produce cast iron. The forerunner to the modern blast furnace was developed in Belgium in the fifteenth century. The blast of air was blown into the haematite and charcoal mixture by a bellows driven by a water wheel.

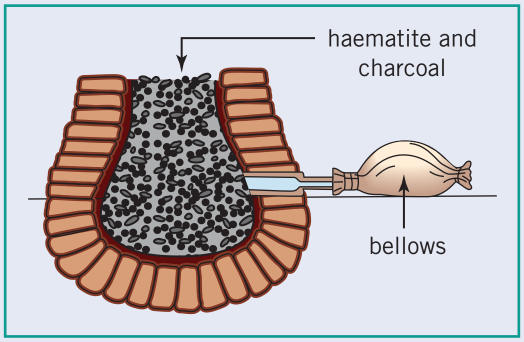


Figure 6.18 An early furnace for extracting iron

6.5 The extraction of metals from their ores

In the production of most metals, four distinct steps are needed to convert ore to refined metal ready for industrial use. These steps—mining, milling, smelting and refining—are summarised in Table 6.6. The total process is called *metallurgy*.

Table 6.6 Metallurgical processes

Process				Examples of products		
Common name of process	*Other associated names*	*Aim of process*	*End product of process*	*Iron*	*Copper*	*Aluminium*
1 Mining	Excavation, stoping	To extract ore	Crude ore	Haematite, limonite up to 69% Fe	Chalcopyrite, malachite up to 5% Cu	Bauxite up to 30% Al
2 Milling	Concentrating, beneficiation, flotation, leaching	To concentrate or purify ore usually by physical means	Ore concentrate	Iron concentrate pellets, sinter 60–70% Fe	Copper concentrate 15–30% Cu	Refined alumina 53% Al
3 Smelting	Metal extraction	To extract crude metal by chemical means	Crude metal	Pig iron 80–95% Fe	Blister copper 98–99% Cu	Commercial aluminium 99.3–99.6% Al
4 Refining	Electrolytic refining, fire refining	To purify crude metal	Pure metal	Steel cast iron 98–99% Fe	Refined copper 99.9% Cu	Refined aluminium 99.99% Al

Extraction of copper from its ore

Australia is one of the world's major copper producers. The main copper ore bodies in Australia are at Mount Isa in Queensland, Roxby Downs in South Australia and Mount Lyell in Tasmania. Copper is extracted principally from sulfide ores, particularly chalcopyrite ($CuFeS_2$). The copper ore may be on the surface and easy to excavate, or may be underground and require more sophisticated methods of excavation. The crude ore from the mine often contains less than 0.5% copper by mass and must be milled before the metal can be extracted. *Milling* refers to the concentration or purification of an ore. Usually this involves physical processes to separate the required mineral from the rock, clay and sand, collectively called *gangue*, also present in the ore. The techniques used to separate the mineral from the impurities vary according to the physical properties of the materials involved, but include those described in Chapter 2, such as sieving, sedimentation, magnetic separation, solution, filtration, evaporation and crystallisation. Copper is concentrated using a method called *froth flotation* (Figure 6.20). In this process, air is bubbled through a suspension of the pulverised ore in water containing a flotation or frothing agent. The desired copper mineral particles adhere to rising bubbles and are skimmed off as froth, leaving the unwanted silicate minerals to settle out. In this way, the copper ore is separated from the gangue.

The concentrated ore, which is now about 15% copper, is then roasted in air, which converts the FeS to FeO but leaves the CuS unaffected.

$$2CuFeS_2(s) + 3O_2(g) \rightarrow 2CuS(s) + 2FeO(s) + 2SO_2(g)$$

Figure 6.19 Stages in the metallurgical process (a) Mining (b) Concentrating ore by froth flotation (c) Smelting (d) Electrorefining

The product is then heated at 1100°C with ground limestone, sand and additional concentrated ore. This converts the FeO to a molten slag and converts the copper(II) sulfide to copper(I) sulfide.

$$\mathrm{FeO(s)} + \mathrm{SiO_2(s)} \rightarrow \mathrm{FeSiO_3(l)}$$

In the final smelting step, the copper(I) sulfide is roasted in air so that part of it is converted to copper(I) oxide.

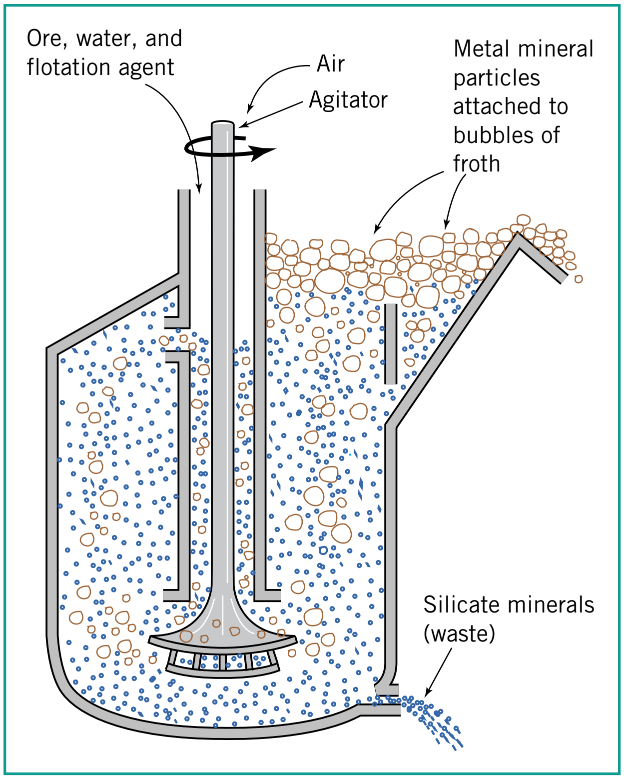
$$\mathrm{2Cu_2S(s)} + \mathrm{3O_2(g)} \rightarrow \mathrm{2Cu_2O(s)} + \mathrm{2SO_2(g)}$$

The two copper(I) compounds, copper(I) sulfide and copper(I) oxide, then react together to form copper metal and sulfur dioxide.

$$\mathrm{2Cu_2O(s)} + \mathrm{Cu_2S(s)} \rightarrow \mathrm{6Cu(l)} + \mathrm{SO_2(g)}$$

This process requires a significant input of energy to maintain the temperatures required for this reaction.

The smelting process produces crude copper of about 98% purity, which is called *blister copper* because of the bubbly appearance produced by escaping sulfur dioxide. To obtain the 99.9% purity required for electrical wiring, the blister copper is refined electrolytically.



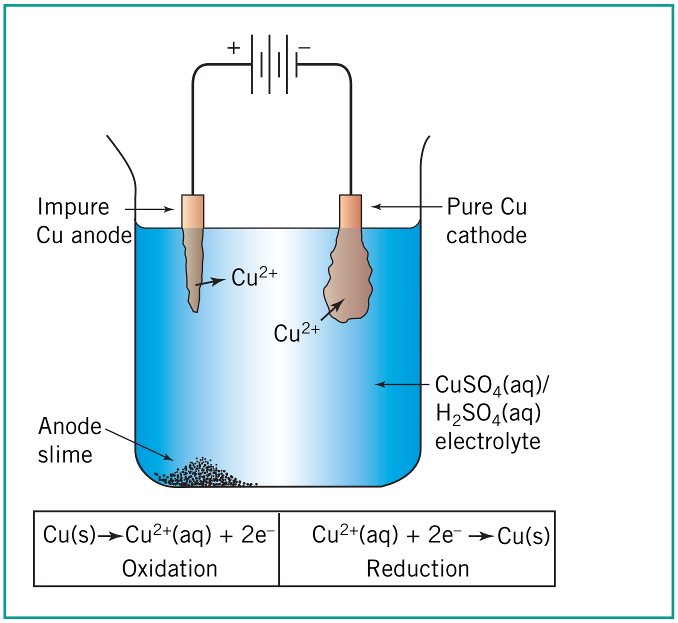


Figure 6.20 Froth flotation is used to concentrate copper ore by separating it from gangue.

Figure 6.21 The electrorefining of copper

The impure blister copper is cast into slabs and made the anode (positive electrode) of an electrolytic cell (Figure 6.21). The cathode is a thin sheet of pure copper and the electrolyte is copper(II) sulfate solution, acidified with sulfuric acid.

The copper and reactive metal impurities such as zinc, iron and nickel present in the anode dissolve and enter the solution as ions. As the anode slab dissolves, the more inert metal impurities such as gold, silver and platinum fall to the bottom of the cell. In a finely divided state, they form an 'anode slime', which is a profitable source of these metals.

A small voltage is used so that pure copper deposits at the cathode (negative electrode). The ions of the more reactive metals remain in solution. These are removed periodically so that their concentrations do not build up sufficiently to cause them to also deposit at the cathode. The copper that deposits at the cathode is extremely pure because almost all of the impurities present in the blister copper have been removed.

❇ Review exercise 6.5

1 Briefly **outline** the main steps in the extraction of a metal from its ore.

2 **Identify** the physical properties that allow copper ores to be separated from gangue in the froth flotation process.

3 In the extraction of metallic copper from chalcopyrite, **explain**:

  a how the iron is removed

  b what causes the blisters in blister copper.

4 **Explain** how the metal impurities in blister copper are removed in the electrorefining process.

6.6 Factors affecting the use of metals

As described earlier in this chapter, metals have a vast range of uses. These uses are determined to a considerable extent by their physical and chemical properties. For example, gold has always been a highly sought-after metal. This popularity results from its attractive appearance, its ability to be shaped easily to make different objects, its very high conductivity and reflectivity, and its resistance to chemical attack. Gold's desirable properties and its rarity make it a very expensive metal.

Apart from their specific properties, other factors that affect the commercial price and extent to which particular metals are used include:

- the abundance of the metal in the ore deposit
- the cost of extraction of the metal
- the demand for the metal.

The crustal abundance, annual world production and price per tonne of several metals are shown in Table 6.7.

Table 6.7 Crustal abundance, annual world production and price per tonne of some metals

Metal	Crustal abundance (ppb by mass)	Method of extraction	Annual world production (000 tonnes)	Price per tonne (2005) ($US)
Aluminium	8.1×10^5	Electrolysis of Al_2O_3	30 000	1 837
Iron	5.0×10^5	Carbon reduction of Fe_2O_3	1 000 000	400
Magnesium	2.1×10^5	Electrolysis of $MgCl_2$	370	3 748
Titanium	4.4×10^4	Conversion to $TiCl_4$; reduction with Na or Mg	120	8 820
Zinc	7.0×10^2	Roasting of ZnS; electrolysis of $ZnSO_4$	7 500	1 396
Nickel	7.0×10^2	Roasting of NiS; hydrogen reduction	900	14 550
Copper	5.0×10^2	Roasting of $CuFeS_2$	8 500	3 782
Tin	30	Carbon reduction of SnO_2	200	6 880
Lead	1.3×10^2	Carbon reduction of PbO	5 500	902
Mercury	0.8	Roasting of HgO	5	7 253
Gold	0.05	Leached with cyanide; reduction by zinc or electrolysis	2	1.02×10^7

Metals vary markedly in their abundance in the Earth's crust. For example, some metals are relatively abundant, such as aluminium (about 8%) and iron (about 5%) respectively. Other metals are less abundant, such as copper (0.005%) and lead (0.001%), while others are rarer still, such as mercury (0.000 008%) and gold (0.000 000 5%). More important than the overall abundance of various metals in the Earth's crust is the occurrence of ore deposits that contain a sufficient proportion of a particular mineral to make the mining of the ore and extraction of the metal economical. For example, although zinc makes up only about 0.008% of the Earth's crust, it occurs in ores containing minerals such as zinc blende in sufficient concentration to make the mining and extraction of the zinc economically viable.

The cost of mining an ore and metal extraction is another important factor that affects the use of metals. Despite being the most abundant metal in the Earth's crust, aluminium was once so expensive to extract that its use was severely limited, even though it had very many useful properties. It was only after a commercially viable method of extracting aluminium from bauxite was developed that its cost was reduced and aluminium could be widely used. Iron, on the other hand, has been comparatively cheap for a long period of time. This is partly because iron ores are usually of a high grade and are reasonably abundant. In addition, the iron can be extracted from its ore on a large scale and at reasonably low cost in blast furnaces that run continuously, thereby reducing production costs.

It is worth pointing out that the economic viability of metal extraction can vary depending on factors such as current demand and price, and improvements in metallurgical processes. For example, the efficiency of gold extraction has increased markedly with the development of the modern carbon-in-pulp process. This process makes it possible to profitably extract gold from much poorer ores than was previously possible. This has led to the re-treatment of old mine dumps, known as *tailings*.

Titanium is a highly sought-after metal despite its relative rarity in ores. The particular properties that make titanium so useful include its extreme toughness and durability, and resistance to corrosion. As a result, titanium is quite expensive.

❇ Review exercise 6.6

1 **Identify** three reasons why gold is very expensive.

2 Sodium is widespread in the Earth's crust, including its presence in common salt. Metallic sodium is extracted by electrolysis of molten sodium chloride, a process requiring large inputs of energy. **Evaluate** the influence of these two observations on the price of sodium metal.

3 **Explain** the following:
  - **a** Iron is by far the most extensively used metal.
  - **b** Aluminium is more abundant in the Earth's crust than iron but its price is much higher than that of iron.
  - **c** Mercury is extremely expensive.

6.7 Recycling of metals

Mineral resources are non-renewable and are limited in quantity. Once all the accessible ore bodies of a particular metal have been mined, that metal will no longer be produced.

Mineral resources are being ‘extended’ in several ways. First, new ore bodies are being discovered, often using advanced exploration techniques in geophysics and remote sensing. Second, improving technology is increasing our ability to access some ores, such as those that occur at considerable depth in the Earth’s crust or under the oceans. Third, our ability to extract metals from lower-grade ores is improving. Fourth, as we learn more about factors affecting the rate of corrosion of metals we are better able to protect metal items and structures from corrosion. Despite all these improvements it is important that we manage our mineral and metal resources responsibly, for our own and future generations. An increasingly important option in extending our metal resources, and reducing energy use, is to recycle metals from objects that no longer serve their original purpose. Many metals, particularly iron, steel, copper and aluminium, are recycled. Metal objects such as drink cans, cars or ships can be salvaged and recycled. Once the metal has been sorted and treated it is ready to be re-melted and re-formed. As the costs of metals continue to increase due to decreasing supplies and increasing demand, the cost-effectiveness of recycling will also rise.

Aluminium recycling versus extraction

The recycling of aluminium from drink cans, car engines and body trim, boats and appliances is well established in Australia and many other countries. More than 60% of the aluminium cans produced in Australia are recycled. The aluminium recovered from these and other sources is sorted according to its alloy type. It is then sent to a smelter, where it is melted in specially designed furnaces. The molten aluminium is then analysed and its composition adjusted before being cast into ingots, which are sent to manufacturers who use the recycled aluminium to make new drink cans, engine parts, garden furniture and other products.

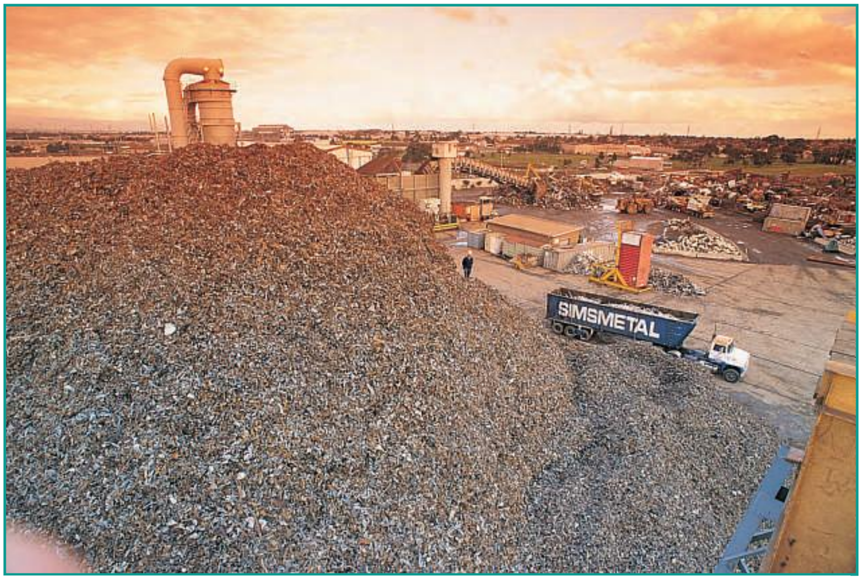


Figure 6.22 In Australia, more than 60% of aluminium cans are recycled.

The recycling of aluminium is very cost-effective compared to extracting the metal from bauxite. The refining of bauxite to produce alumina (Al_2O_3) uses about 15 000 MJ of energy per tonne of alumina produced. Smelting this alumina requires an additional 50 000 MJ per tonne of aluminium produced. Thus the total energy budget for producing aluminium from its ore is 65 000 MJ per tonne of aluminium produced. Melting recycled aluminium requires only 800 MJ of energy per tonne of aluminium produced. Therefore recycling aluminium requires less than 5% of the energy needed to produce the same amount of aluminium from its ore. Recycling not only conserves our reserves of aluminium ore but also is an excellent energy conservation measure because it greatly reduces the amount of electricity needed to produce aluminium.

Vast amounts of energy are required to isolate pure aluminium oxide, alumina, from bauxite and then extract aluminium from alumina. Bauxite is mined extensively in Australia. Major deposits occur in the Darling Range and Mitchell Plateau of Western Australia, at Gove in the Northern Territory and at Weipa in Queensland.

After mining, bauxite must then be separated from its impurities and converted into aluminium oxide (alumina). This process, known as the Bayer process, involves several steps. The bauxite is first heated in hydroxide solution under pressure. The mineral dissolves, forming aluminate solution.

$$Al(OH)_3(s) + OH^-(aq) \rightarrow [Al(OH)_4]^-(aq)$$

Most of the impurities, mainly Fe_2O_3 and SiO_2, settle out as an insoluble 'red mud', which is pumped to disposal ponds. The highly concentrated hot solution of sodium aluminate is then filtered, cooled and 'seeded' with crystals of pure aluminium hydroxide. The precipitation reaction that occurs is the reverse of the solution process.

$$[Al(OH)_4]^-(aq) \rightarrow Al(OH)_3(s) + OH^-(aq)$$

The aluminium hydroxide is filtered off and is decomposed by heating to produce alumina, which is a finely powdered form of pure aluminium oxide.

$$2Al(OH)_3(s) \rightarrow Al_2O_3(s) + 3H_2O(g)$$

The next stage is to extract the aluminium from the alumina by the process of electrolytic reduction. As stated earlier, the ores of reactive metals such as aluminium cannot be reduced chemically. Alumina is reduced to aluminium metal by the Hall-Heroult process. This involves the electrolysis of molten Al_2O_3. However, the high melting point of Al_2O_3 (2045ºC) makes it prohibitively expensive to maintain the electrolyte at that temperature. This problem is reduced significantly by dissolving the alumina in cryolite, which is sodium hexafluoroaluminate (Na_3AlF_6). A mixture containing approximately 80% cryolite allows a molten phase to be maintained at 950ºC to 1000ºC for electrolysis. The electrolytic cell used is shown in Figure 6.23. The carbon anodes are oxidised by combining with O^{2-} and form gaseous products, mainly carbon dioxide.

$$C(s) + 2O^{2-}(l) \rightarrow CO_2(g) + 4e^-$$

Aluminium ions are reduced to the metal at the carbon cathode base and walls of the cell.

$$Al^{3+}(l) + 3e^- \rightarrow Al(l)$$

The molten aluminium is periodically removed from the cell and cast into ingots. The overall equation for the electrolysis is as follows:

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

Although only 5 V is maintained between the electrodes, huge electrical currents, about 1×10^5 A, are needed to convert the aluminium ions to aluminium metal and to keep the electrolyte molten. This makes the extraction process very expensive. It has been estimated that about 5% of electrical energy produced in the United States is used in the extraction of aluminium.

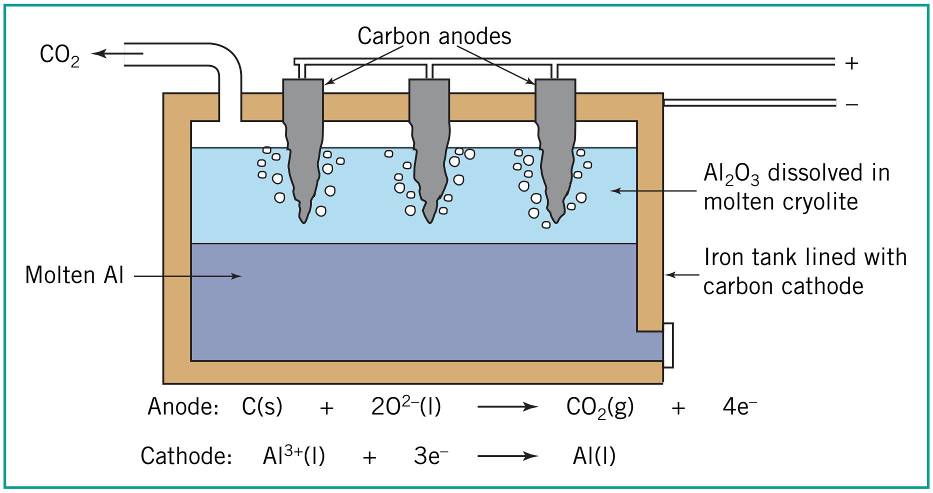


Figure 6.23 The electrolytic cell used in the extraction of aluminium

❋ Review exercise 6.7

1 **Recount** the steps taken in the recycling of aluminium.

2 **Compare** the energy costs involved in the extraction of aluminium from bauxite and the recycling of aluminium.

3 **Account** for the fact that aluminium smelters are usually located near hydroelectricity or power stations.

4 a **Justify** the high rate of recycling of aluminium compared to other metals such as iron and steel.
  b **Clarify** how the recycling of aluminium helps conserve fossil fuel reserves.

*KEY POINTS

- Humans have used metals for at least 14 000 years but their use increased dramatically approximately 7000 years ago when our ancestors began to extract metals from mineral compounds.
- To extract metals from their minerals requires an input of energy to break and rearrange chemical bonds.
- The first metals to be extracted and widely used were copper and iron. Their widespread use is marked by the Copper, Bronze and Iron ages.
- The uses of metals are determined by their physical and chemical properties.
- Aluminium metal was not used widely until a cost-effective method of extraction was developed.
- The current uses of a selection of metals are summarised in Table 6.1.
- Few metals are used in their pure form. Most are combined with other elements to form alloys with modified properties that extend the range of the metal's uses (see Table 6.2).
- Alloys include various types of steel (iron and other elements—see Table 6.3), bronze (copper and tin), brass (copper and zinc), solder (lead and tin) and duralium (aluminium and copper).
- Alloys are generally harder than the metals from which they are made and often are more resistant to corrosion.
- Unreactive metals may be found in their uncombined elemental form.
- Reactive metals are found in minerals, naturally occurring compounds with a definite composition or range of compositions.
- Ores are naturally occurring deposits containing minerals from which a substance, usually a metal, can be economically extracted.
- The steps in the metallurgical process are: mining, milling or concentration, smelting or extraction, and refining.
- In metal extraction, less reactive metals are easier to extract from their ores than more reactive metals.
- The historical use of metals was determined by the abundance of metal ores and the ease of extraction of the metal.
- Copper extraction involves froth flotation to concentrate the chalcopyrite ore, roasting the ore to separate the FeO as slag, further roasting to form blister copper, and electrolytic refining to produce high-purity copper.
- Minerals are non-renewable resources. Metal resources are being extended through improved methods of detecting and accessing new ore deposits, more efficient extraction techniques, reduction of corrosion and increased recycling.
- The commercial price of a metal is determined by its abundance, the cost of production and the demand for the metal (which is often a function of the properties of the metal).

- Aluminium is produced by electrolytic reduction in the Hall-Heroult process. Alumina and cryolite are melted and electrolysed. Molten aluminium is formed at the cathode. The carbon anodes burn away as gaseous carbon dioxide.
- Recycling helps to conserve and extend the use of metals and energy. Many metals including aluminium, copper and steel are recycled.

* APPLICATION AND INVESTIGATION

➲ Investigation

1 a **Identify** the geographical area in which people first learned how to extract copper from its ores.

b **Investigate** and **explain** why the use of metals such as copper and bronze was such an important breakthrough in human cultural development.

c **Identify** some cultures in which the extraction of metals was not evident. **Propose** reasons for why this was so.

➲ Investigation

2 **Gather**, **process** and **analyse** information from secondary sources to describe the extent to which the Bronze or Iron ages spread across different cultures.

3 **Discuss** why iron replaced bronze as the metal of choice in many applications.

4 **Explain** why iron is more useful when it has small amounts of other elements added to it. Support your answer by referring to three specific examples.

➲ Investigation

5 **Investigate** whether alloys are best described as elements, compounds, mixtures or solutions.

6 Alloys are usually harder than their individual component metals. **Discuss** this statement, supporting your answer with examples and **explanations** of why this is the case.

7 For each of the metals listed below, **identify** the property you think is the most important and has led to its widespread use. **Justify** your answer in each case.

a copper

b iron

c aluminium

d titanium

➲ Investigation

8 **Identify** the three most widely used metals today. For each, outline its main uses.

➲ Investigation

9 Titanium is becoming an increasingly important metal. **Investigate** some of its newer and possible future uses, and relate these to its properties.

10 **Discuss** the reasons for the availability of a wider variety of metals today than 200 years ago.

11 **Differentiate**, with examples, between ores, minerals and metals.

12 Copper was extracted from its ores about 7000 years ago, yet aluminium, which is a much more abundant metal, has only been extracted on a commercial scale in the past 50 years. **Explain** these historical observations.

13 **Describe** the process by which copper ores are separated from the other minerals with which they are found.

14 **Explain** how pure copper could be obtained from a piece of impure copper. Include a fully labelled diagram of the apparatus you would require.

15 **Construct** a balanced chemical equation for the chemical reaction of copper(II) oxide (CuO) with carbon.

16 **Discuss** why dissolving alumina in cryolite makes the extraction of aluminium more economically viable.

17 a Aluminium is sometimes described as 'solid electricity'. **Discuss** why this term may be used.

b Comment on the siting of aluminium smelters in terms of the raw materials and energy requirements of the process.

18 Titanium is relatively rare both in terms of its overall abundance in the Earth's crust and in exploitable ores. Titanium is quite expensive, yet despite this, the metal is keenly sought. **Explain** these observations.

⊂ Investigation

19 a **Assess** the validity of the statement: 'The recycling of aluminium is beneficial to the environment'.

b **Investigate** the extent of copper recycling and the techniques used.

CHAPTER 7

CHEMICAL REACTIONS OF METALS

As discussed in the previous chapter, metals have played an important role in the cultural development of humans. The uses of a metal are determined by a number of factors, including the physical and chemical properties of the metal as well as its cost, which is largely determined by its abundance and how readily it can be extracted from its ores. The physical properties of metals were discussed in Unit 3.4 and the uses, extraction and cost of metals were discussed in Chapter 6. This chapter examines some of the chemical reactions of metals.

Metals differ in their reactivity with other substances including oxygen, water and dilute acids. By observing how readily different metals react with oxygen, water and dilute acids it is possible to determine an order of reactivity and thus rank these metals in an activity series.

7.1 Reactions of metals with oxygen

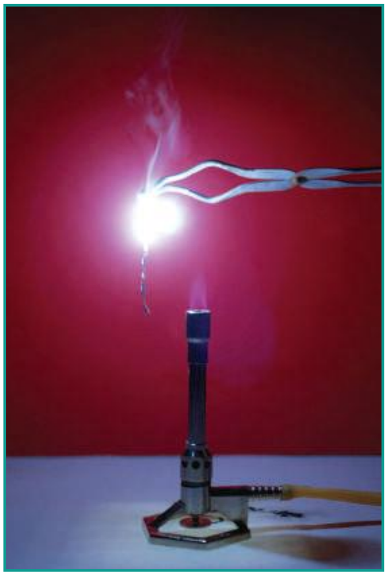


Figure 7.1 Magnesium burns readily in air, releasing heat and light.

Most metals will react with oxygen in the air at room temperature to form metallic oxides. The general word equation for the reaction of oxygen with metals is:

metal + oxygen → metal oxide

Specific examples include:

(1) magnesium + oxygen → magnesium oxide

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

(2) iron + oxygen → iron(III) oxide

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

Metals exhibit widely varied reactivities in their reactions with oxygen. Lithium, sodium and potassium tarnish rapidly when exposed to air and must therefore be stored in liquid paraffin oil. Rubidium and caesium are so reactive that they catch fire in air and must be handled in an inert gas environment such as argon. The equation for the reaction of sodium with oxygen is:

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$

These metals, together with magnesium, calcium, strontium and barium, burn readily in air, releasing large amounts of heat and light. Other metals such as aluminium, zinc and iron will only burn in air if the metal is finely divided. For example:

$$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$$

Less reactive metals do not burn but react slowly with oxygen when heated. For example, copper will react slowly when heated in air to form black copper(II) oxide.

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

Silver, platinum and gold do not react with oxygen in the air even when heated. Table 7.1 summarises the reactivity of different metals with oxygen.

Figure 7.2 Two metals with different reactivities. Gold (left) is so unreactive that it never loses its shine. This statuette of Tutankamun was made in the fourteenth century BC. Sodium (right) is so reactive that it must be stored in paraffin oil to prevent it reacting with air and water.

Table 7.1 The reactivity of metals with oxygen

Metal	Reaction with oxygen
K Na Ca Mg	Burn readily to form oxides
Al Zn Cr Fe Cd Co Ni	Burn to form oxides if finely divided
Sn Pb Cu Hg	React slowly if heated in air or pure oxygen
Ag Pt Au	Do not react with oxygen

CHEMISTRY CONTEXT

❊ CORROSION OF METALS

When metals react with gases in the atmosphere to form new substances, they undergo *corrosion*. This corrosion can cause the metal to lose some of its strength. Oxygen, carbon dioxide, sulfur dioxide and hydrogen sulfide can all react with metals, causing them to corrode. However, because oxygen is the main corrosive agent in the atmosphere, corrosion will generally refer to the reaction of metals with oxygen. The best-known form of corrosion is the rusting of iron, but most metals are susceptible to corrosion to some extent. The corrosion of metals costs Australia several billion dollars annually. A better understanding of the process and the application of appropriate preventative measures could save much of this cost.

In normal atmospheric conditions, most metals form a microscopic surface film of the metal oxide by reaction with oxygen. This is why most metals tarnish and lose their shiny lustre when exposed to air. This layer usually adheres strongly to the metal but can be removed by abrasion with steel wool or emery paper.

Some reactive metals such as aluminium form an inactive coating that immediately re-forms if removed by abrasive action. In these metals this surface oxide layer is impervious to oxygen and therefore protects the underlying metal from further oxidation. This is why aluminium and chromium do not corrode very rapidly in air.

In the case of iron, the oxide layer is relatively porous and allows oxygen to migrate through it to react further with iron atoms. This enables the corrosion of iron to continue.

Common forms of corrosion, including the rusting of iron, often require or are accelerated by the presence of water. The rusting of iron can be represented by the following equation:

$$4Fe(s) + 3O_2(g) + 2H_2O(l) \rightarrow 2Fe_2O_3.H_2O(s)$$

This process may occur in water or in a humid atmospheric environment. Rusting is undesirable for many reasons other than the sheer loss of metal. Corroded structures such as bridges, buildings, cars and machinery are weakened and become dangerous. Electrical connections often corrode and the corrosion products reduce proper contact between terminals and leads. Similarly, corroded fittings such as lids, nuts and bolts, taps, valves and hinges often jam as corrosion products swell and fill the space between moving parts. Tanks, pipes and car radiators may leak as corrosion creates holes in the metal walls.

Figure 7.3 The corrosion of metals is very costly.

❊ Review exercise 7.1

1 With regard to the usefulness of metals, **identify** an example of where the formation of a metal oxide is:
  a a disadvantage
  b an advantage.

2 **Identify** three metals more reactive than iron that do not corrode as readily due to the formation of a protective oxide coating.

3 **Explain** why sodium and potassium are stored in paraffin oil.

4 **Construct** balanced chemical equations for the following reactions:
  a the burning of calcium to form calcium oxide
  b the formation of a surface oxide layer of aluminium oxide.

7.2 Reactions of metals with water

Most metals when placed in cold water undergo no observable changes and show no signs of chemical reaction. However, some metals, including lithium, potassium, sodium and calcium, do react with cold water to form hydrogen and a metal hydroxide.

For example, the reaction of sodium with water is very vigorous.

sodium + water → sodium hydroxide + hydrogen

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

Or, written as an ionic equation:

$2Na(s) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g)$

Figure 7.4 The vigorous reaction of sodium with water. Note the production of hydrogen gas.

The formation of hydrogen in this reaction can be confirmed by collecting a sample of the gas produced and introducing a lighted splint. A small explosion or 'pop' confirms the presence of hydrogen gas. An acid–base indicator such as phenolphthalein or litmus can be used to confirm the production of hydroxide ions.

In this reaction the sodium displaces hydrogen from the water. The reaction involves the transfer of electrons from sodium atoms to hydrogen atoms in the water and is classed as an *oxidation–reduction reaction*. Oxidation–reduction reactions are discussed in detail in Unit 7.5. The loss of electrons by sodium atoms and the gain of electrons by hydrogen atoms can be represented by the following equations:

$Na(s) \rightarrow Na^+(aq) + e^-$

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Another group of somewhat less reactive metals including aluminium, zinc and iron do not react with cold water but will react with steam to produce hydrogen and a metal oxide.

For example, zinc reacts with steam according to the equation:

zinc + steam → zinc oxide + hydrogen

$Zn(s) + H_2O(g) \rightarrow ZnO(s) + H_2(g)$

Less reactive metals such as gold, silver, copper, platinum and lead do not react with water or steam.

Table 7.2 summarises the reactivity of different metals with water.

Table 7.2 The reactivity of metals with water

Metal	Action of water
K Na Ca	React with cold water to form H_2 and hydroxides
Mg	Reacts with hot water to form H_2 and oxide
Al Zn Cr Fe Cd Co Ni	When heated strongly, react with steam or superheated steam to form H_2 and oxides
Sn Pb Cu Ag Hg Pt Au	No reaction

❇ Review exercise 7.2

1 **Construct** word and balanced formula equations for the following reactions:
  - **a** potassium with water
  - **b** calcium with water
  - **c** aluminium with steam.

2 Steam trains use coal to heat water in large boilers to produce the steam needed to turn the wheels. **Propose** why it would be unwise to make these boilers out of iron.

7.3 Reactions of metals with acids

A number of metals that do not react with water will react with dilute acids. The general word equation for this reaction is:

metal + acid → salt + hydrogen

Metals such as magnesium, zinc and iron react quite readily with cold dilute hydrochloric or sulfuric acid to produce hydrogen gas and salts. In fact, the laboratory preparation of hydrogen usually employs the reaction of zinc with dilute hydrochloric or sulfuric acid.

zinc + hydrochloric acid → zinc chloride + hydrogen

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

Or, written as an ionic equation:

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

During the reaction between a metal and an acid, the metal dissolves as it loses electrons and forms positively charged ions. Hydrogen ions from the acid gain electrons to form hydrogen gas. As this reaction involves a transfer of electrons it is an oxidation–reduction reaction. These two simultaneous reactions can be represented by the following equations:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

Similarly, the reaction of magnesium with dilute sulfuric acid is represented as:

$$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$$

or

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

The relevant processes are:

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$$

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

Metals more reactive than magnesium, such as sodium, potassium and calcium, react explosively with dilute hydrochloric and sulfuric acids. Less reactive metals such as copper, silver and gold do not react with these acids.

Table 7.3 summarises the reactivity of different metals with dilute hydrochloric and sulfuric acids.

Table 7.3 Reactivity of metals with dilute hydrochloric and sulfuric acids

Metal	Action of dilute HCl and H_2SO_4
K Na Ca Mg Al Zn Cr Fe Cd Co Ni Sn	React with cold dilute acids to form H_2 and salts
Pb	Reacts with warm dilute acids to form H_2 and salts
Cu Ag Hg Pt Au	No reaction

❇ Review exercise 7.3

1 **Identify** two metals that could be used to construct pipes for the transfer of dilute sulfuric acid in a chemical factory.

2 **Construct** ionic equations and **predict** two observations for the reaction of magnesium with each of the following:

a dilute sulfuric acid

b dilute hydrochloric acid.

3 **Identify** any metals that react with cold dilute hydrochloric acid but not cold water.

4 **Construct** balanced ionic equations for the reaction of aluminium with the following acids:

a dilute sulfuric acid

b dilute hydrochloric acid.

7.4 The activity series and ionisation energy

Table 7.4 The activity series of metals

K	most reactive
Na	↑
Ca	
Mg	
Al	
Zn	
Cr	
Fe	
Cd	
Co	
Ni	
Sn	
Pb	
Cu	
Ag	
Hg	
Pt	
Au	least reactive

At the beginning of this chapter it was stated that by observing how readily different metals react with oxygen, water and dilute acids, it is possible to determine an order of reactivity and thus rank these metals in an activity series. In Table 7.4 some common metals are arranged according to their ability to displace hydrogen from dilute acids and water. The metals are arranged from the most reactive, potassium, to the least reactive, gold. This arrangement is usually called the *activity series* of metals.

A comparison of the activity series for metals with the position of these metals on the periodic table reveals some interesting relationships. The most reactive metals are generally found on the left side of the periodic table, whereas the least reactive metals tend to be found in the middle of the periodic table.

Ionisation energy

The reactions of metals with oxygen, water and dilute acids belong to a class of chemical reactions known as oxidation–reduction reactions (see Unit 7.5). In each case, where a reaction occurs, the metal loses its valence electrons to form a positively charged ion. The relative ease with which a metal loses its valence electrons is a major factor affecting its reactivity. Very reactive metals such as potassium and sodium lose their valence electrons relatively easily. Less reactive metals such as copper do not lose their valence electrons as readily, and gold and silver rarely lose their electrons at all.

Ionisation energy is a measure of the energy needed to remove an electron from the electrostatic attractive force of the positively charged nucleus. The ionisation energy of an atom or ion is defined as the amount of energy required to remove the most loosely bound electron from the atom or ion in the gaseous state. It is the energy required for the process:

$$\begin{array}{ll} \mathrm{M(g)} + \text{energy} \rightarrow & \mathrm{M^{+}(g)} + \mathrm{e^{-}} \\ \text{gaseous atom} & \text{gaseous ion} \end{array}$$

The energy required to remove the first electron from an atom is called the *first ionisation energy*. For a sodium atom, the first ionisation energy is 502 kJ mol^{-1}.

This represents the energy needed for the process:

$Na(g) \rightarrow Na^+(g) + e^-$

In general, reactive metals tend to have low ionisation energies and less reactive metals have higher ionisation energies. Trends in ionisation energies within the periodic table are discussed in Unit 8.3.

❇ Review exercise 7.4

1 **Define** the term ‘activity series’.

2 **Propose** why energy is needed to remove an electron from an atom.

3 **Account** for the order of first ionisation energies for the elements:

$Fe\ (766\ kJ\ mol^{-1}) > Ca\ (596\ kJ\ mol^{-1}) > K\ (425\ kJ\ mol^{-1})$

4 Consider the three metals Na, Mg and Zn. From their positions in the periodic table, **predict** the likely order of first ionisation energies of these elements and their relative reactivities.

7.5 Oxidation–reduction reactions

Because most metals readily undergo corrosion it is not surprising that early chemists studied the reactions of metals with oxygen. Originally *oxidation* was defined as the process in which a substance gained oxygen. The French chemist Antoine Lavoisier was among the first to recognise such oxidation processes. For example, he observed that mercury reacted with oxygen to form red mercury(II) oxide.

$2Hg(s) + O_2(g) \rightarrow 2HgO(s)$

The mercury was said to be oxidised. Similarly, when magnesium burns brightly in air according to the equation

$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

the magnesium is oxidised.

It was a natural development that reactions that involved the loss of oxygen from a compound would be termed *reduction*. For example, copper(II) oxide can be reduced to the metal by reaction with hydrogen.

$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(g)$

Similarly, in the blast furnace production of iron, iron(III) oxide is reduced by carbon monoxide.

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

From a consideration of many oxidation and reduction reactions it became clear that the processes of oxidation and reduction were interdependent. As one substance is reduced by losing oxygen, another reactant can gain the oxygen and be oxidised. For example, in the reduction of lead(II) oxide by carbon,

$2PbO(s) + C(s) \rightarrow 2Pb(s) + CO_2(g)$

the carbon is simultaneously oxidised to carbon dioxide.

Oxidation and reduction as electron transfer processes

With a clearer understanding of atomic structure, closer inspection of oxidation–reduction reactions indicated that they were essentially electron transfer processes. The previous limited view of oxidation–reduction as the gain/loss of oxygen was replaced by a model that interprets these reactions in terms of the transfer of electrons. Consider the combustion of magnesium to form the ionic solid, magnesium oxide.

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

This reaction clearly involves the oxidation of magnesium. The magnesium oxide produced consists of Mg^{2+} ions and O^{2-} ions. Thus, the magnesium atoms have each donated two electrons in the oxidation process.

$$Mg(s) \rightarrow Mg^{2+}(s) + 2e^-$$

A substance that is *oxidised* is one that loses electrons and is therefore an electron donor. Conversely, each oxygen atom has gained two electrons.

$$O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$$

The oxygen is said to have been reduced. A substance that is *reduced* is one that gains electrons and is therefore an electron acceptor.

This view of oxidation and reduction emphasises the interdependence of the two processes. Using this model, the two processes must occur simultaneously. The substance being oxidised must donate electrons to another substance, which is reduced. Because oxidation and reduction must proceed simultaneously, these reactions are often referred to as *oxidation–reduction* or *redox* reactions.

The electron transfer concept of oxidation and reduction is more useful than the former definitions because it can be more generally applied. In particular, it is not restricted to species involving oxygen.

The equations in Figure 7.5 illustrate a range of redox reactions that can be identified by the electron transfer model but would not have been recognised as redox reactions using the previous model.

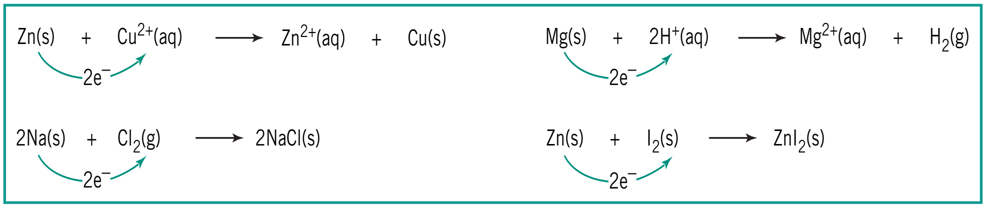
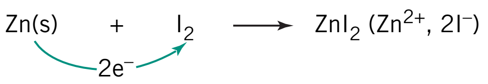


Figure 7.5 Oxidation–reduction reactions are electron transfer processes.

In each of these reactions, the first species donates electrons and is therefore oxidised. The second species accepts the electrons and is therefore reduced.

A substance that causes the oxidation of another substance is called an *oxidising agent* or *oxidant*. It must itself be reduced and therefore be an electron acceptor. In the preceding reactions, the second reactant in each case is an oxidising agent and has accepted electrons. Substances that are readily reduced, such as chlorine and oxygen, are commonly used oxidising agents.

A *reducing agent* or *reductant* is a substance that causes the reduction of another substance. It must be an electron donor and itself undergo oxidation. The first species in the reactions above are reducing agents, as each has donated electrons. Reactive metals, such as magnesium and zinc, are commonly used reducing agents because they tend to donate electrons readily.



Zn	• donates electrons	• is oxidised	• is the reducing agent
I_2	• accepts electrons	• is reduced	• is the oxidising agent

Figure 7.6 The substance oxidised is a reducing agent; the substance reduced is an oxidising agent.

Half-equations

It is useful to consider oxidation–reduction equations in two parts. One part represents the oxidation reaction and the other represents the reduction reaction. Each part is called a *half-equation* as it represents half of the reaction that has occurred. For example, when magnesium reacts with oxygen, the two half-equations are:

Oxidation: $Mg(s) \rightarrow Mg^{2+}(s) + 2e^-$

Reduction: $O_2(s) + 4e^- \rightarrow 2O^{2-}(s)$

As another example, consider the reaction of sodium burning in chlorine gas. This reaction is represented by the equation:

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

The two half-equations are:

Oxidation: $Na(s) \rightarrow Na^+(s) + e^-$

Reduction: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$

Note that half-equations are balanced for charge as well as atoms.

Review exercise 7.5

1 **Identify** the species being oxidised and that being reduced in each of the following.
- **a** $2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$
- **b** $PbO(s) + CO(g) \rightarrow Pb(s) + CO_2(g)$
- **c** $Mg(s) + S(l) \rightarrow MgS(s)$
- **d** $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
- **e** $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
- **f** $Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$

2 **Identify** the oxidising agent and the reducing agent in each of the following.
- **a** $Cl_2(g) + 2Br^-(aq) \rightarrow Br_2(l) + 2Cl^-(aq)$
- **b** $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$
- **c** $2Ag^+(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2Ag(s)$
- **d** $2I^-(aq) + Br_2(l) \rightarrow 2Br^-(aq) + I_2(s)$

3 **Balance** the following half-equations.

- **a** $Mg(s) \rightarrow Mg^{2+}(aq)$
- **b** $Na(s) \rightarrow Na^{+}(aq)$
- **c** $H^{+}(aq) \rightarrow H_2(g)$
- **d** $Cl_2(g) \rightarrow Cl^{-}(aq)$

4 **Construct** oxidation and reduction half-equations for the following reactions.

- **a** $2Na(s) + F_2(g) \rightarrow 2NaF(s)$
- **b** $2Ca(s) + O_2(g) \rightarrow 2CaO(s)$
- **c** $Mg(s) + 2H^{+}(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$
- **d** $Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

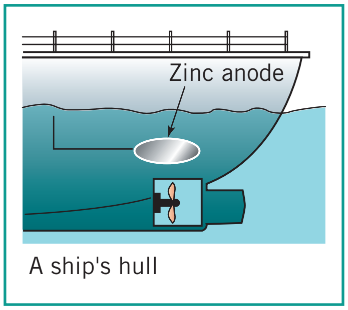
7.6 Metals for different purposes

The uses of a particular metal are determined not only by its physical properties (Units 3.4 and 6.2) but also by its reactivity. Gold, silver and platinum are quite unreactive and undergo little or no corrosion. Because these metals do not readily tarnish, they retain their shiny lustre and make attractive jewellery. Gold is the least reactive of all metals. This has been known since ancient times and throughout history it has been used to make jewellery and fine ornaments. Because gold is an excellent conductor of electricity and does not tarnish, it is also widely used in electrical connections in computer and electronic circuits. Gold also has several applications in the space industry as it is an excellent reflector of infra-red radiation and is chemically inert. For example, the umbilical cord joining astronaut Edward White to his spacecraft during the first 'walk' in space was plated with gold to reflect thermal radiation. Gold was also used on the undercarriage of the *Apollo 11* lunar module, which first placed humans on the moon.

Magnesium is a highly reactive metal and some of its uses are a result of this reactivity. For example, magnesium is used in the cathodic protection of less reactive metals to protect them from corrosion. Steel ships and wharves may have large blocks of magnesium attached to them. Since magnesium is more reactive than the iron in the steel it will corrode first, thus protecting the ship or wharf from corrosion. For this reason the magnesium is called a *sacrificial anode*.

When magnesium burns in oxygen it produces a bright white light. Because of the intensity of this light, magnesium was used in photographic flashbulbs and it continues to be used in modern fireworks.

Owing to its high reactivity, the uses of calcium are restricted to situations where its reactivity can be used to advantage. Calcium is added to some steels to remove any remaining traces of oxygen, sulfur and phosphorus. It is also used in electronic vacuum tubes because it combines with any traces of oxygen that remain, producing a better vacuum.



Figures 7.7 and 7.8 Magnesium, zinc or aluminium blocks are attached to the hull of steel ships to protect them from corrosion.

Zinc is used extensively in galvanised iron production. The galvanised iron is produced by dipping iron into molten zinc. The zinc serves two purposes. First, the zinc forms a protective coating for the iron, excluding oxygen and therefore protecting the iron from rusting. The zinc reacts with the air to form an impervious layer that protects it from corrosion. The second way in which the zinc protects the iron from corrosion is that, in the event that the zinc coating of the iron is damaged, the zinc acts as a sacrificial anode and corrodes in preference to the iron.

The reactivity of zinc also makes it suitable for use in batteries such as dry cells (torch batteries) and button cells (in watches). In these cells the zinc is oxidised and the electrons it loses travel through an external circuit, producing an electric current.

Tin and chromium are used widely to coat a base metal, usually steel, in many applications. This use is due to the low reactivity of these metals together with their shiny appearance. 'Tin' cans commonly used as packaging for foods such as soups, baked beans and canned fruit are actually steel cans coated in tin. The bumper bars of many older cars and so-called chrome trimmings are usually steel coated with chromium metal. Both tin and chromium form an impervious oxide layer that protects the underlying metal from corrosion.

Copper, aluminium and titanium are also widely used because of their low reactivity and/or their resistance to corrosion. Copper is used extensively in the plumbing industry because of its ability to resist corrosion. Unlike the cheaper alternative, iron, copper does not react with hot water and is ideal for hot water tanks and pipes. Aluminium, because of its ability to form a protective oxide layer and its light weight, is extensively used in the building industry. Titanium is used in holding tanks and pipes in desalination plants, which convert sea water into fresh water, and factories producing or using acids. The ability of titanium to resist corrosion makes it an ideal metal in these corrosive environments.

❇ Review exercise 7.6

1 **Account** for the following uses of gold in terms of its reactivity:
   - **a** a wedding ring
   - **b** a component of electrical circuits.

2 **Explain** why more expensive copper pipes are used for carrying hot water rather than cheaper iron pipes.

3 **Propose** why huge aluminium bars are attached to off-shore gas platforms (constructed of steel).

4 **Assess** whether copper would be a suitable sacrificial anode for a steel ship.

*KEY POINTS

- Metals vary in their reactivity with oxygen, water and dilute acids.
- Most metals react with oxygen in an oxidation–reduction process to form a metal oxide. This process is also known as corrosion.
- Reactive metals will burn in air.
- Gold, platinum and silver do not react with oxygen.
- Rusting involves the oxidation of iron by oxygen in the air under moist conditions.
- Some metals such as aluminium form an oxide layer that protects the metal beneath from further corrosion.
- Reactive metals react with water to form hydrogen gas and either an oxide or a hydroxide.
- Most metals react with dilute hydrochloric acid and dilute sulfuric acid to produce a salt and hydrogen gas.
- Gold, platinum, silver, mercury and copper do not react with dilute hydrochloric acid or dilute sulfuric acid.
- By comparing the reactivity of metals it is possible to rank them in an activity series.
- Ionisation energy is the amount of energy required to remove the most loosely bound electron from a gaseous atom.
- Metals on the left-hand side of the periodic table tend to have lower ionisation energies than metals in the middle of the periodic table.
- Metals with low ionisation energies are generally more reactive than those with higher ionisation energies.
- The uses of metals are often related to their reactivity as well as their physical properties.
- Oxidation–reduction (redox) reactions involve the transfer of electrons from one species to another.
- Oxidation and reduction occur simultaneously.
- Oxidation can be defined as the loss or donation of electrons.
- Reduction can be defined as the gain or acceptance of electrons.
- An oxidising agent causes the oxidation of another species and is itself reduced.
- A reducing agent causes the reduction of another species and is itself oxidised.
- An oxidation half-equation shows loss of electrons. A reduction half-equation shows gain of electrons.

- A summary of the reactions covered in this chapter is given in Table 7.5.

Table 7.5

Metal	Reaction with oxygen	Reaction with water	Reaction with dilute acids
K Na Ca	Burn readily to form oxides	React with cold water to form H_2 and hydroxides	React with cold dilute acids to form H_2 and salts
Mg		React with hot water to form H_2 and oxide	
Al Zn Cr Fe Cd Co Ni	Burn to form oxides if finely divided	When heated strongly react with steam or superheated steam to form H_2 and oxides	
Sn Pb	React slowly if heated in air or pure oxygen	No reaction	React with warm dilute acids to form H_2 and salts
Cu Ag			No reaction
Hg Pt Au	No reaction		

✱APPLICATION AND INVESTIGATION

1 **Account** for the fact that the surface of aluminium appears dull rather than shiny.

2 For each of the following mixtures, **predict** whether a reaction will take place. If so, write a balanced equation. If not, write 'no reaction'.

- **a** lead and water
- **b** silver and dilute hydrochloric acid
- **c** powdered zinc and oxygen when heated
- **d** iron and dilute sulfuric acid
- **e** copper and dilute hydrochloric acid

3 Given a piece of titanium metal, **describe** how you could determine its position in the activity series.

4 W, X, Y and Z are metals.

Y reacts with dilute hydrochloric acid and steam but not with hot or cold water.

W does not react with water, steam or dilute hydrochloric acid.

X reacts vigorously with cold water.

Z reacts with hot water.

- **a** **Arrange** these metals in decreasing order of reactivity, that is, from most reactive to least reactive.
- **b** **Identify** metals that could be W, X, Y and Z.

➲ **Investigation**

5 Gather information from appropriate secondary sources to **identify** the ionisation energies of the first 20 elements in the periodic table. Plot a graph of these as a function of atomic number and **identify** any trends.

6 **Explain** why most metals in the Earth's crust are found combined with other elements.

7 **Construct** equations for the reactions that occur when aluminium reacts with:

- **a** dilute hydrochloric acid
- **b** dilute sulfuric acid.

8 **Define** oxidation and reduction in terms of the following:

- **a** oxygen exchange
- **b** electron exchange.

9 **Identify** the oxidising agent in each of the following reactions:

- **a** $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$
- **b** $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
- **c** $Zn(s) + Cl_2(g) \rightarrow ZnCl_2(s)$

10 Rewrite each of the following as two half-equations and label each as oxidation or reduction.

- **a** $2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$
- **b** $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$
- **c** $SnO_2(s) + 2H_2(g) \rightarrow Sn(s) + 2H_2O(l)$

11 **Explain** why hot water tanks are made of copper, yet cold water tanks are made of steel (an alloy of iron).

12 Some hot water tanks are made of steel. **Account** for the practice of suspending a bar of magnesium metal in the water in these tanks.

13 Although gold is commonly found and used as a free element, it also forms compounds. **Identify** the names of some gold compounds. ⊂ **Investigation**

14 Iron is galvanised by coating it with a thin layer of zinc. The zinc itself forms a protective layer by reaction with gases in the atmosphere. ⊂ **Investigation**

- **a** **Identify** the nature of the protective layer formed by the zinc and the chemical reactions involved in its formation.
- **b** **Identify** the chemical reactions that occur during the rusting of iron and explain how the zinc interferes in this process if the zinc coating on the iron is damaged.

CHAPTER 8

THE PERIODIC TABLE

Although a number of metals had been known since ancient times, the beginning of the nineteenth century marked a dramatic increase in the rate at which new elements were being discovered (Figure 8.1). The majority of these discoveries were metals. As new elements were discovered and their physical and chemical properties established, chemists attempted to classify them in some sort of systematic way. The development of the periodic table is an excellent example of how scientific ideas develop as new information becomes available.

Discovery period	Elements in order of discovery										Total number known
ancients	C	S	Au	Cu	Ag	Fe	Pb	Sn	Hg		9
alchemists	Sb	As	Zn	Bi	P						14
1735–1745	Co	Pt									16
1745–1755	Ni										17
1755–1765											
1765–1775	H	N	O	Cl	Mn	F					23
1775–1785	Mo	Te	W								26
1785–1795	U	Zr	Sr	Ti	Y						31
1795–1805	Cr	Be	V	Nb	Ta	Ce	Pb	Rh	Os	Ir	41
1805–1815	K	Na	Ba	Ca	Mg	B	I				48
1815–1825	Li	Cd	Se	Si							52
1825–1835	Al	Br	Th								55
1835–1845	La	Tb	Er	Ru							59
1845–1855											
1855–1865	Cs	Rb	Ti	In							63
1865–1875											
1875–1885	Ga	Yb	Sm	Sc	Ho	Tm					69
1885–1895	Pr	Nd	Gd	Dy	Ge	Ar					75
1895–1905	He	Eu	Kr	Ne	Xe	Po	Ra	Ac	Rn		84
1905–1915	Lu										85
1915–1925	Hf	Pa									87
1925–1935	Re										88
1935–1945	Tc	Fr	At	Np	Pu	Cm					94
1945–1955	Am	Pm	Bk	Cf	Es	Fm					100
1955–1965	Md	No	Lr								103
1965–1999	Db	Rf	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		112

Figure 8.1 The order of discovery of the elements

8.1 Development of the periodic table

Antoine Lavoisier (1734–1794)

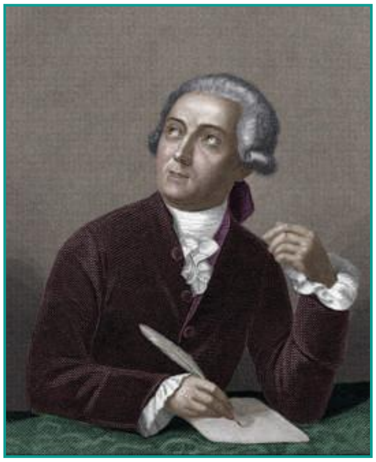


Figure 8.2 Antoine Lavoisier is considered by many to be the father of modern chemistry. Despite his great contributions to chemistry, he was guillotined in 1794 during the French Revolution for his role as a tax collector.

In 1789, Antoine Lavoisier published a table of 33 ‘elements’. His list included some substances now known to be compounds, such as calcium oxide (lime) and silicon dioxide (silica), which at that time could not be broken down into simpler substances. Lavoisier divided his table into metals and non-metals and thus had begun the process of classification of the elements.

Johann Döbereiner (1780–1849)

In 1829, the German chemist Johann Döbereiner reported that several groups, each containing three elements, shared similar physical and chemical properties. He called these groups *triads*. His triads included:

- chlorine, bromine and iodine
- sulfur, selenium and tellurium
- calcium, strontium and barium
- lithium, sodium and potassium.

Döbereiner also noted that when the three elements were arranged in order of increasing atomic mass, the middle element had properties intermediate between the other two, and the atomic mass of the middle element was very nearly the same as the average of the other two.

Figure 8.3 Johann Döbereiner arranged elements exhibiting similar characteristics into groups of three called triads.

Table 8.1 Döbereiner's triads

Triad	Atomic mass	Density (g cm^{-3})	Formula of chloride
Lithium	7	0.53	LiCl
Sodium	23	0.97	NaCl
Potassium	39	0.86	KCl
Calcium	40	1.55	$CaCl_2$
Strontium	88	2.6	$SrCl_2$
Barium	137	3.50	$BaCl_2$

Döbereiner's important contribution to the development of the periodic table was to group elements according to similarities in physical and chemical properties. As new elements were discovered and the atomic masses of more elements became known, other chemists including William Olding discovered new triads and extended some groups to include four or five elements. For example, fluorine was added to the group containing chlorine, bromine and iodine, based on its similarities with the members of this triad.

CHEMISTRY CONTEXT

❇ AN ALTERNATIVE PERIODIC TABLE

Alexandre-Emile Beguyer de Chancourtois (1820–1886)

In 1862 Beguyer de Chancourtois constructed a table of the elements in the form of a helix or 'telluric screw', constructed on a vertical cylinder. The elements were arranged in order of increasing atomic mass in a spiral pattern. Atomic mass was plotted vertically and each rotation of the cylinder corresponded to 16 atomic mass units. Elements with similar properties were arranged directly above one another as shown in Figure 8.4. This classification suggested the regular or periodic recurrence of properties of the elements.

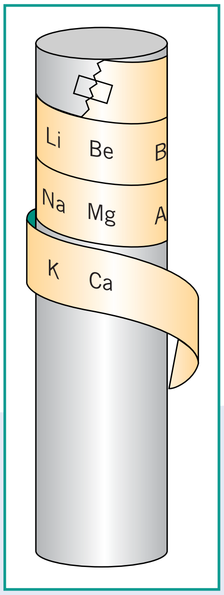


Figure 8.4 The telluric screw shows families of elements arranged vertically.

John Newlands (1837–1898)

In 1864, using 62 elements of known atomic mass, John Newlands observed that the properties of the elements varied periodically with their atomic masses. A year later he published his 'law of octaves' by analogy with the seven intervals of the musical scale. Note that at this stage the noble gases had not been discovered. The elements were divided into seven groups with properties closely related to the first seven elements then known: hydrogen, lithium, beryllium, boron, carbon, nitrogen and oxygen. Newlands stated that when the elements are arranged in order of increasing atomic mass, 'the eighth element starting from a given one is a kind of repetition of the first'. In other words, there is a periodic pattern of properties repeated every seven elements. To make his octaves fit, Newlands occasionally placed two elements in the same position, for example, cobalt and nickel share position 22. In other places in his table he grouped quite dissimilar elements together, for example, copper and silver were placed with lithium, sodium and potassium. For these reasons his work was largely dismissed and even ridiculed. Some unkind scientists claimed that if the elements were arranged alphabetically instead of in order of increasing atomic mass an even better periodic trend might be observed. It was only later that Newlands' contribution to the development of the periodic table was appreciated. He was the first to clearly recognise the periodicity of properties.

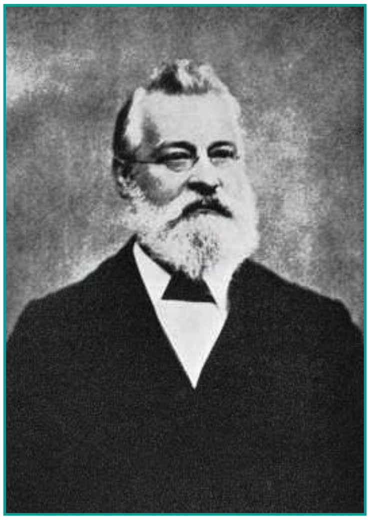


Figure 8.5 John Newlands arranged elements in order of increasing atomic mass. He noticed a repeating pattern every seven elements, which he called 'the law of octaves'.

H 1	**Li** 2	**Be** 3	**B** 4	**C** 5	**N** 6	**O** 7
F 8	9	**Na** 10	**Mg** 11	**Al** 12	**Si** 13	**P S** 14
Cl 15	**K** 16	**Ca** 17	**Cr** 18	**Ti** 19	**Mn** 20	**Fe** 21
Co, Ni 22	**Cu** 23	**Zn** 24	**Y** 25	**In** 26	**As** 27	**Se** 28
Br 29	**Rb** 30	**Sr** 31	**Ce, La** 32	**Zr** 33	**Di, Mo** 34	**Ro, Ru** 35
Pd 36	**Ag** 37	**Cd** 38	**Sn** 39	**U** 40	**Sb** 41	**Te** 42
I 43	**Cs** 44	**Ba, V** 45	**Ta** 46	**W** 47	**Nb** 48	**Au** 49
Pt, Ir 50	**Os** 51	**Hg** 52	**Tl** 53	**Pb** 54	**Bi** 55	**Th** 56

Figure 8.6 Newlands' arrangement of the known elements into seven columns ('octaves')

Lothar Meyer (1830–1895)

In 1869, Dmitri Mendeleev in Russia and Lothar Meyer in Germany, working independently of one another, published similar schemes for the classification of the elements.

Meyer arranged the elements in order of increasing atomic mass and placed them in groups based on their 'combining power' or 'valency', the number of bonds an element can form.

I	II	III	IV	V	VI	VII	VIII	IX
	B = 11.0	Al = 27.3	–	–	–	?In = 113.4	–	Tl = 202.7
	C = 11.97	Si = 28		–		Sn = 117.8	–	Pb = 206.4
			Ti = 48		Zr = 89.7			
	N = 14.01	P = 30.9		As = 74.9		Sb = 112.1		Bi = 207.5
			V = 51.2		Nb = 93.7		Ta = 182.2	
	O = 15.96	S = 31.98		Se = 78		Te = 128?		–
			Cr = 52.4		Mo = 95.6		W = 183.5	
	F = 19.1	Cl = 35.38		Br = 79.75		J = 126.5		–
			Mn = 54.8		Ru = 103.5		Os = 198.6?	
			Fe = 55.9		Rh = 104.1		Ir = 196.7	
			Co = Ni = 58.6		Pd = 106.2		Pt = 196.7	
Li = 7.01	Na = 22.99	K = 39.04		Rb = 85.2		Cs = 132.7		–
			Cu = 63.3		Ag = 107.66		Au = 196.2	
?Be = 93	Mg = 23.9	Ca = 39.9		Sr = 87.0		Ba = 136.8		–
			Zn = 64.9		Cd = 111.6		Hg = 199.8	

Differenz von I zu II und von II zu III ungefähr = 16.
Differenz III zu V, IV zu VI, V zu VII schwankend um 46.
Differenz VI zu VIII, von VII zu IX = 88 bis 92.

Figure 8.7 Meyer's periodic table based on valency

Meyer also plotted graphs of the physical properties of the elements as a function of atomic mass. These graphs clearly demonstrated the periodic variation in physical properties such as melting point, boiling point, density and atomic volume, as shown in Figure 8.8.

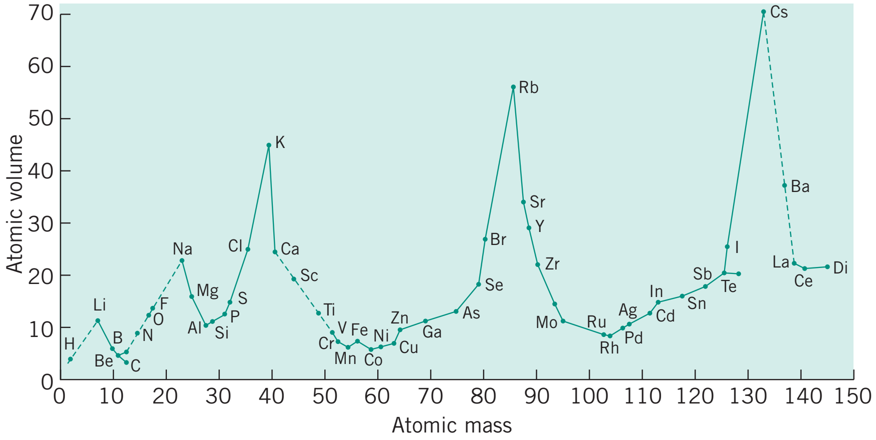


Figure 8.8 Meyer's plot of atomic volume against atomic mass shows a distinct periodic pattern.

Mendeleev (1834–1907)

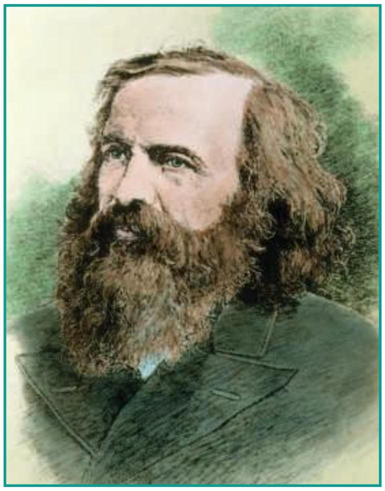


Figure 8.9 Dmitri Mendeleev, 'father' of the periodic table

Mendeleev arranged the elements in horizontal rows in order of increasing atomic mass. Elements with similar properties were arranged in vertical columns in the table. As a result of his work, Mendeleev proposed his periodic law, which states that 'the properties of elements are periodic functions of their atomic masses'. Figure 8.10 shows part of Mendeleev's periodic table.

Elements such as lithium, sodium and potassium, which are all very reactive metals and have many similar properties, were placed in one vertical group. Similarly, the elements fluorine, chlorine and bromine, which are very reactive non-metals that have similar properties, were placed in another common group. Although Meyer and Mendeleev came to essentially the same conclusion about the periodic recurrence of properties, most of the credit for the periodic table goes to Mendeleev. This is because Mendeleev was able to make accurate predictions about elements that had not been discovered. Mendeleev left gaps in his table for elements that

	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
Period 1	H							
Period 2	Li	Be	B	C	N	O	F	
Period 3	Na	Mg	Al	Si	P	S	Cl	
Period 4	K Cu	Ca Zn	? ?	Ti ?	V As	Cr Se	Mn Br	Fe Co Ni
Period 5	Rb Ag	Sr Cd	Y In	Zr Sn	Nb Sb	Mo Te	? I	Ru Rh Pd

Figure 8.10 Mendeleev's periodic table

he thought must exist but were unknown. He suggested that elements would be discovered to fill these gaps and also predicted properties for some of the missing elements and their compounds. Some of the missing elements were discovered within Mendeleev's lifetime and their properties coincided very closely with his predictions. For example, in his periodic table, Mendeleev left a gap for an element between silicon and tin, which he called eka-silicon, which literally means the 'next after silicon'. In 1871 Mendeleev predicted the properties of eka-silicon on the basis of the properties of known adjacent elements in the table. In 1886 the element germanium was discovered and found to have properties very similar to those predicted by Mendeleev for eka-silicon. Table 8.2 outlines the properties of germanium compared with those predicted by Mendeleev for eka-silicon.

Table 8.2 Properties of germanium compared with those predicted by Mendeleev for eka-silicon

Properties of eka-silicon (Es) as predicted by Mendeleev	Observed properties of germanium (Ge) discovered in 1886
Colour grey	Colour grey
Atomic mass 72	Atomic mass 72.6
Density 5.5 g cm^{-3}	Density 5.4 g cm^{-3}
Oxide has formula EsO_2 and density 4.7 g cm^{-3}	Oxide has formula GeO_2 and density 4.2 g cm^{-3}
Chloride has formula $EsCl_4$ and density 1.9 g cm^{-3}	Chloride has formula $GeCl_4$ and density 1.9 g cm^{-3}

The accuracy of Mendeleev's predictions quickly convinced scientists that his ideas were correct, and his periodic table was accepted as a valuable overall summary of the properties of the elements. When Mendeleev constructed the periodic table by arranging the elements in order of increasing atomic mass, he recognised that there were several inconsistencies in the location of certain elements with respect to their properties. For example, the properties of iodine are similar to those of bromine, yet according to its atomic mass iodine should have been placed under selenium. Mendeleev solved the problem by changing the position of tellurium (Te) and iodine, so as to put tellurium under selenium (Se) and iodine under bromine. This portion of the periodic table is illustrated in Figure 8.11.

Group V	Group VI	Group VII
N 14.0	O 16.0	F 19.0
P 31.0	S 32.1	Cl 35.5
As 74.9	Se 79.0	Br 79.9
Sb 121.8	Te 127.6	I 126.9

Figure 8.11 The position of tellurium and iodine in the periodic table—an exception to the arrangement of elements in order of increasing atomic mass

Discovery of the noble gases

Mendeleev's periodic table did not include any of the group VIII elements (the noble or inert gases), because these elements had not been discovered at that time. However, in the period 1893–1898, William Ramsay and co-workers discovered five gases from that group—argon, helium, krypton, neon and xenon. Argon was the first noble gas isolated when Ramsay and Lord Rayleigh made a deliberate attempt to identify any unknown elements in the atmosphere. A year later, Ramsay isolated a new noble gas when the uranium mineral clevite was dissolved in acid. This element exhibited the same spectral lines as those recorded about 30 years earlier as belonging to an element, helium, not previously known on earth but present in the sun. The other three noble gases discovered in this period, krypton, neon and xenon, were isolated from the atmosphere where they occur as minor constituents. The discovery of these elements led to the inclusion of an additional group or column in the periodic table.

Henry Moseley (1887–1915)

The irregularities in Mendeleev's table were clarified when the English physicist Henry Moseley proposed the concept of atomic number in 1913. The atomic number is the number of protons in the nucleus of an atom (Unit 3.1). This also equals the number of electrons surrounding the nucleus in a neutral atom. It was eventually recognised that the fundamental factor that determines chemical properties is atomic number rather than atomic mass. On the basis of atomic number, tellurium, with atomic number 52, and iodine, with atomic number 53, fell into their correct vertical groups. The modern version of the periodic law is better stated as: 'When the elements are listed in order of increasing atomic number, similar chemical properties recur periodically'. The periodic variation of elements' properties was better understood when it was realised that these properties are determined by the electron structure of atoms, in particular the valence or outer energy level electron configuration. From this knowledge it is possible to explain a modern version of the periodic table.

❇ Review exercise 8.1

1 **Propose** why Döbereiner rejected carbon, oxygen and nitrogen as a triad even though the atomic mass of nitrogen (14) is equal to the average of the atomic masses of carbon (12) and oxygen (16).

2 **Outline** the major flaws in Newlands' periodic table that led to his work being dismissed.

3 a **Explain** how Mendeleev knew where to leave gaps for undiscovered elements in his periodic table.
  b **Describe** how Mendeleev was able to so accurately predict the properties of 'eka-silicon'.

4 a **Explain** why Mendeleev's periodic table initially did not include the noble gases.
  b **Account** for the fact that the noble gases remained undiscovered until late in the nineteenth century.

5 **Recount** the modern statement of the periodic law.

8.2 The modern periodic table

In the modern periodic table, the symbols for the elements are placed in order of increasing atomic number and are arranged into groups and periods (see Figure 8.12).

Periods

The horizontal rows in the periodic table are called *periods*. The periods contain different numbers of elements. The first period contains only hydrogen (H) and helium (He). The second period contains eight elements starting with lithium (Li) and ending with neon (Ne). There is a steady change in the properties of the elements across periods. In the third period, for example, there is a decrease in the metallic properties of the elements starting with the highly reactive metal, sodium (Na), and ending with argon (Ar), an unreactive gas. These trends are discussed in more detail in Unit 8.3.

Groups

The vertical columns in the periodic table are called *groups* and are numbered I and II on the left-hand side, and III to VIII on the right-hand side.* The most obvious difference between the periodic table shown in Figure 8.12 and that proposed by Mendeleev is the removal of a set of elements known as the *transition elements* from the simple groups. In period four, for example, ten transition elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) have been removed from the simple groupings suggested by Mendeleev and placed in the modern periodic table between Ca in group II and Ga in group III.

Elements within a particular group share some similarities in properties. The group I elements lithium to caesium are all soft metals with relatively low melting points and are very reactive. These elements, the alkali metals, have only one valence electron and readily form +1 ions in their reactions.

The group II elements, the alkaline earth metals, are also very reactive but not as reactive as the alkali metals. They have two valence electrons and tend to form +2 ions in their reactions.

The group VII elements, the halogens, are very reactive non-metals. These elements all exist as diatomic molecules (X_2). The halogens have a strong attraction for electrons—they are said to have high *electronegativities*—with fluorine having the strongest attraction of all the elements. In their reactions with metals the halogens tend to form ions with a –1 charge, as each atom gains an electron from the metal. For example, magnesium burns in chlorine to form magnesium chloride ($MgCl_2$).

The elements in group VIII, helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn), exist as simple atoms and are all unreactive gases. They are the least reactive of all the elements and until the 1960s it was thought that they did not form any compounds at all. However, in 1962 Neil Bartlett found that xenon could form compounds with other elements, in particular with highly reactive fluorine. Examples of compounds of xenon that have been prepared are XeF_2, XeF_4 and XeF_6. Because of this the group VIII elements are now known collectively as the noble gases rather than the inert gases.

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* In an alternative system, groups in the periodic table are numbered 1 through 18 from left to right. References to groups in this textbook use the roman numerals I to VIII.

KEY

3 ← Atomic number
Lithium ← Name of element
Li ← Symbol of element
6.94 ← Atomic mass

I	II	IIIa	IVa	Va	VIa	VIIa	VIII			Ib	IIb	III	IV	V	VI	VII	VIII
																	2 Helium **He** 4.00
3 Lithium **Li** 6.94	4 Beryllium **Be** 9.01								1 Hydrogen **H** 1.008			5 Boron **B** 10.8	6 Carbon **C** 12.0	7 Nitrogen **N** 14.0	8 Oxygen **O** 16.0	9 Fluorine **F** 19.0	10 Neon **Ne** 20.2
11 Sodium **Na** 23.0	12 Magnesium **Mg** 24.3											13 Aluminium **Al** 27.0	14 Silicon **Si** 28.1	15 Phosphorus **P** 31.0	16 Sulfur **S** 32.1	17 Chlorine **Cl** 35.5	18 Argon **Ar** 39.9
19 Potassium **K** 39.1	20 Calcium **Ca** 40.1	21 Scandium **Sc** 45.0	22 Titanium **Ti** 47.9	23 Vanadium **V** 50.9	24 Chromium **Cr** 52.0	25 Manganese **Mn** 54.9	26 Iron **Fe** 55.8	27 Cobalt **Co** 58.9	28 Nickel **Ni** 58.7	29 Copper **Cu** 63.5	30 Zinc **Zn** 65.4	31 Gallium **Ga** 69.7	32 Germanium **Ge** 72.6	33 Arsenic **As** 74.9	34 Selenium **Se** 79.0	35 Bromine **Br** 79.9	36 Krypton **Kr** 83.8
37 Rubidium **Rb** 85.5	38 Strontium **Sr** 87.6	39 Yttrium **Y** 88.9	40 Zirconium **Zr** 91.2	41 Niobium **Nb** 92.9	42 Molybdenum **Mo** 95.9	43 Technetium **Tc** (98)	44 Ruthenium **Ru** 101.1	45 Rhodium **Rh** 102.9	46 Palladium **Pd** 106.4	47 Silver **Ag** 107.9	48 Cadmium **Cd** 112.4	49 Indium **In** 114.8	50 Tin **Sn** 118.7	51 Antimony **Sb** 121.8	52 Tellurium **Te** 127.6	53 Iodine **I** 126.9	54 Xenon **Xe** 131.3
55 Cesium **Cs** 132.9	56 Barium **Ba** 137.3	57 Lanthanum **La** 138.9	72 Hafnium **Hf** 178.5	73 Tantalum **Ta** 180.9	74 Tungsten **W** 183.9	75 Rhenium **Re** 186.2	76 Osmium **Os** 190.2	77 Iridium **Ir** 192.2	78 Platinum **Pt** 195.1	79 Gold **Au** 197.0	80 Mercury **Hg** 200.6	81 Thallium **Tl** 204.4	82 Lead **Pb** 207.2	83 Bismuth **Bi** 209.0	84 Polonium **Po** (209)	85 Astatine **At** (210)	86 Radon **Rn** (222)
87 Francium **Fr** (223)	88 Radium **Ra** 226	89 Actinum **Ac** 227	104 Rutherfordium **Rf** (261)	105 Dubnium **Db** (262)	106 Seaborgium **Sg** (263)	107 Bohrium **Bh** (262)	108 Hassium **Hs** (269)	109 Meitnerium **Mt** (266)	110 Ununnilium **Uun** (269)	111 Unununium **Uuu** (272)	112 Ununbium **Uub** (277)						

Lanthanides	58 Cerium **Ce** 140.1	59 Praseodymium **Pr** 140.9	60 Neodymium **Nd** 144.2	61 Promethium **Pm** (145)	62 Samarium **Sm** 150.4	63 Europium **Eu** 152.0	64 Gadolinium **Gd** 157.2	65 Terbium **Tb** 158.9	66 Dysprosium **Dy** 162.5	67 Holmium **Ho** 164.9	68 Ersium **Er** 167.3	69 Thulium **Tm** 168.9	70 Ytterbium **Yb** 173.0	71 Lutetium **Lu** 175.0
Actinides	90 Thorium **Th** 232.0	91 Protactinium **Pa** 231.0	92 Uranium **U** 238.0	93 Neptunium **Np** 237	94 Plutonium **Pu** (244)	95 Americium **Am** (243)	96 Curium **Cm** (247)	97 Berkelium **Bk** (247)	98 Californium **Cf** (251)	99 Einsteinium **Es** (252)	100 Fermium **Fm** (257)	101 Mendelevium **Md** (258)	102 Nobelium **No** (259)	103 Lawrencium **Lr** (260)

Figure 8.12 The modern periodic table

Hydrogen—an unusual element

The position of hydrogen in the periodic table presents something of a dilemma. Often hydrogen is placed in group I, above lithium. Although hydrogen is similar to the alkali metals in that it has one valence electron, it shares very few physical or chemical properties with the group I metals. It is a non-metallic covalent molecular substance, existing as diatomic H_2 molecules rather than forming a metallic lattice. Sometimes hydrogen is classified as a group VII element because it is one electron short of a noble gas electron configuration. This is not a very satisfactory classification either, as hydrogen does not form –1 ions as readily as the halogens. In fact, hydrogen does not fit readily in any group of the periodic table. For this reason hydrogen is placed by itself in some periodic tables.

Metals and non-metals

As described in Unit 2.4, a diagonal line is marked from the top of the third group of the periodic table to the lower right corner. This diagonal separates metals to the left and below the diagonal from non-metals to the right and above the diagonal. Hydrogen is an exception to this generalisation. Elements adjacent to the diagonal, such as silicon, germanium and arsenic, are sometimes difficult to classify as metals or non-metals. They are referred to as *semi-metals*.

Transition metals

The *transition metals* are the 'middle' block, which comprises 10 columns of the periodic table. The transition metals occur in the fourth, fifth and sixth rows of the periodic table. The electron configurations of the 10 fourth-row transition metals are given in Table 8.3. In these elements the third electron energy level is being filled from 8 to its capacity of 18 electrons. Similarly in the fifth and sixth rows, the transition elements correspond to increasing the numbers of electrons in the fourth and fifth energy levels from 8 to 18.

Table 8.3 Electron configurations of the 10 fourth-row transition elements

Element	Symbol	Atomic number	Electron configuration
Scandium	Sc	21	2, 8, 9, 2
Titanium	Ti	22	2, 8, 10, 2
Vanadium	V	23	2, 8, 11, 2
Chromium	Cr	24	2, 8, 13, 1
Manganese	Mn	25	2, 8, 13, 2
Iron	Fe	26	2, 8, 14, 2
Cobalt	Co	27	2, 8, 15, 2
Nickel	Ni	28	2, 8, 16, 2
Copper	Cu	29	2, 8, 18, 1
Zinc	Zn	30	2, 8, 18, 2

The transition metals share certain common properties, which are listed below.

1. They are hard, fairly dense metals.
2. They have high tensile strength.

3 They are good conductors of heat and electricity.

4 They have high melting and boiling points.

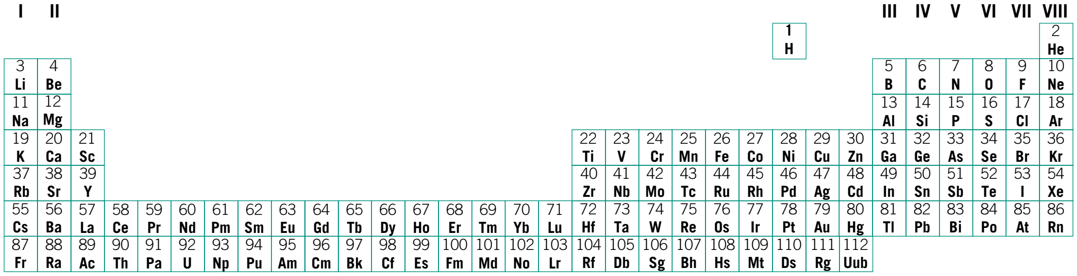
5 They are not as reactive as group I and II metals.

6 They may have various valencies, for example, Fe^{2+} and Fe^{3+}, Cu^{+} and Cu^{2+}.

7 They commonly form coloured compounds.

Lanthanides and actinides

The lanthanide series (elements 58–71) and actinide series (elements 90–103) form another block of elements within the periodic table. In these elements the numbers of electrons in the fourth and fifth energy levels respectively are increasing from 18 to 32. The most common form of the periodic table (for example, Figure 8.12) places these series below the main body of the table. Figure 8.13 is a wide (or long) form of the periodic table, which incorporates the lanthanide and actinide elements within the body of the table.



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

Figure 8.13 The periodic table (wide form)

❇ Review exercise 8.2

1 For the elements listed below, **identify** those that are:

- **a** elements in group VII, the halogens
- **b** elements in the third period
- **c** transition metals.

Ag, Al, Br, Ca, Cl, Cu, F, Fe, Na, Ne, S

2 From the periodic table, **classify** as metals, semi-metals or non-metals the elements Li, Zn, Se, Ce, Te, Br and Xe.

3 **Identify** the pair of elements in the following list that would show the greatest similarity in chemical and physical properties, and **justify** your choice.

Ca, Na, Al, Ba, Cl, C

4 **Identify** the elements that occupy the following positions in the periodic table:

- **a** period 3, group VII
- **b** period 2, group II
- **c** period 5, group VI
- **d** the transition element with 47 protons in the nucleus
- **e** the transition element in the sixth period that is a liquid at room temperature.

5 **Explain** why hydrogen is placed in different positions on different versions of the periodic table.

8.3 Trends in the periodic table

Trends in properties across periods

The development of the periodic table brought a systematic approach to the study of the properties of elements. By organising the elements systematically and recognising trends in the properties of elements, a vast amount of chemical information can be more easily summarised and understood.

In this section the variations in properties of the elements across periods of the periodic table will be examined. Particular attention will be paid to the first 20 elements. Table 8.4 shows values for various physical properties for the first 20 elements. Some of the information in Table 8.4 is also presented graphically in Figures 8.14 to 8.16.

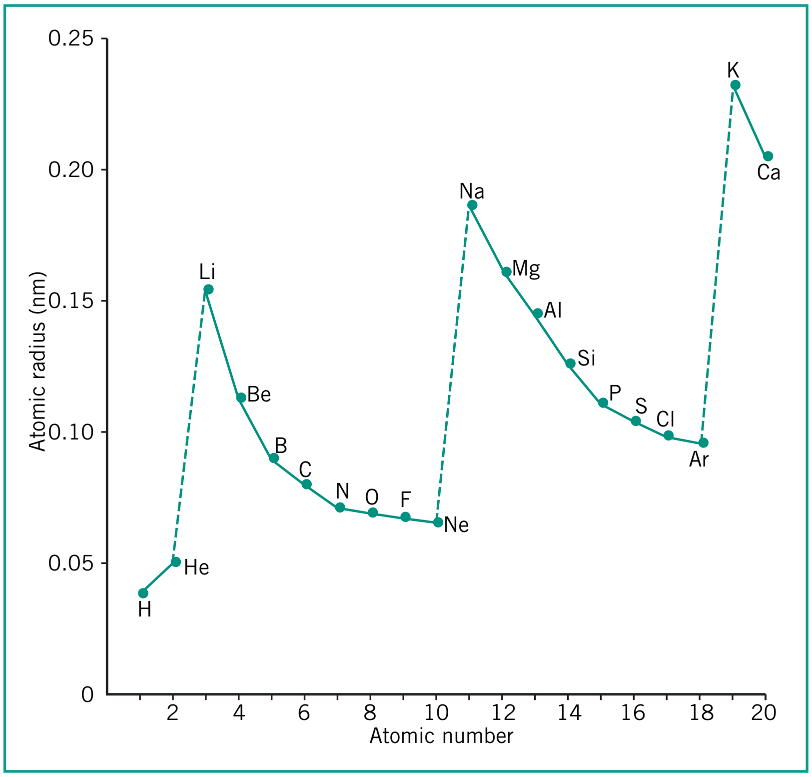


Figure 8.14 Atomic radii of the first 20 elements

By examining the data in Table 8.4 and the graphs in Figures 8.14 to 8.17, the following trends and periodic recurrence of properties are evident:

- Moving from left to right across a period, there is a general decrease in atomic radius (Figure 8.14). The radius decreases because the increasing positive charge of the nucleus attracts the outermost electrons, which are in the same energy level, closer to the nucleus (Figure 8.16).
- The graph of first ionisation energies of the elements as a function of atomic number shows an increase in ionisation energy across each period, reaching a maximum at a noble gas (Figure 8.15). The increase in ionisation energy across a period is due to each successive element having one more proton in its nucleus. The extra electron for successive elements in a period occurs in the same energy level as other valence electrons. There is therefore a gradual increase in the attractive force between the nucleus and the valence electrons, leading to an increase in ionisation energy.

Table 8.4 Various physical properties of the first 20 elements

Element	Symbol	Atomic number	Relative atomic mass	Atomic radius (nm)	Density (g cm^{-3})	Hardness[*] (mohs)	Electrical conductivity[*] (MS m^{-1})	Melting point (°C)	Boiling point (°C)	Ionisation energy (kJ mol^{-1})	Electronegativity	Combining power
Hydrogen	H	1	1.008	0.037	8.2×10^{-5}	–	–	–259	–253	1 318	2.2	1
Helium	He	2	4.003	0.031	1.6×10^{-4}	–	–	–272	–269	2 379	–	0
Lithium	Li	3	6.941	0.152	0.53	0.6	10.6	180	1 342	526	0.98	1
Beryllium	Be	4	9.012	0.112	1.85	–	27	1 278	2 970	906	1.57	2
Boron	B	5	10.81	0.085	2.34	9.5	10^{-10}	2 300	3 660	807	2.04	3
Carbon (graphite)	C	6	12.01	0.077	2.26	0.5	0.07	3 727	4 830	1 093	2.55	4
Carbon (diamond)					3.51	10	10^{-17}	>3 550				
Nitrogen	N	7	14.01	0.075	1.13×10^{-3}	–	–	–210	–196	1 407	3.04	3
Oxygen	O	8	16.00	0.073	1.30×10^{-3}	–	–	–219	–183	1 320	3.44	2
Fluorine	F	9	19.00	0.072	1.63×10^{-3}	–	–	–220	–188	1 687	3.98	1
Neon	Ne	10	20.18	0.071	8.4×10^{-4}	–	–	–249	–246	2 087	–	0
Sodium	Na	11	22.99	0.186	0.97	0.4	21	98	883	502	0.93	1
Magnesium	Mg	12	24.30	0.160	1.74	2	22	650	1 110	744	1.31	2
Aluminium	Al	13	26.98	0.143	2.70	2.8	37	660	2 450	584	1.61	3
Silicon	Si	14	28.09	0.118	2.33	7	10^{-3}	1 410	3 267	793	1.90	4
Phosphorus	P	15	30.97	0.110	1.82	0.5	10^{-15}	44	280	1 018	2.19	3
Sulfur	S	16	32.07	0.103	2.07	2	10^{-21}	113	445	1 006	2.58	2
Chlorine	Cl	17	35.45	0.100	2.91×10^{-3}	–	–	–101	–35	1 257	3.16	1
Argon	Ar	18	39.95	0.098	1.66×10^{-3}	–	–	–189	–189	1 527	–	0
Potassium	K	19	39.10	0.227	0.86	0.5	14	63	760	425	0.82	1
Calcium	Ca	20	40.08	0.197	1.55	1.5	29	839	1 484	596	1.00	2

[*] Values for hardness and electrical conductivity are not applicable to gases.

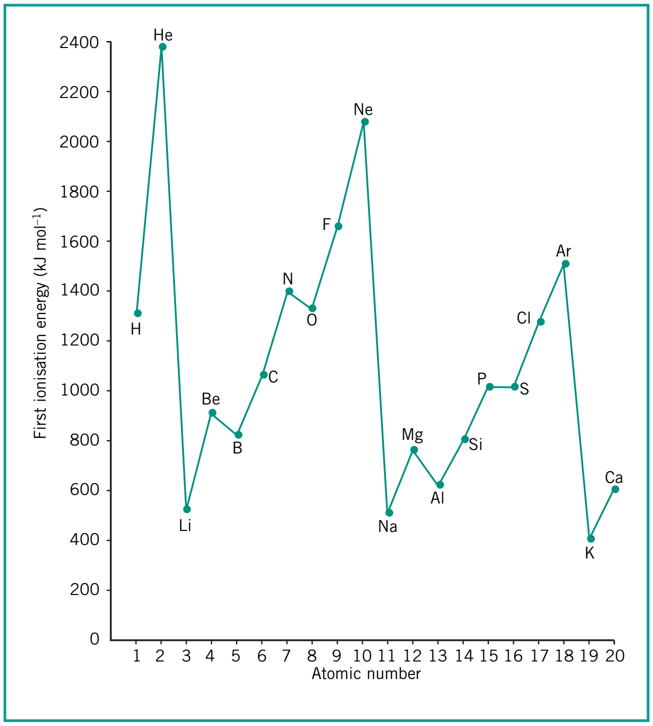


Figure 8.15 First ionisation energies of the first 20 elements

- The melting points and boiling points generally rise to the elements in group IV and then decrease (Figure 8.17).

As was mentioned in Unit 8.1, many properties of elements are determined by the valence or outer energy level electron configurations of the atoms. Because the number of valence electrons varies periodically with the atomic number, it would be expected that the physical and chemical properties would also tend to vary in a periodic manner.

Some other trends across periods in the periodic table can be identified. These include the following, moving across a period from left to right:

- there is an increase in electronegativity of the elements. The electronegativity of an atom is a numerical measure of the electron-attracting power of the atom.
- the elements change from metals through semi-metals to non-metals.

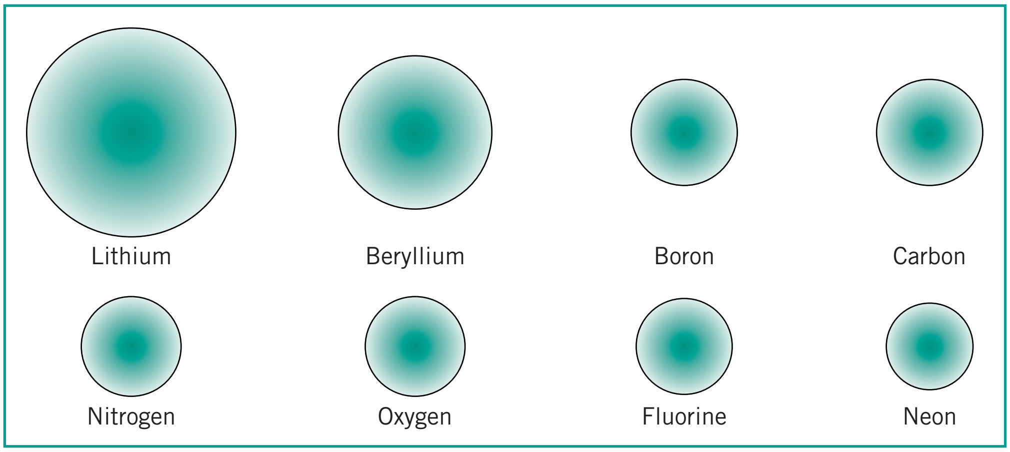


Figure 8.16 The atomic size of Period 2 elements

Table 8.5 Formulas of chlorides and hydrides of the elements in periods 2 and 3

Period 2	Li	Be	B	C	N	O	F	Ne
Formula of chloride	LiCl	$BeCl_2$	BCl_3	CCl_4	NCl_3	Cl_2O	ClF	Does not exist
Formula of hydride	LiH	BeH_2	BH_3 (B_2H_6)	CH_4	NH_3	H_2O	HF	Does not exist
Period 3	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
Formula of chloride	NaCl	$MgCl_2$	$AlCl_3$ (Al_2Cl_6)	$SiCl_4$	PCl_3	SCl_2	Cl_2	Does not exist
Formula of hydride	NaH	MgH_2	AlH_3	SiH_4	PH_3	H_2S	HCl	Does not exist

- the bonding in the elements varies from metallic to covalent network to covalent molecular.
- the electrical and thermal conductivities decrease.
- there is a regular pattern in the combining power of the elements. The pattern is of increasing (to group IV) and then decreasing combining power across each period. This pattern can be detected by examining the formulas of the compounds formed by these elements. Table 8.5 shows the formulas of the chlorides and hydrides of the elements of periods 2 and 3.

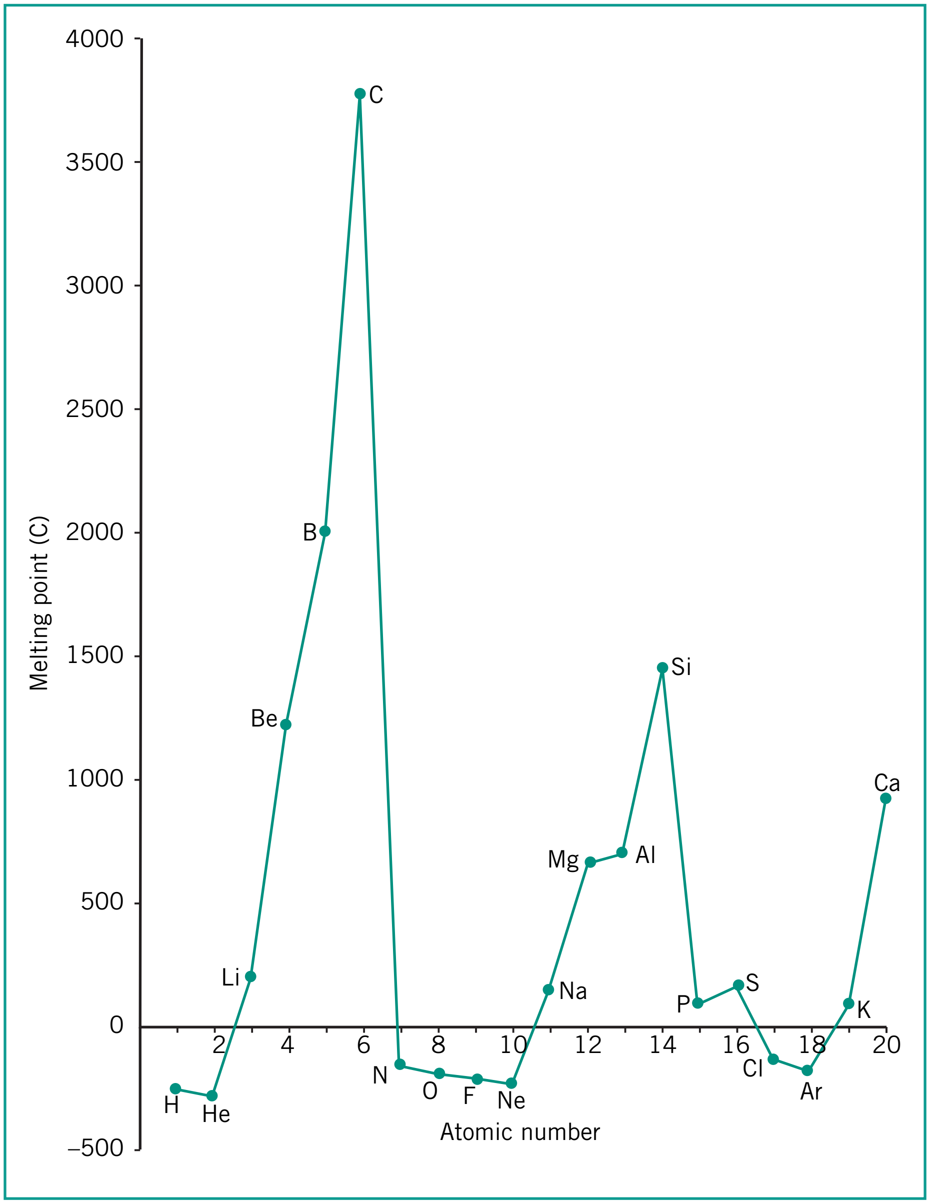


Figure 8.17 Melting points of the first 20 elements

Trends in properties down groups

Elements in the same group of the periodic table have the same number of electrons in their valence or outermost energy level, and as a result have similar properties. However, there is usually a gradual change in properties going down a group. The trends that are evident moving down groups in the periodic table include:

- an increase in atomic radius. This occurs because each new period adds another electron energy level or shell that is more distant from the nucleus than the previous energy level.
- a decrease in first ionisation energy. This occurs because the valence or outer energy level electrons are further from the nucleus in each successive period.
- a decrease in electronegativity. This occurs because the valence electron energy level is at a greater distance from the nucleus in each successive period.
- an increase in metallic character. In group IV, for example, the elements change from a typical non-metal, carbon, at the top of the group, through the semi-metals silicon and germanium, to the typical metals tin and lead.

❇ Review exercise 8.3

1 **a** **Describe** and **explain** the trend in ionisation energies from sodium to argon.
  b **Outline** the relationship between ionisation energy and metallic properties.

2 **a** **Describe** and **explain** the trends in the bonding of the elements from sodium to argon.
  b **Relate** the trends in bonding of the elements to the melting points shown in Figure 8.17.

3 **Explain** the trends in electrical and thermal conductivity (see Table 8.4) across a period.

4 **Describe** the trends in the formulas of the period 3 (third row) chlorides and relate these to the electron configurations of the elements.

5 Consider the period 2 elements: lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine and neon. **Describe** the trends across the period in the following properties:
  a atomic radius
  b metallic character
  c first ionisation energy
  d electronegativity
  e formula of the oxides.

6 **Explain** why elements in the same group show similar chemical properties.

7 **Explain** the general trend in first ionisation energy going down a group of the periodic table.

8 The formula for ammonia is NH_3. **Predict** the formula for the corresponding hydride of:
  a phosphorus
  b arsenic.

9 **Predict** the most metallic element in group V. On what basis did you make your choice?

*KEY POINTS

- The development of the periodic table began as an attempt to systematically classify the known elements.
- Mendeleev identified the periodic variation in the properties of the elements when they are arranged in order of increasing atomic mass.
- In the modern form of the periodic table, the elements are listed in order of atomic number, and the periodic law states that 'the properties of the elements are a periodic function of atomic number'.
- In the periodic table:
  - Metals occur to the bottom and left.
  - Non-metals occur to the top and right.
  - A small number of elements called semi-metals or metalloids have properties in between those of metals and non-metals.
- Periods are horizontal rows of elements in the periodic table. There is a steady change in the properties of elements across a period.
- Groups are vertical columns of elements in the periodic table. Elements in the same group in the periodic table have the same valence electron configuration and share similar properties.
- The group I elements, the alkali metals, are very reactive metals that tend to form +1 ions.
- The group II elements, the alkaline earth metals, are reactive metals that tend to form +2 ions.
- The group VII elements, the halogens, are reactive non-metals that tend to form –1 ions.
- The group VIII elements, the noble gases, are non-reactive gases.
- Hydrogen is placed in different positions on different versions of the periodic table because its properties are unusual and do not fit readily into any one group.
- The transition metals are located in 10 columns in the centre of the periodic table and correspond to building up the electron configurations of the third and subsequent energy levels from 8 to 18.
- The lanthanides and actinides are located in 14 columns in the periodic table and correspond to building up the electron configurations of the fourth and subsequent energy levels from 18 to 32.
- The trends in the properties of the main group elements in the periodic table are illustrated in Figure 8.18.

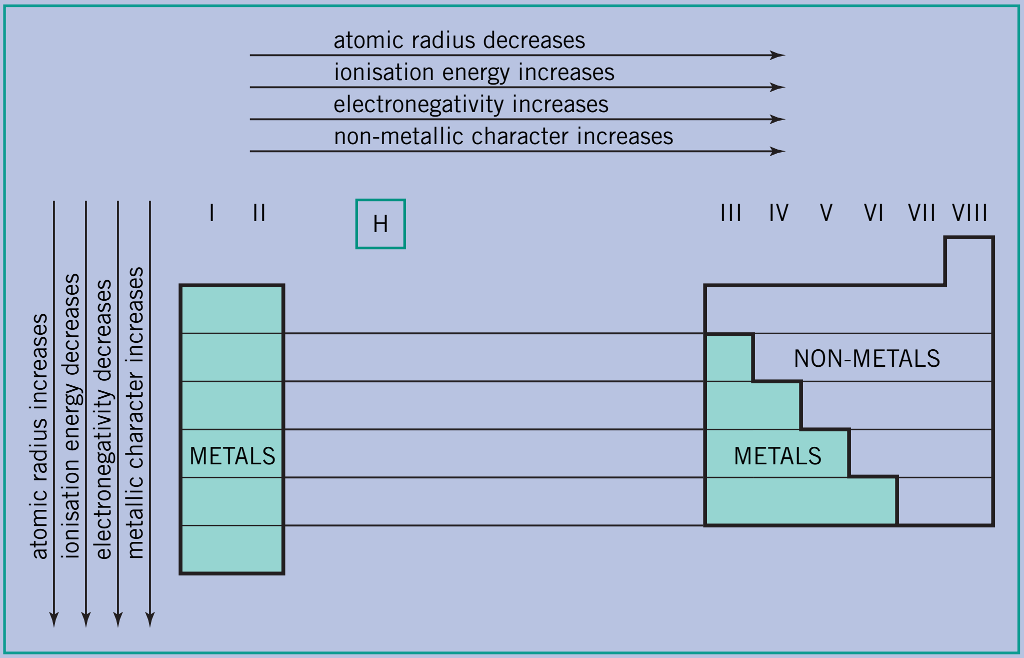


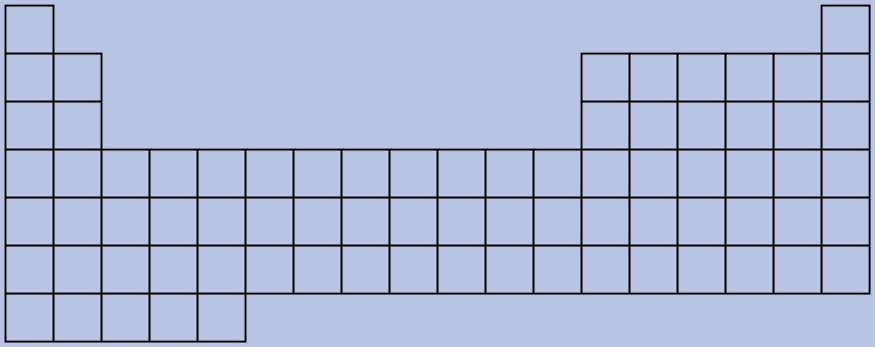
Figure 8.18 Trends in the periodic table

∗APPLICATION AND INVESTIGATION

➲ Investigation

1 The element lawrencium (Z = 103) was discovered in 1961. **Investigate** which elements have been discovered since that time and the names (or atomic numbers) and dates of the discoveries.

2 In the outline of the periodic table provided, **identify** the following:



a the non-metals
b the transition metals
c the period 4 elements
d the group 7 elements
e the alkali metals.

3 Write the formulas for the chlorides of calcium, caesium, gallium, germanium, phosphorus and barium.

4 Using the data in Table 8.4, **construct** a graph to determine whether the boiling points of the elements of periods 2 and 3 show periodicity. Comment on any trends that are apparent.

5 Refer to Figure 8.14. **Identify** the elements that are found at the peaks of the graph of atomic radius as a function of atomic number. **Describe** other properties they have in common.

6 Within any group of the periodic table, the metallic character increases down the group. **Explain** this trend, with particular reference to the group IV elements.

7 The bottom member of the group VII elements in the periodic table is astatine. From the properties of the other halogens, **predict** the following:

a the molecular formula of astatine

b the formula of hydrogen astatide

c the formula of magnesium astatide

d the type of bonding in astatine.

8 By reference to Figure 8.15, **predict** whether the first ionisation energy for krypton would be greater than or less than 1500 kJ mol^{-1}.

9 Consider the abbreviated form of the periodic table below and answer the following questions.

a **Identify** the element that has the largest atomic radius.

b **Identify** the two elements that will react most vigorously to produce an ionic compound.

c **Identify** the elements that have the following electron configurations:

i 2, 8, 3

ii 2, 8, 8

d **Identify** which of the elements in **c** is more reactive. **Explain** why.

e **Identify** which of the elements Na, Rb and Cl has the highest first ionisation energy.

f **Identify** which of the elements S, Br, P, Cs, Cl and Na are good conductors of electricity.

3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K						35 Br	
37 Rb						53 I	
55 Cs						85 At	

10 Use the periodic table to **predict** the most metallic of each of the following:

a S, Se, Te

b Al, Si, P

c Ga, Tl, B

11 Using only a periodic table, consider the following list of elements:

Na, Mg, As, O, Li, Ar, S, Cr, Se, K.

Identify the element that is:

a a semi-metal

b the most reactive metal

c the most reactive non-metal

d a transition metal.

12 **Explain** in terms of electron configuration:

a why the atomic radius of sodium is smaller than that of potassium

b why bromine and iodine have similar properties.

13 Imagine that a group of astronauts is trapped in another universe in which the elements are different from those found in our universe. The astronauts **identify** a series of elements with properties as shown in the table.

Symbol	Relative atomic mass	State	Colour	Relative electrical conductivity	Relative reactivity
A	3.2	solid	silvery	high	medium
D	13.5	gas	colourless	low	high
E	5.3	solid	golden	very high	medium
G	15.4	solid	silvery	high	medium
J	27.9	solid	silvery	high	medium
L	21.6	liquid	colourless	low	medium
M	11.2	gas	colourless	low	low
Q	9.0	liquid	colourless	low	medium
R	1.0	gas	colourless	low	high
T	33.8	solid	colourless	low	medium
X	23.7	gas	colourless	low	low
Z	36.2	gas	colourless	low	medium
B	29.8	solid	golden	very high	medium

a **Arrange** these elements into an alternative periodic table.

b **Assess** whether there appear to be any elements that have yet to be discovered. If so, **describe** the likely properties of these elements.

c A new element is discovered with a relative atomic mass of 25.8. **Predict**:

  i where the element would fit in the alternative periodic table

  ii the likely properties of the element.

CHAPTER 9

MEASURING THE AMOUNTS OF SUBSTANCES: THE MOLE

9.1 Relative atomic mass

In Dalton's atomic theory it was proposed that atoms of a particular element have a unique mass. It was also stated in Unit 3.1 that virtually all of an atom's mass is contained in its nucleus. Because the nucleus consists of protons and neutrons that have almost identical masses, the mass of an atom will depend mainly on the number of protons and neutrons in the nucleus. Hydrogen atoms, with just one proton in the nucleus, are the lightest atoms. Helium atoms, with two protons and two neutrons in the nucleus, have a mass about four times that of hydrogen atoms.

Similarly, carbon atoms, with six protons and six neutrons in the nucleus, are about twelve times the mass of hydrogen atoms.

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

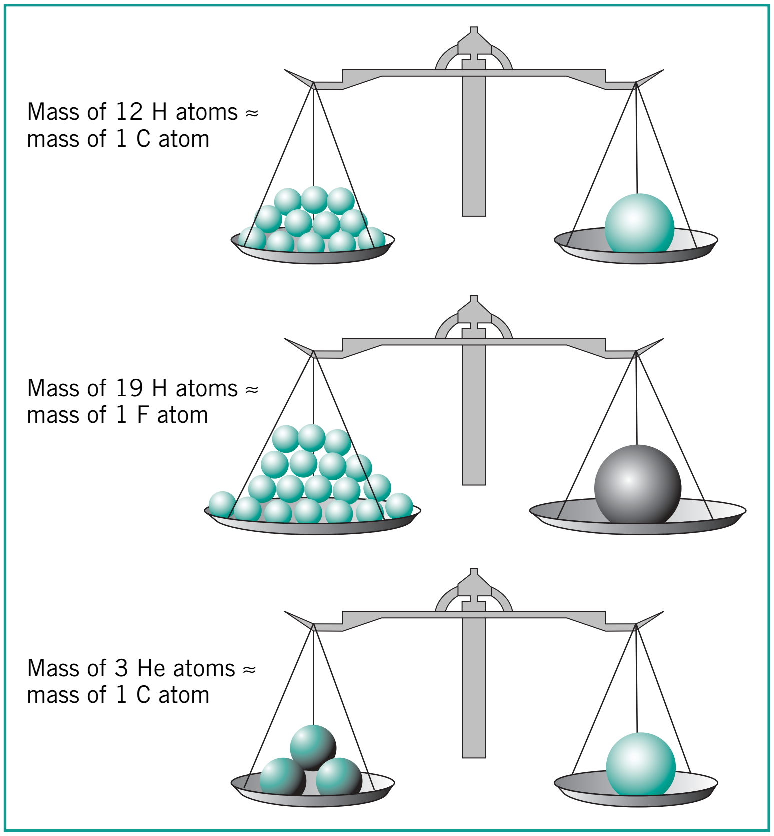


Figure 9.1 Relative masses of atoms of different elements

The actual mass of an atom is exceedingly small. For example, an atom of fluorine has a mass of 3.16×10^{-23} g, or 0.000 000 000 000 000 000 000 031 6 g, while an atom of the isotope carbon-12 has a mass of 1.99×10^{-23} g.

Because atomic masses are so small it is more convenient to describe the mass of an atom by comparing its mass with those of other atoms. Initially the masses of atoms were compared with the mass of the hydrogen atom, the lightest known atom. Thus oxygen, which consists mainly of atoms about 16 times as heavy as an atom of hydrogen, has a relative atomic mass of 16. Gold, with a relative atomic mass of 197, consists of atoms that are about 197 times heavier than hydrogen atoms.

In 1961 the International Union of Pure and Applied Chemistry (IUPAC) defined the masses of atoms relative to the isotope carbon-12, which was assigned a mass of 12.0000. Thus the relative atomic mass (A_r) of an element is defined as the mass of an atom of that element compared with $\frac{1}{12}$th of the mass of an atom of carbon-12.

Because the relative atomic mass is a ratio of two masses, it has no units. The relative atomic masses of some common elements are presented in Table 9.1.

For several of the elements in Table 9.1, the relative atomic masses are close to whole-number values. For example, aluminium has a relative atomic mass of 26.98, gold 197.0, nitrogen 14.01, phosphorus 30.97 and sodium 22.99. These values closely correspond to the sum of the numbers of protons and neutrons in the nuclei of these elements. Aluminium has 13 protons and 14 neutrons (27 in total) in the nucleus, gold 79 protons and 118 neutrons (197 in total) and so on.

Table 9.1 The relative atomic masses* (A_r) of some common elements

Element	Symbol	Relative atomic mass	Element	Symbol	Relative atomic mass
Aluminium	Al	26.98	Lead	Pb	207.2
Barium	Ba	137.3	Magnesium	Mg	24.31
Boron	B	10.81	Mercury	Hg	200.6
Bromine	Br	79.90	Nitrogen	N	14.01
Calcium	Ca	40.08	Oxygen	O	16.00
Carbon	C	12.01	Phosphorus	P	30.97
Chlorine	Cl	35.45	Potassium	K	39.10
Chromium	Cr	52.00	Silicon	Si	28.09
Copper	Cu	63.55	Silver	Ag	107.9
Gold	Au	197.0	Sodium	Na	22.99
Helium	He	4.003	Sulfur	S	32.07
Hydrogen	H	1.008	Tin	Sn	118.7
Iodine	I	126.9	Zinc	Zn	65.41
Iron	Fe	55.85			

*Also known as the atomic weights of the elements.

Further examination of Table 9.1 indicates that many elements have relative atomic masses that are not close to whole-number values. This is because most elements in nature consist of several isotopes. For this reason, the relative atomic masses of elements are weighted averages of the relative atomic masses of the various isotopes that occur naturally.

The relative atomic mass of an element depends on the masses and proportions of each isotope present in nature. Naturally occurring copper consists of two isotopes with relative atomic masses of 63 and 65 respectively. The observed atomic mass of 63.55 indicates that copper-63 is the most abundant isotope. Although carbon and oxygen also have naturally occurring isotopes, one isotope of each element is by far the most abundant, so that their relative atomic masses are very close to whole-number values. Example 9.1 shows how the relative atomic mass of an element can be calculated given the proportions of each of its isotopes.

➜ Example 9.1

Naturally occurring chlorine consists of about 75% chlorine-35, which has a relative atomic mass of 35.0, and 25% chlorine-37, with a relative atomic mass of 37.0. Calculate the approximate relative atomic mass of naturally occurring chlorine.

$$A_r(\mathrm{Cl}) = \frac{75 \times A_r(\mathrm{Cl}-35) + 25 \times A_r(\mathrm{Cl}-37)}{100}$$

$$= \frac{75 \times 35.0 + 25 \times 37.0}{100}$$

$$= \frac{2625 + 925}{100}$$

$$= \frac{3550}{100}$$

$$= 35.5$$

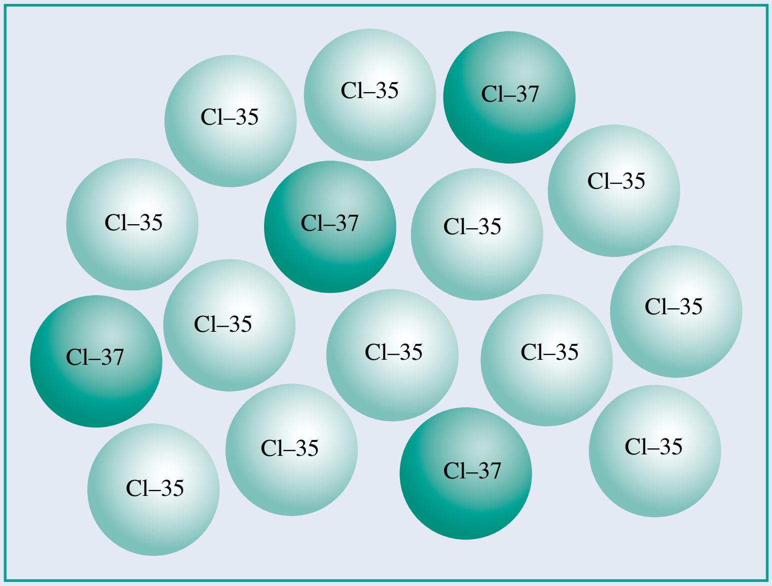


Figure 9.2 Distribution of Cl-35 and Cl-37 atoms in nature

❇ Review exercise 9.1

1. Fluorine occurs as only one isotope in nature and has a relative atomic mass of 19.00. If the relative atomic mass scale was defined relative to $\frac{1}{19}$th the mass of a fluorine-19 atom, **predict** the effect this would this have on the relative atomic masses of the elements.
2. Magnesium occurs in nature as a mixture of three isotopes with relative atomic masses of 24.0, 25.0 and 26.0. Given that the relative atomic mass of naturally occurring magnesium is 24.30, **predict** which isotope is most abundant and **justify** your prediction.
3. Naturally occurring boron contains the isotopes ${}^{10}_{5}\mathrm{B}$ and ${}^{11}_{2}\mathrm{B}$ in about 20% and 80% abundance.

   Calculate the expected relative atomic mass for boron. **Compare** this with the value in Table 9.1 and comment on any difference.

9.2 Relative molecular and formula mass

Just as the relative atomic mass is used to describe the masses of atoms, the relative molecular mass is used to describe the masses of molecules. The relative molecular mass (M_r) of a substance is the mass of a molecule of that substance compared with $\frac{1}{12}$th the mass of an atom of carbon-12. As with relative atomic masses, relative molecular masses have no units. The relative molecular mass of an element or compound is calculated by adding the relative atomic masses of the constituent atoms.

➜ Example 9.2

Calculate the relative molecular mass of ethanol, C_2H_5OH.

$$\begin{aligned} M_r(C_2H_5OH) &= 2\times A_r(C) + 6\times A_r(H) + 1\times A_r(O) \\ &= 2\times 12.01 + 6\times 1.008 + 1\times 16.00 \\ &= 24.02 + 6.048 + 16.00 \\ &= 46.07 \end{aligned}$$

Ionic compounds consist of cations and anions combined in definite proportions that are indicated by the formula of the compound. For example, in aluminium sulfate, $Al_2(SO_4)_3$, there are two aluminium ions for every three sulfate ions. Because ionic compounds do not contain molecules, the sum of the relative atomic masses of the atoms in the formula is called the *relative formula mass*. This is also given the symbol M_r.

➜ Example 9.3

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

$$\begin{aligned} M_r(Na_2CO_3.10H_2O) &= 2\times A_r(Na) + 1\times A_r(C) + 3\times A_r(O) + 20\times A_r(H) + 10\times A_r(O) \\ &= 2\times 22.99 + 1\times 12.01 + 3\times 16.00 + 20\times 1.008 + 10\times 16.00 \\ &= 45.98 + 12.01 + 48.00 + 20.16 + 160.00 \\ &= 286.15 \end{aligned}$$

❇ Review exercise 9.2

1 Using a copy of the periodic table of elements, **calculate** the relative molecular masses of the following:

a	oxygen gas	O_2
b	carbon dioxide	CO_2
c	phosphorus	P_4
d	glucose	$C_6H_{12}O_6$

2 Using a copy of the periodic table of elements, **calculate** the relative formula masses of the following:

a sodium chloride
b barium nitrate
c calcium sulfate-2-water
d magnesium phosphate.

3 A gas in a sample of polluted city air is found to have a relative molecular mass of 46. **Identify** which of the following gases it could be:

N_2, O_2, CO, CO_2, C_3H_8, NO_2, O_3

9.3 Avogadro's number and the mole

Atoms and molecules are far too small to weigh out individually. Using a laboratory balance capable of weighing as little as 0.001 g of a substance, 10^{20} atoms or molecules of most substances would have to be weighed out to obtain a reading on the balance.

Just as it is convenient to group eggs into cartons of a dozen, or sheets of paper into reams (500 sheets), chemists measure the amount of any substance in terms of moles (mol). A *mole* is defined as the amount of a substance that contains the same number of particles as there are atoms in exactly 12 g of carbon-12. Chemists have determined that the number of atoms in 12 g of carbon-12 is 6.022×10^{23}.

This number is called *Avogadro's number* (N_A) after the Italian scientist Amadeo Avogadro. One mole of any substance contains 6.022×10^{23} particles of that substance.

Avogadro's number is so large that it is difficult to comprehend. An impression of the size of this number can be gained by noting that a mole of oranges would form a sphere the size of the earth. Alternatively, a mole of rice grains would cover Australia to a depth of about one kilometre.

When working with mole quantities, the particles or units being counted should be stated as atoms, molecules, ions or formula units. For example, 1 mole of iron (Fe) consists of 6.022×10^{23} atoms of iron, 1 mole of nitrogen gas (N_2) consists of 6.022×10^{23} molecules of nitrogen, and 1 mole of sodium chloride (NaCl) consists of 6.022×10^{23} formula units of NaCl. The term *formula unit* is used for ionic compounds, metals and some network substances such as SiO_2 that do not exist as simple molecules.

Chemists 'count' particles by weighing, in the same way that a bank teller counts five cent coins by weighing. For the bank teller it is much quicker to count a large number of five cent coins by weighing them and comparing their mass with that

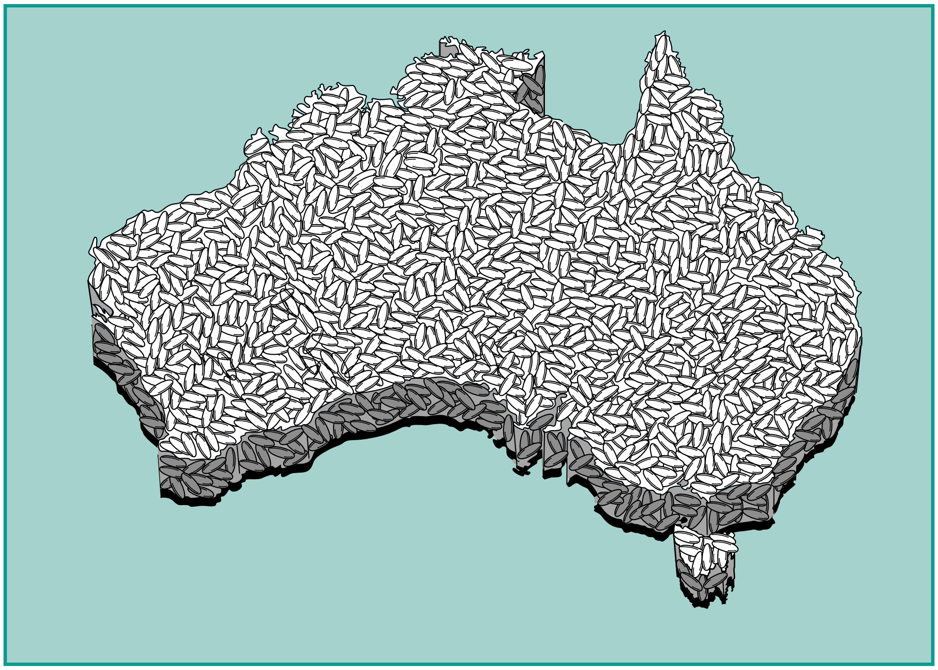


Figure 9.3 A mole of rice grains would cover Australia to a depth of about one kilometre.

of a standard 100-coin roll. For the chemist it is simply not possible to count out atoms or molecules directly. However, the number of particles can be counted indirectly, in moles, by weighing.

Molar mass

Avogadro's number is a particularly useful number with which to work because a mole of any substance has a mass equal to its relative atomic mass, relative molecular mass or relative formula mass expressed in grams. This is known as the *molar mass* (M) of a substance. Thus the molar mass of iron (Fe) is 55.85 g mol^{-1}, nitrogen gas (N_2) is 28.02 g mol^{-1}, and sodium chloride (NaCl) is 58.44 g mol^{-1}.

❇ Review exercise 9.3

1 **Distinguish** between the following terms: relative atomic mass, relative molecular mass, relative formula mass, molar mass. **Identify** the units for each of these.

2 **Calculate**, using appropriate units:
  - **a** the relative atomic mass of nitrogen
  - **b** the molar mass of nitrogen atoms
  - **c** the relative molecular mass of nitrogen gas
  - **d** the molar mass of nitrogen gas.

3 **Calculate** the molar masses of the following:
  - **a** carbon
  - **b** carbon dioxide
  - **c** iron(III) carbonate
  - **d** uranium hexafluoride.

9.4 Moles and numbers of particles

The relationship between the number of moles (n) of a substance and the number of particles (N) of the substance is given by:

$$\text{Number of moles} = \frac{\text{number of particles}}{\text{number of particles in 1 mole}}$$

$$n = \frac{N}{N_A}$$

$$n = \frac{N}{6.022 \times 10^{23}}$$

Using this relationship it is possible to calculate the number of particles or basic units of a substance from the number of moles of that substance.

➜ Example 9.4

1 How many atoms of sulfur (S) are there in 0.250 mol of sulfur atoms?

$$n(\text{S}) = \frac{N}{6.022 \times 10^{23}}$$

$$0.250 = \frac{N}{6.022 \times 10^{23}}$$

$$N = 0.250 \times 6.022 \times 10^{23}$$

$$= 1.50 \times 10^{23} \text{ atoms of S}$$

2 How many moles of calcium carbonate formula units are there in 2.50×10^{24} calcium carbonate formula units?

$$n(\text{CaCO}_3) = \frac{N}{6.022 \times 10^{23}}$$

$$= \frac{2.50 \times 10^{24}}{6.022 \times 10^{23}}$$

$$= 4.15 \text{ mol of CaCO}_3 \text{ formula units}$$

Interpretation of formulas

In the molecular formulas of elements and compounds, the subscripts represent the numbers of atoms of each element present in a molecule of the substance. The subscripts also represent the numbers of moles of atoms of each element present in a mole of molecules of the substance. For example, one mole of ammonia molecules (NH_3) contains one mole of nitrogen atoms and three moles of hydrogen atoms.

The same applies in ionic compounds. One mole of potassium carbonate (K_2CO_3) formula units contains two moles of potassium ions (K^+) and one mole of carbonate ions (CO_3^-).

➜ Example 9.5

Calculate the numbers of moles of NH_4^+ ions, CO_3^{2-} ions and H atoms in 3.0 mol of ammonium carbonate formula units.

1 1 mol of $(NH_4)_2CO_3$ contains 2 mol of NH_4^+ ions.

$$\begin{aligned} n(NH_4^+ \text{ ion}) &= 2 \times n((NH_4)_2CO_3) \\ &= 2 \times 3.0 \\ &= 6.0 \text{ mol of } NH_4^+ \text{ ions} \end{aligned}$$

2 1 mol of $(NH_4)_2CO_3$ contains 1 mol of CO_3^{2-} ions.

$$\begin{aligned} n(CO_3^{2-} \text{ ion}) &= n((NH_4)_2CO_3) \\ &= 3.0 \text{ mol of } CO_3^{2-} \text{ ions} \end{aligned}$$

3 1 mol of $(NH_4)_2CO_3$ contains 8 mol of H atoms.

$$\begin{aligned} n(\text{H atoms}) &= 8 \times n((NH_4)_2CO_3) \\ &= 8 \times 3.0 \\ &= 24 \text{ mol of H atoms} \end{aligned}$$

❇ Review exercise 9.4

1 **a** **Calculate** the number of molecules of water in 3.50 mol of water molecules.

b **Calculate** the number of moles of sodium carbonate formula units in 3.01×10^{22} formula units of sodium carbonate.

2 **a** **Calculate** the number of moles of Fe^{3+} ions, CO_3^{2-} ions, C atoms and O atoms contained in 6.0 mol of iron(III) carbonate, $Fe_2(CO_3)_3$.

b **Calculate** the number of moles of ammonium hydrogenphosphate, $(NH_4)_2HPO_4$, that contains 2.0 mol of hydrogen atoms.

3 **Calculate** the number of oxygen atoms contained in 0.50 mol of calcium hydrogencarbonate, $Ca(HCO_3)_2$.

9.5 Moles and mass

The mass of one mole of any substance is equal to its relative atomic, molecular or formula mass expressed in grams. The relationship between the number of moles (n) and mass (m) of a substance is given by:

$$\text{Number of moles} = \frac{\text{mass}}{\text{mass of 1 mole}}$$

$$n = \frac{m}{M}$$

where n is the number of moles (mol),
m is the mass (g), and
M is the molar mass (g mol^{-1}).

From this relationship it is possible to calculate the number of moles of any substance in a given mass, or the mass of a substance in a given number of moles.

➜ Example 9.6

1 How many moles of ethanol molecules are there in 9.25 g of ethanol?

$$n(C_2H_5OH) = \frac{m}{M} \qquad M(C_2H_5OH) = 46.07 \text{ g mol}^{-1}$$

$$= \frac{9.25}{46.07}$$

$$= 0.201 \text{ mol of } C_2H_5OH \text{ molecules}$$

2 Calculate the mass of 4.00 mol of sodium hydroxide formula units.

$$n(NaOH) = \frac{m}{M} \qquad M(NaOH) = 40.00 \text{ g mol}^{-1}$$

$$4.00 = \frac{m}{40.00}$$

$$m(NaOH) = 4.00 \times 40.00$$

$$= 160.0$$

$$= 1.60 \times 10^2 \text{ g}$$

3 Calculate the mass of nitrogen in 28.02 g of ammonium nitrate, NH_4NO_3.
Calculate the number of moles of NH_4NO_3.

$$n(NH_4NO_3) = \frac{m}{M} \qquad M(NH_4NO_3) = 80.05 \text{ g mol}^{-1}$$

$$= \frac{28.02}{80.05}$$

$$= 0.3500 \text{ mol of } NH_4NO_3$$

Calculate the number of moles of N atoms.

1 mol of NH_4NO_3 contains 2 mol of N atoms.

$$n(\text{N atoms}) = 2 \times n(NH_4NO_3)$$

$$= 2 \times 0.3500$$

$$= 0.7000 \text{ mol of N atoms}$$

Calculate the mass of nitrogen.

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

$$0.7000 = \frac{m}{14.01}$$

$$m = 0.7000 \times 14.01$$

$$= 9.807 \text{ g of nitrogen}$$

❇ Review exercise 9.5

1 **Calculate** the mass of the following:
  - **a** 3.50 mol of magnesium atoms
  - **b** 0.750 mol of carbon dioxide molecules
  - **c** 0.0250 mol of sodium carbonate-10-water ($Na_2CO_3.10H_2O$) formula units.

2 **Calculate** the number of moles of atoms, molecules or formula units contained in each of the following:
  - **a** 64.0 g of oxygen gas (oxygen molecules)
  - **b** 19.95 g of argon gas (argon atoms)
  - **c** 390.0 g of acetylene (C_2H_2 molecules)
  - **d** 2.31 g of lead(II) iodide (PbI_2 formula units).

3 **Calculate** the mass of aluminium in 20.4 g of alumina Al_2O_3.

4 **Calculate** the mass of urea, $CO(NH_2)_2$, that contains 15.0 g of nitrogen.

9.6 Percentage composition

The *percentage composition* of a chemical compound specifies the percentage by mass of each of the different elements present in the compound. For example, water consists of 11.1% hydrogen and 88.9% oxygen by mass. A 100 g sample of water therefore contains 11.1 g of hydrogen and 88.9 g of oxygen.

The percentage composition of a compound can be calculated using the formula of the compound and the relative atomic masses of the elements in the compound.

➜ Example 9.7

Calculate the percentage composition of sulfuric acid, H_2SO_4. One mole of H_2SO_4 contains 2 mol H atoms, 1 mol S atoms, 4 mol O atoms.

$$2 \times 1.008 \text{ g H}, \quad 1 \times 32.07 \text{ g S}, \quad 4 \times 16.00 \text{ g O}$$

$$M(H_2SO_4) = 98.09 \text{ g mol}^{-1}$$

$$\%H = \frac{2 \times 1.008}{98.09} \times 100 = 2.055\%$$

$$\%S = \frac{1 \times 32.07}{98.09} \times 100 = 32.69\%$$

$$\%O = \frac{4 \times 16.00}{98.09} \times 100 = 65.25\%$$

A knowledge of the percentage compositions of compounds can be quite useful. From the data in Table 9.2 it is apparent that haematite and magnetite contain higher percentages of iron than iron pyrites. Such considerations can be important in the economics of the mining and metal extraction industries.

Table 9.2 Percentage of iron in three iron compounds

Iron compound	Formula	Percentage of iron
Haematite	Fe_2O_3	70
Magnetite	Fe_3O_4	72
Iron pyrites	FeS_2	46

Review exercise 9.6

1 **Calculate** the percentage composition of the following:

a methane, CH_4

b oxalic acid, $H_2C_2O_4.2H_2O$

2 **Calculate** the percentage by mass of nitrogen in NH_4NO_3, $(NH_4)_2SO_4$ and NH_3.

Assuming that all the nitrogen in each compound is equally accessible to plants, which compound would be most effective, on a mass of nitrogen per gram of compound basis, as a nitrogenous fertiliser?

9.7 Empirical and molecular formulas

The *empirical formula* of a compound specifies the simplest whole-number ratio of the numbers of atoms or ions of each element in the compound. This contrasts with the *molecular formula*, which specifies the actual number of atoms of each element in a molecule. For the compound hydrogen peroxide, the molecular formula is H_2O_2. Each hydrogen peroxide molecule contains two hydrogen atoms and two oxygen atoms bonded together. However, the empirical formula of hydrogen peroxide is HO. This represents the simplest whole-number ratio of the numbers of atoms of each element.

In many compounds, such as water (H_2O), ammonia (NH_3) and carbon dioxide (CO_2), the empirical and molecular formulas are the same. The empirical and molecular formulas of some common compounds are shown in Table 9.3. Note that where the empirical and molecular formulas are different, the molecular formula is always a multiple of the empirical formula.

Table 9.3 Empirical and molecular formulas of some common substances

Substance	Molecular formula	Empirical formula
Water	H_2O	H_2O
Hydrogen peroxide	H_2O_2	HO
Methane	CH_4	CH_4
Ethene (ethylene)	C_2H_4	CH_2
Ethyne (acetylene)	C_2H_2	CH
Benzene	C_6H_6	CH

Table 9.3 *Continued*

Substance	Molecular formula	Empirical formula
Glucose	$C_6H_{12}O_6$	CH_2O
Sucrose	$C_{12}H_{22}O_{11}$	$C_{12}H_{22}O_{11}$
Ammonia	NH_3	NH_3
Sodium chloride	*	NaCl
Calcium chloride	*	$CaCO_3$
Silicon dioxide	*	SiO_2

*Do not occur as simple discrete molecules.

It is possible for different compounds to have the same empirical formula. Acetylene and benzene are two compounds with the empirical formula CH. The molecular formulas for these compounds are C_2H_2 and C_6H_6 respectively.

The empirical formula of a substance can be established experimentally. This is achieved by determining the percentage composition of the substance by chemical analysis. This is then used to calculate the empirical formula of the substance.

➜ Example 9.8

1 A chemical analysis of glucose indicated its composition to be 40.0% carbon, 6.6% hydrogen and 53.3% oxygen. Calculate the empirical formula of glucose.

2 Given that the relative molecular mass of glucose is 180.16, what is its molecular formula?

1 Elements	C	H	O
%	40.0	6.6	53.3
Mass (in 100 g)	40.0	6.6	53.3
Moles ($\frac{m}{M} = n$)	$\frac{40.0}{12.01} = 3.33$	$\frac{6.6}{1.008} = 6.55$	$\frac{53.3}{16.00} = 3.33$
Simplest ratio	$\frac{3.33}{3.33}$	$\frac{6.55}{3.33}$	$\frac{3.33}{3.33}$
	1.00	1.97	1.00

Empirical formula = CH_2O

2 Relative empirical formula mass $= 1 \times 12.01 + 2 \times 1.008 + 1 \times 16.00$

$$= 12.01 + 2.016 + 16.00$$

$$= 30.03$$

$$\frac{\text{Relative molecular mass}}{\text{Relative empirical formula mass}} = \frac{\text{molecular formula}}{\text{empirical formula}}$$

$$\frac{180.16}{30.03} = \frac{\text{molecular formula}}{CH_2O}$$

$$\text{molecular formula} = \frac{180.16}{30.03} \times CH_2O$$

$$= 6 \times CH_2O$$

$$= C_6H_{12}O_6$$

Review exercise 9.7

1 **Calculate** the empirical formula of freon-12 with composition: 9.9% carbon, 31.4% fluorine and 58.7% chlorine.

2 A 5.00 g sample of an unknown compound contained 1.86 g of C, 0.39 g of H, and 2.75 g of Cl. **Calculate** the empirical formula of the compound.

3 The empirical formula of nicotine is C_5H_7N. Given that the relative molecular mass of nicotine is 162, **calculate** its molecular formula.

4 Ethanol, common alcohol, contains 52.2% carbon, 34.8% oxygen and 13.0% hydrogen. **Calculate** its empirical formula. Given that the relative molecular mass of ethanol is 46.1, what is its molecular formula?

9.8 Gay-Lussac's law and Avogadro's hypothesis

Experiments measuring the combining volumes of gases led to an improvement in our understanding of the formulas of substances and the development of the mole concept. The French chemist Joseph Luis Gay-Lussac (1809) found that there was a simple relationship between the volumes of gases involved in chemical reactions. For example, in the reaction of hydrogen and oxygen gas to produce water, the relationship is as follows:

hydrogen gas		oxygen gas		steam
$2H_2(g)$	+	$O_2(g)$	→	$2H_2O(g)$
2 L of	+	1 L of	→	2 L of
hydrogen		oxygen		steam

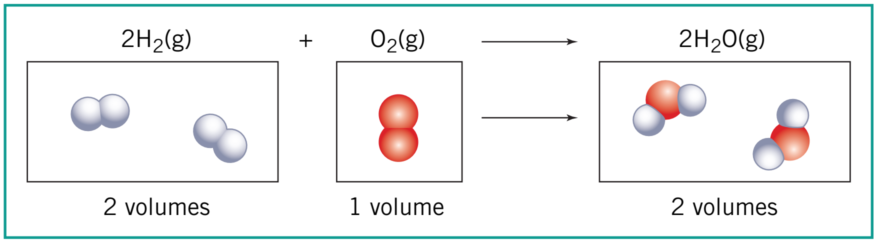


Figure 9.4 Gay-Lussac found that there was a simple relationship between the volumes of reacting gases.

Similar simple ratios are found to exist for other reactions involving gases. An example is the reaction of hydrogen gas and chlorine gas to produce hydrogen chloride.

hydrogen gas		chlorine gas		hydrogen chlorine gas
$H_2(g)$	+	$Cl_2(g)$	→	$2HCl(g)$
1 volume of	+	1 volume of	→	2 volume of
hydrogen		chlorine		hydrogen chlorine

Gay-Lussac's law of combining gas volumes can be stated as follows:

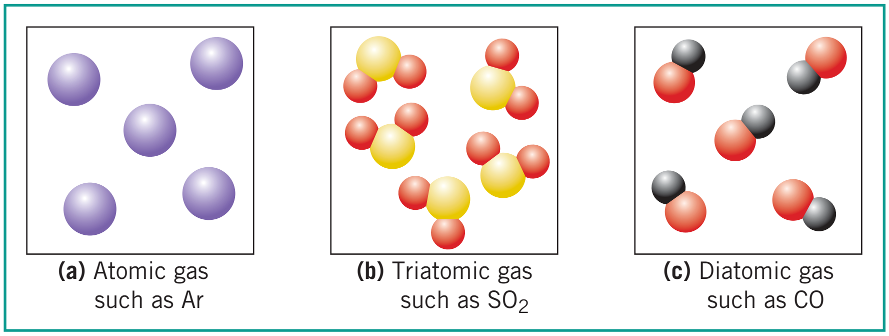
'The ratios of the volumes of gases involved in a reaction, if measured at the same temperature and pressure, are expressed by small, whole numbers.'

Gay-Lussac's law was difficult to interpret at that time because the molecular formulas for hydrogen, oxygen and water were not known with certainty. However, in 1811, Amadeo Avogadro proposed that both hydrogen and oxygen consisted of diatomic molecules and that in the reaction between them the molecules actually split apart and recombined to form water molecules containing two atoms of hydrogen and one of oxygen.

In an attempt to show how the volume of a gas varied with the amount of gas present, Avogadro proposed the following hypothesis:

'Equal volumes of all gases, measured at the same temperature and pressure, contain equal numbers of molecules.'

For example, this means that in 2 L of hydrogen gas there must be the same number of molecules as there are in 2 L of oxygen gas. It also means that the greater the volume of gas, the greater the number of molecules it will contain. For example, in 2 L of hydrogen gas there must be twice the number of molecules there are in 1 L of oxygen gas, provided the volumes are measured at the same temperature and pressure.


(a) Atomic gas such as Ar

(b) Triatomic gas such as SO_2

(c) Diatomic gas such as CO

Figure 9.5 Equal volumes of gases under the same conditions contain equal numbers of particles.

Avogadro's hypothesis explained Gay-Lussac's observations regarding the ratios of the volumes of gases involved in chemical reactions. These simple number ratios occurred because the molecules of the gases combined in simple number ratios, the coefficients in the equations.

It is possible to extend Avogadro's hypothesis to a consideration of the numbers of moles of gases. Because equal volumes of gases contain equal numbers of particles, at the same temperature and pressure, it follows that these equal volumes of gases also contain the same number of moles of gas.

➜ Example 9.9

1 Calculate the volume of hydrogen that will combine with 6.0 L of nitrogen to form ammonia.

What volume of ammonia would be produced, assuming the reaction goes to completion?

The equation for the reaction is as follows.

$$\begin{array}{ccccc} N_2(g) & + & 3H_2(g) & \rightarrow & 2NH_3(g) \\ 1\text{ mol} & + & 3\text{ mol} & \rightarrow & 2\text{ mol} \\ 1\text{ volume} & + & 3\text{ volumes} & \rightarrow & 2\text{ volumes} \end{array}$$

$$V(H_2) = 3 \times V(N_2)$$
$$= 3 \times 6.0$$
$$= 18 \text{ L}$$
$$V(NH_3) = 2 \times V(N_2)$$
$$= 2 \times 6.0$$
$$= 12 \text{ L}$$

2 What volume of oxygen is required to burn 1.0 L of ethane (C_2H_6)? If all the products are gaseous, what is their combined volume, assuming they are measured under the same conditions?

The equation for the reaction is:

$2C_2H_6(g)$	+	$7O_2(g)$	→	$4CO_2(g)$	+	$6H_2O(g)$
2 mol	+	7 mol	→	4 mol	+	6 mol
2 volumes	+	7 volumes	→	4 volumes	+	6 volumes

$$V(O_2) = \frac{7}{2} \times V(C_2H_6)$$
$$= \frac{7}{2} \times 1.0$$
$$= 3.5 \text{ L}$$
$$V(\text{products}) = \frac{10}{2} \times V(C_2H_6)$$
$$= 5 \times 1.0$$
$$= 5.0 \text{ L}$$

❊ Review exercise 9.8

1 **a** **Calculate** the volume of hydrogen gas that would be required to react with 100 L of oxygen gas if measured under the same conditions of temperature and pressure.

b **Calculate** the volume of steam produced.

2 Ammonia decomposes according to the following equation:

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

Given that 10 L of nitrogen is produced, **calculate** the following:

a the volume of ammonia that is decomposed

b the volume of hydrogen produced.

3 Draw a diagram similar to Figure 9.4 showing the volumes of gases involved, together with molecular representations, when methane burns with oxygen to form carbon dioxide and steam.

4 Ammonia can be oxidised according to the following equation:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

Given that 5.0 L of NO are produced, **calculate** the following:

a the volumes of NH_3 and O_2 required

b the volume of H_2O produced.

9.9 Chemical equations and reacting masses

You are already aware that chemists use word and balanced chemical (formula) equations to represent the reactants and products in chemical reactions. A chemical equation shows the relationship between the numbers of moles of reactants and products in a chemical reaction. For example, the equation representing the combustion of butane gas

$$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$$

indicates that for every two moles of C_4H_{10} that react, 13 moles of O_2 are needed and that 8 moles of CO_2 and 10 moles of H_2O are produced. From the relationships between the coefficients in the balanced equation, the number of moles of one substance that will react with, or be produced from, a second substance can be calculated.

➜ Example 9.10

If 4.5 mol of butane is burnt in oxygen, calculate:

1 the number of moles of oxygen gas required to react completely with it

2 the number of moles of carbon dioxide produced

3 the number of moles of water produced.

$$\begin{array}{ccccccc} 2C_4H_{10}(g) & + & 13O_2(g) & \rightarrow & 8CO_2(g) & + & 10H_2O(g) \\ 2\text{ mol} & + & 13\text{ mol} & \rightarrow & 8\text{ mol} & + & 10\text{ mol} \end{array}$$

1 13 mol of O_2 reacts with 2 mol of C_4H_{10}

$$\begin{aligned} \therefore n(O_2) &= \frac{13}{2} \times n(C_4H_{10}) \\ &= \frac{13}{2} \times 4.5 \\ &= 29 \text{ mol of } O_2 \end{aligned}$$

2 8 mol of CO_2 are produced from 2 mol of C_4H_{10}

$$\begin{aligned} \therefore n(CO_2) &= \frac{8}{2} \times n(C_4H_{10}) \\ &= 4 \times n(C_4H_{10}) \\ &= 4 \times 4.5 \\ &= 18 \text{ mol of } CO_2 \end{aligned}$$

3 10 mol of H_2O are produced from 2 mol of C_4H_{10}

$$\begin{aligned} \therefore n(H_2O) &= \frac{10}{2} \times n(C_4H_{10}) \\ &= 5 \times n(C_4H_{10}) \\ &= 5 \times 4.5 \\ &= 22 \text{ mol of } H_2O \end{aligned}$$

Mass–mass calculations from equations

Chemical equations indicate the relationships between the numbers of moles of reactants and products in a chemical reaction. Because the masses of substances are related to the numbers of moles ($m = nM$), chemical equations can be used to determine the relationships between the masses of reactants and products.

For example, in the combustion of carbon to form carbon dioxide, the mass relationships between the reactants and products are:

$$\begin{array}{ccccc} C(s) & + & O_2(g) & \rightarrow & CO_2(g) \\ 1\text{ mol} & + & 1\text{ mol} & \rightarrow & 1\text{ mol} \\ 12\text{ g} & + & 32\text{ g} & \rightarrow & 44\text{ g} \end{array}$$

For every 12 g of carbon that burns, 32 g of oxygen is consumed and 44 g of carbon dioxide is produced.

In the reaction between nitrogen and hydrogen to produce ammonia, the mass relationships are:

$$\begin{array}{ccccc} N_2(g) & + & 3H_2(g) & \rightarrow & 2NH_3(g) \\ 1\text{ mol} & + & 3\text{ mol} & \rightarrow & 2\text{ mol} \\ 28\text{ g} & + & 6\text{ g} & \rightarrow & 34\text{ g} \end{array}$$

A very important part of chemistry is the ability to calculate the masses of substances that react with, or are produced from, other substances. It is essential in analytical chemistry, which is concerned with determining the composition of substances. Also, it is a vital part of chemical manufacturing, which includes the metal, fertiliser, petroleum and plastics industries and many others.

In carrying out mass–mass calculations it is useful to remember the following method.

$$\boxed{\text{Mass of known}} \xrightarrow{n = \frac{m}{M}} \boxed{\text{Moles of known}} \xrightarrow{\text{from equation}} \boxed{\text{Moles of unknown}} \xrightarrow{n = \frac{m}{M}} \boxed{\text{Mass of unknown}}$$

This method of calculation will be further developed to deal with most of the calculations encountered in chemistry.

➜ Example 9.11

The equation for the production of glucose by photosynthesis is:

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$$

Calculate the mass of carbon dioxide required to produce 3.61 g of glucose.

$$\begin{array}{ccccccc} 6CO_2(g) & + & 6H_2O(l) & \rightarrow & C_6H_{12}O_6(s) & + & 6O_2(g) \\ 6\text{ mol} & + & 6\text{ mol} & \rightarrow & 1\text{ mol} & + & 6\text{ mol} \end{array}$$

Calculate the number of moles of the known (glucose).

$$M(C_6H_{12}O_6) = 180.16\text{ g mol}^{-1}$$

$$\begin{aligned} n(C_6H_{12}O_6) &= \frac{m}{M} \\ &= \frac{3.61}{180.16} \\ &= 0.02004\text{ mol of }C_6H_{12}O_6 \end{aligned}$$

Calculate the number of moles of the unknown (carbon dioxide).

6 mol of CO_2 produces 1 mol of $C_6H_{12}O_6$

$$\begin{aligned} n(CO_2) &= 6 \times n(C_6H_{12}O_6) \\ &= 6 \times 0.02004 \\ &= 0.1202 \text{ mol of } CO_2 \end{aligned}$$

Calculate the mass of unknown (carbon dioxide).

$$n(CO_2) = \frac{m}{M} \qquad M(CO_2) = 44.01 \text{ g mol}^{-1}$$

$$0.1202 = \frac{m}{44.01}$$

$$\begin{aligned} m &= 0.1202 \times 44.01 \\ &= 5.29 \text{ g of } CO_2 \end{aligned}$$

❇ Review exercise 9.9

1 For the balanced chemical equations provided, **calculate** the following:

a $CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$

The number of moles of CH_3OH produced in terms of the number of moles of H_2 consumed.

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

The number of moles of Fe produced in terms of the number of moles of CO consumed.

c $TiCl_4(l) + 2H_2O(g) \rightarrow TiO_2(s) + 4HCl(g)$

The number of moles of $TiCl_4$ consumed in terms of the number of moles of HCl produced.

d $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$

The number of moles of O_2 consumed in terms of the number of moles of C_2H_6 consumed.

2 The equation for the burning of magnesium in air is as follows:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

If 8.0 mol of magnesium was burnt, **calculate** the following:

a the number of moles of oxygen molecules required to react completely with it

b the number of moles of magnesium oxide formula units that would be produced.

3 The equation for the decomposition of nitric acid by light is as follows:

$$4HNO_3(aq) \rightarrow 4NO_2(g) + 2H_2O(l) + O_2(g)$$

If 3.0 mol of oxygen gas was produced, **calculate** the following:

a the number of moles of HNO_3 that must have decomposed

b the number of moles of nitrogen dioxide produced.

4 Ethane, C_2H_6, undergoes combustion in the presence of oxygen to produce carbon dioxide and water. If 5.5 mol of ethane reacts, **calculate** the following:

a the number of moles of oxygen gas consumed

b the number of moles of carbon dioxide and water produced.

5 **Calculate** the mass of zinc that can be obtained from the reaction of 16.3 g of zinc oxide according to the following equation:

$$ZnO(s) + C(s) \rightarrow Zn(s) + CO(g)$$

6 **Calculate** the mass of copper(I) sulfide that would need to be roasted to produce 25.4 g of copper according to the following reaction:

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

7 Octane, C_8H_{18}, when burnt in oxygen produces carbon dioxide and water. When 91.2 g of octane is burnt, **calculate** the following:

a the mass of oxygen consumed

b the mass of carbon dioxide produced

c the mass of water produced.

9.10 Limiting reagents and theoretical yields

In industry, chemical reactions are carried out on a vast range of scales, from reactions involving milligrams of reactants to those involving thousands of tonnes. Regardless of the scale used, it is almost always important to use measured amounts of reactants. In extraction and synthesis it is to ensure the most efficient and economic use of resources. This section develops this idea in relation to a simple reaction, that of hydrogen reacting with water, and then applies it to an industrial example.

Limiting reagents

From the balanced equation for a chemical reaction it is possible to calculate the exact quantities of reactants that are consumed and products that are formed. For example, consider the reaction between hydrogen gas and oxygen gas to form water. The equation for the reaction is:

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

From the balanced equation it is evident that for every mole of O_2 that reacts, two moles of H_2 are needed and two moles of H_2O will be produced. This is referred to as the *stoichiometric ratio*.

However, consider the situation where the ratio of the numbers of moles of reactants available is not the same as the ratio of coefficients in the balanced chemical equation. In this situation, one of the reactants will be the limiting reagent and the other will be present in excess. This situation is illustrated in terms of molecules in Figure 9.6 and in terms of moles in Table 9.4. Figure 9.6 illustrates three examples in which differing numbers of molecules of H_2 and O_2 are mixed and undergo reaction. In example (a), the ratio of the number of molecules of H_2 to the number of molecules of O_2 is 2:1, the same as the ratio of the coefficients in the balanced equation. There is just enough hydrogen to react with all the oxygen and there is no limiting reagent. In example (b) there are more oxygen molecules than needed to react with all the hydrogen. The oxygen is present in excess and some remains unreacted after the reaction. Hydrogen is the limiting reagent, as the amount of hydrogen present limits how much water is formed. In example (c) there are more hydrogen molecules than are needed to react with all the oxygen. The hydrogen is present in excess and some remains unreacted after the reaction. Oxygen is the limiting reagent in this case.

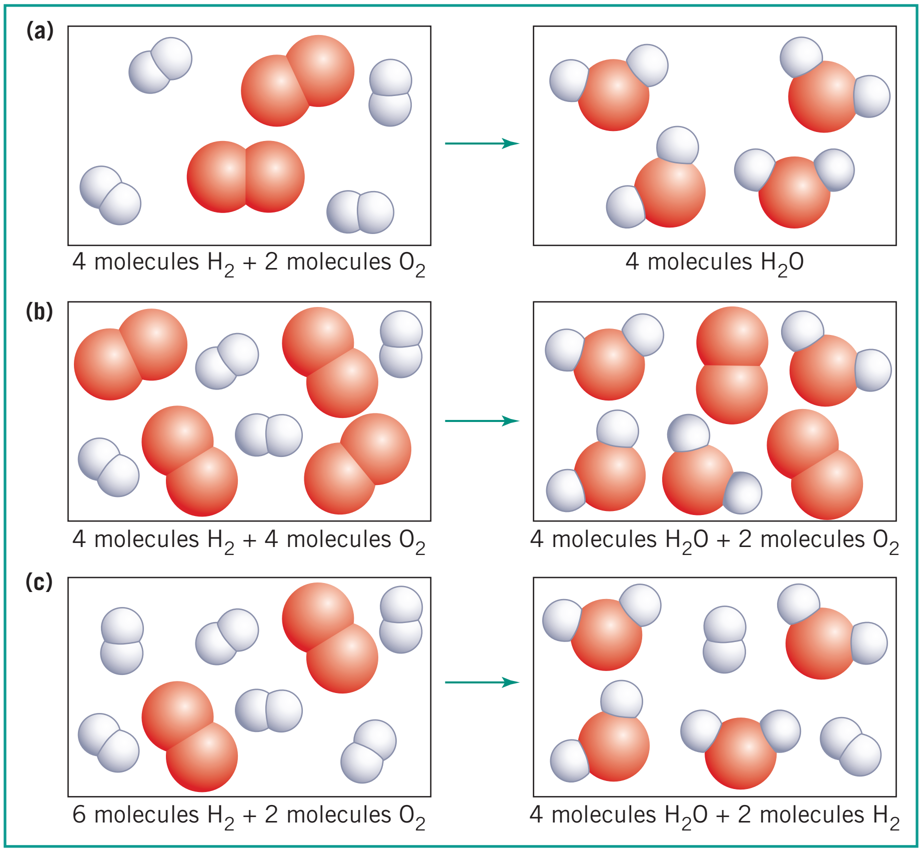


Figure 9.6 Limiting reagent for the reaction $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

Table 9.4 Limiting reagent in the reaction $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

Moles of H_2	Moles of O_2	Ratio of moles of H_2 to moles of O_2	Ratio of coefficient of H_2 to coefficient of O_2	Limiting reagent	Reagent present in excess	Moles of H_2O produced
2.0	1.0	2.0	2.0	—	—	2.0
2.0	2.0	1.0	2.0	H_2	O_2	2.0
3.0	1.0	3.0	2.0	O_2	H_2	2.0
1.0	1.0	1.0	2.0	H_2	O_2	1.0
1.5	0.5	3.0	2.0	O_2	H_2	1.0

Table 9.4 includes five examples in which differing numbers of moles of H_2 and O_2 are mixed and undergo reaction. Note that when the ratio of the number of moles of H_2 to the number of moles of O_2 is greater than two, then H_2 is present in excess. The limiting reagent is then O_2 and the amount of the product, H_2O, is determined from the number of moles of O_2.

When the mole ratio is less than two, H_2 is the limiting reagent and O_2 is present in excess. The amount of H_2O produced under these conditions is determined from the number of moles of H_2.

➜ Example 9.12

Hydrogen gas can be produced by the reaction of zinc with hydrochloric acid. If hydrochloric acid containing 2.74 g of HCl is added to 3.27 g of zinc, calculate:

1 the limiting reagent

2 the mass of hydrogen gas produced

3 the mass of the excess reagent that remains unreacted.

$$\mathrm{Zn(s)} + \mathrm{2HCl(aq)} \rightarrow \mathrm{ZnCl_2(aq)} + \mathrm{H_2(g)}$$

$$1\ \mathrm{mol} + 2\ \mathrm{mol} \rightarrow 1\ \mathrm{mol} + 1\ \mathrm{mol}$$

1 Calculate the numbers of moles of both reactants.

$$n(\mathrm{Zn}) = \frac{m}{M} \qquad M(\mathrm{Zn}) = 65.39\ \mathrm{g\ mol^{-1}}$$

$$= \frac{3.27}{65.39}$$

$$= 0.05001\ \mathrm{mol\ of\ Zn}$$

$$n(\mathrm{HCl}) = \frac{m}{M} \qquad M(\mathrm{HCl}) = 36.46\ \mathrm{g\ mol^{-1}}$$

$$= \frac{2.74}{36.46}$$

$$= 0.07515\ \mathrm{mol\ of\ HCl}$$

Compare the stoichiometric and actual mole ratios.

i Stoichiometric ratio

$$\frac{n(\mathrm{HCl})}{n(\mathrm{Zn})} = \frac{2}{1} = 2$$

ii Actual mole ratio

$$\frac{n(\mathrm{HCl})}{n(\mathrm{Zn})} = \frac{0.07515}{0.05001} = 1.50$$

Actual mole ratio < stoichiometric ratio.

∴ HCl is the limiting reagent.

2 Calculate the numbers of moles of H_2.

2 mol of HCl produces 1 mol of H_2.

$$n(\mathrm{H_2}) = \frac{1}{2} \times n(\mathrm{HCl})$$

$$= \frac{1}{2} \times 0.07515$$

$$= 0.03758\ \mathrm{mol\ of\ H_2}$$

Calculate the mass of H_2.

$$n(\mathrm{H_2}) = \frac{m}{M} \qquad M(\mathrm{H_2}) = 2.016\ \mathrm{g\ mol^{-1}}$$

$$0.03758 = \frac{m}{2.016}$$

$$m = 0.0758\ \mathrm{g}$$

3 Calculate the number of moles of Zn that reacted.

1 mol of Zn reacts with 2 mol of HCl.

$$n(\text{Zn reacted}) = \frac{1}{2} \times n(\text{HCl})$$

$$= \frac{1}{2} \times 0.07515$$

$$= 0.03758\text{S mol of Zn}$$

Calculate the number of moles of Zn that remained unreacted.

$$n(\text{Zn unreacted}) = n(\text{Zn initial}) - n(\text{Zn reacted})$$

$$= 0.05001 - 0.03758$$

$$= 0.01243 \text{ mol of Zn}$$

Calculate the mass of zinc unreacted.

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

$$0.01243 = \frac{m}{65.39}$$

$$m = 0.01243 \times 65.39$$

$$= 0.813 \text{ g}$$

Theoretical yield

The *theoretical yield* in a chemical reaction is the quantity of product predicted from the chemical equation when known quantities of reactants undergo the reaction. In Example 9.12, the theoretical yield of hydrogen was 0.0758 g. This is the mass of hydrogen that would be formed in the reaction and that could be collected. This theoretical yield assumes that all of the limiting reactant, HCl in this case, has reacted.

➜ Example 9.13

The extraction of lead from lead(II) oxide occurs according to the following equation:

$$2\text{PbO(s)} + 2\text{C(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{Pb(l)} + 2\text{CO}_2\text{(g)}$$

1 What is the theoretical yield of lead if 1000 kg (1×10^6 g) of lead(II) oxide is reduced?

2 How much carbon would be needed to reduce this quantity of ore?

3 What mass of carbon dioxide would be produced?

$$\begin{array}{ccccccccc} 2\text{PbO(s)} & + & 2\text{C(s)} & + & \text{O}_2\text{(g)} & \rightarrow & 2\text{Pb(l)} & + & 2\text{CO}_2\text{(g)} \\ 2 \text{ mol} & & 2 \text{ mol} & & 1 \text{ mol} & & 2 \text{ mol} & & 2 \text{ mol} \end{array}$$

1 Calculate the number of moles of lead(II) oxide:

$$n(\text{PbO}) = \frac{m}{M} \qquad M(\text{PbO}) = 223.2 \text{ g mol}^{-1}$$

$$= \frac{1 \times 10^6}{223.2} \text{g mol}^{-1}$$

$$= 4480.3 \text{ mol of PbO}$$

According to the stoichiometric mole ratio:

$$n(\text{Pb}) = n(\text{PbO})$$

$$\therefore n(\text{Pb}) = 4480.3 \text{ mol of Pb}$$

$$\begin{aligned} m(\text{Pb}) &= n \times M \qquad\qquad M(\text{Pb}) = 207.2 \text{ g mol}^{-1} \\ &= 4480.3 \times 207.2 \\ &= 9.283 \times 10^5 \text{ g} \\ &= 928.3 \text{ kg} \end{aligned}$$

2 According to the stoichiometric mole ratio:

$$\begin{aligned} n(\text{C}) &= n(\text{PbO}) \\ \therefore n(\text{C}) &= 4480.3 \text{ mol of C} \\ m(\text{C}) &= n \times M \qquad\qquad M(\text{C}) = 12.01 \text{ g mol}^{-1} \\ &= 4480.3 \times 12.01 \\ &= 5.381 \times 10^4 \text{g} \\ &= 53.81 \text{ kg} \end{aligned}$$

3 According to the stoichiometric mole ratio:

$$\begin{aligned} n(\text{CO}_2) &= n(\text{PbO}) \\ \therefore n(\text{CO}_2) &= 4480.3 \text{ mol of CO}_2 \\ m(\text{CO}_2) &= n \times M \qquad\qquad M(\text{CO}_2) = 44.01 \text{ g mol}^{-1} \\ &= 4480.3 \times 44.01 \\ &= 1.972 \times 10^5 \text{ g} \\ &= 197.2 \text{ kg} \end{aligned}$$

➜ Example 9.14

The extraction of iron from iron(III) oxide occurs according to the following equation:

$$\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \rightarrow 2\text{Fe}(\text{l}) + 3\text{CO}_2(\text{g})$$

What is the theoretical yield of iron if 500 kg (5×10^5 g) of iron(III) oxide is reduced?

$$\begin{array}{ccccccc} \text{Fe}_2\text{O}_3(\text{s}) & + & 3\text{CO}(\text{g}) & \rightarrow & 2\text{Fe}(\text{l}) & + & 3\text{CO}_2(\text{g}) \\ 1 \text{ mol} & & 3 \text{ mol} & \rightarrow & 2 \text{ mol} & & 3 \text{ mol} \end{array}$$

Calculate the number of moles of iron(III) oxide:

$$\begin{aligned} n(\text{Fe}_2\text{O}_3) &= \frac{m}{M} \qquad\qquad M(\text{Fe}_2\text{O}_3) = 159.7 \text{ g mol}^{-1} \\ &= \frac{5 \times 10^5}{159.7} \text{ g mol}^{-1} \\ &= 3130.9 \text{ mol of Fe}_2\text{O}_3 \end{aligned}$$

According to the stoichiometric mole ratio:

$$\begin{aligned} n(\text{Fe}) &= 2 \times n(\text{Fe}_2\text{O}_3) \\ \therefore n(\text{Fe}) &= 6261.7 \text{ mol of Fe} \\ m(\text{Fe}) &= n \times M \qquad\qquad M(\text{Fe}) = 55.9 \text{ g mol}^{-1} \\ &= 6261.7 \times 55.9 \\ &= 3.500 \times 10^5 \text{ g} \\ &= 350.0 \text{ kg} \end{aligned}$$

❃ Review exercise 9.10

1 **Describe** what is meant by the term ‘limiting reagent’.

2 Aluminium metal burns in chlorine according to the equation:

$$2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$$

For the reacting systems in **a** to **d** below:

- **i** **identify** the limiting reagent
- **ii** **calculate** the number of moles of $AlCl_3$ produced
- **iii** **calculate** the number of moles of the excess reagent remaining after the reaction.

a 6 mol of Al and 6 mol of Cl_2

b 6 mol of Al and 9 mol of Cl_2

c 6 mol of Al and 12 mol of Cl_2

d 9 mol of Al and 6 mol of Cl_2

3 The reaction between hydrogen sulfide and sodium hydroxide solution is given by the following equation:

$$H_2S(g) + 2NaOH(aq) \rightarrow Na_2S(aq) + 2H_2O(l)$$

2.48 g of sodium hydroxide is dissolved in water and 1.30 g of hydrogen sulfide bubbled through the solution.

a **Identify** the limiting reagent.

b **Calculate** the mass of Na_2S produced in solution.

c **Calculate** the mass of the excess reagent that remains unreacted.

4 Copper is extracted from chalcopyrite ($CuFeS_2$) according to the equation

$$2CuFeS_2(s) + 5O_2(g) + 2SiO_2(s) \rightarrow 2Cu(l) + 4SO_2(g) + 2FeSiO_3(l)$$

If 1.00 kg of chalcopyrite and 1.00 kg of silica (SiO_2) are heated in an abundant supply of oxygen, **determine** the following:

a the limiting reactant

b the theoretical yield of copper that will be extracted

c the mass of SO_2 produced.

*KEY POINTS

- The relative atomic mass (A_r) of an element is the mass of an atom of that element compared with $\frac{1}{12}$th the mass of an atom of carbon-12.
- Elements that occur mainly as one isotope have a relative atomic mass close to a whole number that is equal to the sum of the number of protons and neutrons in the nucleus.
- Elements that occur as several isotopes have a relative atomic mass that depends on the masses and proportions of each isotope present.
- The relative molecular or formula mass (M_r) of a substance is the mass of a molecule or formula unit of that substance compared with $\frac{1}{12}$th the mass of an atom of carbon-12.
- The relative molecular or formula mass of a substance is calculated by adding the relative atomic masses of the constituent atoms.
- A mole of any substance is the amount of substance that contains Avogadro's number (6.022×10^{23}) of atoms, molecules or formula units of that substance.
- One mole of any substance has a mass equal to its relative atomic, molecular or formula mass expressed in grams. This is the molar mass (M) of the substance.
- The relationship between the number of moles (n) of a substance and the number of atoms, molecules or formula units (N) of the substance is:

$$n(\text{mol}) = \frac{N}{6.022 \times 10^{23}(\text{mol}^{-1})}$$

- The relationship between the number of moles (n), mass (m) and molar mass (M) of any substance is:

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

- The percentage composition of a chemical compound specifies the percentage mass of each of the different elements in the compound.
- The empirical formula of a compound specifies the simplest whole number ratio of the numbers of atoms of each element in the compound.
- The molecular formula of a compound specifies the actual number of atoms of each element in a molecule of the compound.
- Gay-Lussac's law of combining gas volumes states that the ratios of the volumes of gases involved in a reaction, if measured at the same temperature and pressure, are expressed by small, whole numbers. This ratio is the same as the ratio of the coefficients in the balanced equation.
- Avogadro's hypothesis states that equal volumes of gases measured under the same conditions of temperature and pressure contain equal numbers of molecules.
- Chemical reactions are represented by chemical equations.
- Chemical equations show the relationships between the following:
  - the numbers of particles of reactants and products in a chemical reaction

  - the number of moles of reactants and products in a chemical reaction.

- To calculate the mass of a substance that reacts with or is produced from another substance in a chemical reaction, the following procedure can be used:

$$\text{Mass of known} \xrightarrow{n = \frac{m}{M}} \text{Moles of known} \xrightarrow{\text{from equation}} \text{Moles of unknown} \xrightarrow{n = \frac{m}{M}} \text{Mass of unknown}$$

- The limiting reagent in a chemical reaction is the substance that is completely consumed in the reaction. A reactant that is not consumed completely is said to be present in excess.
- The theoretical yield in a chemical reaction is the quantity of product predicted from the chemical equation when known quantities of reactants undergo the reaction.

APPLICATION AND INVESTIGATION

1 A silver atom is about nine times as heavy as a carbon atom. **Calculate** the relative atomic mass of silver.

2 The element neon occurs as three naturally occurring isotopes with the following abundances: Ne-20 is 90.9%, Ne-21 is 0.3%, and Ne-22 is 8.8%. **Calculate** the relative atomic mass of naturally occurring neon.

3 **Calculate** the relative molecular or formula masses of the following:
  a ozone (O_3)
  b phosphorus trichloride
  c calcium hydrogencarbonate
  d iron(II) phosphate.

4 **Identify** how many moles of hydrogen atoms are in each of the following:
  a 1 mol of hydrogen atoms
  b 1 mol of hydrogen molecules
  c 1 mol of hydrogen chloride molecules
  d 1 mol of sulfuric acid molecules
  e 1 mol of ammonium hydrogenphosphate formula units
  f 1 mol of copper(II) sulfate-5-water formula units.

5 Gather information from secondary sources to **investigate** how chemists came to estimate Avogadro's number as 6.02×10^{23}.

Investigation

6 **Calculate** the mass of each of the following:
  a 0.0250 mol of anhydrous sodium carbonate formula units
  b 2.00 mol of nitric acid (HNO_3) molecules
  c 1.50×10^{-2} mol of sucrose ($C_{12}H_{22}O_{11}$) molecules
  d iron in 2.00 kg of iron(III) oxide (Fe_2O_3)
  e chlorine in 0.375 g of silver chloride.

7 **Calculate** the number of moles of the following:
   - **a** chlorine molecules and chlorine atoms in 14.2 g of chlorine gas
   - **b** sodium chloride formula units in 1.20 kg of sodium chloride
   - **c** sulfur dioxide molecules, sulfur atoms and oxygen atoms in 5.45 g of sulfur dioxide
   - **d** vitamin C molecules ($C_6H_8O_6$) in 500 mg of vitamin C.

8 **Calculate** the percentage composition of:
   - **a** nickel(II) sulfide
   - **b** phosphoric acid (H_3PO_4)
   - **c** saccharin ($C_7H_5NO_3S$)

9 **Calculate** the empirical formulas of the following compounds:
   - **a** a copper oxide containing 79.9% copper and 20.1% oxygen
   - **b** teflon, which consists of 24% carbon and 76% fluorine
   - **c** a uranium oxide, given that 59.0 g of the oxide produces 50.0 g of uranium.

10 Glycerol (glycerine) consists of 39.1% carbon, 52.2% oxygen and the remainder is hydrogen. **Calculate** the empirical formula of glycerol. Given that its relative molecular mass is 92.0, predict its molecular formula.

11 A poisonous compound isolated from rhubarb consists of 19.0% carbon, 4.8% hydrogen and 76.2% oxygen. **Calculate** its empirical formula. Given that the compound's relative molecular mass is 126.0 and it occurs as a dihydrate (i.e. it has two waters of crystallisation), what is its molecular formula?

12 Ethylene glycol is often used as an antifreeze in car radiators. It consists of 38.7% carbon, 9.7% hydrogen and 51.6% oxygen. **Calculate** its empirical formula. Given that its relative molecular mass is 62.07, predict its molecular formula.

13 If epsom salt, $MgSO_4.xH_2O$, is heated to 250°C all the water of hydration is lost. After heating a 2.024 g sample of the hydrate, 0.989 g of anhydrous $MgSO_4$ remains. **Calculate** how many molecules of water there are per formula unit of $MgSO_4$.

14 Nitrogen dioxide reacts with water according to the following equation:

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$

If 0.50 mol of nitrogen dioxide reacted, **calculate** the following:
   - **a** the number of moles of nitric acid produced
   - **b** the number of moles of nitric oxide produced.

15 The smelting of chalcopyrite, $CuFeS_2$, is represented by the following equation:

$$2CuFeS_2(s) + 5O_2(g) \rightarrow 2Cu(s) + 2FeO(s) + 4SO_2(g)$$

If 22.0 kg of chalcopyrite reacts, **calculate** the following:
   - **a** the mass of copper formed
   - **b** the mass of sulfur dioxide formed
   - **c** the mass of oxygen consumed.

16 Titanium dioxide (TiO_2), a white pigment used in paints and some sunscreen lotions, is produced together with HCl by the reaction of liquid $TiCl_4$ and steam. If 14.0 g of $TiCl_4$ reacts, **calculate** the following.
   - **a** the mass of TiO_2 produced
   - **b** the mass of H_2O consumed
   - **c** the mass of HCl produced.

17 A sample of iron wire is oxidised to iron(III) oxide by reaction with oxygen. If 2.85 g of iron wire produces 4.00 g of iron(III) oxide, **calculate** the percentage purity of the iron wire.

18 Aspirin is produced from salicylic acid and ethanoic acid by the following reaction:

$$\underset{\text{salicylic acid}}{C_6H_4(OH)COOH(s)} + \underset{\text{ethanoic acid}}{CH_3COOH(l)} \rightarrow \underset{\text{aspirin}}{C_6H_4(OCOCH_3)COOH(s)} + \underset{\text{water}}{H_2O(l)}$$

Calculate the mass of salicylic acid needed to prepare a tablet containing 300 mg of aspirin.

19 The equation for the fermentation of glucose is as follows:

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

If 5.25 g of carbon dioxide was produced, **calculate** the following:

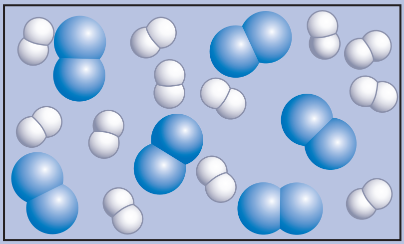
a the mass of ethanol produced

b the mass of glucose consumed.

20 Ammonia is formed by the reaction of nitrogen and hydrogen:

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

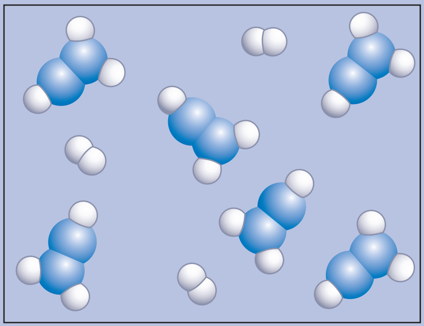
a **Identify** which of the diagrams **i** to **iv** below represents the product mixture.



The starting mixture is represented by the above diagram where ●● represents N_2 and ○○ represents H_2.

b **Identify** which of the reagents is the limiting reagent.

i



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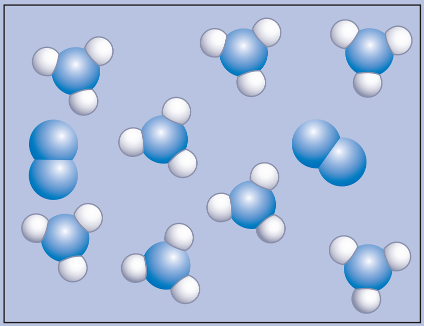

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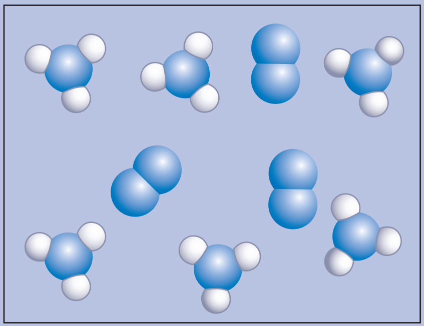

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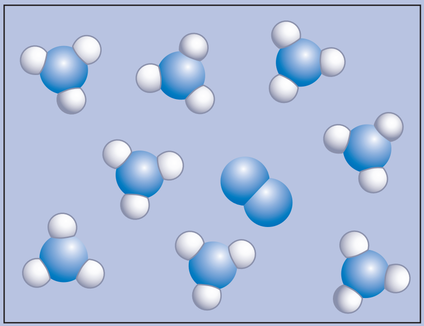


21 The reaction for the production of sulfuric acid can be represented by the following equation:

$$2SO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 2H_2SO_4(l)$$

If 3 mol of SO_2, 1 mol of O_2 and 5 mol of H_2O are allowed to react, **calculate** the numbers of moles of SO_2, O_2, H_2O and H_2SO_4 present after the reaction.

22 When manganese dioxide reacts with concentrated hydrochloric acid, the products are manganese(II) chloride, chlorine gas and water. If 2.17 g of manganese dioxide is treated with hydrochloric acid containing 2.74 g of hydrogen chloride:

a **identify** the limiting reagent

b **calculate** the mass of chlorine produced

c **calculate** the mass of the excess reagent left after the reaction.

23 The fertiliser ammonium sulfate is produced by the following reaction:

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

a **Calculate** the theoretical yield of ammonium sulfate produced from 15.0 g of ammonia.

b If the process were only 85% efficient, **calculate** the mass of ammonium sulfate that would be produced.

*MODULE 2 REVIEW

MULTIPLE-CHOICE QUESTIONS

1 Freshly prepared aluminium filings react more vigorously with water than do freshly prepared iron filings, yet pots and pans are more likely to be made of aluminium than iron.

This is because

A aluminium is less likely to react than iron.
B iron rapidly forms an oxide coating, whereas aluminium forms such a coating only slowly.
C a uniform protective oxide film covers aluminium, whereas iron does not form such a coating.
D aluminium is not oxidised as rapidly, at high temperatures, as is iron.

2 Which one of the following factors could be important in determining whether a mineral deposit is an economic ore body?

A geographical location of the mineral deposit
B concentration of metal in the mineral deposit
C selling price of the metal
D all of the above

3 A metal can often be isolated by heating a mixture of the metal oxide with carbon. In a particular experiment, samples of oxides of copper, sodium, iron and aluminium were mixed with powdered carbon and heated in an oven. As the temperature of the mixture increased, the first metal to appear would be

A copper.
B sodium.
C iron.
D aluminium.

4 Which one of the following oxides <u>cannot</u> be smelted with coke under the conditions found in a blast furnace to yield the metal?

A Ag_2O
B Al_2O_3
C PbO
D Fe_2O_3

5 A 'period' in the periodic table is

A a row of the periodic table.
B a column of the periodic table.
C elements with the same electronegativity.
D elements with different numbers of valence electrons.

6 Elements in different groups of the periodic table (for example, sodium and chlorine) generally have different chemical properties because:

A they have different numbers of valence electrons.
B they have different shells as their outer shell.
C they have atoms that are different in size.
D they have different mass numbers.

7 Which one of the following reactions represents a 'redox' reaction?

A $Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$
B $CaCO_3 \rightarrow CaO + CO_2$
C $Ag^+ + Cl^- \rightarrow AgCl$
D $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$

8 In the reaction $CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(g)$, the reducing agent is

A $H_2(g)$.
B Cu in CuO(s).
C O in CuO(s).
D H in $H_2O(g)$.

9 The number of moles of chlorine molecules (Cl_2) that could be obtained from 3.85 g of $FeCl_3$ is closest to

A 0.024
B 0.036
C 0.072
D 0.108

10 A sample of Fe_3O_4 contains 0.30 mole of iron atoms. The total mass of oxygen in the sample of Fe_3O_4 is closest to

A 6.4 g.
B 4.8 g.
C 3.2 g.
D 1.6 g.

SHORT-ANSWER QUESTIONS

11 a The mineral haematite, present in iron ore, consists of iron(III) oxide. One method of extracting iron from this ore is to react the iron(III) oxide with carbon monoxide gas at high temperatures. **Construct** a balanced chemical equation for the extraction of iron from haematite.

b Another type of iron ore is magnetite (Fe_3O_4). The extraction of iron from this ore can be represented by the following equation:

$$Fe_3O_4(s) + 4C(s) \rightarrow 3Fe(s) + 4CO(g)$$

Calculate the mass of iron that can be extracted from 5.00×10^3 g of ore if it contains 90.0% Fe_3O_4.

12 a In 1817 a German scientist, J. W. Döbereiner, proposed that some elements could be grouped together in groups of three, or triads. One such triad was calcium, strontium and barium. With reference to specific properties, **explain** why Döbereiner suggested that there was a link between these three elements.

b i **Identify** the basis for the arrangement of elements in the modern periodic table.

ii **Discuss** how this differs from the basis used by Mendeleev to develop his periodic table.

13 Metallic iron is produced in the blast furnace from iron ore using a variety of materials.

a Coke is one of two solid materials added to the iron ore in the blast furnace. **Discuss** the purpose of coke in the blast furnace.

b Limestone is the other solid material added to the iron ore in the blast furnace. **Identify** the purpose of limestone in the blast furnace.

c Although iron oxides are reduced in the blast furnace to metallic iron, one of the raw materials used in the process is oxygen, O_2, from the air. Use a chemical equation to **explain** the use of oxygen in the blast furnace.

14 Copper metal reacts with concentrated nitric acid to produce nitric oxide (nitrogen(II) oxide) gas according to the equation:

$$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

a **Calculate** the mass of copper(II) nitrate that would be produced if exactly 2.50 g of copper reacted completely according to the above equation.

b **Calculate** the mass of nitric oxide (nitrogen(II) oxide) gas that would be produced.

c **Explain** why this reaction is an oxidation–reduction reaction.

15 The first ionisation energies (kJ mol^{-1}) of representative elements are shown in the table below.

H 1318							He 2380
Li 527	Be 904	B 807	C 1090	N 1410	O 1320	F 1690	Ne 2090
Na 502	Mg 745	Al 586	Si 791	P 1020	S 1000	Cl 1260	Ar 1530

From the data, several general trends have been proposed. One of them is that the first ionisation energies increase across a period.

a Taking the third period (Na → Ar) as an example, **discuss** the general trend in first ionisation energies in terms of atomic radii.

b **Identify** the trend in ionisation energies down a group and **explain** this trend using the alkali metals (group I) as an example.

16 **Assess** the contributions of Döbereiner, Newlands and Mendeleev to the development of the periodic table.

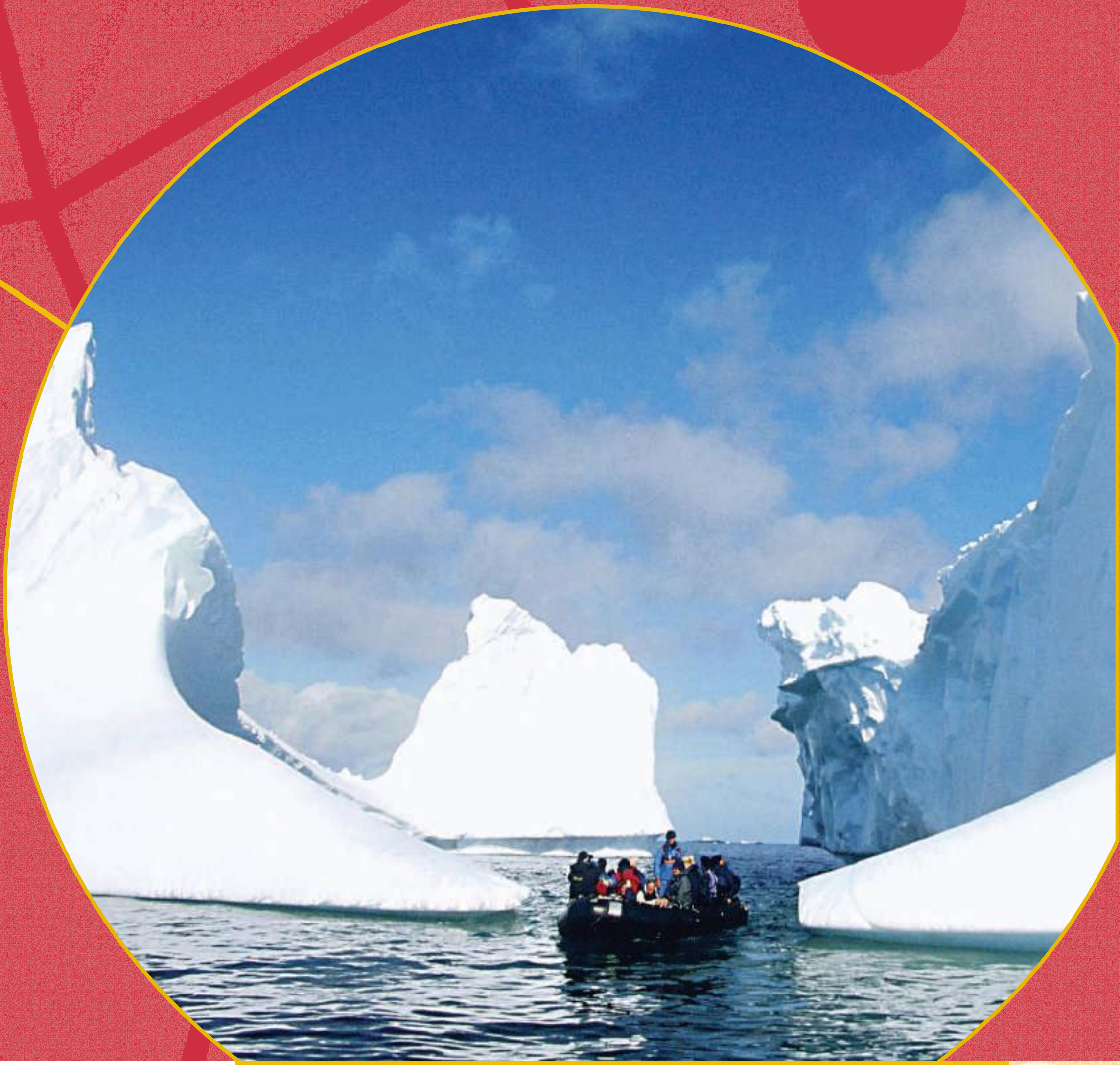
17 Most metals found in the Earth's crust are combined with other elements in naturally occurring compounds called minerals. Depending on the reactivity of the metal, different techniques are used to extract these metals from their ores. Some information about the extraction of three different metals is shown below.

Metal	Formula of main mineral	Method of extraction
Iron	Fe_2O_3	Reduction with carbon or carbon monoxide
Aluminium	$Al_2O_3.3H_2O$	Electrolysis
Copper	Cu_2S	Roasting in air

- **a** **Arrange** these metals in order of increasing reactivity. **Justify** your choice with reference to the method of extraction.
- **b** **Explain** why the order of reactivity given in **a** is also the same order in which these metals were initially used by humans.
- **c** **Account** for the fact that aluminium metal is more expensive than iron.

3

MODULE



water

This module will cover the following material:

- distribution and importance of water on the Earth
- the shapes and polarities of molecules
- intermolecular forces—forces between molecules
- water's properties and their relationship to the molecule's structure and hydrogen bonding
- water as a solvent and the solution process
- solubility of substances in water and precipitation reactions
- reversible reactions and equilibria in physical systems
- concentrations of solutions
- calculations on equations involving solutions
- heat capacity of water
- energy changes in chemical processes and heats of reaction
- thermal pollution of water.

CHAPTER 10

WATER ON EARTH

10.1 The distribution of water on Earth

Although there is evidence of water having existed on other planets and their moons at some time in their history, the presence of water on Earth in the solid, liquid and gaseous states is unique within our solar system. The amount of water that exists on Earth is essentially fixed and was produced early in the Earth's history. The fact that the Earth has retained this water is a result of the planet's gravitational force, determined by its mass, and the Earth's temperature, which is determined by its distance from the sun. Water has played a central role in the evolution of life on Earth and remains critical to the maintenance of life on the planet. In fact, water is considered so important to living organisms that the search for life within our universe centres upon the search for water.

Water is the only pure substance on Earth commonly found in all three states. Of the total water on Earth, 97.2% exists as salt water in seas and oceans, 2.15% in the polar ice caps and glaciers, 0.63% as fresh liquid water and only 0.001% as vapour in our atmosphere. Water has some remarkable properties that are crucial to the maintenance of all living systems. Some of these properties and their significance are summarised in Table 10.1.

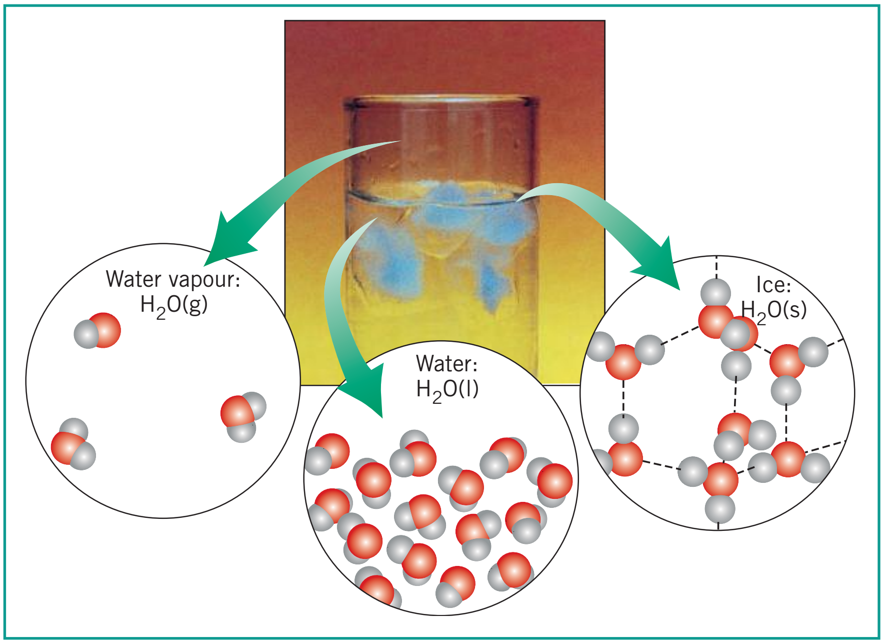


Figure 10.1 The three physical states of water

Table 10.1 Important properties of water

Property	Significance
Ice is less dense than liquid water at 0°C	Ice floats, allowing many aquatic life forms to survive below the surface in cold climates
Transparent to visible light	Allows photosynthesis to occur in aqueous systems
High heat of fusion and vaporisation	Stabilises air temperature
High surface tension	Important in some physiological processes; capillary action in soils and plants
Excellent solvent	Allows biological processes to occur in aqueous solutions; serves as a transport system for nutrients and waste products in living things

The properties described in Table 10.1 are determined by the molecular structure of water and the intermolecular forces that exist between water molecules. The relationship between structure and properties will be explored throughout this module, together with the importance of the unique properties of water in sustaining life on planet Earth.

Liquid water covers nearly 75% of the Earth's surface in the form of oceans, seas, lakes, ground water and rivers, which are collectively referred to as the *hydrosphere*. Sea water is an approximately 3.5% solution of various ionic compounds, of which the most abundant is sodium chloride. Water in rivers and freshwater lakes is generally much less saline than sea water but does contain variable quantities of dissolved salts, including sodium, potassium, calcium and magnesium salts, commonly as chlorides, carbonates, hydrogencarbonates and sulfates. Water also occurs in vast quantities beneath the surface as ground water stored in *aquifers*, layers of water-bearing rocks. The famous Great Artesian Basin of Australia stretching from Queensland through New South Wales and into Victoria and South Australia is one significant example.

Figure 10.2 Earth—The Blue Planet. Water covers nearly 75% of the Earth's surface.

The polar ice caps cover another portion of our planet, dominating the regions north of the Arctic Circle and south of the Antarctic Circle. The solid water found in the polar ice caps, above the snowline at higher latitudes and in glaciers, usually contains lower concentrations of dissolved salts because water generally freezes as a pure substance.

Our atmosphere contains varying amounts of gaseous water, water vapour, in the range 0–5%. Although this represents only a small percentage of the atmosphere, it allows for the transport of vast quantities of water through the earth's water cycle.

Water in the lithosphere can occur as moisture or permafrost within soils and rocks, and as water of crystallisation within minerals. *Water of crystallisation* or *water of hydration* refers to water molecules that form part of the crystal structure of many ionic substances. Common examples are hydrated copper(II) sulfate, $CuSO_4.5H_2O$, which has five water molecules associated with each formula unit, and hydrated sodium carbonate, $Na_2CO_3.10H_2O$. Examples of minerals containing waters of crystallisation include gypsum $CaSO_4.2H_2O$, and gibbsite $Al_2O_3.3H_2O$. The forces holding the water molecules within the crystal structure are not strong, so waters of crystallisation can generally be removed by heating.

Water is the major constituent of living matter, representing approximately 70% of the biosphere. It is a component of all cells, the transport system for nutrients and waste products in living things, a reaction medium for many biochemical processes, and, together with carbon dioxide, is a reactant in photosynthesis.

The states and amounts of water in the biosphere, lithosphere, hydrosphere and atmosphere are summarised in Table 10.2.

Table 10.2 State and percentage of water in various reservoirs on Earth

	Biosphere	Lithosphere	Hydrosphere	Atmosphere
Percentage of water	70%	variable	96–100%	0–5%
State of water	liquid	liquid	liquid	gas
		water of crystallisation	solid ice	
		solid ice		

❊ Review exercise 10.1

1 **Identify** the most common state in which water is found in:
   - **a** the biosphere
   - **b** the hydrosphere
   - **c** the atmosphere.

2 List three natural reservoirs of liquid water that occur on the Earth.

3 **Explain** the term 'water of crystallisation', using an example to support your answer.

10.2 Solutions

The oceans and seas dominate our planet. They are not pure substances, but mixtures containing large quantities of dissolved substances, called *solutions*.

Solutions are defined as homogeneous mixtures. In a solution, one substance, known as the *solute*, is dissolved in another substance, the *solvent*. For example, when sugar is dissolved in water, water is the solvent and sugar is the solute.

Aqueous solutions

Solutions in which the solute is dissolved in water are called *aqueous solutions* and are indicated in chemical equations by the use of the symbol (aq) to the right of the solute. For example, a solution of glucose in water is indicated as $C_6H_{12}O_6(aq)$ and an aqueous solution of sodium chloride as NaCl(aq). Common naturally occurring aqueous solutions include sea water, blood plasma, stomach acid, sap in plants and drinks like coffee and lemonade.

Saturated and unsaturated solutions

If sugar is continually added to water, there comes a point at which no more will dissolve. At this stage the solution is said to be 'saturated'. A *saturated* solution is one in which no more solute will dissolve under the existing conditions of temperature and pressure (Figure 10.3). An *unsaturated* solution is a solution that contains less than the quantity of solute needed to saturate it under the existing conditions.

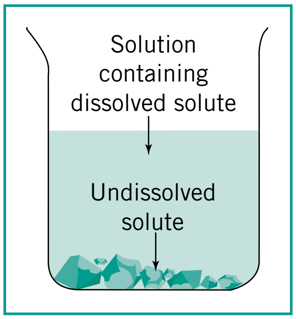


Figure 10.3
A saturated solution contains as much solute as will dissolve under a particular set of conditions

Solubility

Different substances can exhibit very different solubilities in a particular solvent. For example, salt is an example of a substance that is readily soluble in water, while oxygen is less soluble and sand is virtually insoluble. Table 10.3 gives some examples that demonstrate the wide range of solubilities in water found among gases, liquids and solids. The solubilities of different substances are discussed in greater detail in Chapter 12.

Table 10.3 The solubilities of some substances in water

	Solute	Solubility in water
Gases	ammonia	high
	carbon dioxide	slight
	hydrogen	low
Liquids	alcohol	high
	olive oil	low
Solids	calcium nitrate	high
	calcium sulfate	slight
	calcium carbonate	low

CHEMISTRY CONTEXT

❇ GROWING CRYSTALS—SATURATED SOLUTIONS

Crystals are formed from a regular repeated pattern of connected particles such as ions, atoms or molecules. The basic technique for growing crystals involves three steps. First make a saturated solution, then produce small seed crystals, and finally use the seed crystals to grow larger crystals, or allow the seed crystals to continue to grow if there is enough dissolved solute remaining.

Crystals grow by a process called *nucleation*. In this process the dissolved particles bump into each other and connect with each other and continue to grow in the same way. Eventually, this crystal nucleus becomes so large that it crystallises or falls out of solution. Other solute particles will continue to attach to the surface of the crystal, causing it to grow until a balance or equilibrium is reached between the solute molecules in the crystal and those in the solution. Using a saturated solution increases the chance of the solute particles joining and crystals forming.

Seed crystals can easily be produced by hanging a piece of string in a saturated solution or letting a saturated solution evaporate slowly, giving the crystals time to grow. These seed crystals can then be suspended on string or placed in a saturated solution or supersaturated solution and allowed time to grow.

Under certain conditions it is possible to prepare a solution that contains more solute than is contained in a saturated solution. For example, if a saturated solution of sugar in water at 25°C was heated to 50°C, more sugar could dissolve. If more sugar was dissolved in the solution at 50°C and the solution was then carefully cooled back to 25°C, the additional solute may remain dissolved. Such a solution is known as a *supersaturated solution*. A supersaturated solution is a solution that contains more solute than a saturated solution would normally hold under the existing set of conditions. Some supersaturated solutions are relatively stable. For example, toffee is basically a supersaturated solution of sugar in water. It is prepared as a saturated solution at high temperatures and then cooled back to room temperature. Sometimes the toffee will crystalise and needs to be re-melted.

Figure 10.4 Copper sulphate ($CuSO_4$) crystals

Many supersaturated solutions, however, are unstable and the presence of dust, a piece of string or the addition of a small quantity of solid solute will cause the excess solute to crystallise out from solution relatively rapidly.

Substances that can easily grow crystals include: sugar, sodium chloride (salt), magnesium sulfate, copper sulfate, nickel chloride, potassium aluminium sulfate (alum), nickel sulfate, sodium thiosulfate, nickel ammonium sulfate, sodium nitrate, potassium sodium tartrate and sodium borate (borax).

❇ Review exercise 10.2

1 **Outline** the differences between compounds, mixtures and solutions.

2 The solubility of sodium chloride in water is 36 g per 100 g of water at 25°C. **Identify** the following solutions as saturated or unsaturated at 25°C:

- **a** 30 g of NaCl in 100 g of water
- **b** 38 g of NaCl in 100 g of water
- **c** 18 g of NaCl in 50 g of water.

10.3 The importance of water in Earth processes

In Unit 10.1 the distribution and abundance of water on Earth was outlined. The movement of water through the atmosphere, lithosphere, hydrosphere and biosphere is referred to as the *water cycle* and is illustrated in Figure 10.5. This section highlights some of the important functions and processes involving water on planet Earth.

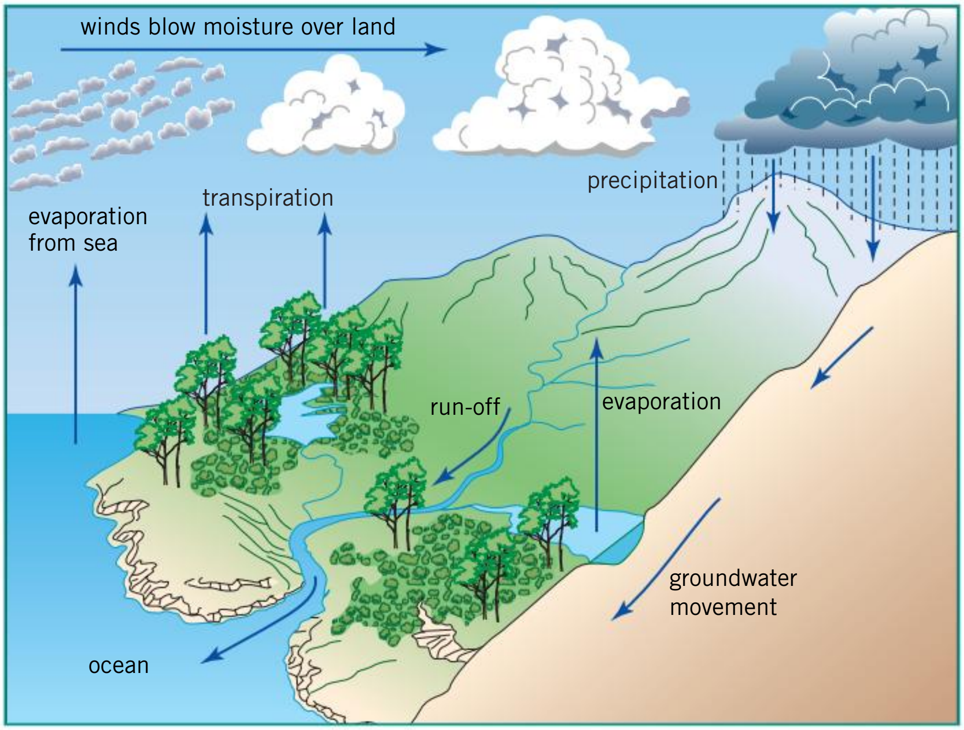


Figure 10.5 The water cycle illustrates the movement of water through various components in the Earth's environment.

Water for life

Water makes up approximately 70% of the biosphere and has a critical role in the maintenance of life on Earth. Together with carbon dioxide it is an essential reactant in the production of glucose by the process of photosynthesis.

$$6CO_2(g) + 6H_2O(l) + \text{light energy} \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$$

This reaction forms the basis for most life on Earth, as glucose is the basic currency of energy in the biosphere. Cellular respiration is essentially the reverse reaction to photosynthesis and provides the energy required to sustain life.

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(aq) + 6H_2O(l) + \text{energy}$$

The vital role of water in the maintenance of life cannot be over-emphasised. Its ability to act as a solvent for many solutes is a particularly important property. Water dissolves, at least to some extent, oxygen, various salts and nutrients, and is therefore important in supporting plant and animal life. Also, many waste products such as carbon dioxide, ammonia and urea are soluble in water, providing an important mechanism by which plant and animal wastes can be removed. The human body is over two-thirds water, with blood, our life-maintaining transport system, being over 80% water. Without water, blood would not be able to flow in arteries, veins and capillaries and transport essential nutrients and waste products. Water is also a major component of our lymph system, and the moisture lining our lungs allows the gases oxygen and carbon dioxide to be transferred between the air we breathe and our respiratory system. A further function of water is the transfer of heat energy around our body from cells performing respiration to our skin, where it can escape.

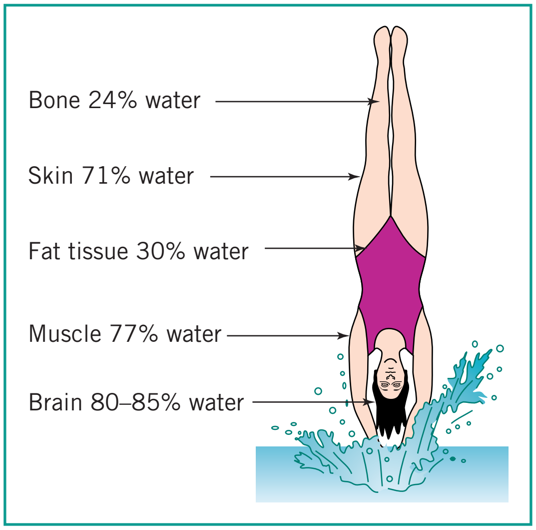


Figure 10.6 The distribution of water in the human body

Water moderates temperature

One of the many important properties of water is that it has a relatively high heat capacity, which means it can absorb (and release) large quantities of heat energy with relatively small temperature changes. While air temperatures in New South Wales can vary greatly throughout the year, from below zero to maximums well above 40°C, the water temperature off the coast of New South Wales varies within a small range of about 17°C to 23°C. This is discussed in greater detail in Chapter 14. The high heat capacity of water in the ocean also has a significant moderating effect on the air temperatures experienced in regions close to the coast. A simple example is the fact that the daily air temperatures of Sydney, or

Figure 10.7 On hot weekends, many people travel to the coast to enjoy the cooler temperatures.

any other coastal location in New South Wales, are always more moderate than temperatures in places such as Mudgee or Hay, located well away from the coast. This moderation of temperature is a direct result of the ability of water to absorb and re-radiate large quantities of heat energy.

Weathering of the lithosphere

Water performs a vital role in both the formation of landforms and the production of soil. It contributes to both weathering and erosion of rocks. *Weathering* is the physical and chemical breakdown and decay of rocks. *Erosion* refers to the processes by which rock fragments are transported by rivers, oceans and wind.

Weathering includes physical processes that cause rocks to break into fragments. This can occur through the constant motion of water, often carrying suspended matter, continually wearing away the rock surfaces. In addition, in areas of extreme cold temperatures the expansion of water as it freezes in joints and cracks of rocks causes weathering.

Water is also an important factor in the chemical weathering of rocks. This occurs over long periods through water dissolving or reacting with some of the minerals present in rocks. For example, water reacts with the rock-forming mineral orthoclase, a feldspar, to form the clay mineral kaolinite and, after prolonged weathering, the mineral gibbsite. The chemical nature of this process is illustrated below.

$$\begin{array}{ccccccc} \text{orthoclase feldspar} & + & \text{water} & \rightarrow & \text{kaolinite} & \rightarrow & \text{gibbsite} \\ KAlSi_3O_8 & + & H_2O & \rightarrow & AlSi_2O(OH)_4 & \rightarrow & Al_2O_3\ 3H_2O \end{array}$$

The prolonged weathering of ancient granite landscapes can result in a profile such as that shown in Figure 10.8. This profile shows granite at depth, overlain by kaolinite clay (a result of extensive weathering of granite minerals), with upper levels consisting of bauxite ore (a result of even greater weathering) that contains the mineral gibbsite together with quartz, iron(III) oxide and clay.

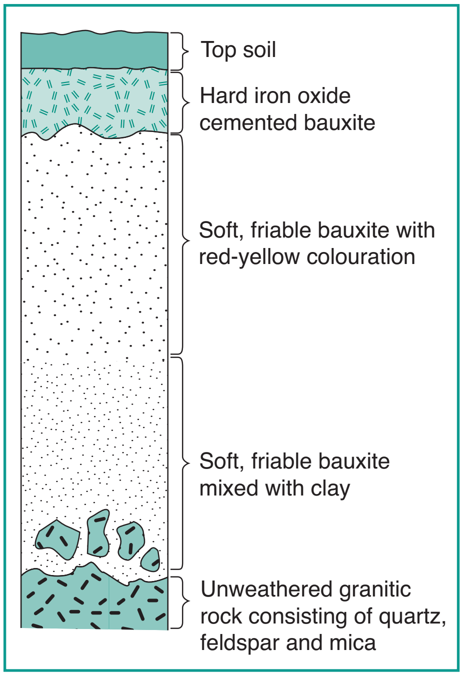


Figure 10.8 A schematic cross-section of a typical bauxite deposit

As rocks are broken down, the smaller pieces are carried away through the process of erosion. The movement of water in the form of waves produces amazing landforms such as ocean cliffs, beaches and rock platforms. Rivers, particularly in times of flood, can cause vast changes to their surrounding landscape.

Ice also plays a role in changing the face of the Earth. The massive glaciers of past ice ages have produced landforms such as the fjords of Scandinavia, and Milford Sound in New Zealand. The slow movement of glaciers causes a gradual and constant grinding away of the underlying rocks, producing particularly rich soils when the glacier recedes during warmer climatic episodes.

Water for humans

Water has already been shown to be critical to the survival of humans as living creatures. It also plays a significant role in human existence in other ways. A consistent and reliable supply of good quality water is a central requirement of modern societies. This water is used for drinking, washing, growing crops and in many industrial processes. These water sources may take several forms, including dams constructed across rivers or the tapping of underground aquifers. Water is usually treated to make it safe to drink.

Figure 10.9 Water plays a significant role in shaping the Earth, as can be seen in this coastal landscape.

Oceans and rivers constitute a transport system, still important in moving great quantities of food, raw materials and consumer products around the planet. Water also serves as a source of great entertainment and enjoyment to many people. Over 80% of the population of Australia resides around our coastal fringe, and enjoys the benefits of fishing, swimming, sailing and other water sports. Those who cannot access the oceans take similar delight from rivers and artificial water play areas such as swimming pools.

❇ Review exercise 10.3

1 **Account** for the importance of water to living things.

2 **Explain** the effect that water's capacity to store heat energy has on the climate of a coastal area.

3 **Identify** and **compare** the processes by which water brings about the physical and chemical weathering of rocks.

10.4 Water density

The density of liquid water, like all other matter, is defined as follows:

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

Mass is usually measured in kilograms (kg) or grams (g) and volume in cubic metres (m^3) or cubic centimetres (cm^3). The units for density are therefore usually expressed as $kg\ m^{-3}$ or $g\ cm^{-3}$.

The density of water at room temperature is approximately $1.0\ g\ cm^{-3}$; that is, one cubic centimetre of water (also 1 mL) has a mass of one gram, or one cubic metre of water has a mass of 1000 kg.

As the temperature of a substance increases, it usually expands, and its volume increases. The increase in volume is caused by the increased kinetic energy of the particles. As a result, the density of the substance decreases because of the increase in volume, while mass remains constant. This decrease in density with increasing temperature occurs for most substances in the solid, liquid and gaseous states. Conversely, most substances increase in density when they freeze, again because a decrease in volume occurs during the freezing process.

The density of water as a function of temperature is shown in Table 10.4. Water's density is unusual in two ways. First, water expands when it changes from the liquid to the solid state. Ice at 0°C has a density of 0.9167 g cm^{-3}, which is lower than that of its liquid form (0.9998 g cm^{-3}) at the same temperature, a totally unexpected result. The lower density of ice in relation to liquid water allows ice to float on top of water, a situation that is critical to life forms in polar and other regions that experience extremely cold weather conditions. Second, as liquid water is cooled, its density increases until it reaches 4°C, but below this temperature its density decreases. This occurs because water initially contracts with cooling but at temperatures below 4°C it expands due to the intermolecular forces in water causing the water molecules to arrange themselves in a particular way. This will be discussed further in Chapter 11.

Table 10.4 Density of water as a function of temperature

Temperature (°C)	Density of water (g cm^{-3})
100	0.9584
50	0.9880
25	0.9970
10	0.9997
6	0.9999
4	1.0000
0 (water)	0.9998
0 (ice)	0.9167
–2	0.9170

Figure 10.10 Icebergs float in surface waters due to the lower density of this solid form of water.

❇ Review exercise 10.4

1 **Explain**, in terms of the particle theory of matter, why the density of substances usually decreases when temperature increases.

2 The density of ice at –2°C is 0.917 g cm^{-3}. **Calculate** the mass of 1 litre (1 dm^{-3}) of ice at this temperature.

3 a **Explain** the unusual variation in the density of water as a function of temperature.
  b **Outline** how this density variation is important for life on Earth.
  c Use Table 10.4 to **identify** the temperature at which water is most dense.

*KEY POINTS

- Water is the only pure substance on Earth commonly found in all three states.
- Water is found in significant quantities and plays a major role in the biosphere, lithosphere, hydrosphere and atmosphere.
- Solutions are defined as homogeneous mixtures.
- Solutions can be thought of in terms of a solvent that 'does the dissolving' and a solute that 'is dissolved'.
- A saturated solution is one in which no more solute will dissolve under the existing conditions of temperature and pressure.
- An unsaturated solution is a solution that contains less than the quantity of solute needed to saturate it under the existing conditions.
- Different substances can exhibit very different solubilities in water.
- Water is essential for living things for many reasons:
  - It provides a transport system.
  - It provides a heat transfer system.
  - It is an essential chemical in many reactions, including photosynthesis.
- Water plays an important role in the physical and chemical weathering of rocks. The action of solid and liquid water has resulted in the formation of many of the Earth's landforms.
- The density of liquid water, like all other matter, may be calculated using the equation:

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

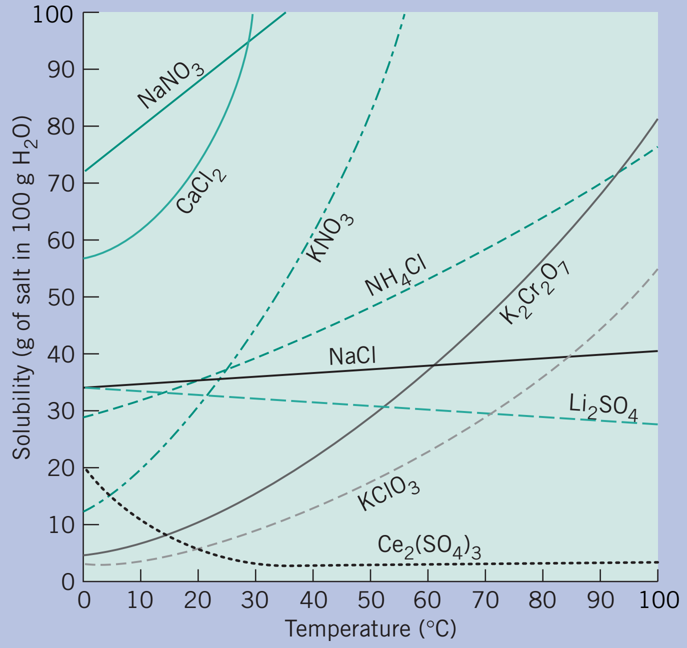
- The densities of substances decrease as temperature increases. This is due to the increase in volume that occurs as the kinetic energy of the particles increases.
- The density of liquid water increases, unusually, for a short temperature range between 0° and 4°C.

*APPLICATION AND INVESTIGATION

➲ Investigation 1 The Latin word for water is 'aqua'. List four words that contain 'aqua' or a derivative of 'aqua' and **define** each word.

➲ Investigation 2 Some hydrated ionic substances lose waters of crystallisation to the atmosphere under certain conditions. These are known as efflorescing hydrates. Other hydrated substances absorb water from the atmosphere and are called hygroscopic. Some hygroscopic substances absorb so much water from the atmosphere that they go into solution. These are called deliquescent substances. Use secondary sources to **investigate** examples of each of these substances and **identify** possible uses.

3 Solubility curves are graphs of the solubility of substances as a function of temperature. **Interpret** the solubility curves below to answer the questions that follow.



a Determine the solubility of the following solids at 25ºC.

  i potassium nitrate

  ii sodium nitrate

b **Identify** the temperature at which the solubility of potassium nitrate is:

  i 50 g per 100 g of water

  ii 100 g per 100 g of water.

c **Compare** the solubilities of ammonium chloride and lithium sulfate at 0ºC and 100ºC.

d **Calculate** the mass of sodium chloride that needs to be dissolved in 200 g of water at 50ºC to make a saturated solution.

e **Predict** what will happen if a solution containing 50 g of NH_4Cl per 100 g of water at 100ºC is slowly cooled to 0ºC.

4 A student is given an aqueous solution of a salt and a crystal of the salt.

a **Outline** how the student could use this crystal to determine whether the solution is unsaturated, saturated or supersaturated.

b **Identify** any experimental variables that would need to be controlled.

5 Use secondary sources to **investigate** and **compare** the composition and functions of blood plasma and plant sap. **Investigation**

6 Use secondary sources to **investigate** and **summarise** the processes used in the treatment of ground water to make it suitable for drinking. **Investigation**

➲ Investigation

7 a Use secondary sources to **investigate** and **identify** the main dissolved solids in:

   - **i** Sydney tap water
   - **ii** two brands of bottled water
   - **iii** de-ionised water.

  b **Identify** and **assess** any health issues associated with drinking these different ‘types’ of water.

8 Use the information in Table 10.4 to draw a graph of the density of water against temperature. **Explain** any notable features of the graph.

9 **Explain** why, in the middle of winter in cold climates, the warmest place in a lake is at the bottom.

10 **Analyse** why astronomers are searching for evidence of water on other planets or their moons as an indication of the potential for life to exist.

CHAPTER 11

THE MOLECULAR STRUCTURE OF WATER AND HYDROGEN BONDING

11.1 The shapes of simple molecules

The properties of water are directly related to the structure and shape of the water molecule and the way in which water molecules interact with each other and with other substances.

In Unit 3.4, Lewis electron dot structures were introduced. The Lewis electron dot structure for the water molecule is shown in Figure 11.1. This structure indicates that in a molecule of water there are two bonding pairs of electrons and two non-bonding or lone electron pairs. The water molecule is described as being V-shaped or bent, as shown in Figure 11.2.

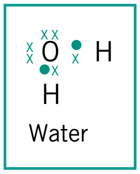


Figure 11.1 The Lewis electron dot structure for water

The shape of a molecule depends on the arrangement of the electron pairs surrounding the central atom in the molecule. To predict the shapes of molecules, the *Valence Shell Electron Pair Repulsion* (VSEPR) model is used. The main idea of the electron pair repulsion model is that the electron pairs in the valence energy level of an atom repel each other and are therefore arranged as far apart as possible to minimise the repulsion between them. The electron pairs that influence molecular shape include both bonding pairs and non-bonding or lone pairs in the valence energy level.

Consider a molecule of hydrogen fluoride (HF). Obviously, a molecule in which there are only two atoms must be linear, regardless of the arrangement of the electron pairs of either atom.

For molecules such as BeF_2, the central Be atom has two electron pairs in its valence energy level after forming a covalent bond with each F atom. The two electron pairs achieve maximum separation by taking up positions on opposite sides of the central atom. The shape of BeF_2 is therefore *linear*, as shown in Figure 11.3.

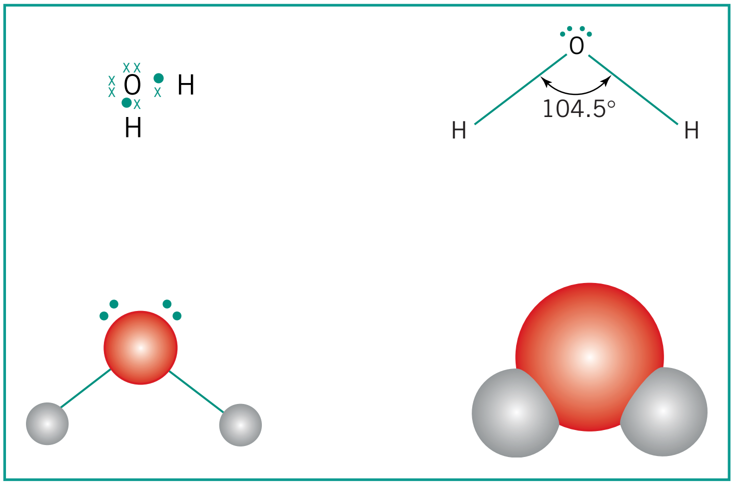


Figure 11.2 The shape of the water molecule

Repulsion between three electron pairs is minimised by a triangular arrangement about the central atom such that the electron pairs are in the same plane with an angle of 120° between them. The shape of BF_3, which has three electron pairs in its valence energy level, is described as *triangular planar* (Figure 11.3).

The geometric arrangement of four electron pairs that minimises repulsion is *tetrahedral*. An example of a tetrahedral molecule is CH_4. In CH_4 the four hydrogen atoms lie at the corners of a tetrahedron with the carbon atom at its centre. For a tetrahedral molecule, the bond angles are 109.5° (Figure 11.3).

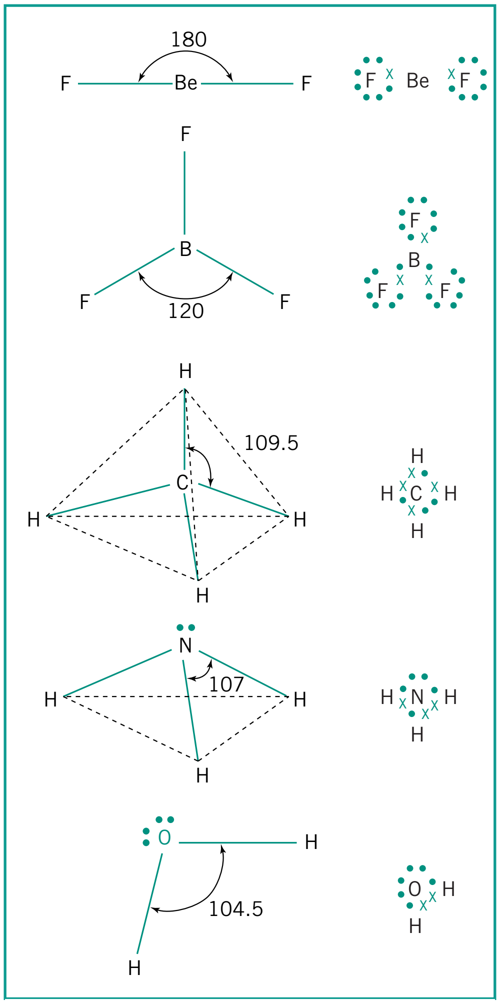


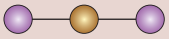
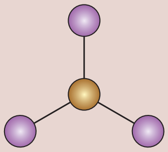
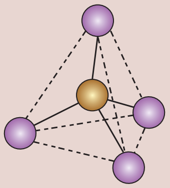
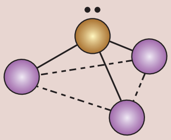
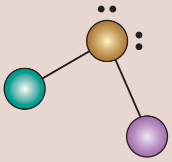
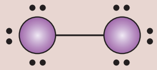
Figure 11.3 The shapes of simple molecules and their Lewis electron dot structures

The NH_3 molecule has four electron pairs around the central atom, but one pair is a lone pair. The arrangement of electron pairs will therefore be tetrahedral, but the arrangement of the atoms is *pyramidal*, with the nitrogen atom at the apex of the pyramid and the three hydrogen atoms forming its base. The lone pair of electrons exerts a slightly stronger repulsive force on the bonding pairs and so the H–N–H bond angle is slightly less than the tetrahedral angle, being about 107°.

In the H_2O and H_2S molecules, there are two lone pairs of electrons. The arrangement of electron pairs will again be tetrahedral, but the arrangement of atoms is *bent* or *V-shaped*. The bond angle of 104.5° is smaller than the tetrahedral angle because the repulsion due to the two lone pairs is slightly greater than the repulsion due to the two bonding pairs.

The shapes of simple molecules are summarised in Table 11.1.

Table 11.1 The shapes of molecules

Number of electron pairs in valence level of central atom	Number of bonding pairs attached to central atom	Number of lone pairs attached to central atom	Shape (with respect to atoms)	Representation of shape	Examples
1	1	0	linear		H_2, HCl
2	2	0	linear		BeF_2
3	3	0	triangular planar		BF_3
4	4	0	tetrahedral		CH_4, CF_4
4	3	1	pyramidal		NH_3, PCl_3
4	2	2	V-shaped (bent)		H_2O, F_2O
4	1	3	linear		Cl_2, F_2

❇ Review exercise 11.1

1 **Outline** the fundamental principle underlying the use of the valence shell electron pair repulsion model to predict molecular shapes.

2 Draw Lewis electron dot diagrams for the covalent molecules listed in **a** to **h** below. For each molecule:

  i **deduce** the number of electron pairs in the valence energy level of the central atom

  ii **identify** the number of atoms bonded to the central atom

  iii **predict** the shape of the molecule, and draw it.

a HCl

b $BeCl_2$

c BCl_3

d CCl_4

e NCl_3

f H_2S

g SiH_4

h CH_3Cl

3 **Predict** the shapes of the following molecules and ions:

a SF_2

b Cl_2O

c C_2H_2

d PH_4^+

11.2 Polarity of bonds and molecules

Electronegativity

The concept of electronegativity was introduced in Chapter 8, where the electronegativity of an atom was described as a numerical measure of the electron-attracting power of the atom within a covalent bond.

Electronegativity is related to, but different from, ionisation energy. Ionisation energy is the energy needed to remove an electron from an atom, whereas the electronegativity relates to an atom's attraction for electrons. Electronegativity values for the main group elements are given in Table 11.2.

Non-metals have a strong attraction for electrons and so have higher electronegativities, whereas metals tend to have lower values. Electronegativities increase across periods in the periodic table up to group VII. The increase can be explained in terms of the increase in nuclear charge across a period. Although an extra electron is also added for each element, this does not fully shield the effect of the increased nuclear charge. As a consequence, the electronegativity increases across the period.

Electronegativities decrease as you move down the groups of the periodic table. This occurs because, in moving down a group, the size of the atoms increases and the attractive force of the shielded nucleus is therefore diminished.

Table 11.2 Electronegativities of the main group elements

H						
2.2						
Li	Be	B	C	N	O	F
1.0	1.6	2.0	2.6	3.0	3.4	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.3	1.6	1.9	2.2	2.6	3.2
K	Ca	Ga	Ge	As	Se	Br
0.8	1.0	1.8	2.0	2.2	2.6	3.0
Rb	Sr	In	Sn	Sb	Te	I
0.8	1.0	1.8	2.0	2.0	2.1	2.7
Cs	Ba	Ti	Pb	Bi	Po	At
0.8	0.9	2.0	2.3	2.0	2.0	2.2
Fr	Ra					
0.7	0.9					

Polar bonds

A bond formed between two atoms that differ greatly in electronegativity, such as Li and F, will be ionic because of the strong tendency for an electron to be transferred completely from the metallic element to the non-metallic element.

When a bond is formed between two identical atoms such as two Cl atoms in Cl_2 the electrons are shared equally, and the bond is non-polar covalent.

When two different types of atoms form a covalent bond, the electron pair is not shared equally between the two atoms. The electron pair would spend more time in the vicinity of the more electronegative atom. Covalent bonds in which there is an uneven charge distribution are called *polar bonds*. The range of bond polarity from purely covalent to ionic bonds is illustrated in Figure 11.4.

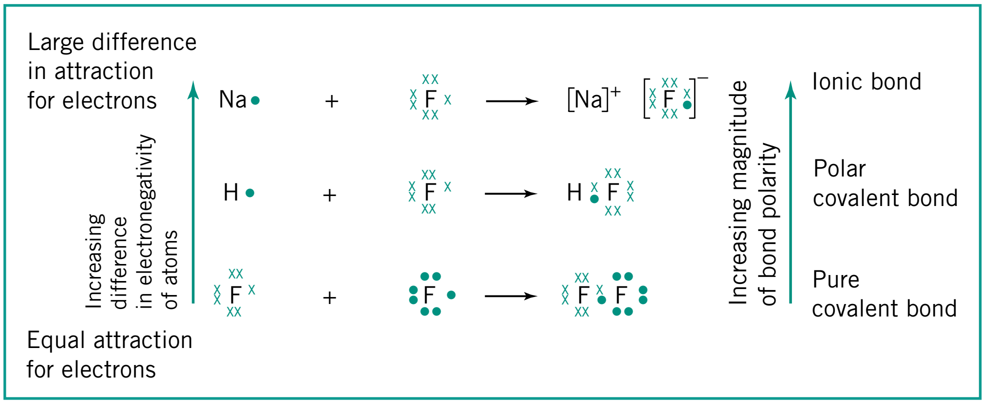


Figure 11.4 The range of bond polarity from purely covalent to ionic bonds

Polar molecules

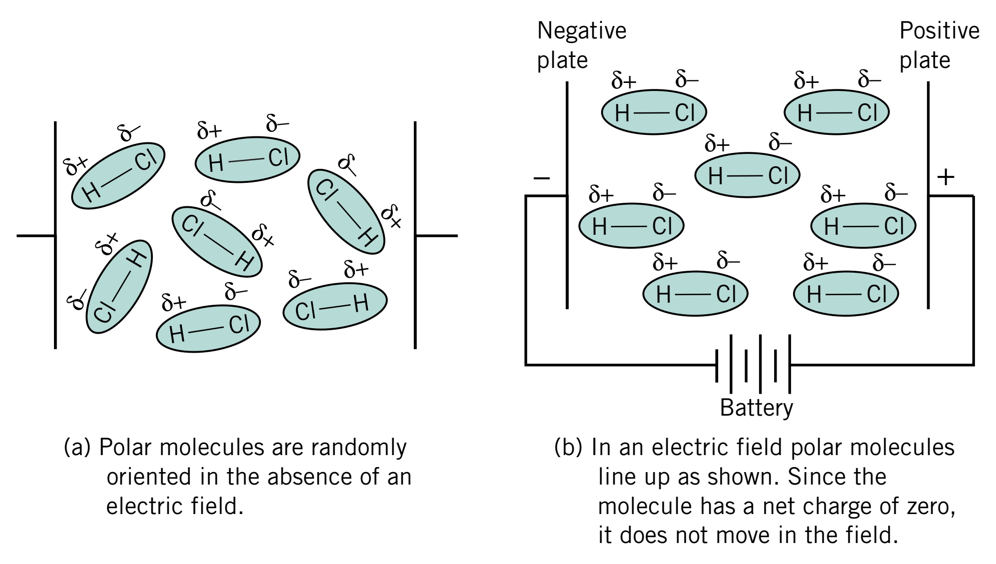
Molecules in which there is an uneven charge distribution are called *polar molecules*. As a result of the unequal sharing of electrons in any bond, one atom acquires a small positive charge, represented by the Greek letter delta (δ^+), and the other acquires an equal small negative charge (δ^-).

In the HCl molecule, for example, the Cl atom is more electronegative (3.2) than the hydrogen atom (2.2). As a result, there is a greater probability of finding the bonding electrons in the vicinity of the chlorine atom than the hydrogen atom. The result is that the chlorine end of the molecule acquires a small negative charge (δ^-) and the hydrogen end acquires a small positive charge (δ^+). Therefore hydrogen chloride is a polar molecule and may be represented as follows:

$$\overset{\delta^+}{\mathrm{H}}-\overset{\delta^-}{\mathrm{Cl}}$$

The occurrence of a positive charge and an equal negative charge separated by some fixed distance is called an *electric dipole*. The HCl molecule has a permanent electric dipole.

If a polar molecule such as HCl is placed in an electric field, it tends to align itself within the field, as shown in Figure 11.5. Note that the positive end of the molecule is oriented towards the negative plate and the negative end is oriented towards the positive plate.



(a) Polar molecules are randomly oriented in the absence of an electric field.

(b) In an electric field polar molecules line up as shown. Since the molecule has a net charge of zero, it does not move in the field.

Figure 11.5 Alignment of HCl molecules in an electric field

Shapes and polarities of molecules

Where a molecule contains more than one polar bond, the polarity of the molecule is found by adding each of the individual bond dipoles. The bond dipoles are represented by arrowheads representing the negative end of the dipoles. From the known molecular shapes, the molecular dipole can be determined by adding the arrows representing each of the individual bond dipoles.

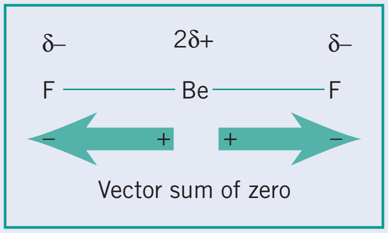
For a molecule to be polar, the following conditions must apply:

- The molecule must contain one or more polar bonds.
- The molecule must not be completely symmetrical.

➜ Example 11.1

BeF_2

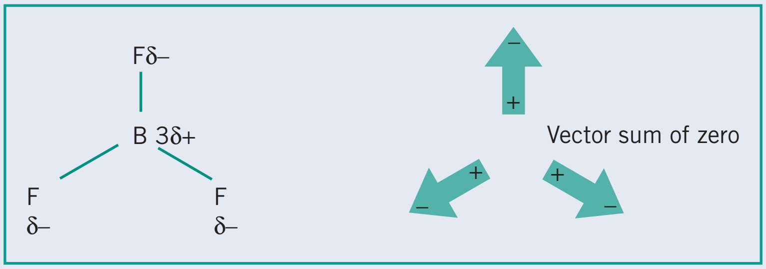
According to the electron pair repulsion model, BeF_2 is linear. The fluorine atoms, being more electronegative, attract the bonding electrons more strongly than the beryllium atom, so the Be-F bonds are polar. The dipoles of the two bonds have the same magnitude but opposite directions. The vector sum of the dipoles is therefore zero and the molecule is non-polar.



➜ Example 11.4

BF_3

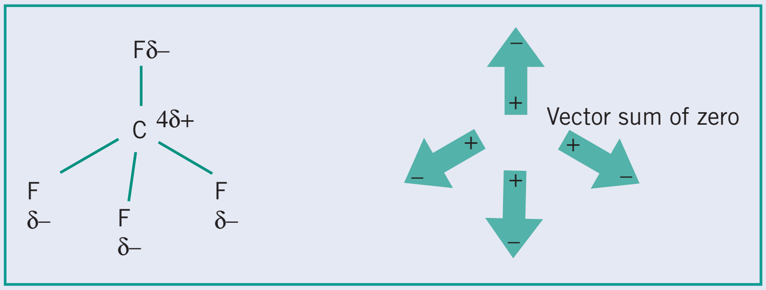
Since the electronegativity of fluorine is greater than boron, boron trifluoride has three polar bonds. The molecule is triangular planar and there is no net molecular dipole because the sum of the vectors is zero. The molecule is therefore non-polar.



➜ Example 11.4

CF_4

A fluorine atom attracts electrons more strongly than a carbon atom. CF_4 therefore has four polar bonds. The molecule is tetrahedral and because the sum of the vectors is zero there is no net dipole and the molecule is non-polar.

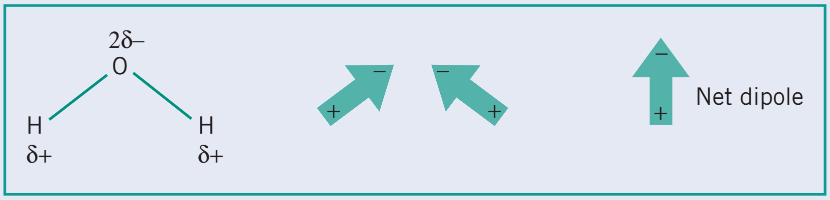


The molecules illustrated in examples 11.1, 11.2 and 11.3 are non-polar despite the fact that the individual bonds are polar. This occurs because each of the molecules is totally symmetrical. A molecule will only be polar if it contains polar bonds and is not completely symmetrical. This is illustrated in the following examples.

➜ Example 11.4

H_2O

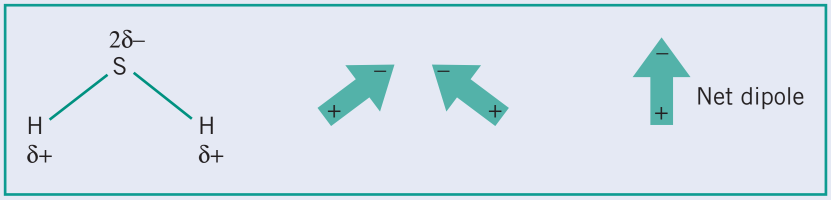
An oxygen atom attracts electrons more strongly than a hydrogen atom and both O–H bonds are polar. The vector sum of these two dipoles produces a net molecular dipole as shown. Thus the water molecule is a polar molecule. This can be shown to be true by holding a charged rod close to a stream of water running from a tap. The attraction between the rod and the polar water molecules causes the stream of water to deflect.



➜ Example 11.5

H_2S

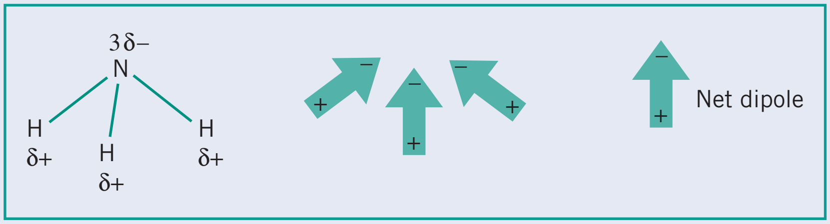
A hydrogen sulfide molecule is very similar in shape to a water molecule. A sulfur atom attracts electrons more strongly than a hydrogen atom and both S–H bonds are polar. The vector sum of these two dipoles produces a net molecular dipole. Therefore the hydrogen sulfide molecule is a polar molecule.



➜ Example 11.6

NH_3

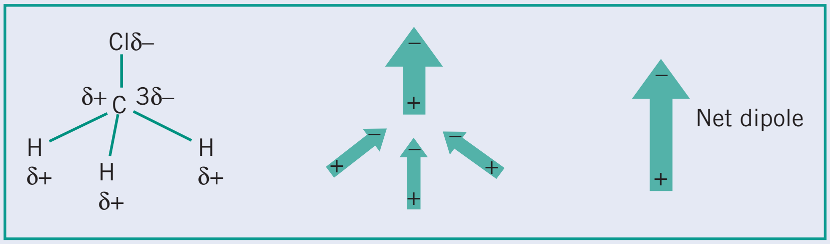
As the electronegativity of nitrogen is greater than hydrogen, the three N–H bonds in ammonia are all polar. Because the molecule is not completely symmetrical, the vector sum of these dipoles is non-zero and an ammonia molecule is therefore polar.



➜ Example 11.7

CH_3Cl

The electronegativity of chlorine is greater than that of carbon and the electronegativity of carbon is slightly greater than that of hydrogen. Although the shape of a molecule of CH_3Cl is tetrahedral, the polarity of the C–Cl bond is different from the C–H bonds, so there is an unsymmetrical distribution of charge. The vector sum of the dipoles is therefore not zero and the molecule is polar.



❊ Review exercise 11.2

1 **Predict** which of the following bonds would be polar.
  - **a** P–Cl in PCl_3
  - **b** O=O in O_2
  - **c** S–O in SO_2
  - **d** N–H in NH_3
  - **e** Sn–Cl in $SnCl_4$
  - **f** Br–Br in Br_2
  - **g** O–F in OF_2
  - **h** S–H in H_2S

2 **a** **Distinguish** between a polar bond and a polar molecule.
  - **b** **Explain** how it is possible for a non-polar molecule to have polar bonds.
  - **c** What are the two conditions that must occur for a molecule to be polar?

3 **Predict** which of the following molecules would be polar.
  - **a** $BeCl_2$
  - **b** CF_4
  - **c** Cl_2O
  - **d** ClF
  - **e** HBr
  - **f** CH_3F
  - **g** CCl_2F_2
  - **h** PF_3

4 For each of the following substances, **predict** whether you would expect the bonds to be ionic, pure covalent or polar covalent.

- **a** NaF
- **b** I_2
- **c** $SiBr_4$
- **d** MgI_2
- **e** PH_3
- **f** CO_2
- **g** MgO
- **h** OF_2

11.3 Forces between molecules

The melting and boiling points of covalent molecular substances are much lower than those of ionic and metallic substances. This implies that the forces of attraction between the molecules in a molecular solid are relatively weak. The weak forces between molecules in molecular solids and liquids are called *van der Waals forces*, after the Dutch scientist who first attempted to explain them. Although all intermolecular forces are referred to as van der Waals forces, they can be further classified as dipole–dipole forces, dispersion forces or hydrogen bonds.

Dipole–dipole forces

If two polar molecules such as HCl approach, they will tend to orient themselves in such a way that the positive end of one molecule is close to the negative end of another molecule, as shown in Figure 11.6. This orientation leads to a lower potential energy.

The force of attraction between the oppositely charged ends of neighbouring polar molecules is called *dipole–dipole attraction*. The ordered structure illustrated in Figure 11.6 is most pronounced in the solid state. In the liquid state, the molecules are not as ordered, due to their higher kinetic energy.

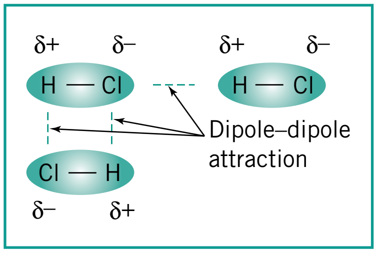


Figure 11.6 Dipole–dipole attraction between HCl molecules

The charged ends of a dipole have a relatively small charge compared with the charges of ions in ionic substances. Consequently, dipole–dipole attractive forces are relatively weak compared with the attractive forces between oppositely charged ions. Therefore solid HCl, a polar molecular solid, melts at –114°C whereas NaCl, an ionic solid, melts at 801°C.

Dispersion forces

If there were no intermolecular forces between the molecules of some substances then these substances would exist only as gases, because there would be no forces to attract the molecules together. However, every substance can be condensed to a liquid and then also to a solid if it is cooled to a low enough temperature. Therefore some form of intermolecular force must exist in every substance, even when the molecules consist of identical atoms, as in O_2 or N_2, and do not possess a permanent dipole.

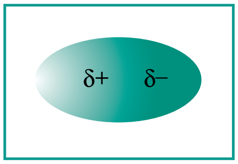


Figure 11.7 Temporary dipole due to unsymmetrical electron charge cloud

Intermolecular forces between non-polar molecules arise from the fact that at any instant a molecule may have a temporary dipole. The temporary dipole occurs at any moment when the electrons in an atom or molecule are not symmetrically distributed. This means that the electron charge cloud will not be symmetrical, as indicated in Figure 11.7.

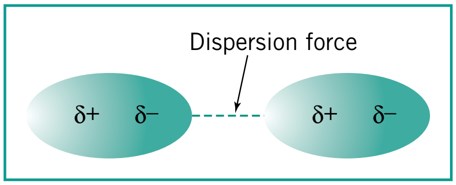
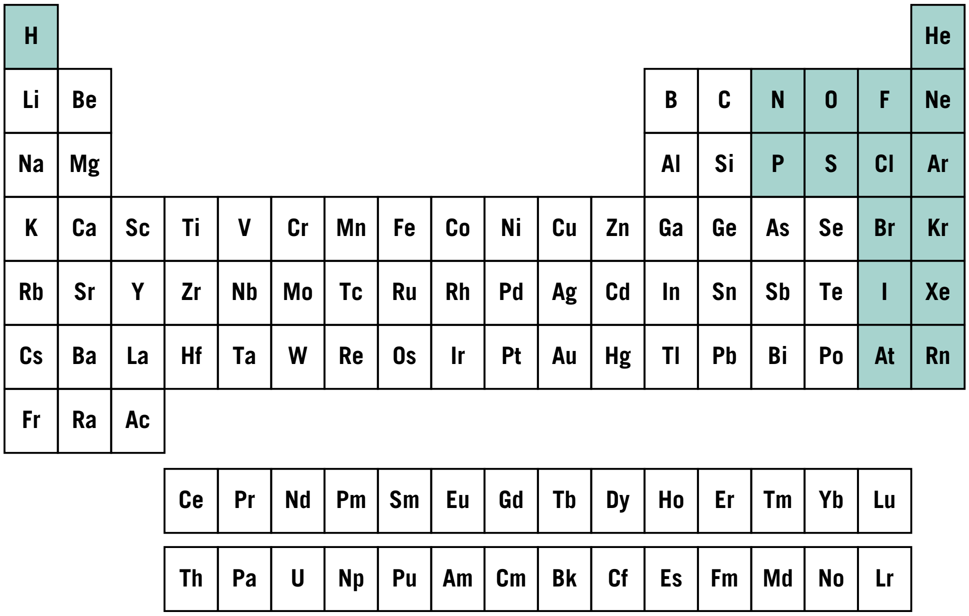


Figure 11.8 Attractive forces between two species with temporary dipoles

When an atom or molecule with a temporary dipole is near another atom, it influences the charge distribution in the second atom. The temporary dipole is said to induce a dipole in the neighbouring atom. The two species then attract each other, as shown in Figure 11.8.

The weak forces of attraction between atoms or molecules arising from such temporary dipoles are known as *dispersion forces*. It should be noted that any particular temporary dipole exists only for an instant, because the distribution of electrons changes constantly. Elements that form molecular solids held together by dispersion forces include hydrogen and the non-metals on the right-hand side of the periodic table, as shown in Figure 11.9. Polyatomic molecules that are non-polar, such as CCl_4, also form molecular solids held together by dispersion forces.



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

Figure 11.9 Elements that form covalent molecular solids in which the intermolecular forces are dispersion forces

Dispersion forces between molecules increase in strength with the number of electrons present in the molecules. Because the number of electrons is greater in larger molecules, it follows that the strength of dispersion forces is also related to molecular size and mass. This is illustrated by examining the melting point trends of the noble gases and halogens shown in Table 11.3.

Table 11.3 Melting points of the noble gases and the halogens

Noble gas	Atomic mass	Number of electrons	Melting point (°C)
He	4	2	–272
Ne	20	10	–249
Ar	40	18	–189
Kr	84	36	–157
Xe	131	54	–112
Halogen	**Molecular mass**	**Number of electrons**	**Melting point (°C)**
F_2	32	18	–220
Cl_2	71	34	–101
Br_2	160	70	–7
I_2	254	106	114

It should be noted that dispersion forces contribute to the attractive forces between all molecules. However, in the case of highly polar molecules, the dipole–dipole forces are much stronger and the effect of the dispersion forces is not as significant. Between molecules that are non-polar or only slightly polar, dispersion forces are the main intermolecular forces acting. Consider the melting points of the compounds HCl, HBr and HI, shown in Table 11.4.

Table 11.4 Melting points of HCl, HBr and HI

Substance	Molecular mass	Melting point (°C)
HCl	36.5	–114
HBr	81	–87
HI	128	–51

Although the HCl molecule is the most polar of the series, HI has the highest melting point. In this series of compounds, the increase in dispersion forces more than compensates for the decrease in dipole–dipole forces as the electronegativity of the halogen element decreases.

The shapes of molecules also influence the strength of dispersion forces but discussion of the reasons for this is beyond the scope of this book.

Hydrogen bonding

The graphs in Figure 11.10 show the melting points and boiling points of the hydrides of the group 14, 15, 16 and 17 elements. There is a general increase in melting and boiling points with increasing relative molecular mass for the hydrides of the group IV elements.

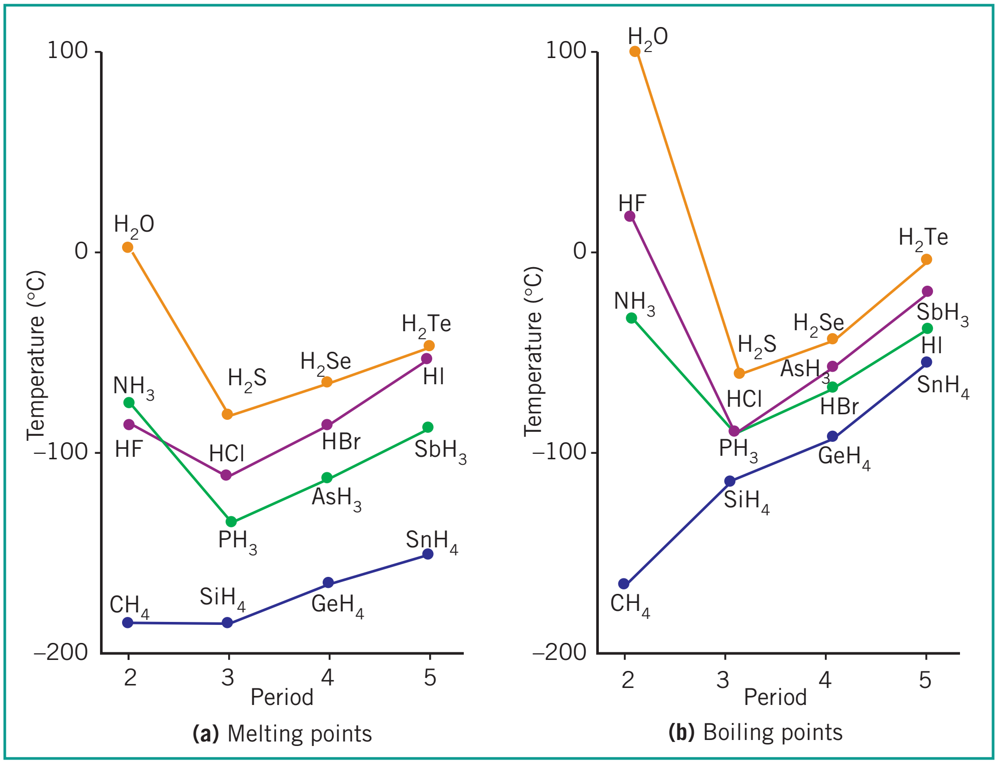


Figure 11.10 Variation in the melting and boiling points of the hydrides of groups IV, V, VI and VII

The regular increase in melting and boiling points also occurs for the compounds H_2S through H_2Se to H_2Te, but H_2O has a higher melting and boiling point than expected. A similar pattern occurs with the hydrides of groups 15 and 17, where NH_3 and HF have higher melting and boiling points than the trends would suggest. The higher melting and boiling points for NH_3, H_2O and HF indicate that there must be unusually strong intermolecular forces between the molecules of these substances.

HF, H_2O and NH_3 are all highly polar because they contain three of the most highly electronegative elements, fluorine, oxygen and nitrogen, bonded to hydrogen, which has a relatively low electronegativity. This results in very polar molecules and much stronger intermolecular forces than expected for dipole–dipole interactions. These particularly strong intermolecular forces are referred to as *hydrogen bonds*.

Hydrogen bonding is a special form of dipole–dipole attraction. It is found in systems where a hydrogen atom is bonded to an atom of oxygen, nitrogen or fluorine. When hydrogen is bonded to the highly electronegative fluorine, oxygen or nitrogen atoms, the resulting bond is very polar and the shared electrons are strongly attracted towards the more electronegative atom. Because the hydrogen atom in these circumstances has an appreciable partial positive charge, it experiences a strong attractive force with lone pairs of electrons on oxygen, nitrogen or fluorine atoms of nearby molecules. Hydrogen bonding is particularly strong in solid HF, which consists of long chains of HF molecules, shown in Figure 11.11.

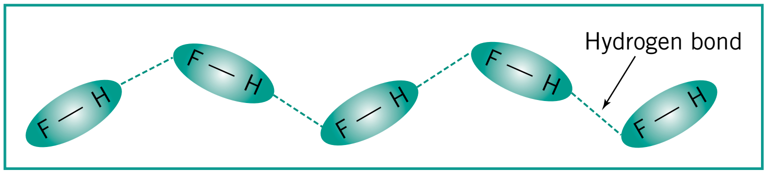


Figure 11.11 Hydrogen bonding in solid HF

Other electronegative elements such as chlorine, bromine and sulfur do not form hydrogen bonds. Although H–Cl, H–Br and H–S bonds are polar, the attractive force between the partially positive hydrogen atoms and the lone electron pairs on other chlorine, bromine and sulfur atoms is not as strong. The chlorine, bromine and sulfur atoms are much larger and the lone pair electrons are not as accessible to the partial positively charged hydrogen atoms.

The essential requirements for hydrogen bonding are:

- a hydrogen atom bonded to N, O or F so that the hydrogen atom has an appreciable partial positive charge due to the unequal sharing of the pair of electrons in the covalent bond
- an unshared pair of electrons on a neighbouring N, O or F atom that can attract the partially positive hydrogen atom.

The strength of hydrogen bonds is in general about ten times that of dipole–dipole forces but about one-tenth that of ionic or covalent bonds. Hydrogen bonding is important in many chemical systems. Some examples are included in Figure 11.12. These include the formation of hydrogen bonds between simple molecules such as

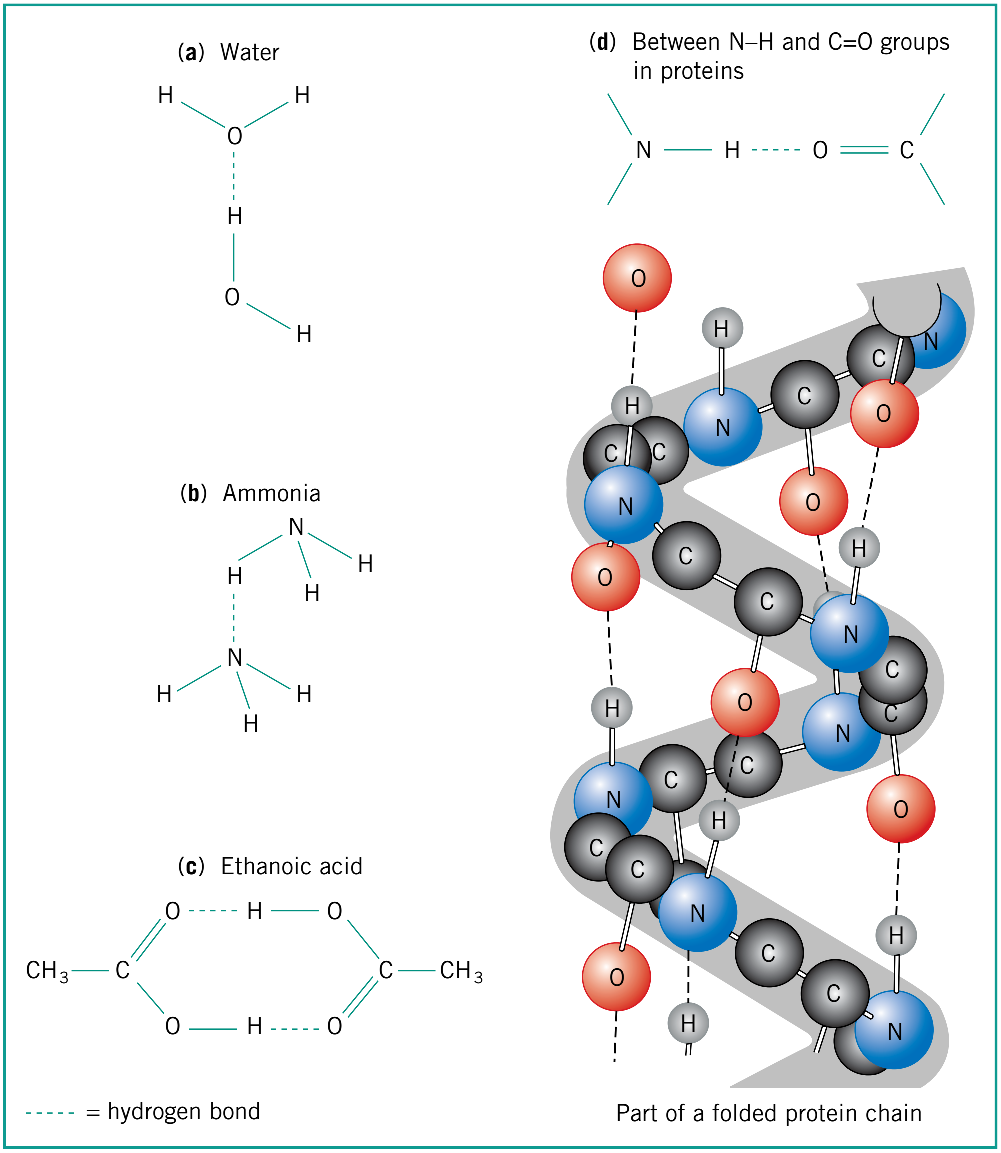


Figure 11.12 Some examples of hydrogen bonding

H_2O, NH_3 and CH_3COOH. Figure 11.12 also illustrates the formation of hydrogen bonds between N–H and C=O groups. Hydrogen bonds such as these are extremely important in biological systems and play a critical role in determining the structure of proteins and the double helix of DNA.

The presence of hydrogen bonding accounts for many of the unique properties of water. For example, the arrangement of water molecules in ice creates a very open structure that causes the density of ice to be less than that of liquid water. Figure 11.13 illustrates the arrangement of water molecules in ice. When ice melts, the regular lattice breaks up and the water molecules can pack more closely to form a liquid of somewhat higher density. Without hydrogen bonding, ice would sink to the bottom of oceans and lakes, a process that in cold climates would cause the death of fish and other aquatic life.

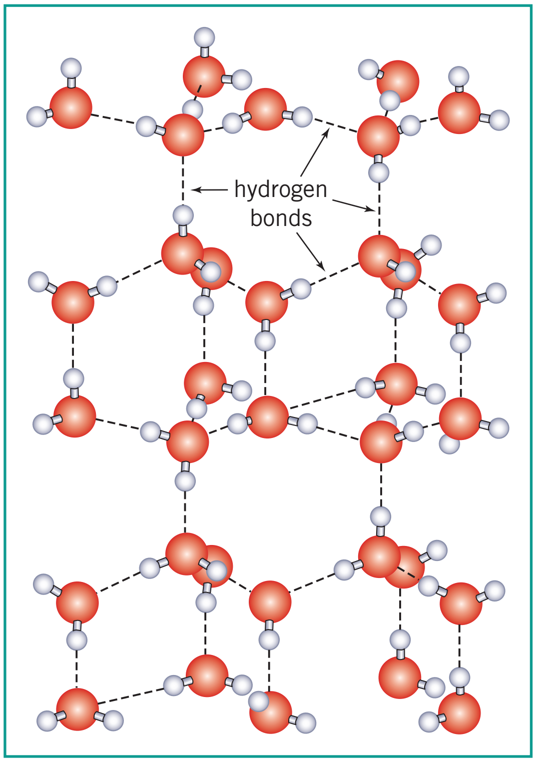


Figure 11.13 Hydrogen bonding in ice

Review exercise 11.3

1 List, in order of increasing strength, the three types of van der Waals forces that may exist between molecules of covalent molecular substances.

2 **Explain** the trend in melting points of the following groups of molecules:

   a F_2 –220°C, Cl_2 –101°C, Br_2 –7°C, I_2 114°C

   b CF_4 –187°C, CCl_4 –23°C, CBr_4 91°C, CCl_4 171°C (decomposes).

3 **Identify** the type of intermolecular attraction (dispersion forces, dipole–dipole forces or hydrogen bonding) that would be most significant in the following:

   a Br_2(l)

   b NH_3(l)

   c CH_3CH_2OH(l)

   d I_2(s)

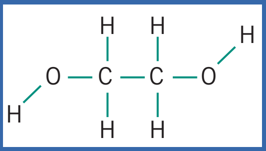
   e HCN(l)

   f CH_3COOH(l)

   g P_4(s)

   h CCl_4(l)

   i CCl_2F_2(l)

   j  (l)

4 In each of the following pairs, **predict** the substance you would expect to have a higher boiling point. **Explain** your prediction.

   a He or N_2

   b CH_4 or CH_3OH

   c HF or HCl

11.4 Properties of water

The ability of water to form droplets and to flow is a result of the intermolecular forces, particularly hydrogen bonds, that exist between water molecules. Various terms are used to describe the ability of water molecules to stick together, a behaviour that accounts for many properties of water that enable it to perform life-maintaining functions.

Figure 11.14 When water sits on a leaf surface, a droplet forms because of the relatively strong hydrogen bonding between water molecules.

Surface tension

The water molecules at the surface of a beaker of water are not surrounded by other water molecules in the same way as those molecules in the centre of the beaker, as shown in Figure 11.15. The result is that the molecules on the surface have an overall attractive force downwards into the rest of the water. This downward force creates a tension on the surface of the water, so that it behaves like a tightly stretched skin. This is known as *surface tension* and is a property of all liquids. The strength of the surface tension is directly proportional to the strength of the forces between the particles of the liquid, so water has a relatively strong surface tension. It is this property that allows many insects to 'walk on water' and the paper clip shown in Figure 11.16 to float.

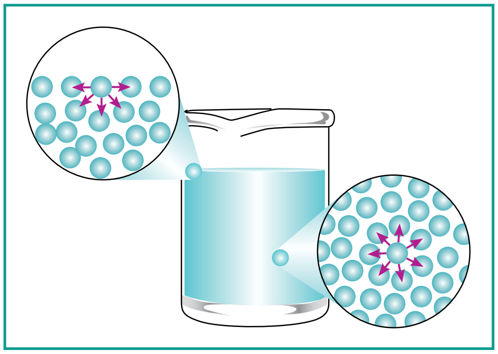
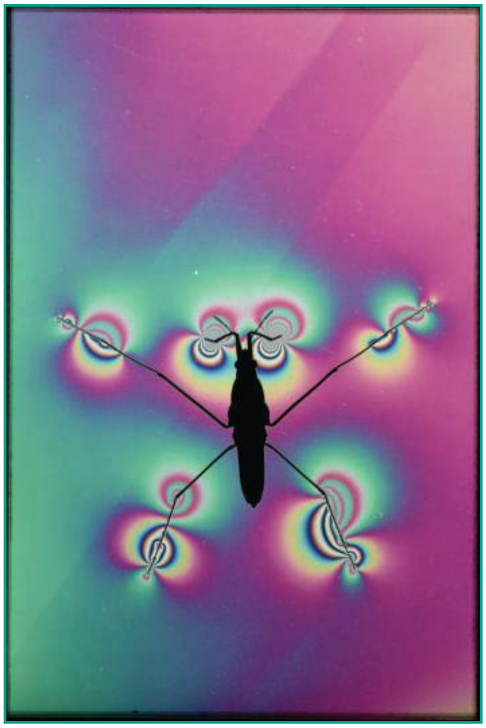


Figure 11.15 The difference between forces on particles at the surface of a liquid and those within the liquid is responsible for surface tension.

(a)



(b)

Figure 11.16 Surface tension enables
(a) a paper clip to float and
(b) insects to walk on the surface of water.

Viscosity

Viscosity refers to how easily a fluid (gas or liquid) flows, and is defined as the resistance of a fluid to flow. A thick fluid such as honey is said to have a high viscosity. Blood and motor oil have somewhat lower viscosities. The viscosity of water is lower again, but is higher than that of many other liquids and, of course, air. When poured, viscous fluids flow more slowly than less viscous fluids. Viscous fluids offer more resistance to movement than less viscous fluids. For example, it is more difficult to move through water than air.

Viscosity is another property that relates directly to the strength of the forces between the particles of the fluid and to the size of the particles. These forces determine how easily the molecules of the fluid move past each other. The viscosity of water is greater than many other liquids such as kerosene, petrol or acetone because the intermolecular forces are much stronger in water than in other liquids. Viscosity decreases as temperature increases, due to the increased motion of the particles. For this reason, motor oil contains additives that change shape on heating. This compensates for the decrease in viscosity of the oil that occurs due to heating.

Figure 11.17 Honey is a fluid of high viscosity.

CHEMISTRY CONTEXT

❈ CAPILLARITY IN TREES

The Grandis in Myall Lakes National Park is probably the tallest tree in New South Wales. How does such a tall tree transport water from its roots to its leaves against the force of gravity, a distance of around 80 metres? Scientists have proposed a theory known as the Cohesion-Adhesion-Transpiration (C-A-T) theory, which accounts for the movement of water through plants by a consideration of the chemistry of water, to answer this question.

Cohesion

Cohesive forces are forces that act between 'like' particles. Water, because of the relatively strong hydrogen bonds between its molecules, has strong forces of cohesion.

Adhesion

Adhesion results from the forces of attraction between unlike particles. Thus the forces between water molecules and water transport tissues of the tree are termed *adhesive forces*.

Capillary action or capillarity

Capillary action is the movement of any liquid such as water up a thin tube due to its cohesive and adhesive properties. The narrower the tube, the greater the ratio of the forces to the weight of the water, and the higher it will rise. This explains how paper towel soaks up water and a wick works in a candle.

Transpiration

Transpiration is the loss of water from the stomates in the leaves of plants. It is a cooling process, just as perspiration cools our bodies. Transpiration provides the pulling force to move the water up a tall tree.

It is the combined action of transpiration, cohesion between water molecules due to hydrogen bonding, and adhesive forces between the water molecules and the vessels in the plant (the latter two combining to produce capillary action) that results in water being able to travel up tall trees.

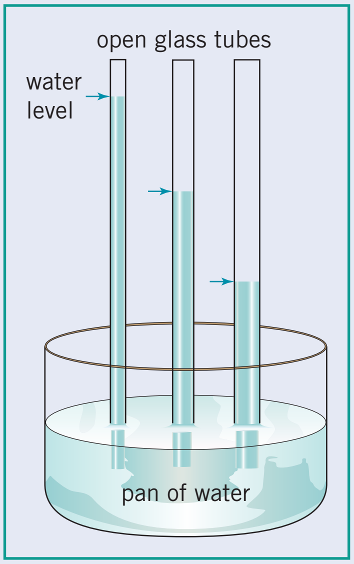
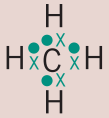


Figure 11.18 Capillarity in three tubes of different diameters

Melting point and boiling point

As discussed previously, the melting and boiling points of water are much higher than would be anticipated for a molecule of its size. The melting and boiling points of water are compared with those of other small molecules in Table 11.5. It can be seen that the values for water are much higher than for molecules of similar mass, reflecting the strength of the hydrogen bonds between its small polar molecules. In an ice crystal the covalently bonded molecules are arranged in a regular pattern, with each molecule being hydrogen bonded to four other water molecules, as shown in Figure 11.13. When ice melts, heat energy is absorbed, increasing the kinetic energy of the molecules so they can break free of the relatively strong hydrogen bonds in the ice lattice.

Table 11.5 Melting and boiling points of some covalent small molecules

Substance	Chemical formula	Relative molecular mass	Electron dot formula	Molecular shape	Melting point (°C)	Boiling point (°C)
water	H_2O	18.0		bent	0	100
ammonia	NH_3	17.0		trigonal pyramidal	–78	–33
hydrogen sulfide	H_2S	34.1		bent	–86	–60
hydrogen fluoride	HF	20.0		linear	–83	20
methane	CH_4	16.0		tetrahedral	–182	–162
carbon dioxide	CO_2	44.0		linear	only forms liquid under high pressure	–78 (sublimes)
nitrogen	N_2	28.0		linear	–210	–196

Review exercise 11.4

1 Given the following information, list the three liquids in order of increasing viscosity.

Liquid	Melting point (°C)	Boiling point (°C)
water	0	100
acetone	–95	56
glycerol	18	290

2 Why does a liquid such as petrol have a lower surface tension than that of water?

3 **Explain** why H_2O has much higher melting and boiling points than H_2S although the molecules have similar shapes.

4 **Analyse** how a water molecule in an ice crystal can form four hydrogen bonds when there are only two O–H covalent bonds in each molecule.

*KEY POINTS

- The Valence Shell Electron Pair Repulsion (VSEPR) model is used to predict the shapes of molecules.
- In the VSEPR model, the electron pairs (bonding and non-bonding) in the valence energy level of an atom are arranged as far apart as possible to minimise the repulsion between them.
- The geometric arrangement of four electron pairs that minimises repulsion is tetrahedral.
- Lone (non-bonding) pairs of electrons exert a slightly stronger repulsive force than bonding electron pairs. This slightly reduces bond angles in molecules such as ammonia or water from the normal tetrahedral angle of 109.5°C.
- Electronegativity of an atom is a numerical measure of the electron-attracting power of the atom.
- When a bond is formed between two atoms, the difference in electronegativity between the atoms determines whether the bond is ionic, polar covalent or non-polar covalent.
  - Where there is a large difference in electronegativity, such as Li and F, the bond will be ionic.
  - Where there is a moderate difference in electronegativity, such as H and Cl, the bond will be polar covalent.
  - Where there is no difference in electronegativity, such as in Cl_2 where the atoms are identical, the bond will be non-polar covalent.
- Covalent bonds in which there is an uneven charge distribution are called polar bonds.
- Molecules in which there is an uneven charge distribution are called polar molecules.
- For a molecule to be polar, the following conditions must apply:
  - The molecule must contain one or more polar bonds.
  - The molecule must not be completely symmetrical.
- The weak intermolecular (between molecules) forces in covalent molecular solids and liquids are called van der Waals forces.
- Intermolecular forces can be further classified as dipole–dipole forces, dispersion forces and hydrogen bonds.
- Dipole–dipole forces are forces of attraction between the oppositely charged ends of neighbouring polar molecules.
- Dipole–dipole attractive forces are relatively weak compared with the attractive forces between oppositely charged ions.
- Dispersion forces are weak attractive forces between non-polar molecules arising from the fact that at any instant a molecule may have a temporary dipole.
- Dispersion forces between molecules increase in strength with the number of electrons present in the molecules.

- Hydrogen bonding is a special, stronger form of dipole–dipole attraction. It occurs between molecules in which a hydrogen atom is bonded to an atom of oxygen, nitrogen or fluorine.
- HF, H_2O and NH_3 are all highly polar because they contain hydrogen bonded to three highly electronegative elements. As a result, strong hydrogen bonds occur between these molecules.
- Molecules on the surface of a liquid have an overall attractive force downwards into the rest of the liquid, which creates a tension on the surface of the liquid known as surface tension.
- Viscosity of a fluid refers to its resistance to flow.
- The melting and boiling points of water are much higher than would be anticipated for a molecule of its size due to the strength of the hydrogen bonds between its molecules.

✱APPLICATION AND INVESTIGATION

1 **Predict** the shapes of the following molecules:
   - **a** BCl_3
   - **b** H_2Te
   - **c** SiH_4
   - **d** SbH_3
   - **e** $BeCl_2$
   - **f** Cl_2O

2 **a** **Explain** why each H–N–H bond angle in an ammonia molecule is approximately the same as each H–C–H bond angle in a methane (CH_4) molecule.

   b Account for any minor differences in the bond angles between ammonia and methane.

3 **Identify** the factors that must be considered to decide whether
   - **a** a bond is polar
   - **b** a molecule is polar.

4 For each of the molecules listed in **a** to **h** below, **predict** whether:
      - **i** the molecule will contain polar bonds
      - **ii** the molecule will be polar.
   - **a** BCl_3
   - **b** C_2H_4
   - **c** PH_3
   - **d** CH_3Cl

  e SO_3
  f SiH_4
  g I_2
  h CO_2

5 **Construct** a table that summarises the conditions in which each of the three types of van der Waals forces will be present in covalent molecular substances, listing examples and comparing the strengths of these three forces.

6 The compounds BF_3 and NF_3 are known to exist. For these two compounds, answer the following questions.

  a **Predict** the types of solids they would form.

  b **Identify** the intermolecular forces that would be present.

  c Which compound would have the higher melting point? **Explain.**

7 Carbon and silicon both have four valence electrons and form compounds with formulas CO_2 and SiO_2, respectively. These oxides have very different properties: CO_2 sublimes at –78°C whereas SiO_2 melts at 1610°C and boils at 2230°C. **Explain** the differences in these properties in terms of the structures of these substances.

8 Consider the information below.

Compound	Boiling point (°C)
SO_2	–10
NH_3	–33
CH_4	–162
H_2O	100

  a Rank the substances in order of increasing strength of intermolecular forces.

  b **Explain** the order in terms of the nature of the intermolecular forces involved.

9 For the molecules listed in **a** to **c** below, **describe**:

    i the bonding within the molecule (intramolecular bond)

    ii the intermolecular forces between molecules.

  a carbon dioxide

  b ammonia

  c hydrogen sulfide

10 For each of the pairs listed in **a** to **c** below:

    i **identify** the nature of the intermolecular forces present

    ii **predict** which member of the pair would have the higher melting point.

  a H_2, O_2
  b CH_4, C_4H_{10}
  c HF, HCl

➲ **Investigation** **11** Water forms a concave meniscus in glass containers that is particularly noticeable when the container is narrow, such as a measuring cylinder. **Explain** the shape of this meniscus in terms of the cohesive and adhesive properties of water.

➲ **Investigation** **12** **Investigate**, using secondary sources, the role that surface tension plays in the ability of insects such as pond skaters to walk across the surface of a pond or lake.

➲ **Investigation** **13** **Investigate**, using secondary sources, the ballpoint pen and **describe** the role of adhesive and cohesive forces as ink from the pen is transferred to paper.

WATER AS A SOLVENT

CHAPTER 12

12.1 The solution process

Solutions were introduced as homogenous mixtures in Unit 10.2. The formation of solutions is related to the forces of attraction between the solvent and solute particles. During the formation of a solution, a rearrangement of particles occurs. For example, when sugar is dissolved in water, the crystal structure of sugar is broken down and the sugar molecules are distributed throughout the solution. For the sugar to dissolve, the following must take place:

- The intermolecular forces between the sugar molecules must be overcome as the crystal dissolves.
- The intermolecular forces between some water molecules must be overcome to make space for the sugar molecules.
- Intermolecular forces must form between the sugar molecules and the surrounding water molecules.

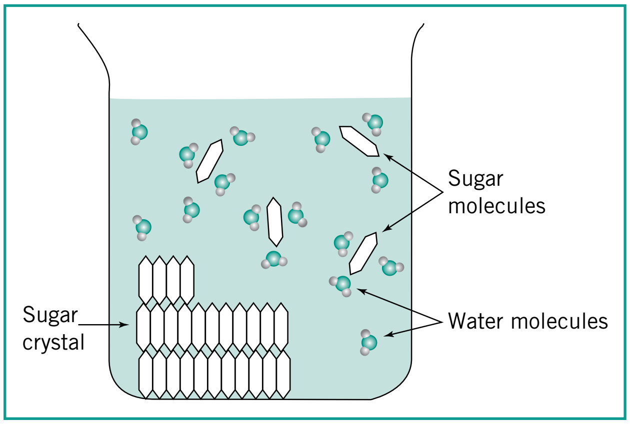


Figure 12.1 A model for sugar dissolving in water

Nature of the solute and solvent

In general, a solute will dissolve in a solvent only if the intermolecular forces within the solute and those within the solvent are similar to those occurring between solute and solvent molecules. Polar solvents tend to dissolve polar solutes and non-polar solvents tend to dissolve non-polar solutes. This generalisation is sometimes expressed as 'like dissolves like' and is illustrated in Table 12.1.

Table 12.1 Solubility tendencies in terms of the nature of the solute and solvent

	Solute	
Solvent	Polar	Non-polar
Polar	Soluble e.g. sugar will dissolve in water	Insoluble e.g. oil will not dissolve in water
Non-polar	Insoluble e.g. sugar will not dissolve in kerosene	Soluble e.g. oil will dissolve in kerosene

Polar solutes tend to dissolve much more readily in polar solvents than in non-polar solvents. This results from the formation of similar intermolecular forces between the solute and solvent molecules compared with those existing between solute molecules and solvent molecules alone. Ethanol (CH_3CH_2OH) and sugar are very soluble in water because both these substances are polar and form hydrogen bonding forces with water molecules. The molecules will tend to be oriented in such a way as to maximise these interactions.

Oil and similar non-polar substances do not dissolve in water because suitable intermolecular interactions do not occur between solute and solvent molecules. In oil the intermolecular forces are mainly dispersion forces, whereas in water, hydrogen bonding forces exist. The hydrogen bonds between water molecules are much stronger than the dispersion forces that could occur between oil and water molecules. As a result, the water molecules do not separate to allow space for the oil molecules to dissolve.

However, oil will dissolve in a non-polar solvent such as kerosene, because suitable interactions occur between the oil molecules and the kerosene molecules. As with oil, the intermolecular forces between the kerosene molecules are dispersion forces. Because of the similar nature of the intermolecular forces, the kerosene molecules will separate to allow space for the oil molecules to dissolve. Dispersion forces are formed between the oil and kerosene molecules.

Although water is the most important industrial solvent, organic solvents are quite widely used. These carbon-based compounds are often non-polar or have low polarity and can therefore be used to dissolve non-polar solutes. Examples include white spirits (a mixture of alkanes) in the paint and varnish industry and perchloroethylene, which is widely used in dry-cleaning.

Review exercise 12.1

1 Which of the following substances would you expect to be soluble in water?
   a $NH_3(g)$
   b $CH_3OH(l)$
   c $CH_4(g)$
   d $HCl(g)$
   e $H_2S(g)$
   f $C_8H_{18}(l)$ (octane).

2 **Identify** which of the following substances you would expect to be soluble in carbon tetrachloride.
   a $MgCO_3(s)$
   b $C_2H_6(g)$
   c $Pb(NO_3)_2(s)$
   d $HF(g)$
   e $C_8H_{18}(l)$
   f $H_2S(g)$

3 **Analyse**, using examples, whether you would expect some substances to be soluble in both water and carbon tetrachloride.

12.2 Relating solubility to structure

Solubility of ionic compounds

It is not possible to make a general statement regarding the solubility of ionic compounds in water. Many ionic compounds like sodium chloride are readily soluble in water but many others, such as silver chloride, are quite insoluble. Where solutions are formed, the charged ions are surrounded by water molecules, as shown in Figure 12.2. For cations (positively charged ions) the surrounding water molecules are oriented with the negatively charged end of the water molecule directed towards the positive ion. For anions (negatively charged ions) the positive end of the dipole is directed towards the ion.

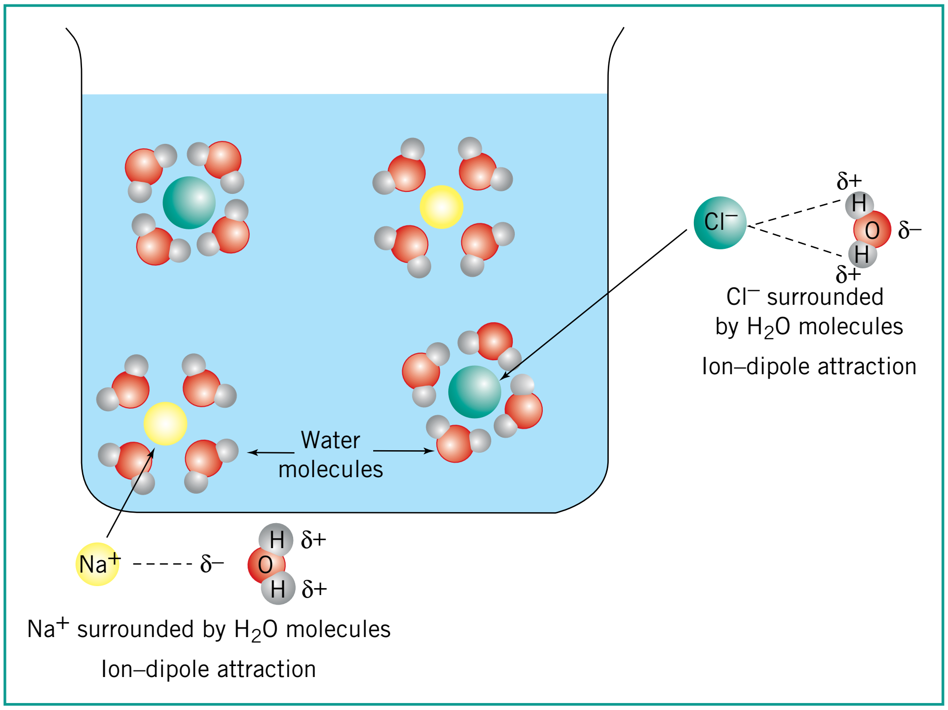


Figure 12.2 In solutions of ionic compounds such as sodium chloride, the ions are surrounded by water molecules.

The insolubility of some ionic compounds in water is due to the particular stability of the crystal lattices of these compounds. The solubility of ionic compounds can be predicted using 'solubility rules', which are discussed in the next chapter.

Aqueous solutions of ionic compounds produce ions in solution by the process known as *dissociation*. The ions in the ionic solid are separated by the solution process. This can be represented as follows:

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$$

Other ionic solids that dissolve in water, such as $Ca(NO_3)_2$ and $CuSO_4$, also dissociate to form ions in solution.

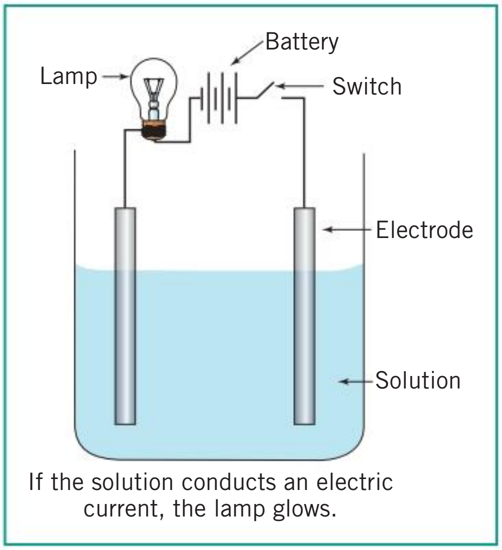


Figure 12.3 A conductivity apparatus used to determine whether a solution conducts electric current

Solutions of ionic compounds are good conductors of electricity. When a salt solution is tested with a conductivity apparatus such as that shown in Figure 12.3, the light bulb glows strongly. The Na^+ and Cl^- ions move through the solution when an electric current flows through it. It is the movement of these ions through the solution that is the current. Substances that produce ions in solution are known as *electrolytes*. Some substances that are not ionic solids also form ions when dissolved in solution. These are discussed later in this chapter.

Solubility of covalent molecular substances

Covalent molecular substances vary greatly in their solubilities in water, from insoluble substances such as paraffin (candle) wax to extremely soluble substances such as ammonia and ethanol. It is a reasonable generalisation that polar substances able to form hydrogen bonds with water are most soluble, followed by polar substances that do not form hydrogen bonds, followed by non-polar substances.

Soluble molecules: covalent molecular compounds that form hydrogen bonds with water

Polar covalent molecular compounds such as ammonia, glucose, sucrose, ethanol and methanol are very soluble in water. Each of these molecules is able to form hydrogen bonds with the water molecules. The intermolecular forces between these substances and water are similar to those within the separate solute and solvent (water).

Figure 12.4 shows the formation of hydrogen bonds between the polar –OH group in methanol and H_2O molecules. Similar hydrogen bonds are formed between water and the other substances listed above.

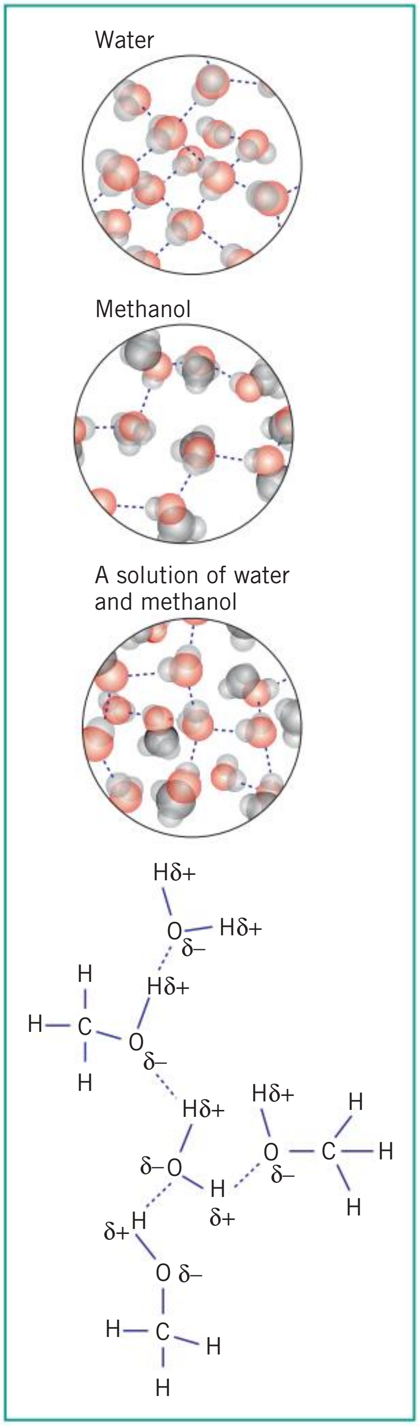


Figure 12.4 Hydrogen bonds between methanol and water.

While fairly small alcohol molecules like methanol (CH_3OH) and ethanol (CH_3CH_2OH) are very soluble in water, larger alcohols such as 1-hexanol ($CH_3CH_2CH_2CH_2CH_2CH_2OH$) and 1-decanol ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$) are much less soluble. Although these larger molecules still contain a polar –OH group capable of forming hydrogen bonds with water, the size of the non-polar hydrocarbon part of the molecule is much larger. The solubility of the alcohol depends on whether the tendency of the –OH group to dissolve in water is greater than the tendency of the hydrocarbon part of the molecule to remain undissolved. In the smaller alcohol molecules, the influence of the –OH group causes the alcohol to be soluble, but in larger alcohol molecules the influence of the hydrocarbon part limits the solubility.

Partially soluble molecules: covalent molecular compounds and covalent molecular elements that do not form hydrogen bonds with water

Covalent molecular substances unable to form hydrogen bonds with water molecules will only form dipole–dipole or dispersion forces with water. As a result, these substances are generally less soluble in water and are sometimes described as being partially or slightly soluble. The lesser solubility of these substances occurs because the intermolecular forces between the solute and water molecules are generally much weaker than the hydrogen bonds that form between water molecules in the solvent.

Partially soluble covalent molecules include both elements and compounds. Elements such as nitrogen and oxygen are non-polar and form only dispersion forces with water. As a result these substances have very limited solubility in water. Covalent molecular compounds may be non-polar or polar. Non-polar compounds such as butane (C_4H_{10}) and carbon tetrachloride (CCl_4) can only form dispersion forces and therefore have very low solubility. Polar molecular compounds such as chloroform ($CHCl_3$) and ether ($C_2H_5OC_2H_5$) form dipole–dipole forces with water molecules. These are slightly stronger than dispersion forces, resulting in slightly greater solubility for these substances.

The solubilities for several molecular gases are given in Table 12.2.

Table 12.2 Solubilities of gases in water at 25°C and 100 kPa pressure

Gas	Solubility (g/100 g)
Hydrogen (H_2)	0.00015
Nitrogen (N_2)	0.0017
Methane (CH_4)	0.0020
Carbon monoxide (CO)	0.0026
Oxygen (O_2)	0.0039
Carbon dioxide (CO_2)	0.14
Hydrogen sulfide (H_2S)	0.33
Chlorine (Cl_2)	0.64
Hydrogen chloride (HCl)	70

The low solubilities of most of these gases are due to the weak intermolecular forces, dipole–dipole forces and/or dispersion forces, between the gas and water molecules. Some substances such as hydrogen chloride and chlorine are more soluble than would be expected. This suggests that when they dissolve, these gases undergo some sort of chemical process, thereby increasing their solubility.

The covalent molecular gas hydrogen chloride (HCl) is very soluble in water. In this case the HCl molecules undergo ionisation when dissolved in water.

$$HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$$

This formation of ions results in a solution of hydrogen chloride being able to conduct electricity. It is therefore classed as an electrolyte.

Similarly, chlorine gas reacts with water, to some extent, as represented in the following equation:

$$Cl_2(aq) + 2H_2O(l) \rightleftharpoons HOCl(aq) + Cl^-(aq) + H_3O^+(aq)$$

In a similar way, carbon dioxide, hydrogen sulfide and ammonia all react with water to varying extents. Thus the solubility of covalent substances can be significantly influenced by whether they react with water.

Both dissociation and ionisation produce ions in solution. The basic difference is that in dissociation of ionic compounds, the ions are already present in the solid and separate to move into solution, whereas in ionisation of a covalent molecular substance, such as HCl, the ions are formed due to the reaction with water.

Insoluble large molecules

Large covalent molecules such as cellulose and polyethylene (polyethene) do not dissolve in water or most other solvents. This is because the very strong covalent bonds that form these large molecules cannot be broken by the weaker intermolecular forces (hydrogen bonds, dispersion forces) that could possibly be formed with the water molecules. In some cases the molecules have polar components, as shown in Figure 12.5. Despite the presence of these potential hydrogen bond-forming sites, these very large molecules are insoluble due to the presence of the large non-polar portion of the molecule and the need to break vast numbers of hydrogen bonds between the solvent water molecules.

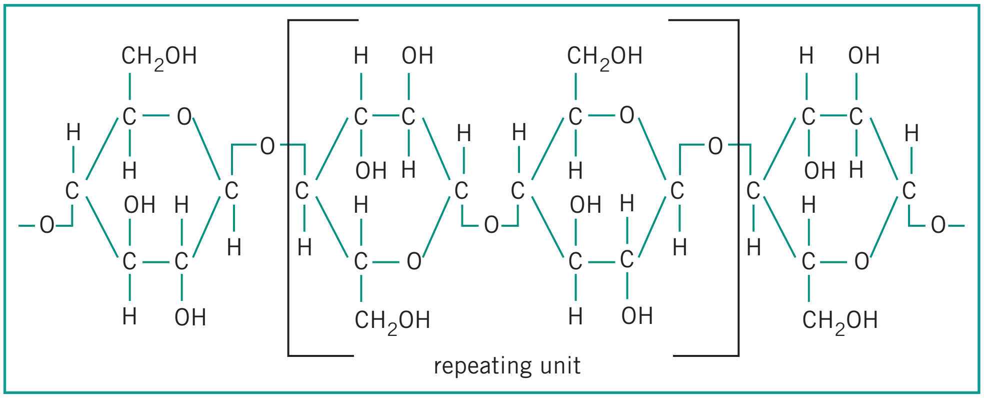


Figure 12.5 Structure of cellulose. Note the presence of polar –OH groups

Solubility of covalent network substances

Covalent network solids such as silicon dioxide and diamond are insoluble in water and most other solvents. This is because the very strong covalent bonds that form the crystal lattices of these substances cannot be broken by the weaker intermolecular forces that could be formed with water molecules.

❇ Review exercise 12.2

1 Draw a diagram to show the orientation of water molecules around the ions in an aqueous solution of KBr.

2 **Construct** a diagram to show the formation of hydrogen bonds between ethanol and water.

3 **Predict** the likely solubility of the following substances in water. Also, **describe** the nature of any intermolecular forces formed between the solute and water molecules.

  a copper(II) sulfate ($CuSO_4$)

  b sulfur dioxide (SO_2)

  c glucose ($C_6H_{12}O_6$), contains polar –OH groups

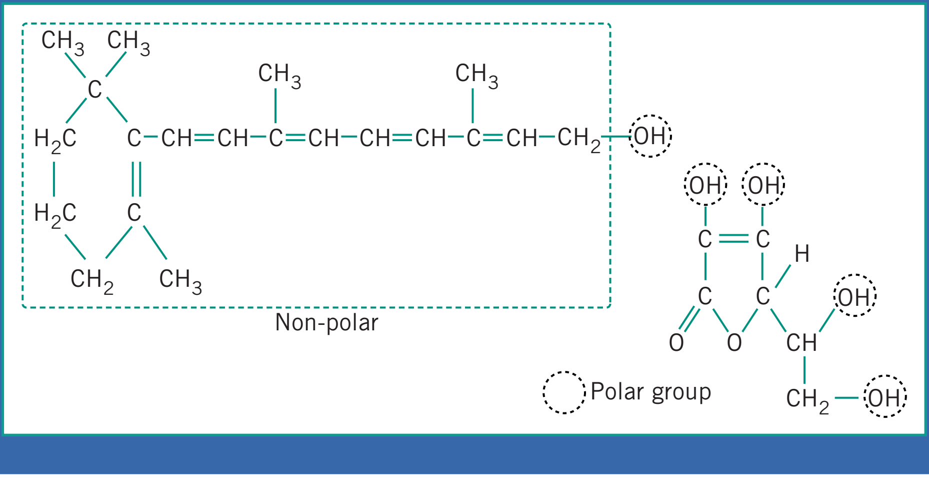
  d octane (C_8H_{18})

  e diamond (C)

  f polyvinyl chloride, PVC (CHClCHCl)*n*

4 **Distinguish** between the processes of ionisation and dissociation to form ions in aqueous solution.

5 Vitamins B and C are water soluble and excess intakes tend to be excreted in urine. Excess intakes of vitamins A, D, E and K are not excreted but tend to be stored in the body's fat. **Identify** which of the following structures represents vitamin A and which is vitamin C.



CHEMISTRY CONTEXT

❇ WATER AS A TRANSPORT SYSTEM FOR CELLS

The aqueous system we call blood plasma has a key role in transporting essential soluble substances such as glucose, oxygen, various salts, carbon dioxide, lactic acid and urea throughout the human body. A similar role is played by sap in plants.

Diffusion, osmosis and active transport play key roles in the movement of nutrients and wastes at the cell level. *Diffusion* is the spread of a substance throughout a space or a liquid due to the continuous random movements of its particles. Gases spread out to fill any container due to their random molecular motion. Diffusion also occurs in liquids. The molecules of the liquid and the particles of any substance dissolved in it move relative to each other due to their kinetic energy (Figure 12.6). Diffusion in liquids is much slower than in gases but will eventually result in the thorough mixing of the substances within the solution. Although the process of diffusion is random in nature, the overall result is that substances diffuse from regions of higher concentration to those of lower concentration.

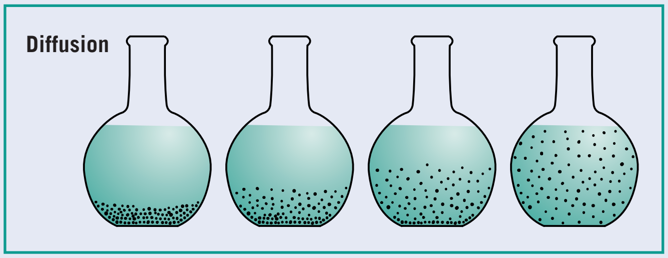


Figure 12.6 Diagrammatic representation of diffusion over a period of time

Diffusion is the basis for the continuous movement of dissolved substances such as small molecules (glucose, lactic acid) and ions (Na^+, Cl^-, K^+) from regions of high concentration to regions of low concentration throughout the body of an organism. Thus glucose, which is produced in the green leaves of plants, moves by diffusion to the plant sap and is then transported to other parts of the plant.

Osmosis is a specific form of diffusion, involving the movement of water from regions where it is highly concentrated to other regions through a semi-permeable membrane such as a cell membrane. These membranes typically allow the passage of water molecules but block the passage of larger solute particles. Osmosis allows water to move freely between cells, through the semi-permeable cell membranes and the liquids bathing them. Solvent water molecules can move in both directions through the membrane. However, the overall or net result is that water moves from the solution that is less concentrated (in solute) to the more concentrated solution (Figure 12.7).

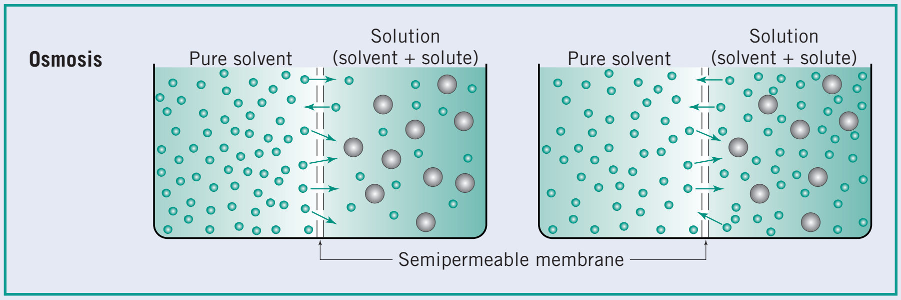


Figure 12.7 Diagrammatic representation of osmosis over a period of time

As well as this simple process of transport across cell membranes, other more complicated processes exist, such as facilitated diffusion and active transport, that allow the passage of particular species across cell membranes. *Active transport* is an endothermic process requiring the cell to use some of its energy supply to transport chemicals, whereas osmosis and diffusion are energy-neutral.

An important application of our knowledge of osmosis is the use of 0.9% saline solutions in hospitals where patients are being fed or provided with drugs intravenously. This concentration is used because it is the same salt concentration as blood plasma. If a different concentration were used, water would move into or out of red blood cells, causing them to swell or shrivel.

*KEY POINTS

- When a solute dissolves in solvent, the following processes must occur:
  - Intermolecular forces between solvent molecules are broken.
  - Intermolecular forces or ionic bonds within the solute are broken.
  - Intermolecular forces form between the solvent molecules and the molecules or ions of the solute.
- In general, a solute will dissolve in a solvent only if the intermolecular forces within the solute and those within the solvent are similar to those occurring between solute and solvent molecules.
  - Polar solvents tend to dissolve polar solutes.
  - Non-polar solvents tend to dissolve non-polar solutes.
  - Water tends to dissolve polar molecular and ionic compounds.
  - The solubility of different types of substances in water varies according to the solute structure and bonding, as shown in Table 12.3.

Table 12.3

Nature of the solute	Solubility in water	Examples
Ionic compounds	Usually soluble but with many exceptions	sodium chloride, copper(II) sulfate, silver nitrate, ammonium sulfate
Covalent molecular compounds capable of forming hydrogen bonds with water	Soluble	glucose, sucrose, ammonia, hydrogen fluoride
Polar and non-polar covalent molecular substances	Slightly soluble—solubility increases with polarity of the solute	hydrogen sulfide, carbon dioxide, chloroform, oxygen, nitrogen, chlorine
Large covalent molecules	Insoluble	polyethylene, cellulose
Covalent network substances	Insoluble	diamond, silicon, silicon dioxide, graphite

- Dissociation is the process in which an ionic solid separates into ions when it dissolves.
- Ionisation is the process in which a covalent molecular substance dissolves to form ions.
- An electrolyte is a substance that, when dissolved in water, produces ions, resulting in a conducting solution.
- Strong electrolytes are substances that are completely ionised or dissociated in solution.

*APPLICATION AND INVESTIGATION

1 **Explain** in terms of intermolecular forces the term 'like dissolves like'.

2 Urea (NH_2CONH_2), a polar molecular solid, and sodium nitrate ($NaNO_3$) are two compounds used in soluble fertiliser mixtures. **Describe** the form in which these substances exist in aqueous solution.

3 Why is kerosene or petrol, rather than water, used to remove oil and grease?

4 **Explain** the following:

  a Ammonia and methane are both covalent molecular substances but have very different solubilities in water.

  b Water is a good solvent for polar and ionic solutes.

  c The forces between solute and solvent particles change when sodium chloride is dissolved in water.

5 **Identify** which of each of the following pairs of compounds would be expected to be more soluble in water. **Explain** your choice for each.

  a CH_3OH or $CH_3CH_2CH_2CH_2OH$

  b C_6H_{14} or $C_6H_{13}OH$

  c $MgCl_2$ or Cl_2

6 **Predict** the likely solubility of the following substances in water and **identify** the nature of the intermolecular forces between solute particles and water.

  a quartz, SiO_2

  b sodium carbonate, Na_2CO_3

  c nitrous oxide, N_2O

  d ethane, C_2H_6

  e polypropylene

  f hydrazine, N_2H_4

➲ **Investigation**

7 Sulfur dioxide is very soluble in water, suggesting that it reacts with water when it dissolves. **Investigate** using secondary sources the reactions that take place when sulfur dioxide dissolves in water.

8 **Explain** why liquid hydrogen chloride is a non-conductor of electricity but an aqueous solution of hydrogen chloride is a good electrical conductor.

9 Using HCl and NaCl as examples, **distinguish** between ionisation and dissociation when substances are dissolved in water.

➲ **Investigation**

10 **Investigate** the processes involved in the movement of water from the soil through a tree to the atmosphere.

➲ **Investigation**

11 Why would a freshwater fish probably die if placed in sea water?

CHAPTER 13

SOLUBLE AND INSOLUBLE SALTS

13.1 Solubility rules for ionic substances

As discussed in Unit 12.2, the solubilities of ionic substances in water vary considerably. When solutions of different ionic compounds are mixed, they sometimes react to produce a precipitate (insoluble solid). For example, if a solution of silver nitrate is added to a sodium chloride solution, a white solid, silver chloride, is produced immediately, as shown in Figure 13.1. The equation for this can be written as:

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

When two solutions are mixed, precipitation will occur if one or more of the cation–anion combinations produces an insoluble compound. In the preceding example, mixing the two solutions caused insoluble silver chloride to precipitate. The other possible cation–anion combination, $NaNO_3$, is soluble and therefore would not precipitate.

If solutions of NH_4NO_3 and Na_2CO_3 are mixed, no precipitate is produced. Neither of the new cation–anion combinations, $(NH_4)_2CO_3$ and $NaNO_3$, is an insoluble compound.

It is possible to predict whether a precipitation reaction will occur when solutions of ionic compounds are mixed, by using a table of solubilities. Table 13.1 indicates the solubilities of ionic substances in water under normal laboratory conditions.

Table 13.1 Solubility of common ionic substances*

Soluble anions	Exceptions
NO_3^-	none
Cl^-	Ag^+ insoluble, Pb^{2+} slightly soluble
Br^-	Ag^+ insoluble, Pb^{2+} slightly soluble
I^-	Ag^+, Pb^{2+} insoluble
SO_4^{2-}	Ba^{2+}, Pb^{2+} insoluble, Ca^{2+}, Ag^+ slightly soluble
Insoluble anions	**Exceptions**
OH^-	Na^+, K^+, Ba^{2+} soluble; Ca^{2+} slightly soluble Note: NH_4OH exists as $NH_3(aq)$
S^{2-}	Na^+, K^+, NH_4^+ soluble
CO_3^{2-}	Na^+, K^+, NH_4^+ soluble
PO_4^{3-}	Na^+, K^+, NH_4^+ soluble

*This table applies to the cations Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Ag^+, Zn^{2+}, Sn^{2+} and Pb^{2+}.

Figure 13.1 Silver chloride precipitate forms when silver nitrate solution is added to sodium chloride solution.

Table 13.1 is organised in terms of the solubility of various anions. It is easier to remember the solubilities of ionic compounds when they are organised in this way. In addition, one useful generalisation relating to cations is that all sodium, potassium and ammonium salts are soluble. The colours of some of the most commonly encountered precipitates are listed in Table 13.2.

Table 13.2 Colours of common precipitates

Cation	Anion						
	NO_3^-	Cl^-	Br^-	I^-	SO_4^{2-}	OH^-	CO_3^{2-}
Na^+							
K^+							
NH_4^+							
Mg^{2+}						white	white
Ca^{2+}					white	white	white
Ba^{2+}					white		white
Fe^{2+}						green	green
Fe^{3+}						brown	brown
Cu^{2+}						blue	green
Ag^+		white	pale yellow	yellow	white	brown	yellow
Zn^{2+}						white	white
Sn^{2+}						white	white
Pb^{2+}		white	white	yellow	white	white	white

Ionic equations

As mentioned previously, when solutions of silver nitrate and sodium chloride are mixed, a white precipitate of silver chloride is formed. This is illustrated in Figure 13.2, which indicates the ions present in the solutions before and after mixing.

When the two solutions are mixed, the reaction is essentially a reaction between $Ag^+(aq)$ and $Cl^-(aq)$ ions to form solid AgCl. The $Na^+(aq)$ and $NO_3^-(aq)$ ions are not involved in the reaction at all and remain as ions in solution. Ions that are not involved in chemical reactions are often called *spectator ions*. Because spectator ions take no part in chemical reactions, the reaction equations are usually simplified, as shown here.

Equation with formulas:

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

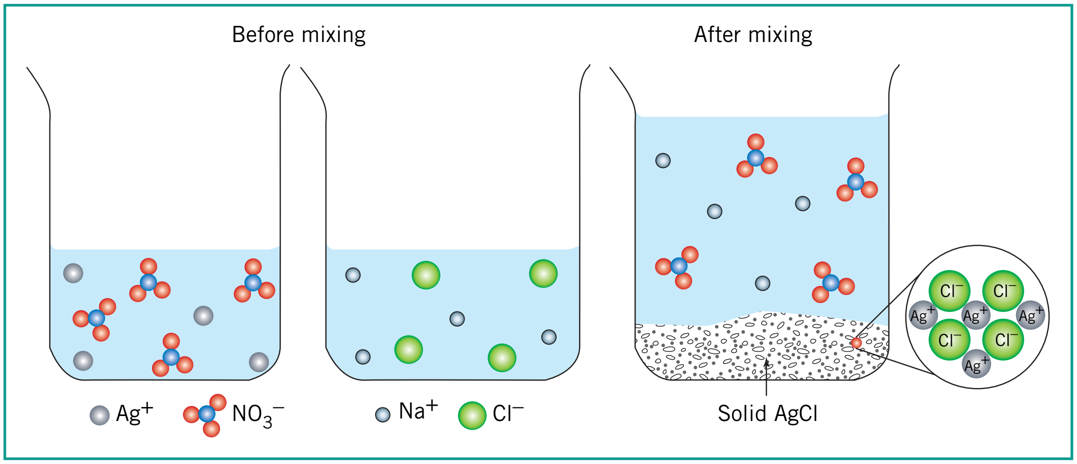


Figure 13.2 Ions present when solutions of NaCl and $AgNO_3$ are mixed

Ionic equation showing all ions:

$$Ag^+(aq) + NO_3^-(aq) + Na^+(aq) + Cl^-(aq) \rightarrow AgCl(s) + Na^+(aq)\ NO_3^-(aq)$$

Net ionic equation with spectator ions removed:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

The net ionic equation most accurately represents what occurs when the reaction takes place. Net ionic equations for other examples of precipitation reactions are shown in Table 13.3.

Table 13.3 Examples of precipitation reactions

Solutions mixed	Precipitate formed	Net ionic equation
$AgNO_3$ and NaBr	AgBr	$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$
$Pb(NO_3)_2$ and KI	PbI_2	$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$
$CaCl_2$ and Na_2CO_3	$CaCO_3$	$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$
$BaCl_2$ and $(NH_4)_2SO_4$	$BaSO_4$	$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$
$Mg(NO_3)_2$ and NaOH	$Mg(OH)_2$	$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$
$FeSO_4$ and K_3PO_4	$Fe_3(PO_4)_2$	$3Fe^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Fe_3(PO_4)_2(s)$

Net ionic equations can be used for reactions other than precipitation reactions. However, they are mainly used for reactions that take place in solution. When writing ionic equations the following rules should be observed.

- Strong electrolytes are written in ionic form.
- Weak electrolytes are written in molecular form.
- Non-electrolytes are written in molecular form.
- Insoluble substances are written as the formulas of the substances.
- Gases are written in molecular form.
- Net ionic equations should not include spectator ions.
- Equations must be balanced in atoms and electrical charge.

In addition to precipitation reactions, other reactions that are better represented by net ionic equations include the following:

- the preparation of carbon dioxide by the reaction of an acid with a carbonate. Depending on whether the acid is added to the solid carbonate or a solution containing carbonate ions, the equation can be written as:

  $Na_2CO_3(s) + 2H^+(aq) \rightarrow 2Na^+(aq) + CO_2(g) + H_2O(l)$

  or

  $CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$

  The acid is written as H^+ in these equations as the anion takes no part in the reaction. The same reaction occurs whether hydrochloric (HCl), sulfuric (H_2SO_4) acid or any other acid is involved.

- the preparation of hydrogen by the reaction of an acid with a metal. The equation when zinc is the metal used is:

  $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

  Again the acid is written as $H^+(aq)$ as the anion is not involved in the reaction.

✻ Review exercise 13.1

1 Using Table 13.1, **identify** which of the following pairs of solutions produce precipitates when mixed, and **construct** ionic equations for the reactions.

  a $CuSO_4(aq)$ and $Na_2CO_3(aq)$
  b $FeCl_3(aq)$ and $KOH(aq)$
  c $AgNO_3(aq)$ and $Na_2S(aq)$
  d $NaNO_3(aq)$ and $(NH_4)_2S(aq)$
  e $Ca(NO_3)_2(aq)$ and $K_3PO_4(aq)$
  f $Ba(NO_3)_2(aq)$ and $CaCl_2(aq)$

2 **Construct** balanced net ionic equations for the following reactions:

  a $HCl(aq) + Na_2CO_3(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$
  b $CaBr_2(aq) + (NH_4)_2CO_3(aq) \rightarrow CaCO_3(s) + NH_4Br(aq)$
  c $Pb(NO_3)_2(aq) + H_2S(g) \rightarrow PbS(s) + HNO_3(aq)$
  d $CaCO_3(s) + CO_2(aq) + H_2O(l) \rightarrow Ca(HCO_3)_2(aq)$

3 Write balanced net ionic equations for the following reactions.

  a Solutions of K_2CO_3 and $BaCl_2$ are mixed.
  b Solutions of $Pb(NO_3)_2$ and $(NH_4)_2CO_3$ are mixed.
  c Magnesium metal is added to hydrochloric acid.
  d Hydrochloric acid is added to marble chips.
  e A solution of $Ca(HCO_3)_2$ is boiled to form calcium carbonate, carbon dioxide and water.
  f Two solutions when mixed form a precipitate of $Ba_3(PO_4)_2$.

13.2 Reversible reactions and equilibrium systems

Reversible reactions

In previous discussions, reactions have been viewed as proceeding in one direction from reactants to products. In many reactions, however, there is a significant reaction in the opposite direction in which product molecules react to regenerate the reactants. Because of this, the terms *forward reaction* and *reverse reaction* are frequently used. For example, if the reaction:

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

is described as the forward reaction, the reaction:

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

will be the reverse reaction. Frequently, a double arrow is used as a way of indicating significant reversibility of a reaction. In the case of the reaction above, this can be represented as:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

When the reactants in a reversible reaction are placed in a closed container under appropriate reaction conditions, products will begin to form by means of the forward reaction. As the concentrations of reactants decrease, the rate of the forward reaction also decreases. This occurs because collisions between reactant molecules become less frequent. As soon as products begin to form, the reverse reaction becomes possible. The reverse reaction rate, which was initially zero, will gradually increase as the concentrations of products increase. Eventually, the rates of the forward and reverse reactions become equal and the system is said to have reached *chemical equilibrium*. When a system of two reversible reactions is at chemical equilibrium, no further observable changes are noted, unless the equilibrium is disturbed. Reaction rate and the factors influencing it will be discussed in greater detail in Chapter 19.

Equilibrium in physical systems

The essential features of dynamic equilibrium are also present in simple physical systems such as solubility equilibria and equilibria between different states. While these are not strictly chemical changes, they illustrate the fundamental aspects that are characteristic of chemical equilibrium.

Solution equilibria

The situation that exists when excess solute is in contact with a saturated solution is an example of dynamic equilibrium. Some of the solid solute continues to dissolve into solution at the same rate as dissolved solute crystallises out of solution.

Consider what happens when 210 g of sugar is mixed with 100 g of water at 20ºC. The solubility of sucrose at this temperature is about 204 g per 100 g of water, so when the solution is saturated, 6 g of undissolved sucrose will be left in contact with the solution. Once the solution is saturated, no changes in the macroscopic properties (observable properties) of the solution take place. However, the processes of dissolving and crystallising continue at equal rates. The evidence for the continual dissolving and crystallisation of the sugar molecules comes from studies using radioactive tracers. This involves adding solid sugar containing radioactive

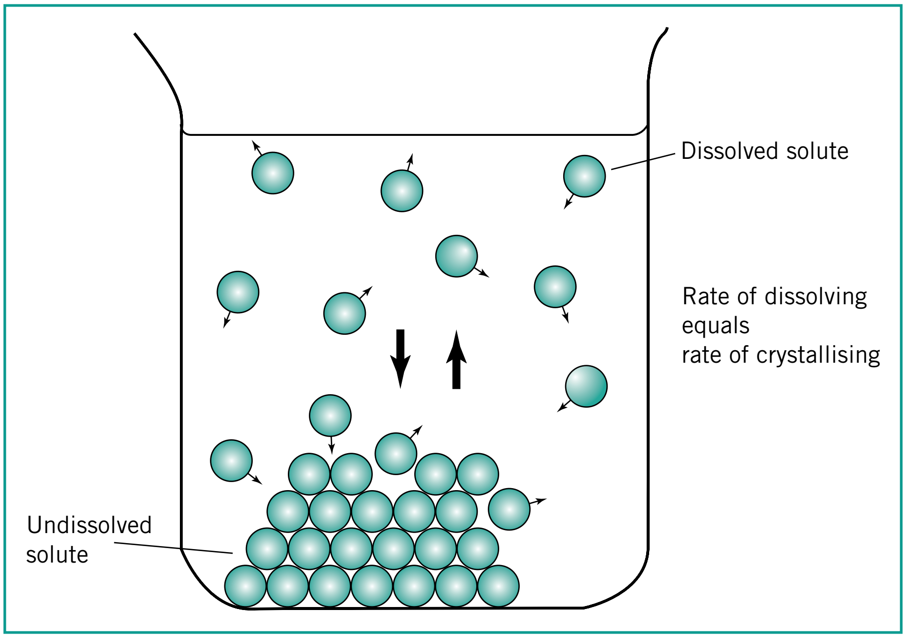


Figure 13.3 When an equilibrium is established between undissolved solute and solute in solution, the rates of dissolution and crystallisation are equal.

carbon-14 to an already saturated solution. At regular intervals, small samples of the solution are removed and the level of radioactivity is recorded. The level of radioactivity of the solution is shown to increase, providing evidence that while the mass of undissolved solute remains constant at the molecular level, dissolution and crystallisation continue to occur. This dynamic equilibrium can be represented as:

$$C_{12}H_{22}O_{11}(s) \rightleftharpoons C_{12}H_{22}O_{11}(aq)$$

If the temperature of the system is reduced, the system will no longer be at equilibrium. The solubility of sucrose is less at lower temperatures, so the mass of dissolved sucrose will decrease. Extra sucrose will crystallise from solution until the solution contains only the mass of sucrose needed to saturate it at the lower temperature.

The change in temperature of the system produces a change in the rates of the processes of dissolving and crystallising. The rate of crystallisation is greater than the rate of dissolution, so the mass of dissolved sucrose decreases as additional solid separates from the solution. Eventually a new equilibrium is established in which the rates of the two processes are again equal.

Saturated solutions in contact with undissolved ionic solute also represent examples of dynamic equilibria. For example, a saturated solution of sodium nitrate in contact with excess undissolved solute can be represented as:

$$NaNO_3(s) \rightleftharpoons Na^+(aq) + NO_3^-(aq)$$

Because the ions dissociate when the solid dissolves, the equilibrium is between undissolved solute and ions in solution.

Model to explain the solubility of ionic solids

In Unit 12.1 the formation of solutions was discussed in terms of the forces of attraction between the solvent and solute particles. When an ionic solid dissolves in water, the crystal structure of the substance breaks down and the ions become distributed throughout the solution. For an ionic solid to dissolve, the following must take place:

- The electrostatic forces of attraction between the positive and negative ions of the ionic solid must be overcome as the crystal dissolves.
- Intermolecular forces between some polar water molecules must be overcome, to make space for the positive and negative ions.
- Attractive forces must form between the positive and negative ions and surrounding water molecules.

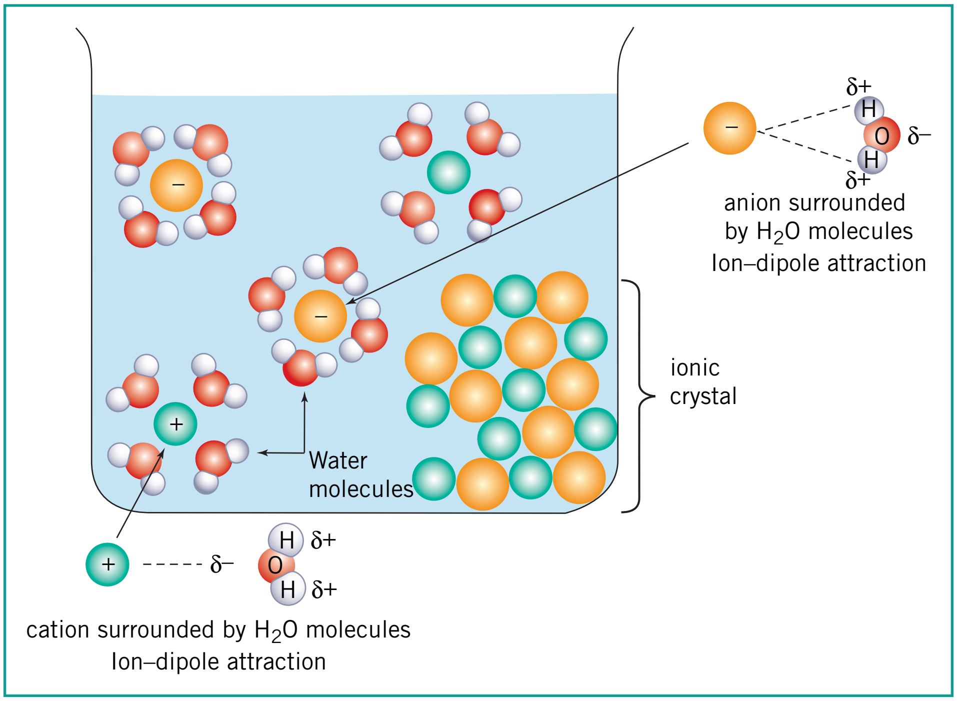


Figure 13.4 A model for an ionic solid dissolving in water

In general, an ionic solid will dissolve in water if the strength of the attractive forces between the dissolved ions and water molecules is sufficient to compensate for the energy needed to separate the ions in the solid and the water molecules in the solvent. In the case of insoluble ionic solids such as silver chloride, the electrostatic forces of attraction between the positive silver ions and the negative chloride ions are too strong to be overcome by the attractive forces that would be formed between the silver and chloride ions and polar water molecules. Conversely, for soluble ionic solids such as potassium nitrate, the attractive forces between the ions and water molecules are sufficient to allow the solute to dissolve. The attractive forces between the ions are broken and the ions become surrounded by the polar water molecules.

A precipitate will form if the forces of attraction between dissolved cations from one solution and dissolved anions from an added solution are stronger than the forces of attraction between the dissolved ions and the water molecules. These cations and anions will join together, gradually forming small crystals that keep growing and eventually fall to the bottom of the container. This is illustrated in Figure 13.5, with the spectator ions removed from the diagram.

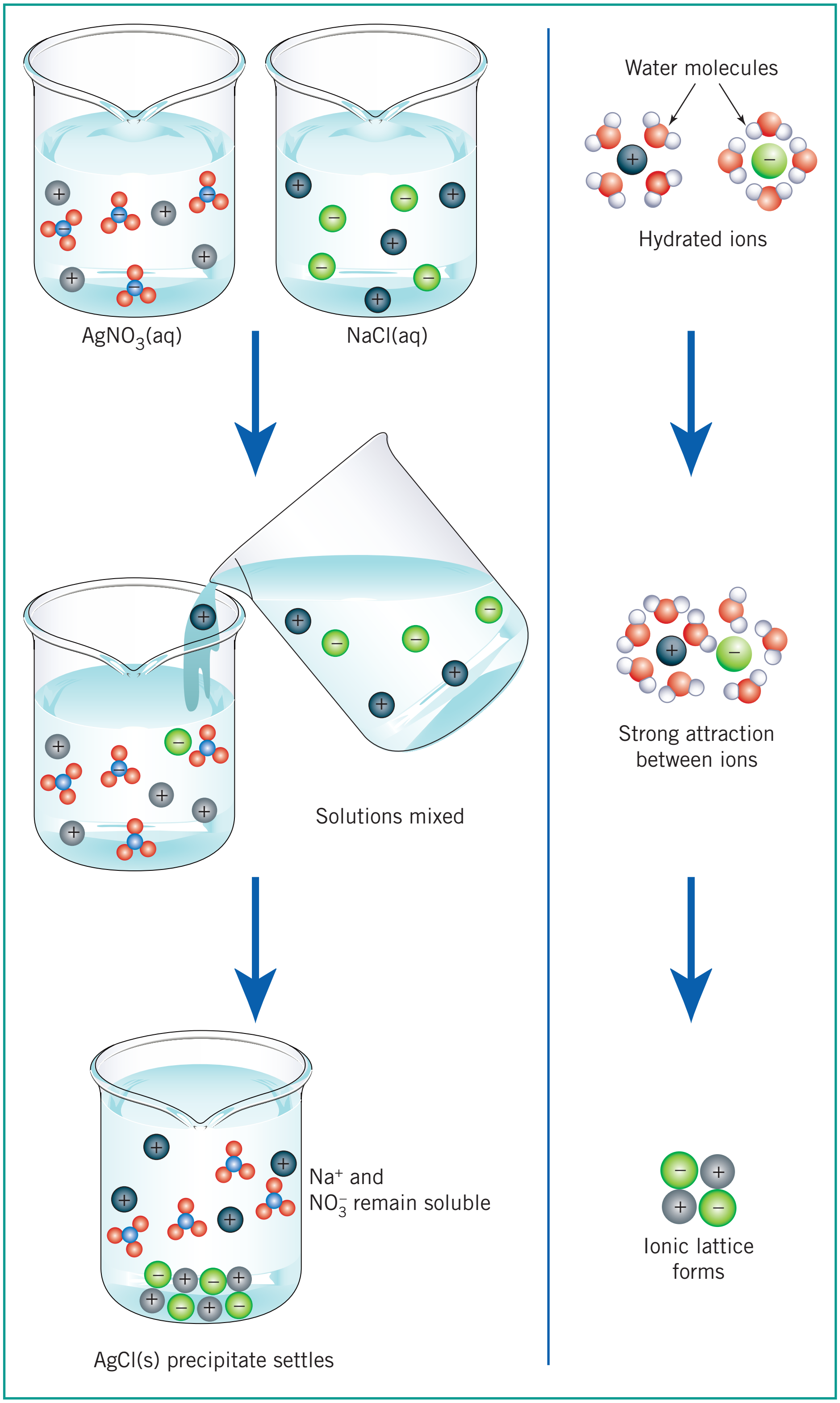


Figure 13.5 A model for a precipitation reaction

CHEMISTRY CONTEXT

❇ LIQUID–VAPOUR EQUILIBRIA

If a closed vessel is partly filled with a liquid such as water, equilibrium is established between the liquid and gaseous states. Some of the liquid evaporates into the gaseous state. As the concentration of the vapour state increases, the chances of gaseous molecules colliding with and re-entering the liquid increase. As a result, the rate of condensation increases. If the temperature is kept constant, the rates of evaporation and condensation will become equal. From this time the masses of the liquid and gaseous states remain constant and the system has constant macroscopic or observable properties. A state of dynamic equilibrium exists, as shown by the following equation:

$$H_2O(l) \rightleftharpoons H_2O(g)$$

If the temperature of the system was increased by 10ºC the system would no longer be in equilibrium. The rate of evaporation would increase because a greater proportion of the liquid molecules would have sufficient kinetic energy to escape from the cohesive forces in the liquid. As the concentration of molecules in the vapour state increased, the condensation rate would also increase. Eventually, the rates of evaporation and condensation would once again be equal and equilibrium would be re-established. Note that at the higher temperature, the mass of liquid would be lower and the vapour pressure would be higher. However, once equilibrium was re-established, the macroscopic properties of the system would remain constant, provided no further changes were made to the conditions.

Important safety considerations arise when transporting liquid fuels because of the liquid–vapour equilibrium.

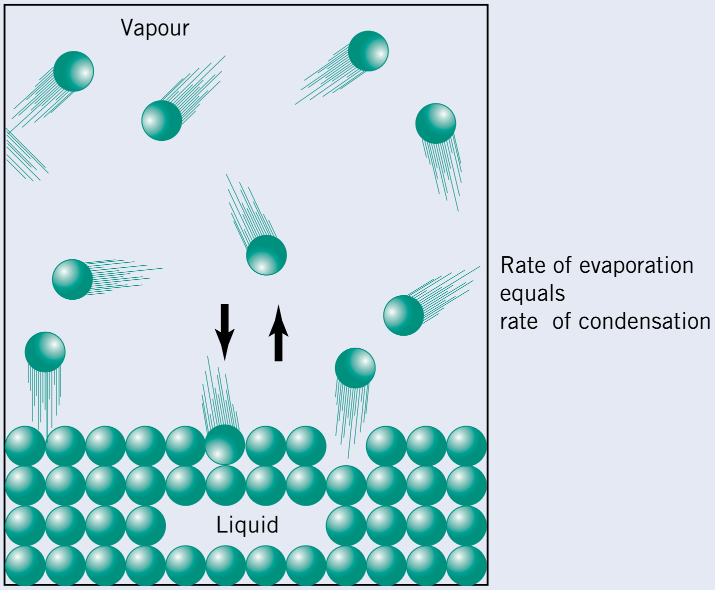


Figure 13.6 When an equilibrium is established between a liquid and its vapour, the rates of evaporation and condensation are equal.

It is the gas state of fuels that combusts, and air can form explosive mixtures with fuels such as petrol, even at low temperatures. It is the amount of air present that determines the size of the potential explosion, as a greater volume of gaseous air than liquid fuel is consumed in the combustion reaction. This is why petrol should only ever be stored and transported in appropriate containers.

Petrol road tankers have a vapour recovery system, which consists of a series of pipes collecting the vapours from the top of the tanker during the loading process to prevent the escape of fuel vapours, and they must load and unload at a slow rate in order to allow vapour and air to exit/enter the tanker and avoid pressure or a vacuum to build up. Road tankers are constructed with multiple compartments and each compartment often has an internal partition as well. This reduces the movement of liquid fuel during transport.

CHEMISTRY CONTEXT, cont.

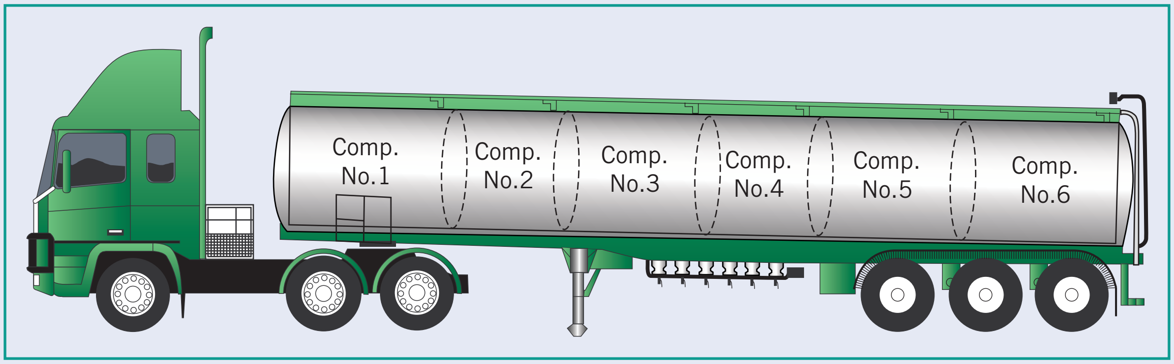


Figure 13.7 Petrol tanker trucks are designed with an understanding of liquid–vapour equilibrium.

❄ Review exercise 13.2

1 The solubility of NaCl per 100 g of water is 36.0 g at 20°C and 37.0 g at 50°C. 40 g of NaCl was added to 100 g of water at 20°C and the system allowed to come to equilibrium. If the system was heated to 50°C, **describe** the changes that would occur.

2 When nitrogen and hydrogen are heated under conditions of high temperature and pressure, ammonia is formed. However, a sample of ammonia when heated produces nitrogen and hydrogen. Write an appropriate symbol equation to represent this reversible system.

13.3 Concentrations of solutions

The concentration of a solution refers to the quantity of solute dissolved in a particular quantity of solvent or solution. Often solutions are qualitatively described as being dilute or concentrated. These terms do not have any precise meaning and only indicate that a concentrated solution contains more solute than a dilute solution containing the same solute.

Quantitative methods of expressing solution concentrations are needed so that the precise quantity of solute in a given volume of solution can be determined. The use of solution concentrations is important in chemical analysis, chemical manufacturing, the prescription of drugs and medicines, and other situations requiring quantitative work. Four methods of expressing solution concentrations are as follows:

- grams per litre
- percentage composition by mass
- parts per million
- moles per litre.

Grams per litre (g L^{-1})

Solution concentrations can be expressed as the number of grams of solute dissolved in a litre of solution. For example, if 200 mL of sea water contained 4.2 g of sodium chloride, the concentration of the solution would be 21 grams per litre, that is, 21 g L^{-1}.

Percentage composition by mass

The percentage composition by mass is the mass of solute in grams dissolved in 100 g of solution. For example, a 3% hydrogen peroxide solution is one that contains 3 g of H_2O_2 in every 100 g of solution. The percentage composition is calculated in the following way.

$$\text{Concentration (\% composition)} = \frac{\text{mass of solute (g)}}{\text{mass of solution (g)}} \times 100$$

➜ Example 13.1

A solution of concentrated hydrochloric acid contains 296 g of hydrogen chloride dissolved in 500.0 g of water. Calculate the percentage composition of the hydrochloric acid.

$$\text{Total mass of solution} = 296 + 500.0 = 796\text{ g}$$

$$\begin{aligned}\text{\% composition} &= \frac{\text{mass of HCl}}{\text{mass of solution}} \times 100 \\ &= \frac{296}{796} \times 100 \\ &= 37.2\%\end{aligned}$$

Parts per million (ppm)

This method of expressing the concentration of solutions is sometimes used for very dilute solutions. For example, the concentration of salt in drinking water is often expressed in parts per million. The concentration in parts per million is the mass of solute, in milligrams, in one kilogram of solution. This is because 1 mg is one-millionth the mass of 1 kg. A sodium chloride solution with a concentration of 250 ppm contains 250 mg of salt in each kilogram of solution. Concentrations in parts per million can be calculated as follows:

$$\text{Concentration (ppm)} = \frac{\text{mass of solute (mg)}}{\text{mass of solution (kg)}}$$

➜ Example 13.2

A sample of tap water was found to contain 0.0537 g of NaCl per 250.0 g of solution. Calculate the concentration of NaCl in parts per million.

$$\begin{aligned}\text{Concentration (ppm)} &= \frac{\text{mass of solute (mg)}}{\text{mass of solution (kg)}} \\ &= \frac{53.7}{0.2500} \\ &= 215\text{ ppm}\end{aligned}$$

This method of measuring concentration is often used when reporting the concentrations of minor components or pollutants in water. For example, the total dissolved salts in drinking water are usually reported in ppm. The World Health Organisation recommends a maximum value of 500 ppm dissolved salts as the desirable limit. Fluoride levels of 1 ppm are often added to water supplies to reduce dental decay. Our water supplies are routinely analysed for dangerous possible pollutants such as lead, mercury and arsenic. In natural aquatic systems, such as rivers and lakes, nitrogen and phosphorus levels are often monitored. This is because N-containing compounds and P-containing compounds can cause algal blooms if their levels exceed a few parts per million.

In the atmosphere, the concentrations of minor constituents and pollutants are also reported as parts per million. In gases, however, this refers to parts per million by volume rather than mass. Thus an air sample containing 10 ppm of carbon monoxide means that the carbon monoxide makes up $\frac{10}{1\,000\,000}$ of the volume of the gas sample.

Moles per litre (mol L^{-1})

The concentration of a solution in moles per litre indicates the number of moles of solute dissolved in a litre of solution. For example, a 1 mol L^{-1} sodium hydroxide solution is one that contains 1 mol of NaOH for every litre of solution. A 2 mol L^{-1} solution would contain two moles of NaOH per litre of solution.

The concentration of a solution in moles per litre is calculated as follows:

$$\text{Concentration (mol L}^{-1}\text{)} = \frac{\text{number of moles of solute (mol)}}{\text{volume of solution (L)}}$$

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

In chemistry, moles per litre is the most frequently used method of expressing concentration. This is because the measurement of a definite volume of solution of known concentration makes it possible to calculate the number of moles of solute present in the solution.

The concentration of a solution in moles per litre is sometimes referred to as the *molar concentration* or *molarity* of a solution and given the symbol M. A 0.50 mol L^{-1} solution is therefore the same as a 0.50 M solution.

➜ Example 13.3

Calculate the number of moles of sulfuric acid in 150.0 mL of 2.50 mol L^{-1} H_2SO_4 solution.

$$\begin{aligned} n &= cV \\ &= 2.50 \times 0.150 \\ &= 0.375 \text{ mol of } H_2SO_4 \end{aligned}$$

➜ Example 13.4

Calculate the concentration, in mol L^{-1}, of a silver nitrate solution prepared by dissolving 5.09 g of $AgNO_3$ in 250.0 mL of solution.

Calculate the number of moles of solute.

$$n = \frac{m}{M} \qquad M(AgNO_3) = 169.9 \text{ g mol}^{-1}$$

$$= \frac{5.09}{169.9}$$

$$= 0.02996 \text{ mol of } AgNO_3$$

Calculate the concentration of the solution.

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

$$= \frac{0.02996}{0.2500}$$

$$= 0.120 \text{ mol L}^{-1}$$

➜ Example 13.5

Calculate the mass of oxalic acid ($H_2C_2O_4.2H_2O$) needed to prepare 500.0 mL of 0.02500 mol L^{-1} oxalic acid solution.

Calculate the number of moles of solute.

$$n = cV$$

$$= 0.02500 \times 0.5000$$

$$= 0.01250 \text{ mol of } H_2C_2O_4.2H_2O$$

Calculate the mass of solute.

$$n = \frac{m}{M} \qquad M(H_2C_2O_4.2H_2O) = 126.07 \text{ g mol}^{-1}$$

$$0.01250 = \frac{m}{126.07}$$

$$m = 0.01250 \times 126.07$$

$$= 1.576 \text{ g}$$

The solubilities of ionic substances were described in Table 13.1 as soluble, slightly soluble and insoluble. These solubilities are defined in terms of the number of moles of solute that will dissolve per litre of solution.

Soluble: more than 0.1 mol L^{-1}

Slightly soluble: between 0.001 and 0.1 mol L^{-1}

Insoluble: less than 0.001 mol L^{-1}

Preparing a solution of known concentration

To prepare a solution of known concentration, a weighed mass of substance is dissolved in water and the solution made up to a definite volume in a volumetric flask. A *volumetric flask* is a flask that has a long, thin neck with a calibration mark that indicates the measured volume. Figure 13.8 illustrates the procedure for preparing 500 mL of approximately 0.02500 mol L^{-1} oxalic acid solution.

Approximately 1.576 g of $H_2C_2O_4.2H_2O$ is accurately weighed out and completely transferred by washing into a 500 mL volumetric flask. Sufficient water is added to dissolve the oxalic acid. Further water is then added to make the solution up to the calibration mark. This indicates that the volume of solution is exactly 500.0 mL. The stoppered flask is then shaken to ensure the solution is thoroughly mixed. From the exact mass of oxalic acid dissolved, the precise concentration of the solution can be calculated.

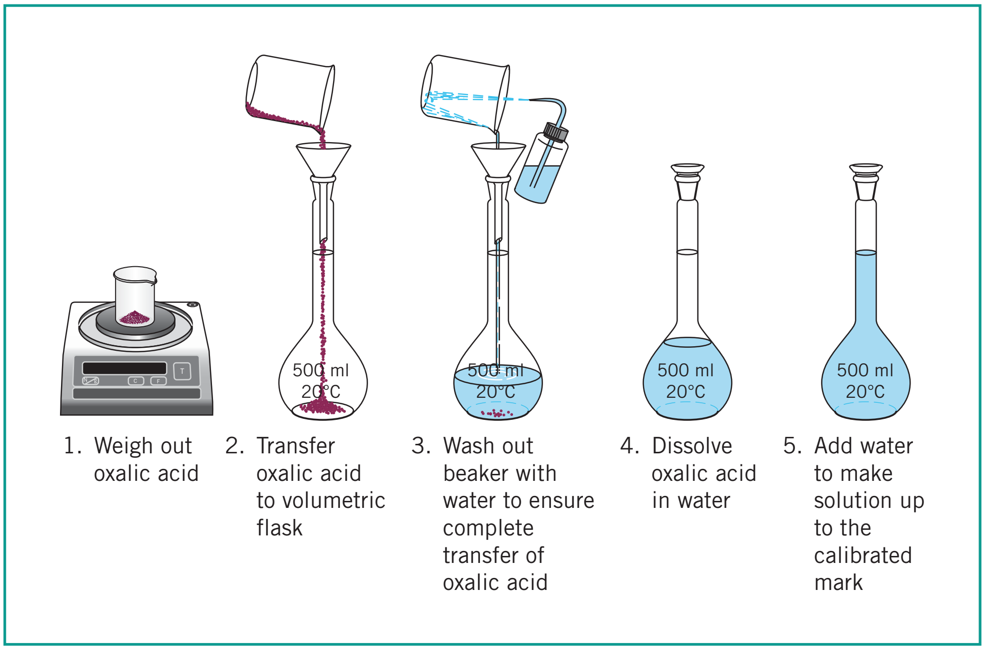


Figure 13.8 The preparation of an oxalic acid solution of known concentration

Concentrations of ions in solutions

As pointed out in Unit 12.2, ionic substances and some covalent substances are electrolytes when dissolved in water. These substances are described as strong electrolytes if they completely ionise or dissociate into ions in solution. For these substances it is possible, from the concentration of the solute, to calculate the concentrations of ions present in solution.

➜ Example 13.6

In 20.0 mL of 0.40 mol L^{-1} $Al(NO_3)_3$ solution, calculate:

1 the concentration of Al^{3+} and NO_3^-

2 the numbers of moles of Al^{3+} and NO_3^-.

$$\begin{array}{ccccc} Al(NO_3)_3(s) & \rightarrow & Al^{3+}(aq) & + & 3NO_3^-(aq) \\ 1\,mol & \rightarrow & 1\,mol & + & 3\,mol \end{array}$$

$$\begin{aligned} c(Al^{3+}) &= c(Al(NO_3)_3) \\ &= 0.40\,mol\,L^{-1} \end{aligned}$$

1

$$\begin{aligned} c(NO_3^-) &= 3 \times c(Al(NO_3)_3) \\ &= 3 \times 0.40 \\ &= 1.2\,mol\,L^{-1} \end{aligned}$$

$$n(\mathrm{Al}^{3+}) = c(\mathrm{Al}^{3+})V$$
$$= 0.40 \times 0.0200$$
$$= 0.0080 \text{ mol of } \mathrm{Al}^{3+} \text{ ions}$$

2 $$n(\mathrm{NO_3^-}) = c(\mathrm{NO_3^-})V$$
$$= 1.2 \times 0.0200$$
$$= 0.024 \text{ mol of } \mathrm{NO_3^-} \text{ ions}$$

❇ Review exercise 13.3

1 **Calculate** the mass of sodium nitrate required to prepare 400.0 mL of $NaNO_3$ solution with a concentration of 5.0 g L^{-1}.

2 A solution is prepared by dissolving 4.50 g of KCl in 250.0 g of water. **Calculate** the concentration of KCl:

- **a** as a percentage composition
- **b** in parts per million.

3 **Calculate** the number of moles of $AgNO_3$ contained in 25.0 mL of 0.215 mol L^{-1} $AgNO_3$ solution.

4 What is the concentration of a sodium carbonate solution, in mol L^{-1}, prepared by dissolving 1.32 g of Na_2CO_3 in 250.0 mL of solution?

5 What mass of $CuSO_4.5H_2O$ could be obtained if 20.0 mL of 0.525 mol L^{-1} copper (II) sulfate solution was evaporated to dryness?

6 Given 50.0 mL of 0.450 mol L^{-1} $Fe(NO_3)_3$ solution, **calculate** the following:

- **a** the concentrations of Fe^{3+} and NO_3^- ions
- **b** the numbers of moles of Fe^{3+} and NO_3^- ions.

13.4 Dilutions

It is often convenient to dilute solutions from one concentration to a lower value by adding more solvent. For example, if a 1.0 mol L^{-1} NaOH solution was available, it would be convenient to prepare a 0.10 mol L^{-1} solution by diluting the 1.0 mol L^{-1} solution. This would be less time-consuming than weighing out another sample of solid NaOH and dissolving this to form a solution of the required concentration. To prepare a 0.10 mol L^{-1} NaOH solution from the 1.0 mol L^{-1} solution, a 1:10 dilution is required. If 10 mL of the concentrated solution was diluted to form 100 mL of solution, the diluted solution would have a concentration of 0.10 mol L^{-1}.

The usual procedure in a dilution of this sort is illustrated in Figure 13.9. A definite volume of the concentrated solution is measured out with a pipette and placed into a volumetric flask. Sufficient solvent is then added to the flask to make the solution up to the calibrated mark.

When calculating the volume of solution needed to produce a particular volume of a more dilute solution, it is useful to remember that the dilution does not alter the number of moles of solute present. The number of moles of solute is the same before and after the dilution.

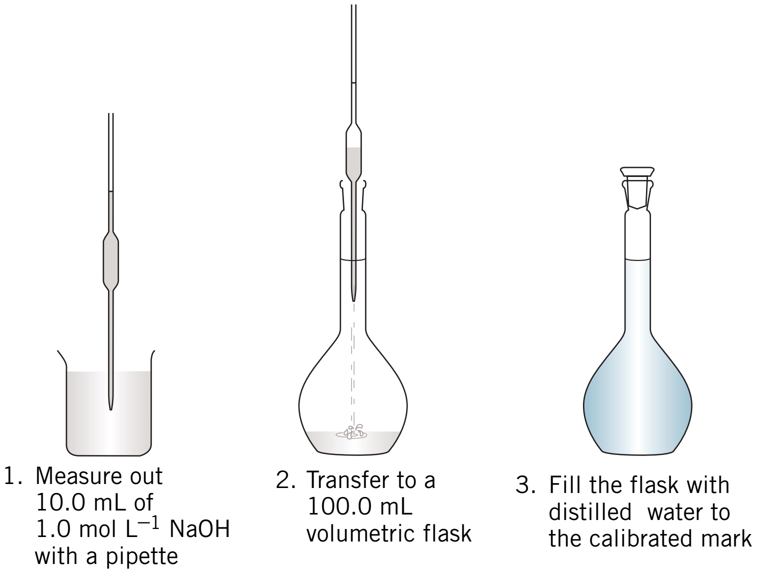


Figure 13.9 Preparing a 0.10 mol L^{-1} NaOH solution by dilution of 1.0 mol L^{-1} NaOH

➜ Example 13.7

What volume of 12.0 mol L^{-1} HCl is required to prepare 500.0 mL of 2.50 mol L^{-1} solution?

$$\begin{aligned} n_1(\text{HCl})\text{ before dilution} &= n_2(\text{HCl})\text{ after dilution} \\ c_1V_1 &= c_2V_2 \\ 12.0 \times V_1 &= 2.50 \times 0.5000 \\ V_1 &= 2.50 \times \frac{0.5000}{12.0} \\ &= 0.104\,\text{L} \\ &= 104\,\text{mL} \end{aligned}$$

❇ Review exercise 13.4

1 A laboratory technician is asked to prepare a dilute solution of sulfuric acid from the concentrated acid. **Calculate** the volume of 18.0 mol L^{-1} H_2SO_4 that is needed to make up 5.0 L of 2.5 mol L^{-1} H_2SO_4.

2 5.00 mL of 4.50 mol L^{-1} battery acid (H_2SO_4) is diluted to 100.0 mL in a volumetric flask. **Calculate** the concentration of the diluted battery acid.

3 100.0 mL of 2.00 mol L^{-1} NaOH is mixed with 80.0 mL of 2.50 mol L^{-1} NaOH. Assuming the volume of the final solution equals the sum of the added volumes, **calculate** the NaOH concentration of the final solution.

13.5 Calculations from chemical equations involving solutions

Now that a relationship between the number of moles of solute and the concentration and volume of a solution has been developed, calculations based on equations can be extended to include those involving solutions. The range of possible calculations is illustrated as follows.

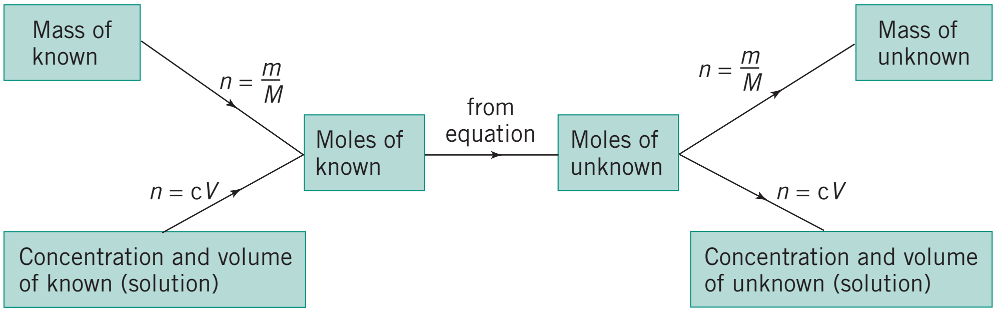


Figure 13.10 Calculations from chemical equations involving solutions

➜ Example 13.8

What mass of silver chloride will be precipitated if excess $AgNO_3$ solution is added to 50.0 mL of 0.400 mol L^{-1} $BaCl_2$ solution?

$$BaCl_2(aq) + 2AgNO_3(aq) \rightarrow 2AgCl(s) + Ba(NO_3)_2(aq)$$
$$1\,\text{mol} \quad + \quad 2\,\text{mol} \quad \rightarrow \quad 2\,\text{mol} \quad + \quad 1\,\text{mol}$$

Calculate the number of moles of $BaCl_2$.

$$\begin{aligned} n(BaCl_2) &= cV \\ &= 0.400 \times 0.0500 \\ &= 0.0200\,\text{mol of }BaCl_2 \end{aligned}$$

Calculate the number of moles of AgCl.

$$\begin{aligned} n(AgCl) &= 2 \times n(BaCl_2) \\ &= 2 \times 0.0200 \\ &= 0.0400\,\text{mol of AgCl} \end{aligned}$$

Calculate the mass of AgCl.

$$n(AgCl) = \frac{m}{M} \qquad M(AgCl) = 143.4\,\text{g mol}^{-1}$$

$$0.0400 = \frac{m}{143.4}$$

$$\begin{aligned} m &= 0.0400 \times 143.4 \\ &= 5.74\,\text{g} \end{aligned}$$

❇ Review exercise 13.5

1 The reaction between barium chloride and potassium sulfate produces solid barium sulfate according to the equation

$$BaCl_2(aq) + K_2SO_4(aq) \rightarrow BaSO_4(s) + 2KCl(aq)$$

Calculate the following:

a the number of moles of barium chloride in 50.0 mL of 0.250 mol L^{-1} solution

b the number of moles of precipitate that would be produced

c the mass of precipitate produced

d the volume of 0.400 mol L^{-1} K_2SO_4 solution that would be needed to react with the $BaCl_2$.

2 Aluminium hydroxide can be used as an antacid. It reacts with excess stomach acidity (dilute hydrochloric acid) according to the equation:

$$Al(OH)_3(s) + 3HCl(aq) \rightarrow AlCl_3(aq) + 3H_2O(l)$$

If an antacid tablet contained 0.500 g of aluminium hydroxide, **calculate** the following:

a the number of moles of aluminium hydroxide in the tablet

b the number of moles of hydrochloric acid that would react with the aluminium hydroxide

c the volume of 0.150 mol L^{-1} HCl that would react

d the number of moles of aluminium chloride produced

e the concentration of aluminium chloride in the final solution if the volume of the solution was 0.500 L.

3 Copper reacts with nitric acid according to the equation:

$$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + H_2O(l)$$

If 7.62 g of copper reacts, **calculate** the following:

a the number of moles of copper

b the number of moles of NO produced

c the number of moles of nitric acid required

d the volume of 4.00 mol L^{-1} HNO_3 required.

*KEY POINTS

- Precipitation reactions occur when two solutions are mixed and an insoluble solid is formed.
- It is possible to predict whether a precipitation reaction will occur when solutions of ionic compounds are mixed, by using a table of solubilities.
- Table 13.4 identifies the solubilities of some ionic compounds.

Table 13.4 Solubility of common ionic substances*

Soluble anions	Exceptions
NO_3^-	none
Cl^-	Ag^+ insoluble, Pb^{2+} slightly soluble
Br^-	Ag^+ insoluble, Pb^{2+} slightly soluble
I^-	Ag^+, Pb^{2+} insoluble
SO_4^{2-}	Ba^{2+}, Pb^{2+} insoluble, Ca^{2+}, Ag^+ slightly soluble
Insoluble anions	**Exceptions**
OH^-	Na^+, K^+, Ba^{2+} soluble; Ca^{2+} slightly soluble Note: NH_4OH exists as $NH_3(aq)$
S^{2-}	Na^+, K^+, NH_4^+ soluble
CO_3^{2-}	Na^+, K^+, NH_4^+ soluble
PO_4^{3-}	Na^+, K^+, NH_4^+ soluble

*This table applies to the cations Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Ag^+, Zn^{2+}, Sn^{2+} and Pb^{2+}.

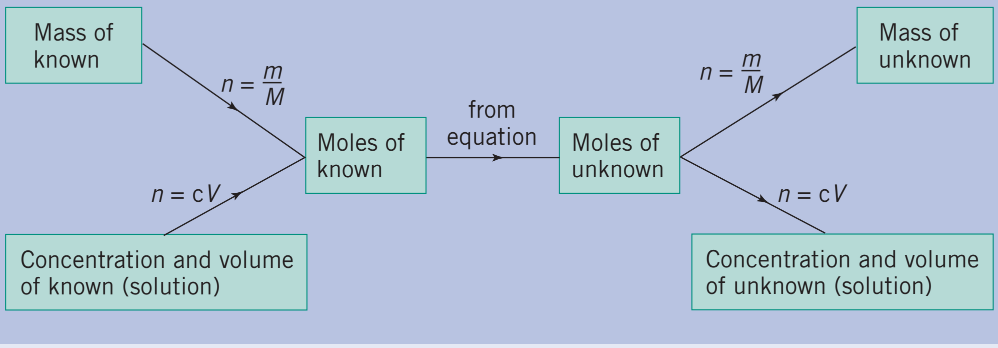
- Net ionic equations are used for solution reactions to indicate more accurately the reaction taking place. Spectator ions are not included.
- Many chemical reactions and processes are reversible.
- In chemical reactions and processes, when the rates of the forward and reverse reactions become equal, the system has reached chemical equilibrium.
- When a system is at chemical equilibrium, there are no observable changes unless the equilibrium is disturbed.
- Equilibrium exists in physical systems, including the equilibrium between undissolved solid and dissolved solute in a saturated solution. For example:

$$C_{12}H_{22}O_{11}(s) \rightleftharpoons C_{12}H_{22}O_{11}(aq)$$

$$PbI_2(s) \rightleftharpoons Pb_2^+(aq) + 2I^-(aq)$$

- Concentrations of solutions can be expressed as g L^{-1}, % composition, ppm and mol L^{-1}.
- The number of moles of solute in a solution is given by the formula $n = cV$.

- When a solution is diluted, the number of moles of solute remains unchanged but the concentration decreases.
- Different calculations involving chemical equations are possible, as summarised below.



*APPLICATION AND INVESTIGATION

1 **Predict** your observations and write balanced net ionic equations for the following:

- **a** mixing solutions of $Pb(NO_3)_2$ and $(NH_4)_2SO_4$
- **b** mixing solutions of $CuCl_2$ and $Ba(OH)_2$
- **c** mixing solutions of $AgNO_3$ and NaBr
- **d** mixing solutions of $NaNO_3$ and $BaCl_2$
- **e** mixing solutions of $Zn(NO_3)_2$ and K_2S
- **f** adding dilute HCl to solid $CuCO_3$
- **g** adding dilute H_2SO_4 to Mg.

2 N_2O_4 is an almost colourless gas, whereas NO_2 is dark brown. **Propose** a method to determine whether the following system was at equilibrium:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

3 An equilibrium system is characterised by constant macroscopic properties. **Describe** some macroscopic properties of a saturated solution of copper(II) sulfate.

4 A saturated solution of iodine in alcohol at 25°C is in equilibrium with some undissolved iodine crystals.

- **a** **Construct** a balanced equation for the equilibrium.
- **b** **Describe** the changes that would occur if the temperature was lowered to 10°C.

5 When the contents of a 375 mL can of soft drink were evaporated to dryness, 51.2 g of sugar remained. **Calculate** the concentration of the original sugar solution in grams per litre.

6 Saline solutions used in intravenous injections have a concentration of 0.90% NaCl. **Calculate** the mass of NaCl required to prepare 500.0 g of this solution.

7 A 3.00 L sample of drinking water of mass 3.00 kg is found by analysis to contain 1.35 g of sodium chloride. **Calculate** the concentration in parts per million.

8 **Calculate** the number of moles of solute in the following:

- **a** 2.50 L of 3.00 mol L^{-1} $CaCl_2$
- **b** 15.50 mL of 0.105 mol L^{-1} HNO_3.

9 **Calculate** the concentrations of the following solutions in moles per litre:

- **a** 14.0 g of NH_4Cl in 250.0 mL of solution
- **b** 8.00 g of NaOH in 2.0 L of solution
- **c** 25.0 g of $BaCl_2.2H_2O$ in 1.50 L of solution.

10 **Calculate** the mass of solute in the following solutions:

- **a** 250.0 mL of 0.050 mol L^{-1} Na_2CO_3
- **b** 4.0 L of 2.0 mol L^{-1} NaOH
- **c** 50.0 mL of 0.500 mol L^{-1} $CuSO_4.5H_2O$.

11 Some home-brewed ginger beer is found to contain 0.510% ethanol (CH_3CH_2OH). Assuming the density of the ginger beer is 1.00 g mL^{-1} **calculate** the following:

- **a** the mass of ethanol in a 250.0 mL glass of ginger beer
- **b** the concentration of ethanol in the ginger beer in mol L^{-1}.

12 **Identify** the ions present in each of the following 1 mol L^{-1} solutions and rank the solutions in order of increasing total concentration of ions: glucose, $FeCl_3$, Na_2SO_4, NaCl, NH_4NO_3, sucrose.

13 **Calculate** the concentrations of ions in the following:

- **a** 0.105 mol L^{-1} HCl
- **b** 2 mol L^{-1} Na_2SO_4
- **c** 0.054 mol L^{-1} $Al_2(SO_4)_3$.

14 **Calculate** the volume of concentrated reagent required to prepare the following diluted solutions:

- **a** 16 mol L^{-1} HNO_3 to prepare 500.0 mL of 6.0 mol L^{-1} HNO_3
- **b** 18 mol L^{-1} H_2SO_4 to prepare 2.50 L of 2.0 mol L^{-1} H_2SO_4.

15 **Calculate** the concentrations when the following solutions are prepared:

- **a** 15.0 mL of 0.500 mol L^{-1} HCl is diluted with water to form 100.0 mL of solution.
- **b** 25.0 mL of 0.105 mol L^{-1} NaOH and 50.0 mL of 0.240 mol L^{-1} NaOH are mixed and the solution is made up with water to 100.0 mL.

16 If solutions of $MgCl_2$ and NaOH are mixed, a precipitate of $Mg(OH)_2$ is formed according to the equation:

$$MgCl_2(aq) + 2NaOH(aq) \rightarrow Mg(OH)_2(s) + 2NaCl(aq)$$

If 10.0 mL of 0.500 mol L^{-1} $MgCl_2$ reacts, **calculate** the following:

a the mass of $Mg(OH)_2$ produced

b the volume of 0.240 mol L^{-1} NaOH needed to react with it.

17 Chlorine gas can be produced in the laboratory by the following reaction:

$$2KMnO_4(s) + 16HCl(aq) \rightarrow 2MnCl_2(aq) + 5Cl_2(g) + 8H_2O(l) + 2KCl(aq)$$

If 6.50 g of $KMnO_4$ reacts, **calculate** the following:

a the volume of 6.00 mol L^{-1} HCl required

b the mass of Cl_2 gas produced.

➲ Investigation

18 **Investigate** how the World Health Organisation determines the recommended levels of various heavy metals used to decide whether water is safe for drinking.

THE HEAT CAPACITY OF WATER

14.1 Specific heat capacity

Unit 10.3 identified the important role that water, particularly the oceans, plays in moderating temperatures. This is because of the relatively large quantities of heat energy absorbed or released when the temperature of water changes. This is illustrated by the fact that water when heated does not increase in temperature as fast as many other materials such as concrete or metals. A bucket of water left out in the sun in the middle of summer warms up during the day, but doesn't increase in temperature to the same extent as the concrete around it. Both substances are exposed to equal amounts of the sun's radiant energy but the water has a much higher specific heat capacity.

Figure 14.1 Anyone with a swimming pool knows that it is cooler during the day and often warmer at night than the surrounding concrete area.

Specific heat capacity (C), also called specific heat, is the amount of heat energy required to change the temperature of 1 g of a substance by 1 Kelvin.* The unit for specific heat capacity is J g^{-1} K^{-1} (or kJ kg^{-1} K^{-1}). Table 14.1 lists the specific heat capacities of a variety of substances. Water has a high specific heat capacity, which makes it very useful in cooling systems such as car radiators and also home heating systems.

*Each unit of temperature on the Kelvin scale is the same as 1 degree Celsius. The difference is that the Kelvin scale has its zero point 273 degrees lower than the zero point of the Celsius scale. For calculations in this course, a temperature difference in degrees Celsius can be used.

Table 14.1 Specific heat capacities of various substances

Substance	Specific heat capacity (J g^{-1} K^{-1})
Water	4.18
Ethanol	1.41
Toluene (methylbenzene)	1.13
Phenol (hydroxybenzene)	1.11
Benzene	1.05
Aluminium	0.90
Chloroform	0.55
Carbon tetrachloride	0.54
Glass	0.50
Iron	0.45
Silver	0.23
Mercury	0.14

The specific heat capacity may be used to determine the energy absorbed or released when the temperature of a known mass of a substance increases or decreases. The equation used to calculate the heat energy involved is:

$$Q = mC\Delta T$$

where:

Q is the heat energy absorbed or released (joules, J)

m is the mass of substance being heated or cooled (g)

C is the specific heat capacity of the substance being heated or cooled (J g^{-1} K^{-1})

ΔT is the temperature change of the substance being heated or cooled (K).

The joule (J) is the scientific unit for energy. An older unit, the calorie, is still sometimes used. One calorie is equal to 4.18 joules.

➜ Example 14.1

How much energy will be required to raise the temperature of 1.00 L of water in a kettle from 17°C to 100°C?

1.00 L of water = 1000 mL = 1000 g (assuming the density of water to be 1 g mL^{-1})

$$\begin{aligned} Q &= mC\Delta T \qquad\qquad C(H_2O) = 4.18\ Jg^{-1}\ K^{-1} \\ &= 1000 \times 4.18 \times (100 - 17) \\ &= 1000 \times 4.18 \times 83 \\ &= 346940\ J \\ &= 347\ kJ \end{aligned}$$

❇ Review exercise 14.1

1 **Calculate** the quantity of heat energy that would be required to warm up 45.0 L of water in a tropical fish tank from 18.0°C to 27.5°C.

2 **Calculate** the specific heat capacity of nickel, if it takes 860.0 J of energy to heat a 150.0 g sample from 25.0°C to 38.0°C.

14.2 Energy changes in chemical reactions

The burning of a piece of wood (Figure 14.2) demonstrates that energy changes accompany chemical reactions. When wood burns, energy is released. Some of this energy heats the surroundings and some is released as light. Substances that react to produce large quantities of heat are often useful as fuels. Wood, coal, oil, kerosene and natural gas all produce useful quantities of energy for heating purposes when they react with oxygen in the air. The release of energy in chemical reactions occurs when the reactants have a higher chemical energy than the products. The chemical energy of a substance is a type of potential energy stored within the substance. This stored chemical potential energy is called the heat content or enthalpy of the substance and is given the symbol H. A change in the enthalpy of a substance is given the symbol ΔH and is discussed in more detail in Unit 14.3. Note: The symbol Δ (delta, from the Greek alphabet) means 'change in'.

Figure 14.2 Wood burning, an exothermic reaction

The collection of atoms or molecules involved in a chemical reaction is conveniently referred to as a *system* and anything else around it is called the *surroundings*. If a reaction is carried out in solution, the species involved in the reaction is the system and the solvent is part of the surroundings. In a gaseous reaction, again it is only the reacting molecules that constitute the system.

If the enthalpy decreases during a chemical reaction, a corresponding amount of energy (Q) must be released to the surroundings. For example, when methane burns in air, the heat energy given out corresponds to the decrease in enthalpy that occurs as the reactants are converted to products.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + \text{energy}$$

The release of energy that occurs in this process can be represented as in Figure 14.3. The enthalpy difference (ΔH) between the reactants and products is equal to the amount of energy released to the surroundings. A reaction in which energy (Q) is released to the surroundings is called an *exothermic reaction*. In this type of reaction the *enthalpy*, or stored chemical energy, is lower for the products than for the reactants. In most combustion reactions, heat and light energy are released. Some reactions can also release electrical energy, such as the reaction that occurs when a dry cell operates.

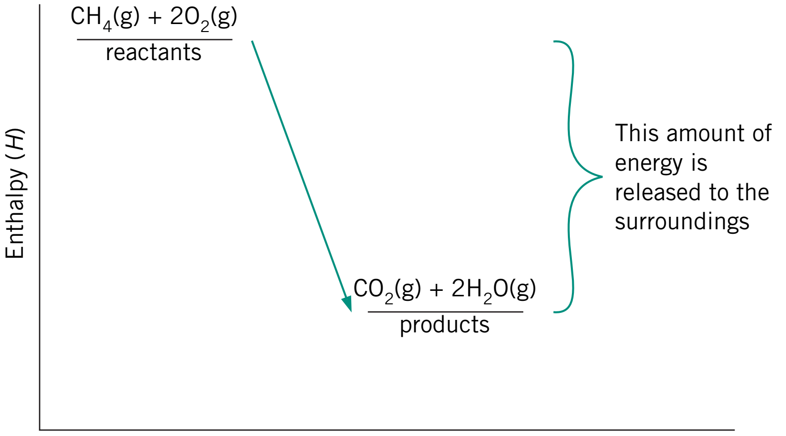


Figure 14.3 Energy is released to the surroundings when methane burns in air.

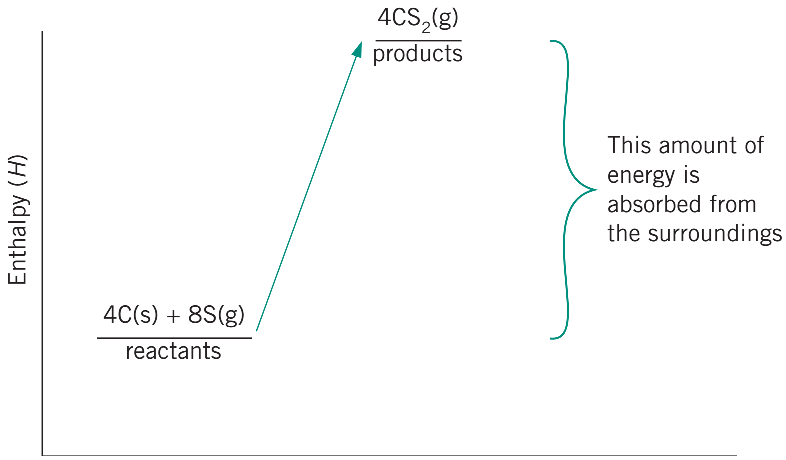


Figure 14.4 Energy is absorbed from the surroundings when carbon reacts with sulfur.

Reactions that absorb energy result in products that have a greater enthalpy than the reactants. For example, the process for manufacturing the solvent carbon disulfide is one that absorbs energy. This process involves passing sulfur vapour over white-hot carbon in an electric furnace.

$$4C(s) + 8S(g) + \text{energy} \rightarrow 4CS_2(g)$$

As the equation indicates, energy is absorbed while the reaction proceeds. The process can be represented as in Figure 14.4.

The enthalpy difference between the reactants and the products is equal to the amount of energy absorbed from the surroundings. A reaction in which energy is absorbed from the surroundings is called an *endothermic reaction*. In endothermic reactions the enthalpy of the products is greater than that of the reactants.

As with exothermic reactions, it is possible for various forms of energy to be involved in endothermic reactions. For example, the reaction of carbon with sulfur to produce carbon disulfide absorbs heat energy, whereas photosynthesis absorbs light energy. During the recharging of a car battery, chemical reactions occur that require electrical energy.

Because reactions release or absorb energy, they affect the temperature of their surroundings. Exothermic reactions release energy, causing the surroundings to heat up. In contrast, endothermic reactions absorb energy from the surroundings, causing them to cool down.

Review exercise 14.2

1 For each of the processes **a** to **d** below:

- **i** **identify** whether the reactants or products have the higher enthalpy
- **ii** **recall** whether the process would be exothermic or endothermic
- **iii** **identify** whether heat would be absorbed from or released to the surroundings.

a burning kerosene

b mixing solid $Ba(OH)_2$ and solid NH_4SCN. The following reaction takes place and the reaction mixture becomes cold:

$$Ba(OH)_2(s) + 2NH_4SCN(s) \rightarrow Ba^{2+}(aq) + 2SCN^-(aq) + 2NH_3(g) + 2H_2O(l)$$

c melting ice at 0°C

d condensing steam at 100°C

2 **Explain** why the process of burning wood is regarded as an exothermic reaction.

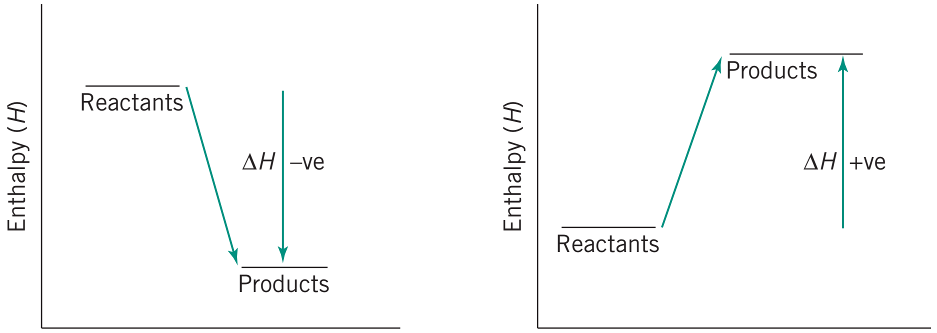
14.3 Heat of solution and reaction

Describing energy changes in chemical reactions

As discussed in the previous chapter, the change in enthalpy during a reaction is known as the heat of reaction and is given the symbol ΔH. The following expression shows the relationship between the heat of reaction and the enthalpies of reactants and products. The symbol Σ is used to indicate ‘sum of’.

$$\underset{\text{heat of reaction}}{\Delta H} = \underset{\text{enthalpy of products}}{\sum H(\text{products})} - \underset{\text{enthalpy of reactants}}{\sum H(\text{reactants})}$$

ΔH values are negative for exothermic reactions and positive for endothermic reactions. This is illustrated in Figure 14.5. In exothermic reactions the final enthalpy is less than the initial enthalpy, so ΔH is negative. This loss of enthalpy by the system (ΔH) is accompanied by the release of energy to the surroundings (Q). In endothermic reactions the final enthalpy is greater than the initial enthalpy and ΔH is positive. The gain in enthalpy by the system is accompanied by the transfer of energy from the surroundings to the system.



- Exothermic reaction
- ΔH negative
- Heat released to surroundings

- Endothermic reaction
- ΔH positive
- Heat absorbed from surroundings

Figure 14.5 Enthalpy changes for exothermic and endothermic reactions

The enthalpy change for a chemical reaction can therefore be calculated by the amount of heat released to the surroundings using an amended version of the equation introduced in Unit 14.1 where the energy absorbed by the surroundings, Q, is replaced by the chemical energy released, ΔH.

$$\Delta H = -mC\Delta T$$

where:

ΔH is the chemical energy released or absorbed (joules, J)

m is the mass of substance being heated or cooled (g)

C is the specific heat capacity of the substance being heated or cooled (J g^{-1} K^{-1})

ΔT is the temperature change of the substance being heated or cooled (K).

The sign of ΔH therefore indicates the change in enthalpy of the system. The surroundings must undergo an equal but opposite energy change to that experienced by the system.

Values for the heat of reaction are usually given per mole of one of the reactants or products. For example, in the decomposition of water referred to in Chapter 7:

$$H_2O(l) \rightarrow H_2(g) + \tfrac{1}{2}O_2(g)$$

ΔH is +286 kJ. This means that 286 kJ of energy are absorbed in the decomposition of one mole of water.

Two commonly used methods for indicating the heat of chemical reactions are illustrated as follows:

$$H_2O(l) \rightarrow H_2(g) + \tfrac{1}{2}O_2(g) \quad \Delta H = +286\ \text{kJ}$$

$$H_2O(l) + 286\ \text{kJ} \rightarrow H_2(g) + \tfrac{1}{2}O_2(g)$$

In the first method, the value for ΔH is given separately from the equation. In the second method, the quantity of heat involved is written as part of the equation for the reaction. The heat term is written as a product in exothermic reactions and as a reactant in endothermic reactions. The first method expresses the change in enthalpy of the reacting system. The second method indicates whether heat is absorbed from or released to the surroundings.

Heat of solution

When solutes dissolve in solvents, energy may be absorbed or released. The heat of solution, ΔH_{soln}, is the enthalpy change when a solute dissolves in solvent to form a solution. This is usually expressed as the molar heat of solution, and refers to the heat energy absorbed or released when one mole of solute dissolves in solution. Solution processes may be exothermic or endothermic. Examples of exothermic and endothermic solution processes are shown below.

$$NaOH(s) \rightarrow Na^+(aq) + 2OH^-(aq) \qquad \Delta H_{soln} = -44.5\ \text{kJ mol}^{-1}$$

The dissolution of sodium hydroxide releases 44.5 kJ of heat energy per mole of NaOH dissolved and is strongly exothermic.

Ammonium nitrate (NH_4NO_3) absorbs energy when it dissolves. The equation for its dissolution is represented as follows.

$$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq) \qquad \Delta H_{soln} = 25.7\ \text{kJ mol}^{-1}$$

Table 14.2 includes the heats of solution of several ionic solutes in water.

Table 14.2 Heat of solution for some ionic solutes

Solute	ΔH_{soln} (kJ mol^{-1})
Sodium chloride	+4
Sodium bromide	–1
Sodium nitrate	+20
Calcium chloride	–83
Calcium bromide	–110
Calcium nitrate	–19
Lithium chloride	–37

Table 14.2 *Continued*

Solute	ΔH_{soln} (kJ mol^{-1})
Lithium bromide	–49
Lithium nitrate	–3
Ammonium chloride	+15
Ammonium bromide	+17
Ammonium nitrate	+26

Heats of solution are the basis for the instant ‘hot packs’ and ‘cold packs’ used in first aid treatment. These packs consist of two compartments, one containing water and the other containing a soluble salt, NH_4NO_3, for cold packs and $CaCl_2$ or $MgSO_4$ for hot packs. The packs are manipulated to break the wall between the compartments and allow the water to dissolve the salt, resulting in the absorption or release of heat as the salt dissolves.

Figure 14.6 Instant cold packs use an endothermic reaction.

Enthalpy changes in the solution process

As described in Unit 12.1, the dissolution process can be considered as three steps:

1. Breaking the electrostatic forces between positive and negative ions in ionic solids or the intermolecular forces between solute molecules. This process uses energy and is therefore endothermic.
2. Breaking the intermolecular forces, hydrogen bonds, between solvent water molecules. This process also uses energy and is therefore endothermic.
3. Forming attractive forces between positive and negative ions and water molecules or between solute molecules and water molecules. This process of hydration releases energy and is therefore exothermic.

The overall heat of solution will depend on the sum of the energy changes for these three processes.

When ammonium nitrate dissolves, the energy released when the ions are hydrated does not compensate for the energy required to break the attractive forces between the ions in the solute and the hydrogen bonds between water molecules. On the other hand, when calcium chloride dissolves, the energy released accompanying the hydration of calcium and chloride ions is significantly greater than the energy needed to break the attractive forces between the ions in the solute and the hydrogen bonds between water molecules. As a result, the dissolution process is strongly exothermic.

Heat of reaction

For any reaction, the heat of reaction is the enthalpy change associated with the conversion of reactants to products. For example, the combustion of methane

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

is exothermic, with ΔH = –890 kJ. This is called the *heat of combustion* of methane.

The highly exothermic nature of the reaction of hydrocarbons with oxygen is the reason that these substances are so widely used as fuels. Hydrocarbon fuels include natural gas (methane), propane, butane, octane and acetylene.

Acid–base neutralisation reactions in aqueous solutions are also typically exothermic. For example, the reaction

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(aq)$$

is *exothermic*, with *heat of neutralisation*, $\Delta H = -57$ kJ.

The heats of neutralisation for several acid–base reactions are shown in Table 14.3. The first four reactions in the table have the same heat of neutralisation because the same reaction is taking place in each case. This reaction can be represented as:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

Table 14.3 Heats of neutralisation (at 25°C)

Acid	Base	ΔH (kJ mol^{-1} of acid)
HCl	NaOH	–57.1
HCl	KOH	–57.2
HNO_3	NaOH	–57.2
HNO_3	KOH	–57.1
H_2SO_4	NaOH	–114.3
H_2SO_4	KOH	–114.4

The other species, K^+, Na^+, Cl^- and NO_3^-, are spectator ions and do not take part in the reaction. The heats of neutralisation per mole of sulfuric acid are double those of the other two acids because each mole of H_2SO_4 reacts with two moles of base to produce two moles of water. Thus, per mole of water produced, the values are almost identical to those of the other acids.

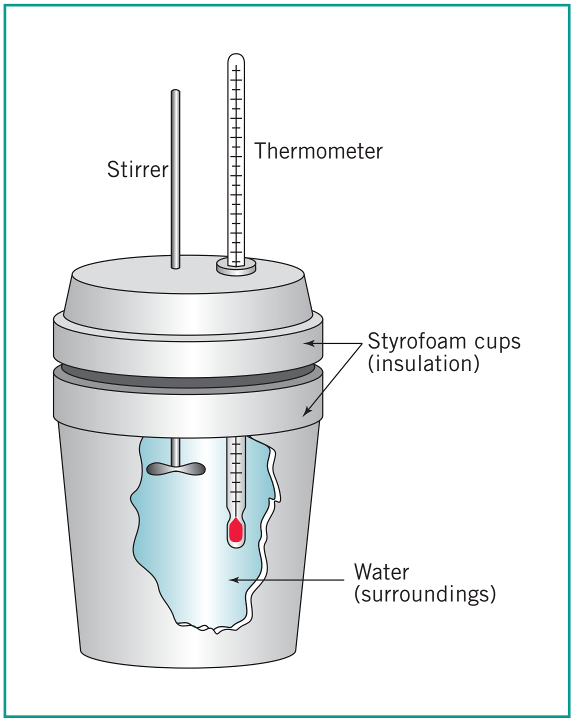


Figure 14.7 A simple calorimeter used to measure heats of reaction in a solution consists of an insulated container enclosing a known mass of water.

Measuring heats of solution and reaction

Heats of reaction are measured using a *calorimeter*. There are different types of calorimeters but generally they consist of a reaction vessel surrounded by an insulated container enclosing a known mass of water. The heat energy released or absorbed in the reaction changes the temperature of the reaction vessel and surrounding body of water. If the temperature change is measured, and the heat capacity of the calorimeter and water are known, the quantity of heat released or absorbed can be calculated.

Many chemical reactions occur in solution. The heat energy released or absorbed by these reacting systems increases or decreases the temperature of the solution (surroundings). In reactions carried out in solution, a simple calorimeter can be constructed from a polystyrene cup, as shown in Figure 14.7.

The polystyrene cup is assumed to have minimal heat capacity and the heat of the solution is calculated from measurements of the temperature change of the solution and the specific heat of the water.

➜ Example 14.2

When 1.00 g of sodium hydroxide is dissolved in 100 g of water, in an insulated cup, the temperature of the water rises from 20.00ºC to 22.66ºC. Calculate the heat of solution for sodium hydroxide.

$$\Delta H = -mC\Delta T$$

ΔH in J g^{-1} of NaOH

$$\Delta H = -(100 \times 4.18 \times 2.66)$$

$$= -1112 \text{ J g}^{-1}$$

ΔH in J mol^{-1} of NaOH　　$M(\text{NaOH}) = 40.00 \text{ g mol}^{-1}$

$$= (-1112 \times 40.00)$$

$$= -44\,480$$

$$= -44.5 \text{ kJ mol}^{-1}$$

➜ Example 14.3

When 100 mL of 1.00 mol L^{-1} sodium hydroxide is added to 100 mL of 1.00 mol L^{-1} hydrochloric acid in an insulated container, the temperature rises from 21.0ºC to 34.6ºC. Calculate the heat of neutralisation for the reaction.

The equation for the reaction is as follows.

$$\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(aq)}$$

$$\Delta H = -mC\Delta T$$

$$= -(200 \times 4.18 \times 13.6)$$

$$= -11369.6 \text{ J}$$

$$= -11.37 \text{ kJ}$$

The number of moles of HCl and NaOH involved in the reaction:

$$n = cV$$

$$= 0.100 \times 1.000$$

$$= 0.100 \text{ mol}$$

ΔH in kJ mol^{-1} of HCl and NaOH

$$\Delta H = -\frac{11.37 \text{ kJ}}{0.100 \text{ mol}}$$

$$\Delta H = -113.7 \text{ kJ mol}^{-1}.$$

❇ Review exercise 14.3

1 For reactions **a** to **c** below:

- **i** **draw** a diagram showing the enthalpy of the reactants and products
- **ii** **identify** whether the reaction is exothermic or endothermic
- **iii** **predict** whether the temperature of the surroundings would increase or decrease.

a $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta H = -283$ kJ

b $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightarrow HI(g) \quad \Delta H = 26$ kJ

c $2S(s) + 3O_2(g) \rightarrow 2SO_3(g) + 792$ kJ

2 **a** For the dissolution of KBr in water, **explain** the changes in the nature of the forces between solute and solvent molecules.

b Given that ΔH for this process is +20 kJ, **compare** the relative strengths of these forces.

3 When 2.40 g of sodium hydroxide is dissolved in 100 mL of water, the temperature of the water increases from 22.0°C to 28.4°C. **Determine** the molar heat of solution of sodium hydroxide.

4 **Predict** the expected final temperature for the solution formed when 50.0 mL of 2.00 mol L^{-1} HCl is added to 100.0 mL of 1.00 mol L^{-1} NaOH. The initial temperature of both solutions was 18.0°C and the molar heat of neutralisation is 57.0 kJ mol^{-1}.

14.4 Thermal pollution

The moderating effect of water on temperature was discussed in Unit 10.3. This moderating effect results from water's high specific heat capacity. In summer, large quantities of heat energy are required to increase the temperature of water, so water remains relatively cool compared to its surroundings. In winter, large quantities of heat need to be lost to decrease the temperature of water. As a result, water remains relatively warm compared to its surroundings. Water bodies of a reasonable size, such as rivers, lakes and oceans, provide relatively stable temperature conditions for living things. Aquatic organisms generally have not evolved with the temperature control mechanisms, such as perspiration and nocturnal activity, that are characteristic of many land-based organisms.

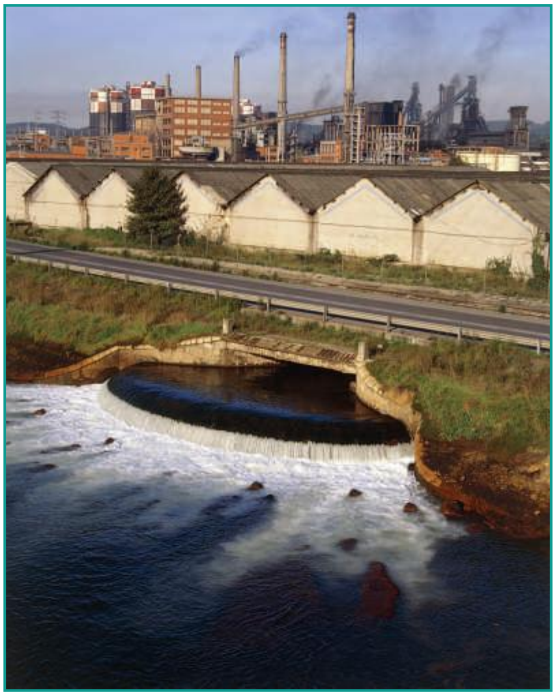


Figure 14.8 Many industries use water for cooling.

It is widely known that chemicals can pollute aquatic systems such as rivers and lakes, making them less suitable environments for naturally occurring organisms. It is less well known that excess heat energy discharged into the environment, *thermal pollution*, can also have a serious effect on aquatic systems and threaten the survival of the aquatic organisms they contain. The heat energy is usually added as a result of an industry that uses water for cooling, such as power generation or steel production. The industrial plant takes in cool water, uses it and then returns hot water to the lake or river. The most important effect of thermal pollution is usually the reduction in the concentrations of dissolved gases such as oxygen and carbon dioxide within the water. Figure 14.9 shows the solubility of gases at different temperatures. Note that, in general, the solubility of gases decreases with increasing temperature.

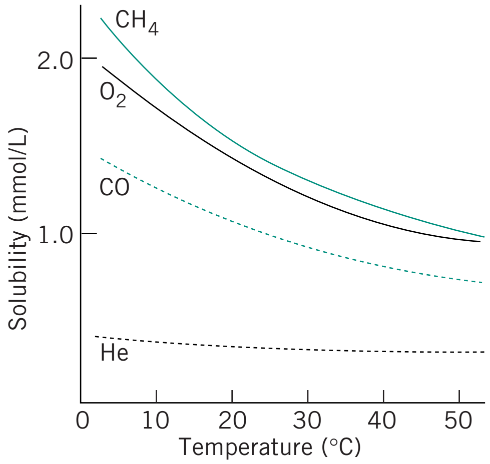


Figure 14.9 Gases have different solubilities in water at different temperatures.

At the higher temperatures associated with thermal pollution, the concentration of dissolved oxygen may fall below that necessary to sustain particular life forms that are present. Severe oxygen depletion may be fatal to fish and other aquatic animals. Fish are particularly susceptible to changes in water temperature. At higher temperatures, fish have a higher metabolic rate, requiring a higher concentration of dissolved oxygen, when in fact the levels of dissolved oxygen are lower. Fish such as trout that thrive in cold water will die if the temperature goes up more than a few degrees. Other ecological effects can include the displacement of plankton, the food base of aquatic ecosystems, by blue-green algae at higher temperatures.

❄ Review exercise 14.4

1. Using Figure 14.9, **compare** the availability of oxygen for animal life in water at 15ºC and 40ºC.
2. If a beaker of cold water is warmed, bubbles of gas form on the sides of the beaker at well below the boiling point. **Identify** the likely composition of the bubbles and **describe** why they form.
3. Use the kinetic theory and your knowledge of intermolecular forces to **account** for the decrease in gas solubility as temperature increases.

*KEY POINTS

- Specific heat capacity is the amount of heat energy required to raise the temperature of 1 g of a substance by 1 Kelvin.
- The unit for specific heat capacity is J g^{-1} K^{-1} (or kJ kg^{-1} K^{-1}).
- Water has a high specific heat capacity of 4.18 J g^{-1} K^{-1}.
- The enthalpy or heat content (H) of a substance is its stored chemical potential energy.
- If the enthalpy changes (ΔH) during a chemical reaction, a corresponding amount of energy (Q) must be released to or absorbed from the surroundings.
- An exothermic reaction is one in which:
  - energy is released to the surroundings
  - there is a decrease in enthalpy of the system
  - there is an increase in the temperature of the surroundings.
- An endothermic reaction is one in which:
  - energy is absorbed from the surroundings
  - there is an increase in enthalpy of the system
  - there is a decrease in the temperature of the surroundings.
- Combustion reactions, in which heat and light energy are released, are examples of exothermic reactions.
- The electrolysis of water (electrical energy absorbed), photosynthesis (light energy absorbed) and thermal decomposition (heat energy absorbed) are examples of endothermic reactions.
- The heat of reaction is the enthalpy change in a system accompanying the reaction:

  $$\Delta H = \sum H(\text{products}) - \sum H(\text{reactants})$$

- ΔH is negative for exothermic reactions and positive for endothermic reactions.
- The energy change in a chemical reaction can be calculated using the equation:

  $$\Delta H = -mC\Delta T$$

  where ΔH is the energy (J), m is the mass (g), C is the specific heat capacity (J g^{-1} K^{-1}) and ΔT is the temperature change (K).
- The heat of reaction can be indicated in two ways:
  - as ΔH—this represents the change in enthalpy of the system
  - as an energy term in the equation—this indicates whether energy is absorbed from, or released to, the surroundings.
- The heat of solution is the enthalpy change when a solute dissolves in a solvent to form a solution.
- The heat of solution can be considered in terms of the following steps:
  1. the endothermic process of separating solute particles
  2. the endothermic process of separating water molecules
  3. the exothermic process of hydration—surrounding solute particles with water molecules.

- The heats of reaction (ΔH) for reactions that occur in solution can be determined by measuring the temperature change of the solution.
- Water has a moderating effect on the temperature of adjacent land masses.
- Water bodies such as rivers, lakes and oceans display a narrower range of temperatures than land masses.
- Thermal pollution occurs when excess heat energy is discharged into the environment. This can have a serious effect on aquatic ecosystems.
- Gases become less soluble as the temperature of water increases.

∗ APPLICATION AND INVESTIGATION

1 **a** **Calculate** the quantity of heat energy that would be required to heat 2.00 L of water in a saucepan from 18.0ºC to 100.0ºC.

b A 126 g sample of ethylene glycol, a car radiator coolant, loses 2680 J of heat. Given that the specific heat capacity of ethylene glycol is 2.42 J g^{-1} K^{-1}, **calculate** the initial temperature if the final temperature is 30.0ºC.

2 **a** **Calculate** the specific heat capacity of lead, if it requires 219.6 J of energy to heat a 50.0 g sample from 20.0ºC to 55.0ºC.

b If the same amount of heat energy were supplied to a 50.0 g sample of aluminium, would the temperature change be the same? **Explain** your answer, making reference to the data in Table 14.1.

3 **Investigate** the development and use of the Kelvin temperature scale.

Investigation

4 For the processes in **a** to **c** below:

- **i** **identify** whether the reactants or products have the higher enthalpy
- **ii** **recall** whether the process would be exothermic or endothermic
- **iii** **identify** whether heat would be absorbed from or released to the surroundings.

a burning magnesium

b sublimation of carbon dioxide

c addition of concentrated sulfuric acid to water, which results in the temperature of the solution increasing

5 **Predict** the sign of ΔH for the following processes:

a the formation of dew

b $O_2(g) \rightarrow 2O(g)$

c $H(g) + I(g) \rightarrow HI(g)$

d $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

6 **Classify** the following reactions as exothermic or endothermic:

a $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \Delta H = -92 \text{ kJ}$

b $6CO_2(g) + 6H_2O(g) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g) \qquad \Delta H = +2803 \text{ kJ}$

c $2C(s) + O_2(g) \rightarrow 2CO_2(g) + 222 \text{ kJ}$

d $2H_2O(g) + 484 \text{ kJ} \rightarrow 2H_2(g) + O_2(g)$

7 824 kJ of energy is released when one mole of iron metal is converted to iron(III) oxide. **Construct** a balanced equation for this reaction, indicating the heat energy involved.

8 Instant cold packs used to treat sporting injuries often contain NH_4NO_3 and a plastic bag of water. When the plastic bag is broken, the ammonium nitrate dissolves, as shown by the equation:

$$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$$

a Is this process exothermic or endothermic?

b Would the products or reactants would have a higher enthalpy? **Explain** your answer.

c **Construct** a diagram showing the enthalpy of the reactants and products.

9 Drano®, a commercial drain cleaner, consists mainly of sodium hydroxide. If a tablespoonful of Drano® with a mass of 50.0 g is dissolved in 100.0 mL of water, **calculate** the temperature change of the solution, assuming no heat losses. The heat of solution for NaOH is -44.5 kJ mol^{-1}.

10 A 0.200 g sample of magnesium ribbon was dissolved in 100.0 mL of 1.0 mol L^{-1} HCl in a polystyrene calorimeter. The temperature of the solution rose from 15.5°C to 24.5°C. Assuming that the density and specific heat capacity of the solution are the same as for water, **calculate** the following:

a the heat released in the reaction

b the value of ΔH for the reaction in kJ mol^{-1} of magnesium dissolved.

11 Pollution control authorities monitor the temperature of natural waterways above and below the water inlets and outlets of large factories. **Account** for this practice.

➲ Investigation

12 **Investigate** the effect of increasing temperature on the functioning of biochemical catalysts called enzymes. What effect would high levels of thermal pollution have on the biochemical reactions of living organisms?

*MODULE 3 REVIEW

MULTIPLE-CHOICE QUESTIONS

1 An ionic solution like NaOH(aq) can conduct an electric current because

- **A** the molecules of NaOH are surrounded by a sea of electrons that can conduct a current.
- **B** in solution the NaOH molecules are polar and the molecules can therefore transfer charge.
- **C** the NaOH dissociates into its constituent ions of Na^+ and OH^- which can move through the solution.
- **D** the NaOH dissociates into its constituent ions of Na^+ and OH^- which allow the electrons to flow.

2 50 mL of 0.10 mol L^{-1} $Ca(OH)_2$ is diluted to 1.0 L with distilled water. The concentration of the diluted solution is closest to

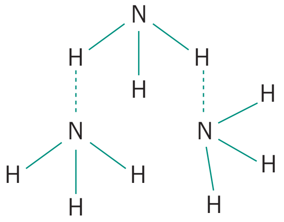
- **A** 0.0010 mol L^{-1}.
- **B** 0.0050 mol L^{-1}.
- **C** 0.050 mol L^{-1}.
- **D** 0.10 mol L^{-1}.

3 The number of moles of potassium nitrate necessary to make 500 mL of 2.0 mol L^{-1} solution would be

- **A** 0.20 mol.
- **B** 0.50 mol.
- **C** 1.0 mol.
- **D** 2.0 mol.

4 The diagram below shows three adjacent molecules of ammonia. The dotted lines between these molecules represent

- **A** dispersion forces.
- **B** polar covalent bonds.
- **C** hydrogen bonds.
- **D** dipole–dipole bonds.



5 The specific heat of water

- **A** is relatively high because it takes considerable heat energy to increase its temperature.
- **B** is relatively high because its temperature rises a great deal with only a small amount of heat added.
- **C** is relatively low because it takes considerable heat energy to increase its temperature.
- **D** is relatively low because its temperature rises a great deal with only a small amount of heat added.

SHORT-ANSWER QUESTIONS

6 **Describe** the three types of intermolecular forces that may exist between molecular compounds.

7 Use your understanding of the solution process to **explain** the generalisation that 'like dissolves like'.

8 Potassium sulfate solution is added by burette to a silver(I) nitrate solution until a precipitate of silver(I) sulfate is just evident. The precipitate is filtered and left to dry.

- **a** **Construct** an ionic equation for the precipitation reaction.
- **b** Will the dried precipitate conduct electricity? **Explain**.
- **c** Will the remaining filtrate conduct electricity? **Explain**.

9 **a** **Outline** what is meant by the 'molarity' of a solution.

- **b** What formula would you use to determine the molarity of a solution made by adding 0.50 moles of sodium hydroxide to make 250 mL of solution?
- **c** **Calculate** the molarity of the above solution.

10 A student added 0.025 L of 2.0 mol L^{-1} copper(II) sulfate solution to 50 mL of sodium hydroxide solution of unknown molarity. A blue precipitate of copper(II) hydroxide was produced. The precipitate was dried and found to weigh 2.35 g.

- **a** **Construct** a balanced equation for the reaction.
- **b** Did all of the copper(II) sulfate react? Use working to **justify** your answer.

11 **Calculate** the mass of solid sodium carbonate that would be required to completely neutralise 5.0 L of 0.050 mol L^{-1} ethanoic acid. **Describe** how you would know the reaction was complete.

12 Consider the information in the table below.

Compound	Formula	Molar mass (g mol^{-1})	Boiling point (°C)
Water	H_2O	18.0	100
Sodium hydride	NaH	24.0	425*d*
Ammonia	NH_3	17.0	–33
d = decomposes			

a **Draw** the electron dot formula for H_2O.

b **Explain** why the boiling point of water is higher than the boiling point of ammonia.

13 16.93 g of sodium carbonate is dissolved in water to make 250 mL of solution. This is then diluted to 500 mL. 25 mL of this solution is then placed into a conical flask.

a **Calculate** the number of moles of sodium carbonate in the original solution.

b **Calculate** the molarity of the diluted sodium carbonate solution.

c How many moles of sodium carbonate are present in the conical flask?

d **Calculate** the volume of 0.010 mol L^{-1} hydrochloric acid that is needed to react completely with the 25 mL of solution in the conical flask. Show all working.

14 Some students were given the task of determining the exact molarity of a 0.5 mol L^{-1} solution of hydrochloric acid that was several years old. Their science teacher told them that it was highly likely the acid was no longer 0.5 mol L^{-1}. The students chose to perform an accurate procedure called a titration in order to determine the actual molarity of the acid. Their method is outlined below.

Step 1 Place some sodium carbonate in an evaporating basin and put it in a drying oven overnight.

Step 2 Accurately weigh approximately 5.3 g of the sodium carbonate and make up to 500 mL of solution. The students' mass of sodium carbonate was exactly 5.259 g.

Step 3 Place 25 mL of sodium carbonate solution in a 100 mL conical flask and add a few drops of indicator.

Step 4 Run the unknown HCl from the burette until the indicator changes colour.

The students' results were as follows:

Titration number	Volume of HCl added (mL)
I	13.5
II	12.95
III	12.90
IV	13.05

a Why did they place the sodium carbonate in a drying oven overnight?

b **Identify** the piece of equipment they would have used in:

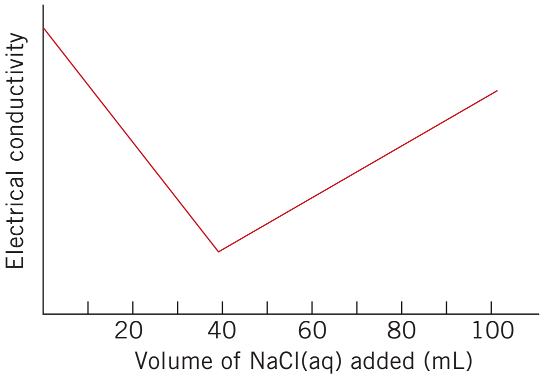
  i step 2 to make up the solution

  ii step 3 to measure the 25 mL of solution.

c **Construct** a balanced symbol equation, including states for the reaction.

d **Calculate** the accurate molarity of the acid.

15 The graph below shows the electrical conductivity of the solution formed when 100 mL of 0.50 mol L^{-1} sodium chloride solution is slowly added to 100 mL of 0.10 mol L^{-1} lead(II) nitrate solution.



a **Calculate** the number of moles of sodium chloride required to make 100 mL of 0.50 mol L^{-1} solution.

b **Construct** a balanced ionic equation for any chemical reaction that occurs when the two solutions are added together.

c **Explain** the pattern in the conductivity of the solution as represented on the graph.

16 A food chemist was given the task of analysing a recently developed soft drink. Her first step was to determine the concentration of sugar in the drink.

a By referring to your knowledge of solutions, **describe** a process the food chemist could use.

b **Identify** a possible unit for concentration that the chemist would use to report her results. **Justify** your choice of this unit.

4

MODULE

energy

- **Chapter 15** SOME COMPOUNDS ARE IMPORTANT SOURCES OF ENERGY
- **Chapter 16** THE VARIETY OF CARBON COMPOUNDS
- **Chapter 17** HYDROCARBONS
- **Chapter 18** COMBUSTION OF HYDROCARBONS
- **Chapter 19** RATES OF CHEMICAL REACTIONS
- **MODULE 4** REVIEW

This module will cover the following material:

- the role of photosynthesis in transforming light energy into chemical energy
- the formation and origins of fossil fuels
- allotropes of carbon
- bonding in carbon compounds
- the naming of straight-chained hydrocarbons using IUPAC nomenclature
- the separation of petroleum by fractional distillation
- dispersion forces and the non-polar nature of hydrocarbons
- the relationship between melting point, boiling point and volatility of hydrocarbons
- combustion of hydrocarbons
- uses of hydrocarbons
- volatility, flash point and ignition temperature of fuels
- the safe use, storage and transport of hydrocarbons
- pollution caused by burning fossil fuels
- energy changes in chemical reactions
- the collision theory and factors affecting the rate of reactions.

CHAPTER 15

SOME COMPOUNDS ARE IMPORTANT SOURCES OF ENERGY

Almost all life on Earth is dependent on the ability of organisms such as plants and blue-green algae (cyanobacteria) to transform light energy from the sun into chemical energy. This process, known as *photosynthesis*, is the beginning of nearly all food chains, and supplies the energy for ecosystems to function. The chemical energy stored in fossil fuels can also be traced back to the process of photosynthesis.

15.1 The production of carbohydrates by plants

Using light energy trapped by chlorophyll, plants combine carbon dioxide and water to form carbohydrates and oxygen. *Carbohydrates* are organic substances containing carbon, hydrogen and oxygen and have the general formula $C_x(H_2O)_y$. Carbohydrates can be classified into the following groups:

- monosaccharides, e.g. glucose and fructose
- disaccharides, e.g. sucrose (common sugar) and maltose
- polysaccharides, e.g. starch, glycogen and cellulose.

The process of photosynthesis is quite complex and involves many steps but the overall reaction can be represented by the equation:

$$\begin{array}{ccccccc} \text{carbon dioxide} & + & \text{water} & \xrightarrow{light} & \text{carbohydrate} & + & \text{oxygen} \\ CO_2 & + & H_2O & \xrightarrow{light} & [CH_2O] & + & O_2 \end{array}$$

Because the carbohydrate glucose, $C_6H_{12}O_6$, is one of the main photosynthetic products of this reaction, the equation is usually written:

$$\begin{array}{ccccccc} \text{carbon dioxide} & + & \text{water} & \xrightarrow{light} & \text{glucose} & + & \text{oxygen} \\ 6CO_2(g) & + & 6H_2O(l) & \xrightarrow{light} & C_6H_{12}O_6(aq) & + & 6O_2(g) \end{array}$$

This reaction is endothermic, as it requires the absorption of energy. Light energy from the sun is transformed into chemical potential energy, which is stored within the glucose molecules.

Figure 15.1 The absorption of solar energy in photosynthesis provides the energy needed to sustain most life on Earth.

The plant will use some of the glucose produced by photosynthesis almost immediately for its own energy requirements, but most is converted into complex carbohydrates (polysaccharides). These include starch, which is used for energy storage, and cellulose, the main component of the cell walls of plants, which provide support and structure.

The chemical energy stored in glucose and other carbohydrates can be released by *respiration*. This reaction makes this energy available to animals, including humans, when they eat plant material containing these carbohydrates. The chemical breakdown of food releases the chemical potential energy stored within the molecules. Most living things obtain energy by the oxidation of carbohydrates.

For example, plants and animals oxidise glucose to produce energy in the process known as *aerobic* (in the presence of oxygen) *respiration*.

$$\text{glucose} + \text{oxygen} \xrightarrow{\textit{enzymes}} \text{carbon dioxide} + \text{water} + \text{energy}$$

$$C_6H_{12}O_6(aq) + 6O_2(g) \xrightarrow{\textit{enzymes}} 6CO_2(g) + 6H_2O\,(l) + \text{energy}$$

Humans and other animals can use the energy stored in sugars such as glucose, fructose and sucrose, which are present in plants. We can also break down the polysaccharide starch in foods such as potatoes, wheat, corn and rice, to form glucose. Ruminants, such as cows and sheep, can also break down cellulose into its constituent glucose units. This is not possible for humans, for whom cellulose is indigestible but an important source of dietary fibre.

❇ Review exercise 15.1

1 **Identify** the process by which light energy is transformed into chemical energy in plants.

2 **Explain** how plants are a link between light energy and the chemical energy in an ecosystem.

3 **Construct** word equations and balanced chemical equations for:
   - **a** photosynthesis
   - **b** respiration.

15.2 Fossil fuels

The types of fuels used by humans have changed considerably during history. The combustion of wood was the major source of energy until the middle of the nineteenth century. The increased energy demands of the industrial revolution led to an increasing use of fossil fuels. Coal, oil and natural gas are the most extensively used fuels at present because of their high energy content, relatively low cost and convenience. However, there are problems with this dependence on fossil fuels. These relate to the limited reserves of these fuels and to the pollution brought about by their use. Major environmental concerns regarding the use of fossil fuels include the formation of acid rain, photochemical smog and global warming. *Fossil fuels* are non-renewable resources and the known reserves of fossil fuels, particularly of oil and gas, are limited. It is estimated that supplies of oil and gas may run out in the next few decades and coal deposits are estimated to be sufficient for only a hundred years or so.

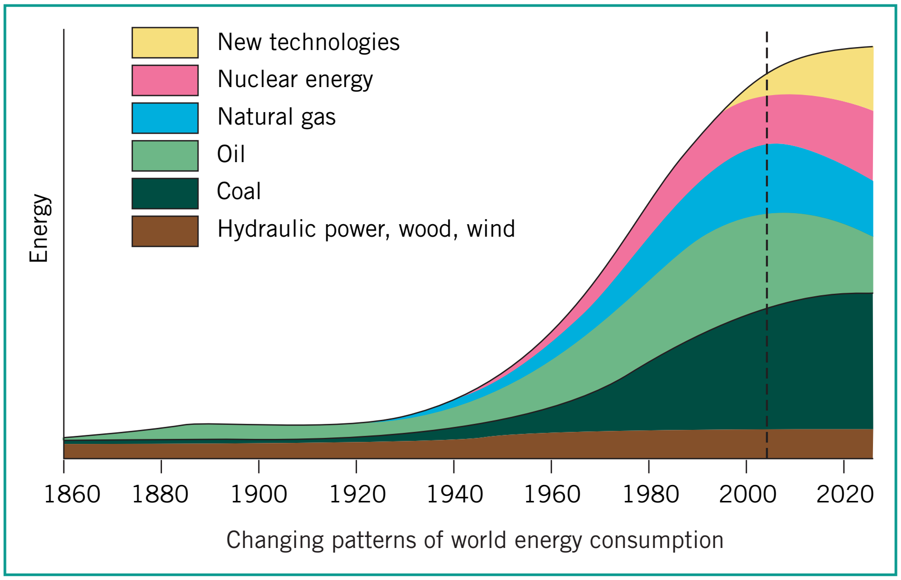


Figure 15.2 Changing patterns of world energy consumption

15.3 The origin of fossil fuels

Fossil fuels such as coal, oil and natural gas are derived from the remains of fossil plants and animals. Usually, when a plant or animal dies, it decays and is broken down by bacteria mainly into carbon dioxide (CO_2) and water (H_2O).

However, the plant and animal remains may be buried beneath sediment before complete aerobic decomposition has taken place. The resulting material contains substantial amounts of carbon and hydrogen. Over a period of millions of years these carbon compounds may be converted into fossil fuels by the action of heat and pressure resulting from various geological processes.

Essentially, fossil fuels are mixtures of *hydrocarbons*, compounds containing only carbon and hydrogen, with small proportions of other elements. Fossil fuels have chemical potential energy that is released when they are burned in air. The source of energy locked in these natural resources can ultimately be traced back to the solar energy captured millions of years ago by prehistoric plants.

Coal

Coal is by far the most abundant fossil fuel. Most of the Earth's coal deposits were formed between 350 and 225 million years ago during the Carboniferous and Permian periods. Coal is produced by the accumulation of plant material in conditions where decomposition by oxidation is negligible. The stagnant waters often associated with swamps, marshes and mangroves are an ideal environment for this process. During the Carboniferous and Permian periods there was an abundance of plant life. Plant debris including leaves, bark and wood accumulated in these ancient swamps and was buried beneath more plant material.

Figure 15.3 Coal formation began in the stagnant waters of swamps during the Carboniferous and Permian periods.

Initially the organic matter was converted into *peat*, a soft, spongy material containing large amounts of water. With increased pressure and temperature, peat was converted into brown coal (*lignite*) then black coal (*bituminous coal*) and finally *anthracite*. The first stage in the formation of coal is *biochemical decomposition* caused by anaerobic bacteria. This results in the loss of volatile compounds such as CO_2, H_2O and CH_4, with an overall increase in the relative carbon content. The second phase, *coalification*, occurs when the peat is buried and compressed by the deposition of sediments. In coalification, the combined effects of temperature and pressure over long periods of time reduce the oxygen content (through release of CO_2) and hydrogen content (through release of CH_4). This results in increasing carbon content through the sequence: peat → lignite → bituminous coal → anthracite. The type of coal produced depends on the degree to which the original material has been changed. For example, low-grade peat can contain carbon, hydrogen and oxygen atoms in the ratios 1:2:1, while in high-grade anthracite the carbon:hydrogen ratio can be as high as 5:2, with virtually no oxygen present.

Figure 15.4 A specimen of bituminous coal

Coal contains numerous impurities in varying levels, particularly sulfur and sediments such as mud, deposited and buried with plant material. When the coal is burnt, these impurities form pollutants including sulfur dioxide and ash. The pollution associated with the combustion of fossil fuels is discussed in Chapter 18. The sulfur content of Australian coals is fairly low and our coal is therefore in great demand.

The Latrobe Valley in Victoria contains some of the world's richest deposits of brown coal, and vast deposits of black coal are found in the Sydney Basin, including the Hunter Valley, Lithgow and Wollongong. The location of Australian coal deposits is shown in Figure 15.5.

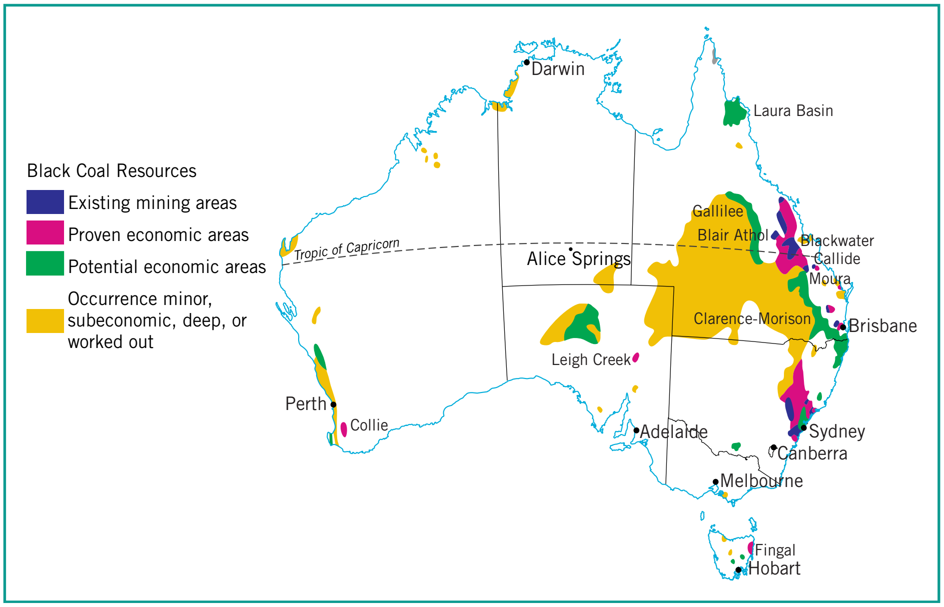


Figure 15.5 The location of Australian black coal deposits

Petroleum

Petroleum consists of a complex mixture of hydrocarbons. Before refining, petroleum is a viscous black liquid often called *crude oil*. Its composition varies from well to well. Like coal, the origins of the chemical energy in petroleum can be traced back to light energy from the sun. This is because most petroleum is derived from the buried remains of marine organisms, particularly bacteria and plankton. The oils and fats in the bodies of these organisms are converted into hydrocarbons by high temperatures and pressures deep in the Earth's crust. Due to its density, the oil tends to migrate upwards, where it may seep out onto the Earth's surface or become trapped beneath impervious rock. In the latter case accumulation of oil and gas occurs, forming an oil field. The separation of crude oil into useful 'fractions' is discussed in Unit 17.3.

Natural gas

Natural gas, like petroleum, has its origin in marine organisms that accumulated as organic sediment in oceans or inland seas. Over long periods of time this organic matter was covered by further sediment. The action of anaerobic bacteria and the increasing temperature and pressure of compaction at depth reduced the organic material to hydrocarbons. These hydrocarbons accumulated in porous pockets in the upper strata of the Earth, trapped by layers of impervious rock, as shown in Figure 15.6.

Natural gas is often found in conjunction with petroleum but can be found by itself, as in the vast reserves currently being developed on the North-West Shelf in Western Australia. Part of the gas produced by these off-shore wells is piped to Perth and other parts of the state, where it is burnt for direct heating or as a fuel in electricity generation. Vast quantities are also liquefied and exported overseas (Figure 15.7) as *liquefied natural gas* (LNG).

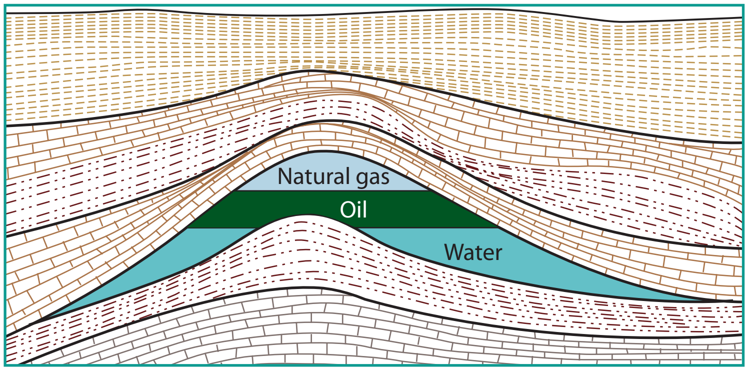


Figure 15.6 Oil and gas trapped in a typical geological structure

Natural gas contains a range of compounds, particularly alkanes (see Unit 17.2) of low molecular mass. Methane (CH_4) is the main component of natural gas, although ethane (CH_3CH_3), propane ($CH_3CH_2CH_3$), butane ($CH_3CH_2CH_2CH_3$), carbon dioxide, nitrogen and hydrogen sulfide are also present in varying amounts, depending on the source of the gas. Generally ethane, propane and butane are extracted from natural gas. The ethane is used in the petrochemical industry, while propane and butane are liquefied under pressure to produce *liquefied petroleum gas* (LPG).

Natural gas is a relatively cheap, clean and convenient fuel. The burning of natural gas can generally be represented by the burning of methane.

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

The combustion of hydrocarbons and their use as fuels is discussed in detail in Chapter 18.

Figure 15.7 A tanker loading liquified natural gas (LNG) off the North-West Shelf

❇ Review exercise 15.2

1 **Identify** three fossil fuels.

2 **Identify** the ultimate source of energy in fossil fuels. **Summarise** how fossil fuels are derived from this source of energy.

3 **Construct** a flow diagram to show the stages of anthracite coal formation.

4 **Identify** the type of environment in which each of the following fossil fuels formed:
   a coal
   b petroleum and natural gas.

5 **Describe** how oil and natural gas can get 'trapped' underground.

6 In general terms, **outline** the conditions required for the conversion of living organic material into fossil fuels.

*KEY POINTS

- The sun is the ultimate source of energy for organisms living on Earth.
- Plants convert light energy into chemical energy by the process of photosynthesis.
- The overall equation for photosynthesis is

$$6CO_2(g) + 6H_2O(l) \xrightarrow{light} C_6H_{12}O_6(aq) + 6O_2(g)$$

- Plants store energy within carbohydrates, which include sugars (mono- and disaccharides such as glucose and sucrose) and polysaccharides (such as starch and cellulose).
- Respiration is the process used by plants and animals to obtain energy stored in carbohydrates.
- The overall equation for respiration is

$$C_6H_{12}O_6(aq) + 6O_2(g) \xrightarrow{enzymes} 6CO_2(g) + 6H_2O\ (l) + \text{energy}$$

- Fossil fuels are naturally synthesised fuels that have formed from the remains of plants and animals over millions of years.
- The conversion of carbon compounds in the remains of organisms into fossil fuels is the result of biochemical processes of bacteria and the action of heat and pressure resulting from various geological processes.
- Coal, petroleum (crude oil) and natural gas are the most important fossil fuels.
- Coal is formed from the remains of plants living in ancient swamps and marshes.
- Oil and natural gas are formed predominantly from the remains of marine organisms.
- Oil and gas may become trapped underground by non-porous rock.

*APPLICATION AND INVESTIGATION

➲ Investigation

1 Gather information from secondary sources to outline some of the steps that take place in the photosynthesis reaction.

2 **Explain** how the energy obtained by a dingo as it digests a rabbit it has eaten can be traced back to its original source, the sun.

3 **Clarify** the derivation of the term ‘fossil fuels’.

4 Fossil fuels are sometimes described as ‘stored solar energy’. **Discuss** what this means.

5 Gather information from secondary sources to **identify** the location of the main Australian oil and natural gas fields. Indicate their location on a map of Australia. ⊂ **Investigation**

6 **Distinguish** between liquefied natural gas (LNG) and liquefied petroleum gas (LPG). ⊂ **Investigation**

7 Gather information from secondary sources to **investigate** Australia's current estimated reserves and projected lifetimes for the following fossil fuels: ⊂ **Investigation**

a coal

b oil

c natural gas.

CHAPTER 16

THE VARIETY OF CARBON COMPOUNDS

16.1 Carbon chemistry

The study of the element carbon and its compounds is often described as organic chemistry. Originally the term ‘organic chemistry’ was used for substances that were derived from living things. Compounds that fitted this classification included urea from urine, lactic acid from milk, citric acid from lemons and tartaric acid from grapes. Any substance that was not obtained from a plant or animal source was classified as inorganic.

CHEMISTRY CONTEXT

❊ DEBUNKING THE VITAL FORCE THEORY

Chemists of the eighteenth century believed that there was an essential difference between organic and inorganic compounds. In 1807 Berzelius described the difference between organic and inorganic compounds in terms of some ‘vital force’ in nature that had to be present before an organic compound could be formed. This theory was challenged in 1828 when the German chemist Wohler prepared urea, a compound all chemists agreed was organic, by heating an aqueous solution of the inorganic compound ammonium cyanate to dryness.

$$\underset{\text{ammonium cyanate}}{NH_4CNO(aq)} \xrightarrow{heat} \underset{\text{urea}}{H_2NCONH_2(s)}$$

This suggested that there was nothing special about the formation of this organic compound.

The ‘vital force’ theory was discredited in 1845 when Kolbe prepared acetic acid in the laboratory from its constituent elements of carbon, hydrogen and oxygen. This showed once and for all that organic compounds were made from elements just like inorganic compounds, and that no special or vital force was necessary for their formation.

Today the distinction between inorganic and organic chemistry is a somewhat arbitrary one. The term *organic chemistry* is generally applied to the study of carbon compounds other than metallic carbonates, hydrogencarbonates and the oxides of carbon. The number of carbon-based compounds is greater than the sum of all other known compounds that do not contain carbon. Several million carbon compounds have been prepared or isolated, so it is convenient to examine this large group of compounds as a separate field of study.

The study of organic compounds is also justified because they exhibit great diversity of properties and are used extensively. Coal, wood, oil, soaps, detergents, antibiotics, rubber, pesticides, wool, alcohols, fuels, carbohydrates, proteins and plastics represent some examples of important organic substances.

Carbon

Carbon has an atomic number of six and is found in group IV of the periodic table. The most common isotope of carbon has a mass number of twelve. Hence the nucleus of a carbon-12 atom contains six protons and six neutrons. Six electrons are distributed in the space around the nucleus of each carbon atom. In the ground or lowest-energy state, a carbon atom has an electron configuration of 2, 4.

KEY

3 ← Atomic number
Li ← Symbol of element
6.94 ← Atomic mass

I	II	IIIa	IVa	Va	VIa	VIIa	VIII			Ib	IIb	III	IV	V	VI	VII	VIII
1 **H** 1.008																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.8	6 **C** 12.0	7 **N** 14.0	8 **O** 16.0	9 **F** 19.0	10 **Ne** 20.2
11 **Na** 23.0	12 **Mg** 24.3											13 **Al** 27.0	14 **Si** 28.1	15 **P** 31.0	16 **S** 32.1	17 **Cl** 35.5	18 **Ar** 39.9
19 **K** 39.1	20 **Ca** 40.1	21 **Sc** 45.0	22 **Ti** 47.9	23 **V** 50.9	24 **Cr** 52.0	25 **Mn** 54.9	26 **Fe** 55.8	27 **Co** 58.9	28 **Ni** 58.7	29 **Cu** 63.5	30 **Zn** 65.4	31 **Ga** 69.7	32 **Ge** 72.6	33 **As** 74.9	34 **Se** 79.0	35 **Br** 79.9	36 **Kr** 83.8
37 **Rb** 85.5	38 **Sr** 87.6	39 **Y** 88.9	40 **Zr** 91.2	41 **Nb** 92.9	42 **Mo** 95.9	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57 **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226	89 **Ac** 227	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (266)	107 **Bh** (264)	108 **Hs** (277)	109 **Mt** (268)	110 **Ds** (271)	111 **Rg** (272)	112 **Uub** (277)						

Lanthanides	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.2	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
Actinides	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)

Figure 16.1 The position of carbon in the periodic table

Carbon has four valence electrons and tends to form four bonds to achieve a share in a valence electron octet. For example in methane, CH_4, carbon forms four single covalent bonds with four separate hydrogen atoms. In carbon dioxide, CO_2, the carbon atom forms two double covalent bonds with two oxygen atoms. The Lewis electron dot diagrams and bonding models for CH_4 and CO_2 are illustrated in Figure 16.3.

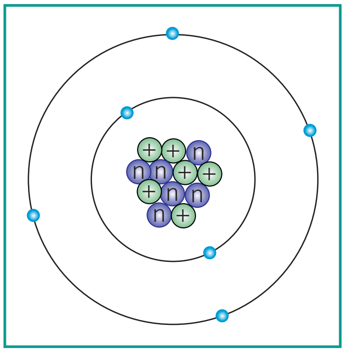


Figure 16.2 An atom of carbon

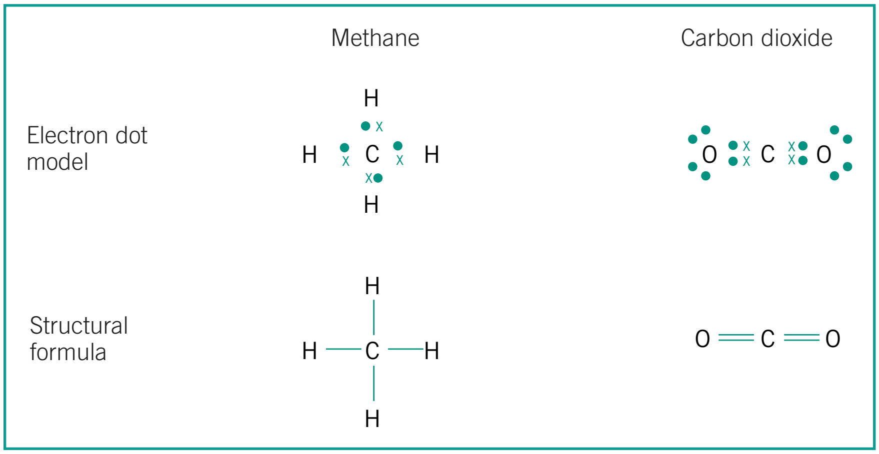


Figure 16.3 Electron dot diagrams and bonding models for CH_4 and CO_2

❇ Review exercise 16.1

1 **Classify** the following substances as either organic or inorganic: glucose ($C_6H_{12}O_6$), carbon dioxide, methane (CH_4), petrol, sodium carbonate, ammonium hydrogencarbonate and carbon disulfide.

2 **Summarise** the properties of carbon under the following headings:
  - **a** Nuclear composition
  - **b** Electron configuration
  - **c** Valence electrons
  - **d** Position in the periodic table.

16.2 Allotropes of carbon

Allotropes are different forms of the same element in the same physical state. Allotropes consist of atoms of the same element, but the atoms are arranged in different crystalline or molecular structures. Consequently, allotropes have distinctly different physical properties such as density, hardness and colour. Until recently, carbon was thought to have only two allotropes, diamond and graphite. However, in 1985 it was discovered that soot contained other molecular forms of carbon called fullerenes. Other elements that exist in allotropic forms include sulfur, phosphorous and tin.

Diamond

Diamond, a crystalline form of pure carbon, is an example of a covalent network substance. It is widely used in jewellery because when cut and polished it sparkles brilliantly. Experimental evidence indicates that in diamond all the C–C bonds are of the same length and all the bond angles are 109.5°. Using this information a diamond crystal can be pictured as a single giant molecule made up of a regular network of carbon atoms extending throughout the crystal. Each carbon atom can be imagined to be at the centre of a regular tetrahedron, surrounded by four other carbon atoms at the corners of the tetrahedron, as illustrated in Figure 16.4.

In this three-dimensional network of atoms, each carbon atom forms four covalent bonds by sharing electrons with each of its four nearest neighbours. The bonding electrons are tightly bound and highly localised and are therefore unable to move freely within the lattice. Therefore diamond crystals are non-conductors of electricity.

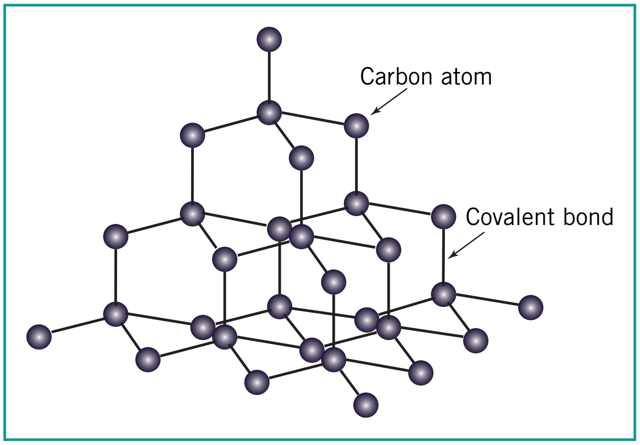


Figure 16.4 The structure of diamond

It is also very difficult to distort diamond, and other covalent network crystals, since this would involve breaking many strong covalent bonds. Consequently, diamond is extremely hard and has a very high melting and boiling point. If the highly directional bonds in diamond are subjected to extreme stress, the crystal is unable to deform in shape and it shatters. Diamond is the hardest known naturally occurring substance. Diamonds unsuitable for gemstones are used in applications such as glass cutting and polishing, mineral exploration drills and dentists' drills.

Graphite

Graphite, a second form or allotrope of pure carbon, has properties quite different from those of diamond. In fact, the properties of graphite are quite unusual for a covalent network substance. Graphite has a high melting and boiling point but is soft and is a good conductor of electricity.

In graphite, the carbon atoms are arranged in flat parallel layers, as shown in Figure 16.5. Within each layer each carbon atom is covalently bonded to three other atoms, forming a hexagonal arrangement. Each layer can be considered a two-dimensional network of carbon atoms. The strong covalent bonds within the layers account for the very high melting point of graphite.

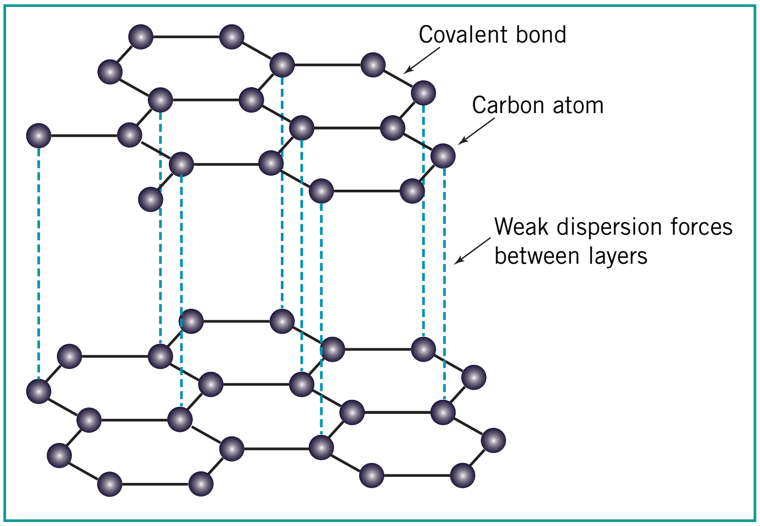


Figure 16.5 The structure of graphite

Each carbon atom shares one of its valence electrons with each of its three neighbouring atoms within the plane. The fourth electron is delocalised. The delocalised electrons are free to move parallel to the layers of carbon atoms but not perpendicular to the layers. The delocalised electrons are responsible for the electrical conductivity of graphite. Because of its electrical conductivity, graphite is used as an electrode in dry cells, in electric furnaces and in electrolytic cells.

The bonding between layers in graphite is relatively weak, consisting only of dispersion forces. As a result, the layers can easily slide over each other. This accounts for the softness and slippery feel of graphite and its use as a dry lubricant. Graphite mixed with clay is also used to make the 'lead' in lead pencils. When a lead pencil is used, the graphite is transferred to the paper. Graphite fibres are used extensively to improve the strength of polyesters and other plastics. These composite materials are used in sporting equipment such as golf clubs, tennis racquets and fishing rods, and in advanced aircraft.

Fullerenes

A third allotrope of carbon was discovered in 1985. This allotrope is a group of molecular structures called *fullerenes*, which are spherical aggregates, or 'cages', of carbon atoms. The most stable of these to be isolated so far is C_{60}, called *buckminsterfullerene* after the noted American engineer R. Buckminster Fuller. More commonly, C_{60} is referred to as 'buckyballs'. Buckyballs have a similar structure to a hollow soccer ball and consist of 12 five-membered and 20 six-membered carbon rings. These are arranged in exactly the same shape as the segments in a soccer ball.

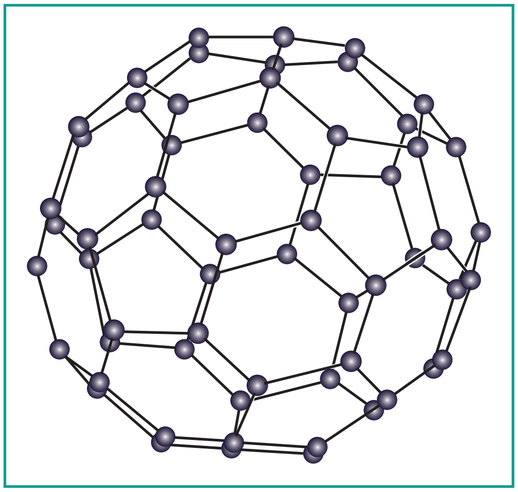


Figure 16.6 The structure of buckminsterfullerene (C_{60})

In a molecule of C_{60} each carbon atom is attached to three other carbon atoms in much the same way as in graphite. As with graphite, this leaves one delocalised electron for each carbon atom in the molecule. Buckminsterfullerene is a covalent molecular substance. It is soluble in non-polar solvents and can be vaporised at moderate temperatures.

Buckyballs are found to a small extent in soot, and new ways of producing larger quantities have been developed. Research is currently in progress, seeking new ways of preparing different fullerenes and investigating their properties and possible uses. A great deal of interest has focused on the potential use of buckyballs as lubricants, in batteries, as superconductors when doped with potassium, and as a trap for radioactive atoms used in radiotherapy. Only the future will determine the extent to which buckyballs are used in these different applications.

Another group of fullerenes are known as *nanotubes*. These can be thought of as a sheet of graphite rolled into a cylinder. Nanotubes have many interesting properties and may have possible applications in the electronics industry.

❇ Review exercise 16.2

1. **Define** the term ‘allotrope’.
2. **Account** for the different physical properties of allotropes.
3. **Compare** the arrangement of carbon atoms in diamond, graphite and buckminsterfullerene.
4. **Explain** why graphite is an electrical conductor but diamond is an electrical insulator.
5. **Explain** why diamond and graphite have high melting and boiling points.

16.3 Bonding in carbon compounds

In organic compounds, carbon atoms almost always form four bonds. This suggests that the carbon atom’s four valence electrons are all involved in bonding. An examination of simple carbon-based molecules like methane (CH_4) and carbon tetrachloride (CCl_4) indicates that in these compounds the carbon atom forms four identical single covalent bonds and that the angles between the bonds are 109.5°. It can be predicted from the valence shell electron pair repulsion (VSEPR) theory (Unit 11.1) that a tetrahedral orientation of the electron pairs is required, to minimise the electrostatic repulsion between them.

The central role of carbon in organic chemistry depends on the fact that carbon has a valency of four and can form a variety of bonds. Consequently, carbon atoms can form chains of virtually unlimited length containing many carbon–carbon bonds. The valence electrons not involved in forming carbon–carbon bonds are used in forming bonds with atoms of other elements such as hydrogen, oxygen, nitrogen and halogens.

Figures 16.7 to 16.10 illustrate the bonding in several representative organic compounds that contain C–H, C–Cl, C–C, C=C and C≡C bonds. These figures include several ways of representing these bonds.

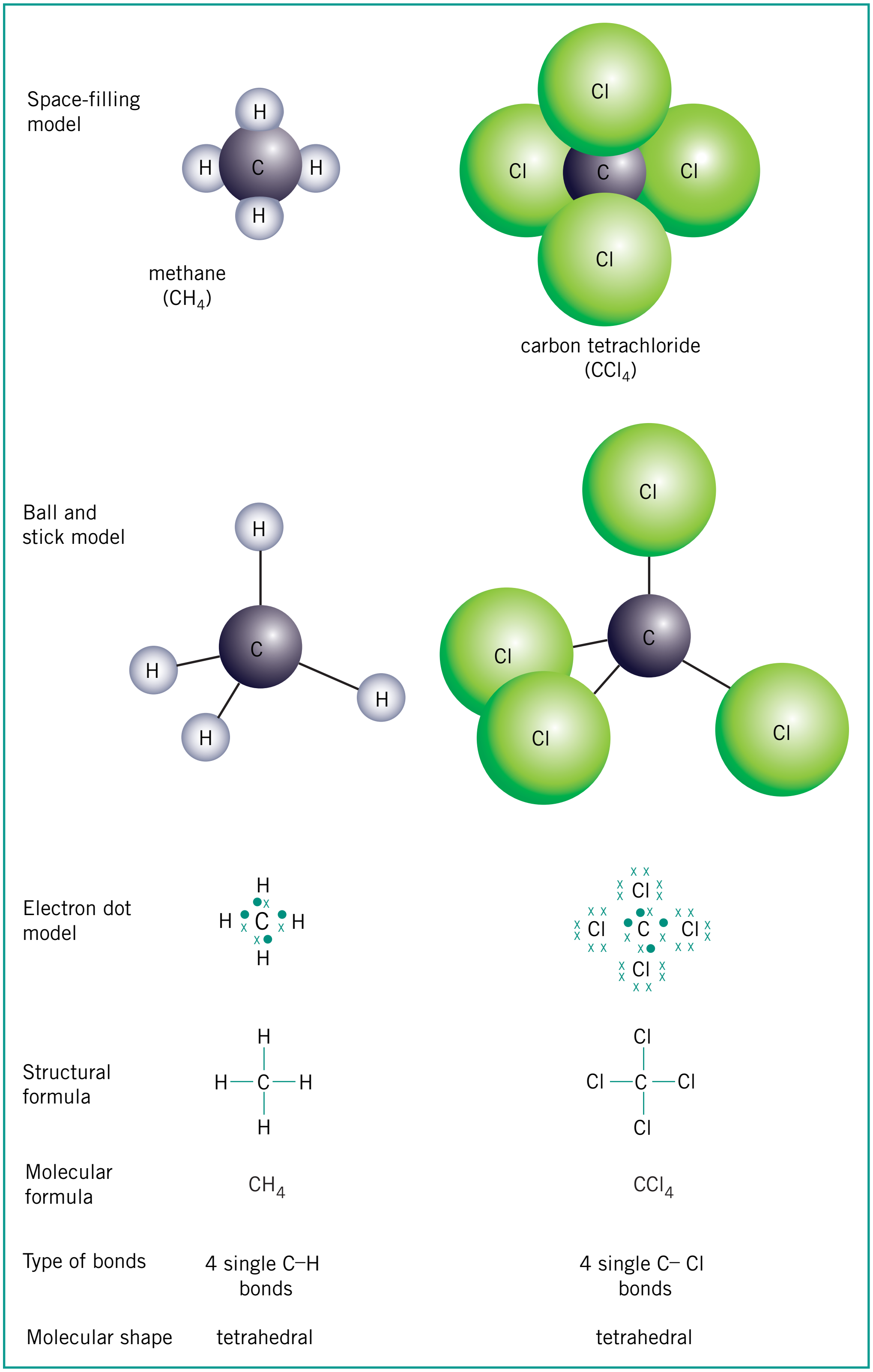


Figure 16.7 **The bonding in methane and carbon tetrachloride**

Carbon–carbon single bonds

The two simplest molecules containing carbon–carbon single bonds are ethane (CH_3CH_3) and propane ($CH_3CH_2CH_3$). In these compounds each carbon atom forms four single bonds, which again have a tetrahedral orientation. In the case of CH_3CH_3 three of the bonds formed by the carbon atoms are C–H bonds, while the other bond is a C–C bond.

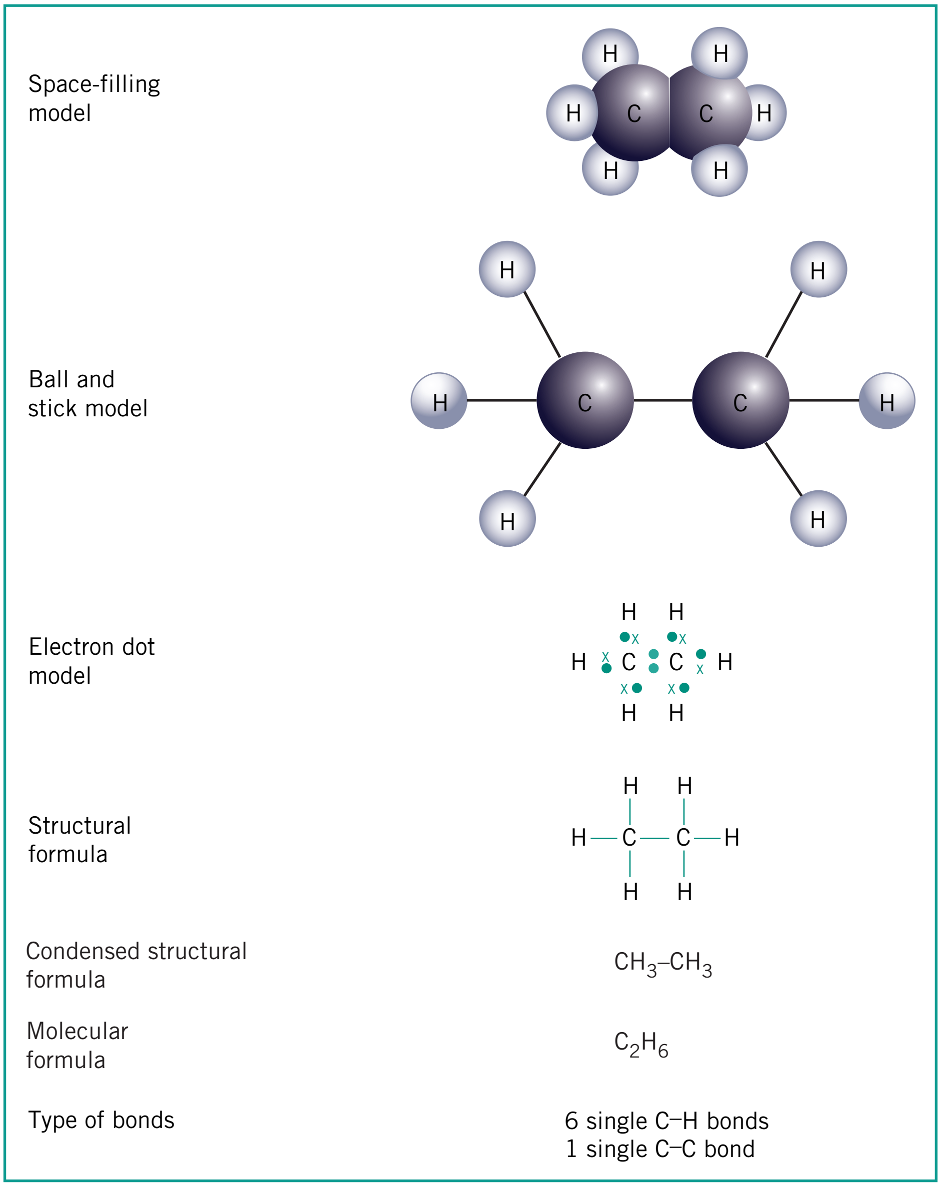


Figure 16.8 The bonding in ethane

Carbon–carbon double bonds

The compound ethene or ethylene (CH_2CH_2) is the simplest carbon compound containing a C=C double bond. In this case only two of each carbon atom's four valence electrons are used in bonding with hydrogen atoms. Hence each carbon atom shares two pairs of electrons with another carbon atom. These two pairs of electrons constitute a double bond.

An examination of compounds such as ethene (CH_2CH_2) indicates that the bond angles are 120º, and the geometric arrangement of the two carbon atoms and adjoining hydrogen atoms is planar. This again can be explained in terms of the VSEPR theory. In using the VSEPR theory, the C=C double bond is viewed as a single region of charge. To minimise electron repulsion, the three electron regions around each carbon atom adopt a planar orientation with bond angles of 120º.

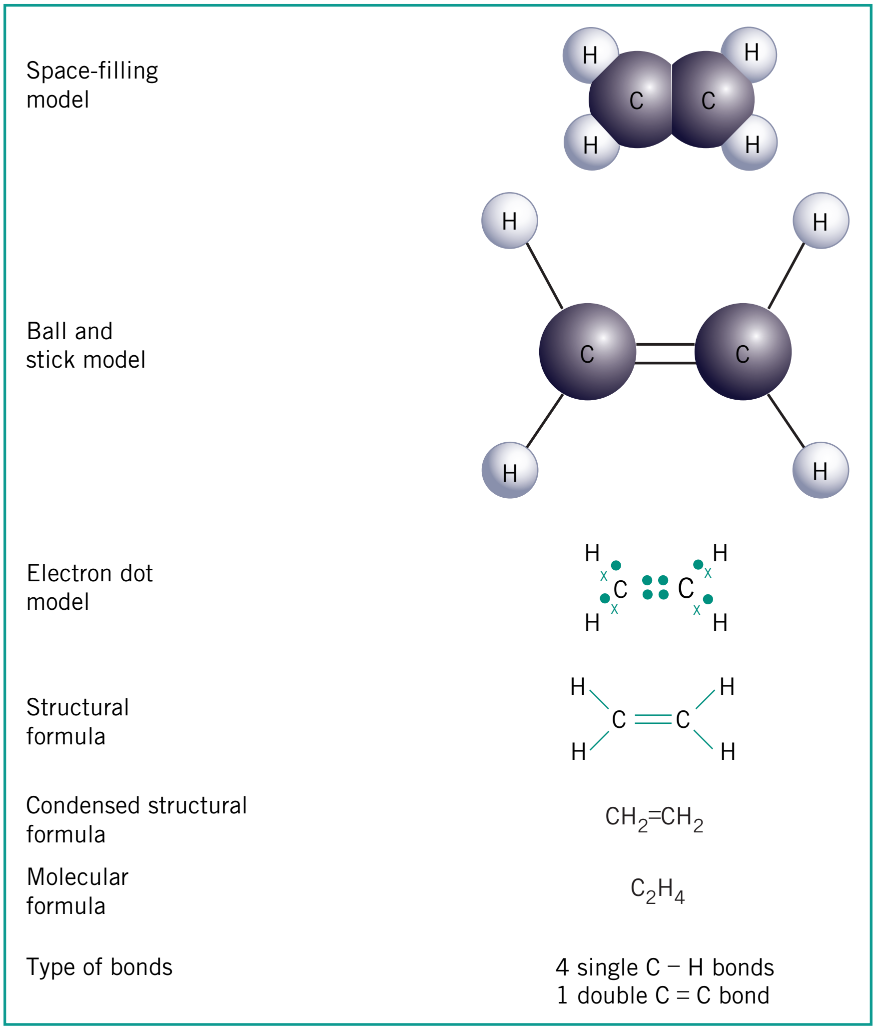


Figure 16.9 The bonding in ethene

Carbon–carbon triple bonds

Ethyne (CHCH) is the simplest carbon compound containing a C≡C triple bond. Each carbon uses only one electron in forming a bond with a hydrogen atom. This allows the carbon atoms to share three pairs of electrons, resulting in the formation of a triple bond.

An examination of compounds such as ethyne (CHCH) indicates that the bond angles are 180°. If the C≡C triple bond is taken to represent one region of charge, then by applying the VSEPR theory the shape of such molecules must be linear, as illustrated in Figure 16.10.

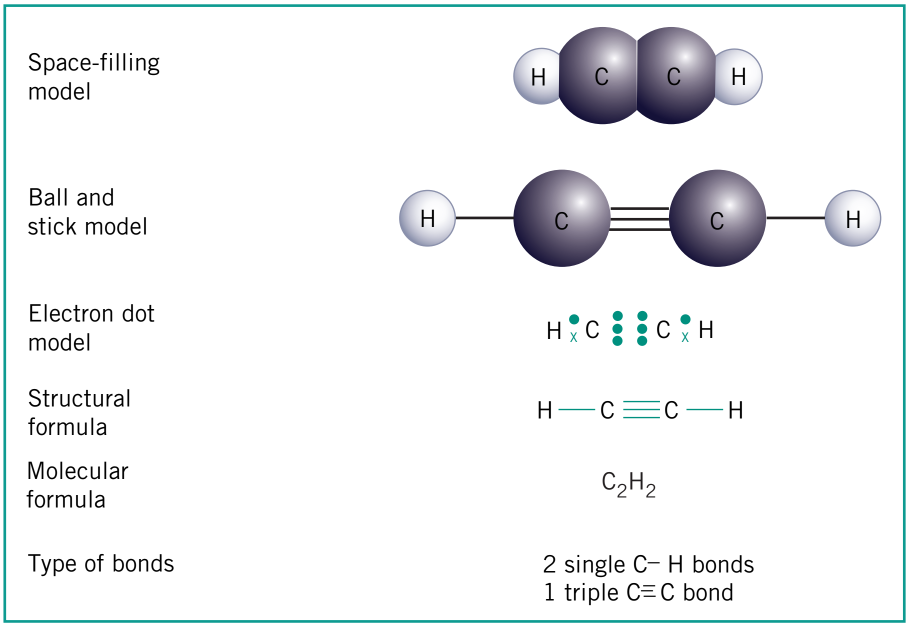


Figure 16.10 The bonding in ethyne

Table 16.1 summarises the characteristics of single, double and triple carbon–carbon bonds. As the number of bonds between the two carbon atoms increases, the bond length decreases. This occurs because of the increased attraction between the bonding electrons and the carbon nuclei. The bond angles and the geometric arrangement of atoms can be determined by using the VSEPR theory.

Table 16.1 Characteristics of single, double and triple carbon–carbon bonds

Type of carbon–carbon bond	Representation	Number of shared pairs of electrons	Bond angles
Single	–C–C–	1	109.5°
Double	–C=C–	2	120°
Triple	–C≡C–	3	180°

Review exercise 16.3

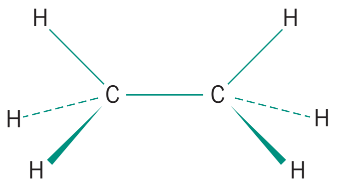
1 Silicon belongs to the same group of the periodic table as carbon. **Describe** why each silicon atom also forms four covalent bonds in its compounds.

2 Chloroform has the formula $CHCl_3$. For a molecule of chloroform, complete the following.
  a **Construct** an electron dot diagram.
  b **Draw** a structural formula showing all the bonds in the molecule.
  c **Predict** the shape of a chloroform molecule. **Justify** your prediction in terms of VSEPR theory.

3 Vinyl chloride (CH_2CHCl) is an important raw material used to manufacture polyvinyl chloride (PVC).
  a **Construct** an electron dot diagram for vinyl chloride.
  b **Draw** the structure of vinyl chloride showing all bonds and unshared valence electrons.
  c **Describe** the shape of a molecule of vinyl chloride and **explain** why such a shape occurs.

16.4 Representing the structures of carbon compounds

Several methods are used to represent the bonding and structures of carbon compounds. These include the space-filling, ball and stick, electron dot and structural formula approaches used in Figures 16.7 to 16.10. In addition, it is possible to draw representations that emphasise the three-dimensional structures of these compounds. Figure 16.11 shows the three-dimensional structure of ethane (CH_3CH_3). The convention used is that a straight line (—) represents a bond in the plane of the page, a dashed line (- - -) represents a bond going into the page, and a wedge shape (◀) represents a bond coming out of the page.



Three-dimensional representation of ethane — all bond angles are 109.5

Figure 16.11 The bonding and structure of ethane

Usually the bonding and structures of carbon compounds are represented by one of the structural formulas shown in Figure 16.12. The simplest structural formula of an organic compound precisely defines the bonding and arrangement of atoms present in the compound. From this formula, all the more complicated representations shown in Figure 16.12 can be derived.

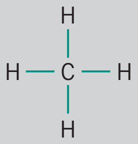
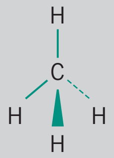
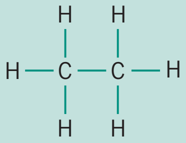
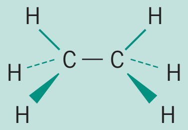
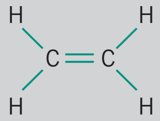
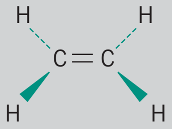
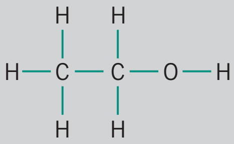
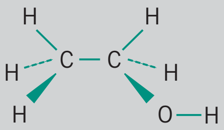
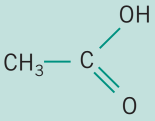
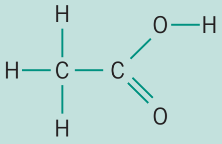
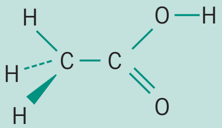
Name	Molecular formula	Condensed structural formula	Structural formula showing some bonds	Structural formula showing all bonds	Three-dimensional diagram showing shape
Methane	CH_4	CH_4	CH_4		
Ethane	C_2H_6	CH_3CH_3	$CH_3—CH_3$		
Ethene	C_2H_4	CH_2CH_2	$CH_2{=}CH_2$		
Ethyne	C_2H_2	CHCH	$CH{\equiv}CH$	$H—C{\equiv}C—H$	$H—C{\equiv}C—H$
Ethanol	C_2H_6O	CH_3CH_2OH	$CH_3—CH_2—OH$		
Ethanoic acid	$C_2H_4O_2$	CH_3COOH			

Figure 16.12 Methods of representing some simple carbon compounds

❇ Review exercise 16.4

1 **Construct** electron dot diagrams for the following compounds:

- **a** CH_3Cl
- **b** $CH_3CH_2CH_3$
- **c** CH_3CHCH_2
- **d** CH_3OH

2 **Draw** structural formulas showing all the bonds in the molecules represented by the following simple structural formulas:

- **a** CF_4
- **b** $(CH_3)_2CHCH_3$
- **c** CH_3CHCH_2
- **d** $(CH_3)_2C(CH_3)_2$
- **e** $CH_3CHCHCH_2CHCHCH_3$
- **f** CH_3CH_2CCH

*KEY POINTS

- Organic chemistry and the chemistry of carbon are interchangeable terms that apply to the study of carbon compounds other than metallic carbonates and hydrogencarbonates and the oxides of carbon.
- Carbon is a non-metal element with four valence electrons and an electron configuration of 2, 4.
- Allotropes are different forms of the same element in the same physical state. Allotropes consist of atoms of the same element, but the atoms are arranged in different crystalline or molecular structures.
- Allotropes have different physical properties because the arrangement of atoms in their crystals or molecules is different.
- Carbon exists in three allotropic forms including diamond, graphite and a group of molecular structures called fullerenes.
- Carbon forms a vast number of different compounds because of the fact that it has a valency of four and can form a variety of bonds, often in chains of virtually unlimited length.
- Carbon can form C–C single bonds, C=C double bonds and C≡C triple bonds.
- Some simple bonding rules for carbon-based compounds are as follows.
  - Carbon atoms must form four bonds.
  - Halogen atoms must form one bond.
  - Oxygen atoms must form two bonds.
  - Nitrogen atoms must form three bonds.
  - Hydrogen atoms must form one bond.
- There are a variety of ways to represent the structures of organic compounds. These include:
  - Lewis electron dot diagrams
  - a variety of structural formulas that are used in different circumstances
  - three-dimensional representations.

✱APPLICATION AND INVESTIGATION

1 **Identify** the property of carbon responsible for the huge number of carbon-based compounds.

➲ **Investigation**

2 Carbon forms four bonds in most of its compounds, as in CH_4 and CO_2. The bonding in CO does not fit this generalisation. **Investigate** and write a brief description of the bonding in CO.

3 **Explain** in terms of its structure and bonding why diamond is a very hard solid with a high melting point that can be used as an abrasive, whereas graphite is a soft, greasy solid with a high melting point that can be used as a lubricant.

➲ **Investigation**

4 Gather information from secondary sources to **investigate** some uses of allotropes of carbon, including potential uses of the fullerenes, and relate these uses to their physical properties.

5 **Explain** why the formation of four identical bonds leads to a tetrahedral arrangement of atoms around a central carbon atom.

6 **Describe** the difference between carbon–carbon single, double and triple bonds in terms of the number of shared pairs of electrons, bond length and arrangement of the atoms.

7 **Describe** the bonding in ethyne (CHCH) and **explain** why molecules of this compound have a linear shape.

8 **Construct** electron dot diagrams for the following:

a CH_2Cl_2
b CH_3CH_2Br
c CH_2CHCl
d C_2H_4
e CO_2
f HCN
g $CH_3CH_2CH_2OH$
h C_2H_6O

9 For the compounds listed in **a** to **f** below:

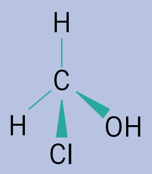
i Draw structural formulas showing all the bonds in each molecule.
ii **Predict** the shape of each molecule.
iii Draw a three-dimensional structure of each molecule.

a CH_2Cl_2
b CH_3CH_2Br
c CH_2CHCl
d C_2H_4
e CO_2
f HCN

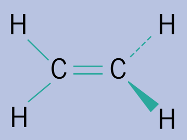
10 Indicate what is wrong with each of the following structures and then rewrite them correctly.

a CH_2Br_2Cl
b $CH_3{=}CBr_2$
c CH_3CH_2O
d $CCl_2{=}H$

e



f



CHAPTER 17

HYDROCARBONS

17.1 Defining hydrocarbons

Classifying hydrocarbons

The most important fossil fuels—natural gas, petroleum and coal—are mixtures of hydrocarbons. *Hydrocarbons* are compounds that contain only carbon and hydrogen. They should not be confused with carbohydrates, which contain the elements carbon, hydrogen and oxygen. There are three major groups of hydrocarbons: aliphatic, alicyclic and aromatic. In this module we will concentrate on the first of these groups, the aliphatic hydrocarbons. Aliphatic hydrocarbons can have either straight-chain or branched-chain structures. Aliphatic hydrocarbons can be divided into three subgroups: alkanes, alkenes and alkynes.

Alkanes are described as *saturated hydrocarbons* because they possess only single carbon–carbon bonds and cannot incorporate more atoms into their structure. For example, in ethane (C_2H_6) each carbon atom forms a single bond with the other carbon atom and each of three hydrogen atoms. Alkenes and alkynes are described as *unsaturated hydrocarbons* because they possess multiple carbon–carbon bonds and can react to incorporate more atoms into their structure. Alkenes contain carbon–carbon double bonds, whereas alkynes contain carbon–carbon triple bonds. In ethene (C_2H_4), each carbon atom forms a double bond with the other carbon atom and single bonds with two hydrogen atoms. If one of the bonds between the carbon atoms is broken, then each carbon can bond with another atom. Similarly, in ethyne (C_2H_2), if the carbon–carbon triple bond is replaced by a single bond, this allows each carbon atom to bond to two additional atoms. Thus both ethene and ethyne are unsaturated because they can undergo reactions that will incorporate more atoms into their structures.

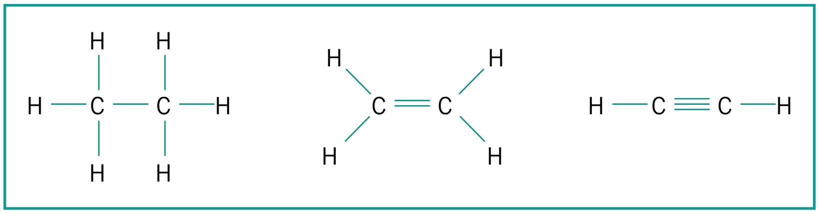


Figure 17.1 Structures of ethane, ethene and ethyne—the multiple carbon–carbon bonds in ethene and ethyne mean these compounds are unsaturated.

Systematic nomenclature

Because there are a vast number of carbon-based compounds, a systematic method for naming them is needed. Originally chemists named newly discovered carbon compounds in an arbitrary way. For example, the names acetic acid (CH_3COOH), chloroform ($CHCl_3$), ethylene (CH_2CH_2), acetylene (CHCH), formaldehyde (HCHO), acetone (CH_3COCH_3) and vinyl chloride (CH_2CHCl) were not systematically determined. As the number and diversity of known compounds grew, this informal naming system (*nomenclature*) became chaotic. As a result, in 1930 the International Union of Pure and Applied Chemistry (IUPAC) drafted a set of rules for the systematic naming of organic compounds. In this book the systematic naming of compounds is preferred. However, the use of traditional names for some compounds is so entrenched that they are still commonly used. Table 17.1 lists some of the non-systematic names that are still in use. As there are a large number of rules in the IUPAC system of nomenclature, these will be introduced as they are needed.

Table 17.1 Traditional and systematic (IUPAC) names of some common organic compounds

Traditional name	IUPAC name	Formula
ethylene	ethene	CH_2CH_2
acetylene	ethyne	CHCH
formaldehyde	methanal	HCHO
acetaldehyde	ethanal	CH_3CHO
acetone	propanone	CH_3COCH_3
formic acid	methanoic acid	HCOOH
acetic acid	ethanoic acid	CH_3COOH
oxalic acid	ethanedioic acid	HOOCCOOH
ethyl acetate	ethyl ethanoate	$CH_3COOCH_2CH_3$
vinyl chloride	chloroethene	CH_2CHCl
chloroform	trichloromethane	$CHCl_3$
carbon tetrachloride	tetrachloromethane	CCl_4
glycerol	1,2,3-propanetriol	$CH_2OHCHOHCH_2OH$

When naming a hydrocarbon (or any organic compound), attention must be given to two characteristics of the compound. These are the number of carbon atoms in the hydrocarbon chain, and the presence of any functional group in the compound. The number of carbons in a hydrocarbon chain determines the 'stem' name of the compound. The functional group determines the 'suffix' added to the stem.

Table 17.2 indicates the stem used for different numbers of carbon atoms in the chain. For chains containing five or more carbon atoms, the stem used is the Latin prefix for that number. The suffix added to the stem depends on the functional group present in each molecule. The specific names for various functional groups will be discussed in later sections.

Table 17.2 The 'stem' names used in continuous chain hydrocarbons

Number of carbon atoms in chain	Stem name	Number of carbon atoms in chain	Stem name
1	meth-	6	hex-
2	eth-	7	hept-
3	prop-	8	oct-
4	but-	9	non-
5	pent-	10	dec-

❇ Review exercise 17.1

1 **Identify** which of the following compounds are hydrocarbons.

a	propane	$CH_3CH_2CH_3$
b	chloromethane	CH_3Cl
c	methane	CH_4
d	glucose	$C_6H_{12}O_6$
e	ethene	CH_2CH_2
f	methanol	CH_3OH
g	sucrose	$C_{12}H_{22}O_{11}$
h	ethanoic acid	CH_3COOH
i	diamond	
j	carbon tetrachloride	CCl_4

2 **Identify** the bonding characteristic the alkenes and alkynes have in common that allow them to be grouped together as unsaturated hydrocarbons.

3 **Deduce** the number of carbon atoms in the following compounds.

- **a** propane
- **b** ethanol
- **c** octane
- **d** cyclohexane
- **e** methanoic acid
- **f** butene

17.2 Naming hydrocarbons

Alkanes

The alkanes are saturated aliphatic hydrocarbons. These compounds possess only single C–C bonds and do not contain a functional group in the usual sense of the term. Their family name is indicated by the suffix '-ane'. The simplest member of this family is called methane, the stem name 'meth-' indicating one carbon and the suffix '-ane' the family name. Similarly the two-carbon compound of this family, with the stem name 'eth-' and suffix '-ane', is called ethane. Figure 17.2 shows the structures of the first three members of the alkanes and Table 17.3 lists the first 10 members.

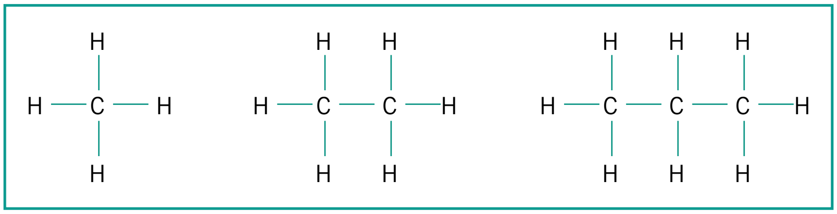


Figure 17.2 The structures of the first three members of the alkanes

Table 17.3 The names and formulas of the first 10 members of the alkanes

Number of carbon atoms in chain	Molecular formula	Structural formula	Name
1	CH_4	CH_4	methane
2	C_2H_6	CH_3CH_3	ethane
3	C_3H_8	$CH_3CH_2CH_3$	propane
4	C_4H_{10}	$CH_3(CH_2)_2CH_3$	butane
5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	pentane
6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	hexane
7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	heptane
8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	octane
9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	nonane
10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	decane

Notice that each member of the family differs by $-CH_2-$ from its two nearest neighbours. Consequently the general formula for the alkanes can be written as C_nH_{2n+2}, where n is any integer. This general formula describes what is called a *homologous series* in which each member differs by CH_2 from its closest members in the family.

Alkenes

Alkenes are unsaturated hydrocarbons that contain at least one C=C double bond. This double bond is the functional group of the alkene homologous series.

When naming members of this family, the longest chain containing the carbon–carbon double bond is considered the parent compound. The chain is numbered from the end that gives the position of the double bond its lowest number. The family name for these compounds is indicated by the suffix '-ene', which is attached to the stem name.

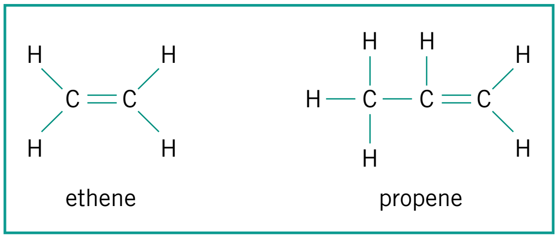


Figure 17.3 The structures of the first two members of the alkenes

The simplest member of this family has two carbon atoms joined by a double bond. The stem name 'eth-' and suffix '-ene' result in the name ethene. Propene, the next member of the family, consists of a three-carbon chain in which a double bond exists between two of the carbon atoms (Figure 17.3).

For alkenes containing four or more carbons in the hydrocarbon, *structural isomerism* occurs. Isomers have the same molecular formula but the atoms in the molecule are arranged differently. For example, the C4 alkene, C_4H_8, exhibits two structural isomers, as can be seen in Figure 17.4. The bonding requirements of carbon and hydrogen are satisfied when the double bond occurs

$CH_3-CH_2-CH=CH_2$

1-butene

$CH_3-CH=CH-CH_3$

2-butene

Figure 17.4 Position structural isomers of butene between the two carbons at the end of the chain or between the middle two carbon atoms. These isomers are known as 1-butene and 2-butene respectively. This is an example of position structural isomerism.

Note that when the double bond occurs between the first and second carbon atoms in the chain, the name is 1-butene. When the double bond is between the second and third carbon atoms, the name is 2-butene. The double bond is identified by the lower-numbered of the two carbon atoms it joins.

Table 17.4 lists some members of the alkene homologous series.

As indicated in Table 17.4, the general formula for this homologous series is C_nH_{2n}. Note that members of this series contain two fewer hydrogen atoms than the corresponding member of the alkane homologous series. This occurs because the alkenes contain a carbon–carbon double bond and require two less hydrogen atoms to satisfy the bonding requirements of the carbon atoms.

Table 17.4 Names, molecular formulas and structural formulas of some straight-chain alkenes

Number of carbon atoms in chain	Molecular formula	Structural formula	Name
2	C_2H_4	$CH_2{=}CH_2$	ethene
3	C_3H_6	$CH_3{-}CH{=}CH_2$	propene
4	C_4H_8	$CH_3{-}CH_2{-}CH{=}CH_2$	1-butene
		$CH_3{-}CH{=}CH{-}CH_3$	2-butene
5	C_5H_{10}	$CH_3{-}CH_2{-}CH_2{-}CH{=}CH_2$	1-pentene
		$CH_3{-}CH_2{-}CH{=}CH{-}CH_3$	2-pentene
6	C_6H_{12}	$CH_3CH_2CH_2CH_2CH{=}CH_2$	1-hexene
		$CH_3CH_2CH_2CH{=}CHCH_3$	2-hexene
		$CH_3CH_2CH{=}CHCH_2CH_3$	3-hexene
7	C_7H_{14}	$CH_3CH_2CH_2CH_2CH_2CH{=}CH_2$	1-heptene
		$CH_3CH_2CH_2CH_2CH{=}CHCH_3$	2-heptene
		$CH_3CH_2CH_2CH{=}CHCH_2CH_3$	3-heptene
8	C_8H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH{=}CH_2$	1-octene
		$CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_3$	2-octene
		$CH_3CH_2CH_2CH_2CH{=}CHCH_2CH_3$	3-octene
		$CH_3CH_2CH_2CH{=}CH\ CH_2CH_2CH_3$	4-octene

❇ Review exercise 17.2

1 **Identify** the straight-chain alkanes containing two, four, six and eight carbon atoms respectively, and draw diagrams showing all the bonds in these compounds.

2 **a** **Write** a general formula for alkenes.
  b **Predict** the molecular formula for the C5 and C7 alkenes.
  c Draw all the possible straight chain structural formulas for the pentenes and heptenes, and give each compound its correct IUPAC name.

3 **Define** the term 'position structural isomerism'. Use examples to **illustrate** your answer.

4 **Identify** the following compounds:
  a $CH_2{=}CH{-}CH_2{-}CH_3$
  b $CH_3{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_3$

5 Draw structural formulas for the following:
  a 2-hexene
  b 2,4,6-octatriene.

6 Write systematic names for the following compounds:
  a $CH_3{-}CH_2{-}CH{=}CH{-}CH_3$
  b $CH_3{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_3$

17.3 Separation of petroleum (crude oil)

Figure 17.5 A fractionating tower at an oil refinery

Petroleum consists of a complex mixture of compounds that are mainly hydrocarbons in the C1 to C40 range. While alkanes are the principal component, petroleum also contains smaller amounts of alkenes, aromatic compounds (carbon compounds containing a benzene ring, C_6H_6) and other organic compounds containing oxygen, nitrogen and sulfur. The actual composition of crude oil varies depending on its source.

The petroleum must be separated into several fractions to make maximum use of the variety of constituents it contains. This is achieved by the process of fractional distillation using a fractionating tower. This separates the petroleum into fractions containing hydrocarbons with similar boiling points.

The petroleum is heated to about 400ºC to produce a hot liquid/vapour mixture that enters the fractionating tower as shown in Figure 17.6. Inside the tower are horizontal trays, each of which contains many bubble caps. As the vapour rises it forces up the bubble caps and bubbles through the condensed liquid in the trays. The higher boiling point components tend to condense to liquid while the lower boiling point components continue to rise up the tower. The lower the boiling point of a component, the higher its vapour will rise in the fractionating tower before it condenses. Because the intermolecular forces involved are only weak dispersion forces, the boiling point depends mainly on the molecular size and shape. The lighter hydrocarbons will condense towards the top of the tower while heavier ones will condense nearer the bottom.

The fractionating tower is designed so that the various fractions can be drawn off as they condense. This is illustrated in Figure 17.6. Table 17.5 outlines some of the major fractions resulting from the refining of petroleum.

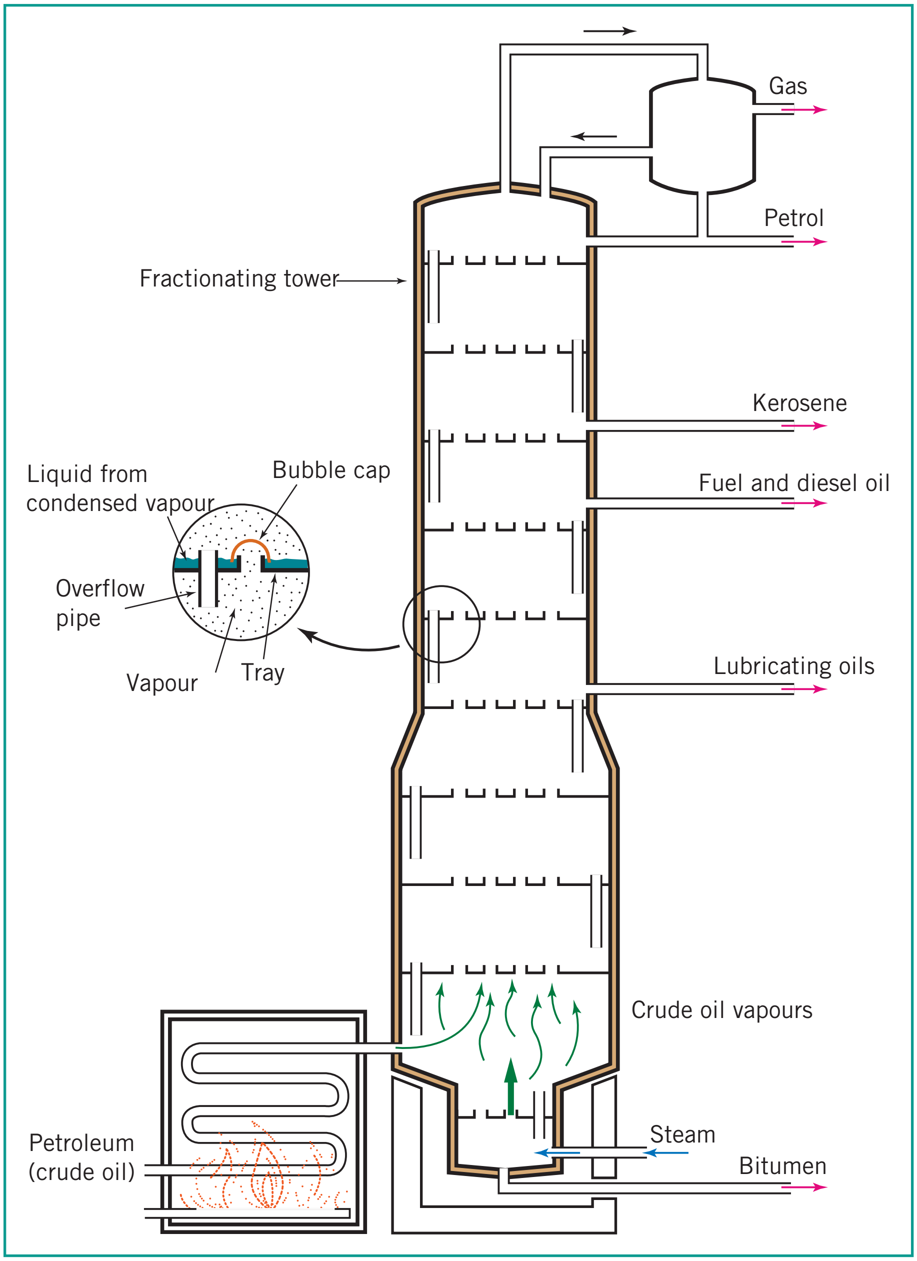


Figure 17.6 A schematic drawing of a fractionating tower used in the refining of crude petroleum

In petroleum refining, the yield of each fraction depends initially on the composition of the crude oil being refined. However, yields of the different fractions can be adjusted to match market demand. For example, ‘cracking’ the longer, higher boiling point components found in kerosene, fuel oils and lubricating oils could increase the yield of petrol. The catalytic cracking process involves reactions that convert straight-chain alkanes into smaller alkanes, alkenes and alkynes. Some of these processes are described in Module 1 of *Chemistry Contexts 2*.

Table 17.5 Some typical fractions obtained from refining crude oil, and their uses

Fraction	Composition	Boiling range (°C)	% of crude oil	Principal uses and comments
Refinery gas	C1–C4	below 30	1–2	Used mainly as a fuel or as starting material in the manufacture of plastics and petrol additives
Gasoline (naphtha, petrol)	C5–C12	30–200	15–30	Motor fuel, naphtha for manufacture of petrochemicals, solvents
Kerosene	C11–C15	180–275	10–15	Aviation fuel, starting material for catalytic cracking process to produce other organic compounds
Diesel and gas oils	C15–C18	275–350	15–20	Diesel fuel, heating fuel oil, fuel for industrial boilers, starting material for catalytic cracking process to produce other organic compounds
Lubricating oils	C16–C20	Above 350	40–50	Lubricating oil, starting material for catalytic cracking process to produce other organic compounds
Paraffin waxes	C20–C40	Low-melting solids		Candles, wax paper
Bitumen	Above C40	Gummy residues		Roofing tar, road bitumen (asphalt)

Uses of hydrocarbons

More than 90% of petroleum is used as a fuel for heating or transport. The highly exothermic nature of the combustion of hydrocarbons makes them very useful as fuels. Natural gas, which consists principally of methane with small quantities of other hydrocarbons, is a very important domestic and industrial fuel. Underground pipes deliver it to homes and industry, where it is burnt for direct heating or as a fuel in electricity generation. In homes, natural gas is used for domestic heating, hot water systems and gas stoves. Liquefied petroleum gas (LPG) is a mixture of volatile hydrocarbons, particularly propane and butane. It is used as a portable fuel in caravans and gas barbeques. Since the 1980s, many cars, particularly taxis, have been converted to run on LPG as well as petrol. Butane gas is easily compressed into a liquid fuel for use in disposable lighters and as camping gas. Petrol for motor vehicles is a mixture of C5–C12 hydrocarbons, and longer chain hydrocarbons are used as aviation and diesel fuels. Ethyne (also known as acetylene) is used as a fuel in oxyacetylene torches, which can cut through and weld metals. When the mix of ethyne and pure oxygen is adjusted, these torches are capable of producing a very hot flame.

Figure 17.7 Complete combustion of ethyne (acetylene) in an oxyacetylene torch produces a very hot flame.

Figure 17.8 Many aerosol spray cans use hydrocarbons as propellants.

Hydrocarbons are not only used for fuels. Ethylene (ethene) and propylene (propene) are used extensively in the petrochemical industry to manufacture a vast range of important plastics including polyethylene, PVC, PVA, PET, polystyrene, perspex, teflon and many others. The manufacture and uses of some of these plastics are discussed in Module 1 of *Chemistry Contexts 2*. Hydrocarbons are also used in the production of ethanol, ethanoic acid, 1,2-ethanediol (ethylene glycol) and glycerol. Hydrocarbons are used as the starting materials in the synthesis of many more useful substances including synthetic fibres, detergents, dyes, pharmaceuticals and insecticides. Gaseous hydrocarbons are used as propellants in many aerosol spray cans. Some higher molecular weight hydrocarbons are used as lubricants such as engine oil, grease and vaseline. Hydrocarbons are also used as solvents in industry including mineral turpentine, ‘turps’, which is used as a solvent for oil-based paints. Turpentine is principally pinene, $C_{10}H_{16}$, and can be derived from pine trees.

❇ Review exercise 17.3

1 a **Outline** the purpose of fractional distillation of crude oil.
  b **Explain** how fractional distillation enables crude oil to be separated into several fractions with distinctive uses.

2 **Outline** the main use of each of the following fractions and **identify** two alkanes recovered from them.
  a gasoline
  b refinery gas

3 Octane is a component of petrol. Write the molecular and structural formulas for straight-chain octane.

4 Many fuels are basically mixtures of hydrocarbons. **Identify** five common fuels that fall into this category.

5 **Describe** four other uses of hydrocarbons.

17.4 Physical properties of hydrocarbons

Intermolecular forces between hydrocarbon molecules

Unit 11.3 outlined the nature of forces that exist between molecules. These intermolecular forces occur between molecules in covalent molecular substances such as O_2, Cl_2, CH_4, C_8H_{18}, $CHCl_3$, CO_2, HCl, $C_6H_{12}O_6$, NH_3 and H_2O. Intermolecular forces are of three types:

- dipole–dipole forces of attraction between the oppositely charged ends of neighbouring polar molecules, for example, HCl, $CHCl_3$
- dispersion forces, which are weak attractive forces between non-polar molecules caused by temporary dipoles
- hydrogen bonds between a hydrogen atom attached to a fluorine, oxygen or nitrogen atom in one molecule and a fluorine, oxygen or nitrogen atom in another molecule.

The strength of intermolecular forces is generally: hydrogen bonds > dipole–dipole forces > dispersion forces. However, the strength of dispersion forces increases with the number of electrons present in the molecules, and is consequently related to molecular size and mass. As a result, dispersion forces may be more significant than dipole–dipole forces where the molecules concerned are weakly polar.

Physical properties of hydrocarbons

Table 17.6 lists the melting points, boiling points and states of the first 10 straight-chain alkanes under normal conditions.

Table 17.6 Physical properties of the first 10 members of the alkanes

Name	Formula	Relative molecular mass	Number of electrons	Melting point (°C)	Boiling point (°C)	State under normal atmospheric conditions
methane	CH_4	16.0	10	–182	–162	gas
ethane	CH_3CH_3	30.1	18	–183	–89	gas
propane	$CH_3CH_2CH_3$	44.1	26	–188	–42	gas
butane	$CH_3(CH_2)_2CH_3$	58.1	34	–138	0	gas
pentane	$CH_3(CH_2)_3CH_3$	72.1	42	–130	36	liquid
hexane	$CH_3(CH_2)_4CH_3$	86.2	50	–95	69	liquid
heptane	$CH_3(CH_2)_5CH_3$	100.2	58	–91	98	liquid
octane	$CH_3(CH_2)_6CH_3$	114.2	66	–57	126	liquid
nonane	$CH_3(CH_2)_7CH_3$	128.2	74	–54	151	liquid
decane	$CH_3(CH_2)_8CH_3$	142.3	82	–30	174	liquid

From Table 17.6 it can be seen that there are trends in the melting and boiling points of the alkanes that are related to the size of the molecules. The melting and boiling points increase with increasing relative molecular mass. At 25°C and one atmosphere pressure, the first four alkanes are gases, the C5 to C17 alkanes are liquids, and alkanes with 18 or more carbon atoms are solids.

The alkenes and alkynes exhibit similar trends in melting and boiling points. This is evident from the fact that at room temperature the smaller members (C2 to C4) are gases, the intermediate members (C5 to C15) are liquids and the larger members (> C16) are solids.

These trends in melting and boiling points can be explained in terms of the intermolecular forces between hydrocarbon molecules. Carbon and hydrogen have similar electronegativities and the arrangement of hydrogen atoms around carbon atoms is fairly symmetrical. As a result, hydrocarbon molecules have very low polarities and are usually considered to be non-polar. The intermolecular forces present in hydrocarbons are therefore weak dispersion forces. These dispersion forces increase in strength with increasing relative molecular mass.

The shapes of molecules also influence the strength of dispersion forces. This can be seen by comparing the boiling points of pentane (36.1°C) and dimethylpropane (9.5°C). As these two compounds have the same molecular formula and molecular mass, the difference in boiling points must be due to the difference in shape of the two molecules (Figure 17.9). The strength of the dispersion forces is greater for pentane than dimethylpropane. This is because there is relatively greater surface contact between pentane molecules, which have a chain-like structure, than dimethylpropane, whose branched-chain structure results in a more spherical shape.

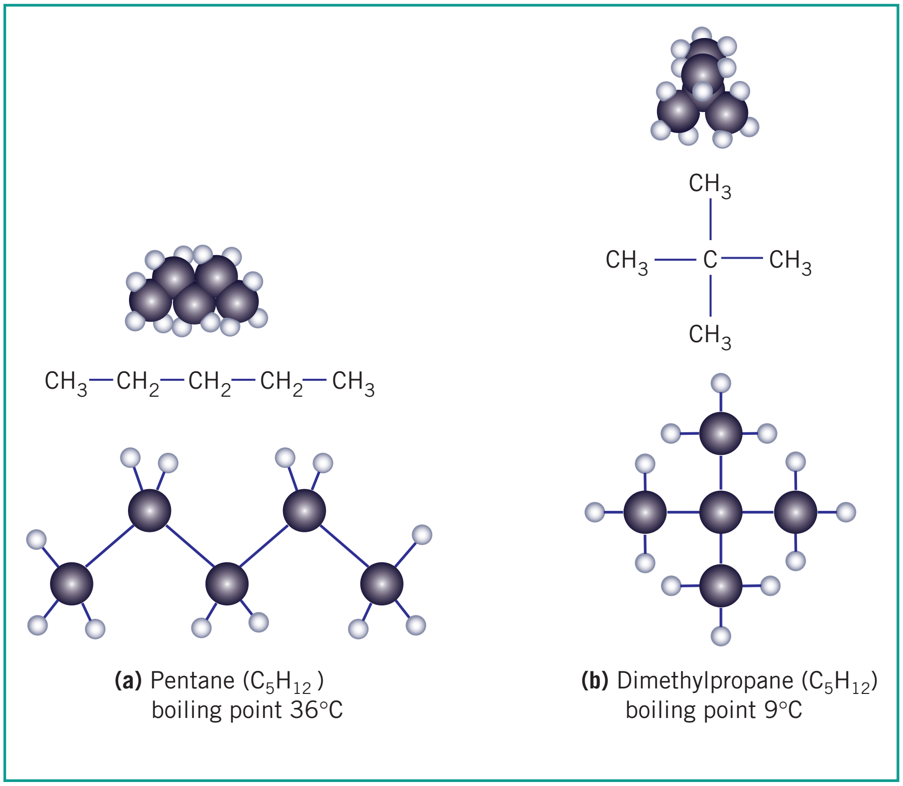


Figure 17.9 Molecular shapes of (a) pentane and (b) dimethylpropane

Density of hydrocarbons

The densities of hydrocarbons increase gradually with increasing relative molecular mass. For example, the density of pentane (C_5H_{12}) is 0.621 g cm^{-3}, decane ($C_{10}H_{22}$) is 0.726 g cm^{-3} and icosane ($C_{20}H_{42}$) is 0.785 g cm^{-3}. Similar trends exist for alkenes and alkynes. All these hydrocarbons have densities less than that of water.

Solubility of hydrocarbons

As described in Chapter 12, solutes tend to dissolve in solvents if the solute–solvent intermolecular forces are similar to those within the solute and those within the solvent. Thus non-polar substances are soluble in non-polar solvents such as carbon tetrachloride but tend to have very limited solubility in polar solvents such as water. In solvents such as carbon tetrachloride the solute–solute, solvent–solvent and solute–solvent intermolecular forces are all dispersion forces and solubility is likely. However, in solvents such as water, the intermolecular hydrogen bonds between water molecules are much stronger than the dispersion forces that would form if a non-polar solute dissolved in it. Hydrocarbons are therefore virtually insoluble in water. This, together with their relative densities, is the reason that crude oil is often found floating on top of water in geological formations and why oil spills can have such catastrophic effects on bird and aquatic life.

The solubility of hydrocarbons in non-polar solvents is the reason that white spirits (a mixture of alkanes) is a commonly used solvent in paints and varnishes, and non-polar solvents are widely used in dry cleaning to remove grease and oil stains.

Review exercise 17.4

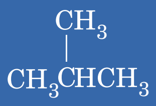
1 **Describe** the intermolecular forces that exist between the molecules in liquid and solid alkanes.

2 **Explain** the trend in the boiling points of the following molecules:

$$CH_4\ -162°C,\ \ CH_3CH_3\ -89°C,\ \ CH_3CH_2CH_3\ -42°C,\ \ CH_3CH_2CH_2CH_3\ 0°C.$$

3 **Identify** which of the following hydrocarbons would be expected to have the higher boiling point. **Justify** your decision.

$CH_3CH_2CH_2CH_3$



$CH_3\overset{\overset{CH_3}{|}}{C}HCH_3$

4 **Explain** in terms of intermolecular forces why greasy engine parts are better cleaned using kerosene or petrol as the solvent rather than water.

17.5 Evaporation, vapour pressure and boiling

Evaporation

If petrol in an open container is left exposed to the atmosphere it eventually evaporates. The petrol that was present as a liquid has changed to the vapour or gaseous state. The process of evaporation is a change from the liquid to the gaseous state that occurs at a temperature below the boiling point of the liquid.

The process of evaporation can be understood in terms of the kinetic theory. From the kinetic theory we know that the molecules in gas and liquid samples have a wide range of velocities and kinetic energies ($KE = \frac{1}{2}mv^2$, where m is mass and v is the velocity of any molecule). This is illustrated in Figure 17.10. Some molecules are moving rapidly and have high kinetic energies, whereas others are moving more slowly and have lower kinetic energies. If the temperature is increased, the average velocity and kinetic energy of the molecules will also be increased. There will still be a range of molecular velocities and kinetic energies but the average values will be greater. Also, a larger proportion of molecules will have very high kinetic energies.

Within any liquid sample at any particular instant, a small fraction of molecules will have a kinetic energy considerably greater than the average value. Some molecules near the surface

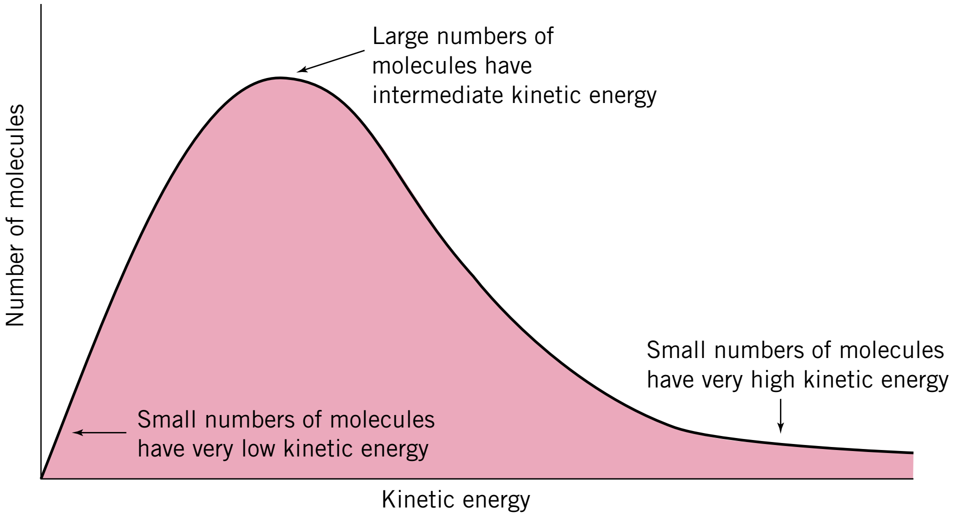


Figure 17.10 Distribution of molecular kinetic energies at a particular temperature

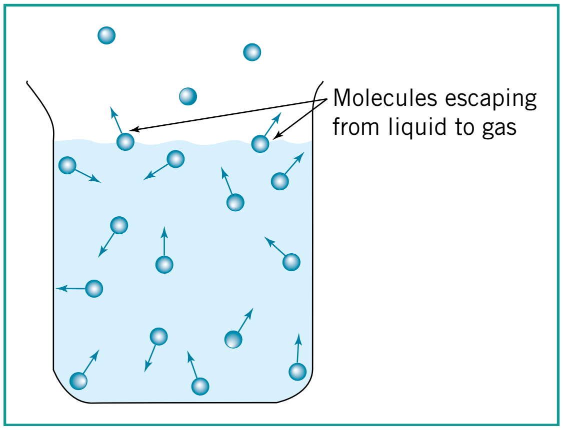


Figure 17.11 Evaporation is the change from liquid to gas at a temperature below the boiling point.

of the liquid may be able to escape from the attractive forces of their neighbouring molecules and pass into the gaseous state. Only molecules with a sufficiently high kinetic energy will be moving fast enough to escape from the liquid.

Because the more energetic molecules are the ones that tend to escape, this will lower the average kinetic energy of the molecules remaining in the liquid. This is the reason that the temperature of a liquid falls as evaporation takes place. The cooling that occurs as a liquid evaporates is used in a variety of ways. Volatile liquids, those that evaporate readily and have low boiling points, are sometimes used in the treatment of sporting injuries. When a liquid such as 2-methylbutane is sprayed onto the affected part it evaporates quite rapidly, cooling as it does so. Heat flows from the surrounding flesh, causing its temperature to fall, thereby reducing the internal bleeding associated with bruising and torn muscles. Perspiration works on the same principle. When overheating occurs, the body starts to perspire. Evaporation of the perspiration results in a loss of heat from the body. This is one way in which body temperature is kept under control.

Volatility

Volatility can be defined as the tendency of the molecules of a substance to escape from the liquid state and enter the gaseous state. Volatile substances are those that evaporate readily and have low boiling points. These substances have weak intermolecular forces. As a result, molecules in the liquid can readily overcome the attractive intermolecular forces of neighbouring molecules and escape into the gaseous state.

If petrol is placed in a closed vessel, evaporation will occur. The more energetic molecules will escape from the surface of the liquid into the gaseous state. As the process continues, the number of gaseous petrol molecules increases. Because the molecules cannot escape, they will collide with other petrol molecules, air molecules and the sides of the container. Also, some molecules will collide with the surface of the liquid in the container and return to the liquid state. Eventually the rate at which molecules are escaping from the liquid will be equal to the rate at which they are returning to it. This is an example of dynamic equilibrium, in which there is no net change but the two processes are continuing to occur. The rates of the two processes, evaporation and condensation, are equal.

CHEMISTRY CONTEXT

❇ VAPOUR PRESSURE, A MEASURE OF VOLATILITY

A liquid stored in a sealed container will eventually reach an equilibrium with its vapour. These gaseous molecules exert a pressure due to their collisions with the walls of the container. This pressure is called the *vapour pressure* of the liquid.

Different liquids exert different vapour pressures, which depend on the relative strengths of the intermolecular forces present in the liquids. Vapour pressure is a measure of the volatility of a liquid. The values in Table 17.7 compare the vapour pressures of some familiar liquids. Water, with strong intermolecular hydrogen bonds, has a lower vapour pressure than molecules with weaker dispersion and dipole–dipole intermolecular forces.

Some solids also have significant vapour pressures. For example, naphthalene, which is used in mothballs, and paradichlorobenzene, which is used as a toilet deodorant, have quite high vapour pressures. As a result they have strong odours and disappear gradually over time.

As temperature increases, the vapour pressure of a liquid also increases. This occurs because at a higher temperature a greater proportion of the molecules have sufficient energy to escape from the liquid. This can be explained in terms of the distribution of molecular kinetic energies, shown in Figure 17.13. At the higher temperature more molecules have the energy needed to escape from the liquid.

Table 17.7 Vapour pressures of some familiar liquids at 20°C

Substance	Vapour pressure (kPa)
Ether	58.9
Pentane	56.6
Chloroform	19.3
Ethanol	5.85
Water	2.34
Mercury	0.000160

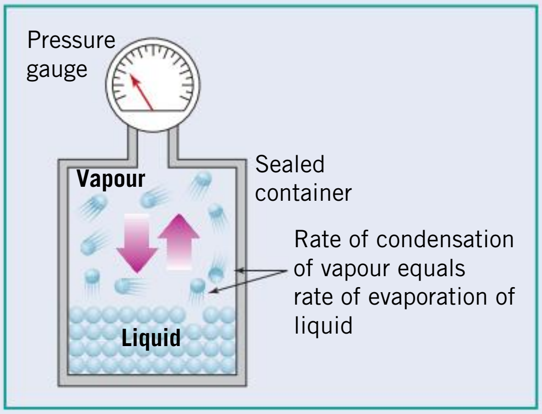


Figure 17.12 The vapour pressure of a liquid is the result of its vapour exerting a pressure on the walls of its sealed container.

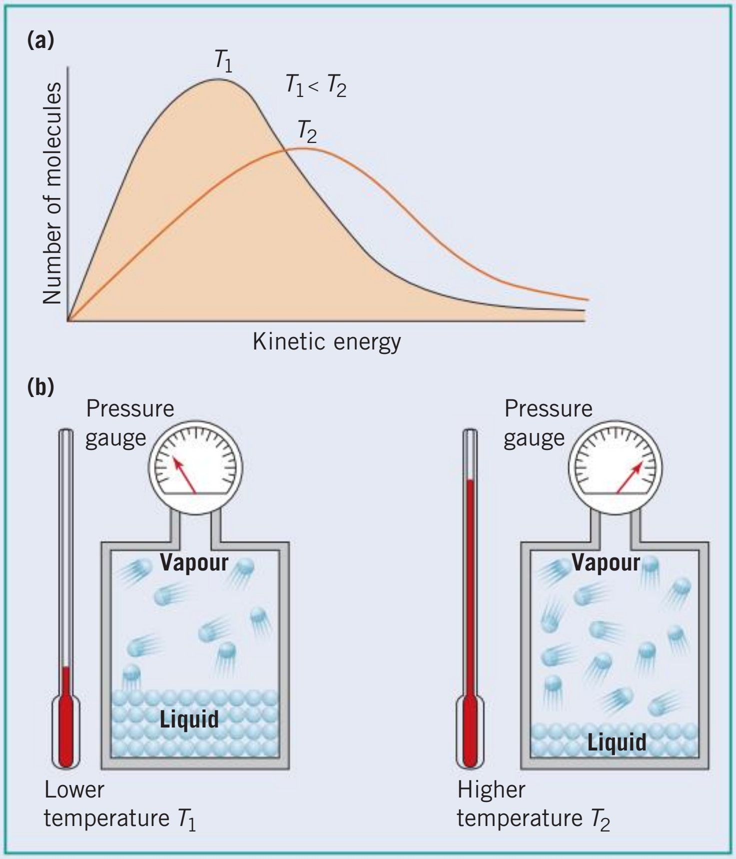


Figure 17.13 (a) Distribution of molecular kinetic energies at different temperatures (b) The vapour pressure of a liquid increases with temperature.

CHEMISTRY CONTEXT, cont.

Figure 17.14 shows the variation in vapour pressure of several liquids as a function of temperature. Other liquids show similar increases in vapour pressure as the temperature is increased.

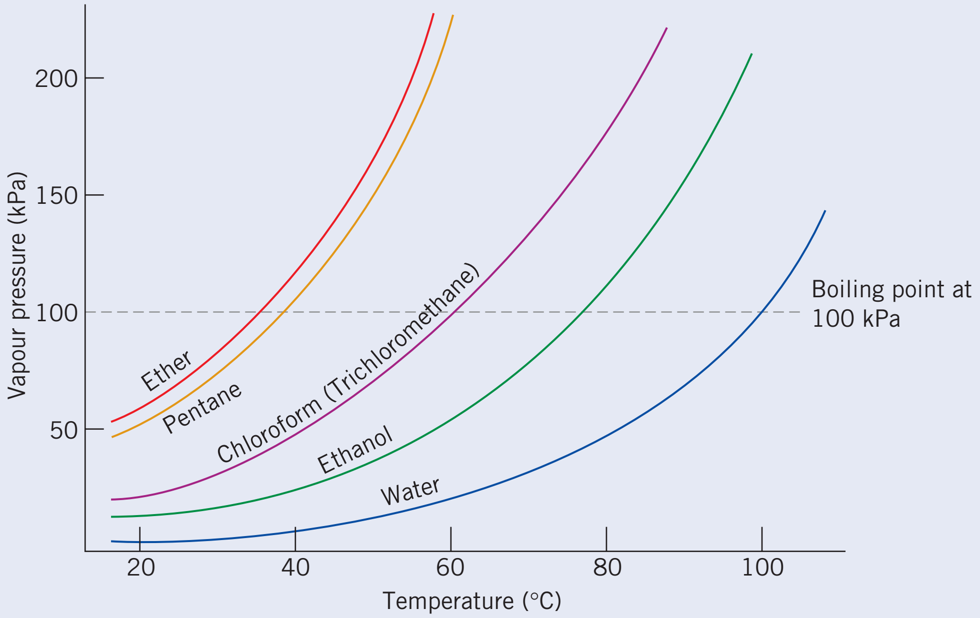


Figure 17.14 Vapour pressure of several liquids as a function of temperature

Boiling

When water is heated to 100ºC, at normal atmospheric pressure, it starts to boil. At this temperature, the vapour pressure of the water equals the atmospheric pressure of the surroundings. When this occurs, vapour forms throughout the liquid, not just at the surface. This vapour produced in the 'body' of the liquid forms the familiar bubbles that are observed during boiling. The vapour pressure within the bubbles is large enough to stop them from collapsing and they rise to the surface of the liquid. The process of bubble formation is illustrated in Figure 17.15. At the boiling point of a substance, continuous vaporisation takes place throughout the liquid. This only occurs when the vapour pressure reaches atmospheric pressure.

It is possible to predict the boiling points of each of the liquids in Figure 17.14 by identifying the temperatures at which the vapour pressures equal atmospheric pressure. Ether, for example, has a boiling point of about 35ºC and ethanol about 78ºC.

As boiling occurs, when the vapour pressure of a liquid reaches atmospheric pressure, it follows that any variation in atmospheric pressure will result in a change in boiling point. The lower the atmospheric pressure, the lower the boiling point will be. Under reduced pressure conditions, the liquid will not have to be heated to such a high temperature for its vapour pressure to reach atmospheric pressure. For example, on the peak of Mt Everest, where atmospheric pressure is about 35 kPa, water boils at about 70ºC.

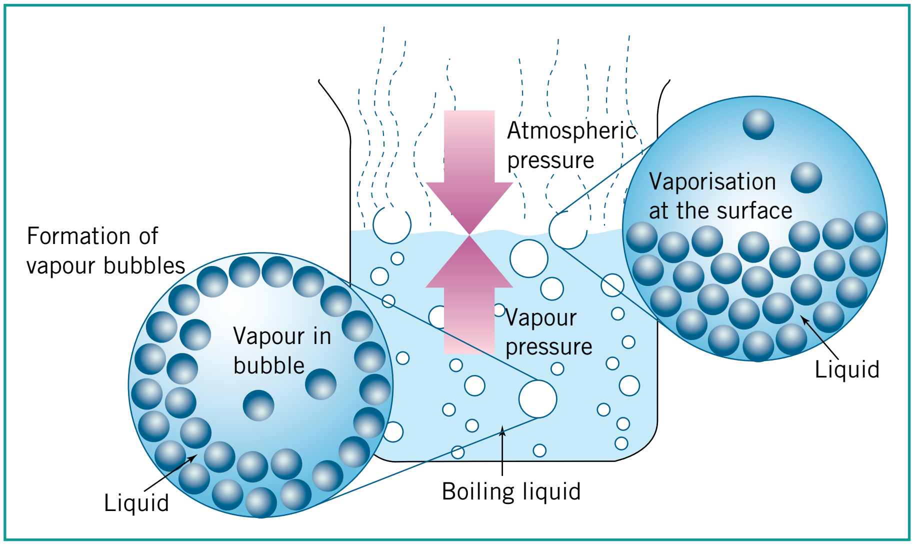


Figure 17.15 When the vapour pressure of a liquid equals the atmospheric pressure, boiling occurs.

❊ Review exercise 17.5

1 **Outline** the effect of increasing the temperature of a liquid or gas sample on the following:
  - **a** the average molecular velocity of the molecules
  - **b** the average kinetic energy of the gas molecules.

2 **Distinguish** between evaporation and boiling in terms of the following:
  - **a** temperature at which it occurs
  - **b** where it occurs in a liquid.

3 Use the kinetic theory to **explain** why wet clothes dry faster on a hot day than on a cold day.

4 At 20°C the vapour pressure of water is 2.34 kPa and that of pentane ($CH_3CH_2CH_2CH_2CH_3$) is 56.6 kPa.
  - **a** **Identify** which liquid would have the higher boiling point.
  - **b** **Compare** the nature and likely strengths of the intermolecular forces of water and pentane.

5 Use Figure 17.14 to **predict** the boiling point of chloroform.

6 **Explain** how it is possible to use a pressure cooker containing liquid water to obtain temperatures well over 100°C. **Assess** the effect this has on the time needed for cooking.

17.6 The safe handling of hydrocarbons

In September 1998, a huge explosion at the Esso gas plant in Longford, Victoria, killed two people, seriously injured eight others and left over a million people without gas for cooking, heating or hot water for several weeks. A young motorist was incinerated at a Sydney petrol station when the cigarette she was smoking caused an explosion. A boat on Sydney Harbour exploded when a spark from the electric starter motor ignited petrol fumes that had accumulated in the cabin. Such incidents highlight the importance of safe handling, storage and transport of hydrocarbon fuels.

Figure 17.16 Explosion at the Longford gas plant in Victoria, 1998

Figure 17.17 Petrol tanker in flames

Volatility, ignition temperature and flash point

The reaction between a fuel and oxygen in the air is called *combustion*. The combustion of a fuel requires a suitable fuel/air mixture and sufficient heat to initiate the reaction. For the fuel/air mixture to burn, the fuel must be in the gaseous state, that is, a vapour. Even the combustion of wood is the burning of flammable wood gases rather than the solid wood itself. Therefore a liquid's volatility will determine the ease of combustion. The smaller hydrocarbons, C1–C4, are gases at normal temperatures and pressures and are clearly highly volatile. Many liquid hydrocarbons, particularly those with five to twelve carbon atoms, readily evaporate to form vapours and are also quite volatile. As discussed in the previous section, the evaporation, vapour pressure and boiling point of a fuel are interrelated and depend on the strength of the intermolecular forces that exist between the molecules of the fuel.

The most commonly used fuels will only burn at room temperature if a mixture of their vapours and air is ignited with a flame, hot filament or a spark. For example, petrol left in an open container at room temperature will not burst into flames unless it is 'set alight'. However, if the temperature is increased to 390ºC, the petrol will spontaneously ignite without a flame being present. The minimum temperature at which a fuel/air mixture spontaneously ignites is called the *ignition temperature* of the fuel.

Table 17.8 Ignition temperatures and flash points of C1 to C8 alkanes and other selected fuels

Fuel	Ignition temperature (ºC)	Flash point (ºC)
Methane	630	–188
Ethane	515	–135
Propane	450	–104
Butane	370	–74
Pentane	260	–49
Hexane	225	–23
Heptane	225	–3
Octane	220	14
Methanol	455	12
Ethanol	363	13
Petrol	390	–43
Kerosene	380	48
Diesel	260	51–124
Hydrogen	500–570	–253

The lowest temperature at which a volatile fuel produces enough vapour to form an explosive mixture when it comes in contact with a flame is called the *flash point* of the fuel. Fuels with a flash point much higher than room temperature, such as diesel and heating oil, are relatively safe to handle because even if they are exposed to a naked flame, spark or hot filament they will not explode. However, a fuel with a flash point below room temperature is potentially very dangerous because a spark or flame can result in a fire or explosion. Natural gas, LPG, petrol and ethanol all have flash points below room temperature. At petrol stations, signs warning motorists to extinguish cigarettes and to switch off the car ignition and mobile phones are recognition of the dangers associated with the low flash point of petrol (–43°C).

Safety precautions

The main danger associated with the use and storage of hydrocarbon fuels is that they are highly flammable. Consequently there is always a risk of explosion. Explosive reactions, which occur as a result of rapid combustion, produce large quantities of heat energy, causing nearby gases to expand rapidly. Explosions are most likely to occur with fuels that vaporise readily, producing a fuel vapour:air ratio favourable for explosive combustion, and that are easily ignited. Therefore the most important indicators of the potential dangers of a fuel are its flash point and volatility. All the C_1 to C_8 hydrocarbons are highly flammable and must be used, stored and transported in such a way that vapours cannot build up to form an explosive fuel vapour/air mixture.

Although natural gas is often piped from gas fields to industry and metropolitan users, and ethyne (acetylene) is usually stored and transported under pressure in gas cylinders, most hydrocarbon fuels are stored and transported as liquids. This is an economical method of transportation because the hydrocarbons occupy much smaller volumes in the liquid than the gaseous state. For example, liquefied natural gas (LNG), methane, is transported overseas from the North-West Shelf in massive ocean tankers. Liquefied petroleum gas (LPG), mainly propane and butane, is also stored and transported under pressure in strong steel cylinders to keep it liquefied at normal temperatures. Pentane, hexane, heptane and octane are volatile, flammable liquid hydrocarbons. They must be stored and transported in sturdy metal or high-density plastic containers that have a narrow neck to reduce evaporation, and tight-fitting lids.

Figure 17.18 LPG, a mixture of propane and butane, must be stored in cool, well-ventilated areas away from naked flames and sparks.

All these fuels have very low flash points and must be stored in cool, well-ventilated areas and kept away from naked flames and sparks, which would ignite them. The valves, regulators and the cylinders themselves must be checked and tested regularly. A foul-smelling compound is added to natural gas so that leaks can be detected before explosive mixtures are produced.

Solid fuels such as coal, coke and wood have low volatilities and are generally less easily combustible. However, coal dust/air mixtures can have low flash points due to the large surface area of the dust.

Some of the safety measures employed in the storage and transportation of hydrocarbons include:

- transportation of gases in strongly constructed pipelines or pressurisation to condense them into liquid form
- sturdy construction and chaining of gas cylinders
- prohibition of flames or sparks of any sort near petrol stations or fuel storage areas
- fitting of road and rail tankers with earthing systems to prevent the build-up of static electricity
- storage of minimal quantities of fuels
- regular checking of tanks and pipelines for leaks
- addition of odorous components in natural gas so that leaks are evident.

❇ Review exercise 17.6

1 **Distinguish** between the flash point and the ignition temperature of a fuel.

2 A fuel has a flash point of –9°C. **Evaluate** whether there is a danger of an explosion with this fuel. **Justify** your answer.

3 **Identify** some of the safety precautions that should be observed when storing and using:

a LPG

b petrol.

*KEY POINTS

- Hydrocarbons contain the elements hydrogen and carbon only.
- Aliphatic hydrocarbons are straight or branched chain hydrocarbons.
- A saturated hydrocarbon contains only single carbon–carbon bonds, while an unsaturated hydrocarbon contains at least one double or triple carbon–carbon bond.
- The properties of the aliphatic hydrocarbons are summarised in Table 17.9.

Table 17.9 A summary of the characteristics of aliphatic hydrocarbons

	Alkanes	Alkenes	Alkynes
General formula	C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}
Family name	ane	ene	yne
Stem name	Depends on the length of the carbon chain		
Melting point Boiling point Density	All relatively low but increase with increasing molecular mass		
Solubility in water	All virtually insoluble		
Simplest member	CH_4	CH_2CH_2	CHCH
IUPAC name of simplest member	methane	ethene	ethyne

- Isomers are different compounds that have the same molecular formula.
- Hydrocarbons are very important as fuels, as shown by the use of natural gas, petroleum and coal.
- Crude oil can be refined by fractional distillation to produce a variety of products including refinery gas, gasoline (petrol), kerosene, diesel and gas oil, lubricating oils, paraffin waxes and bitumen.
- Hydrocarbons have extensive uses as fuels, solvents and aerosol propellants, and as the starting materials in the synthesis of a vast range of substances including plastics, synthetic fibres, detergents, dyes, pharmaceuticals and insecticides.
- Hydrocarbons are essentially non-polar because of the similar electronegativities of carbon and hydrogen and the fairly symmetrical arrangement of hydrogen atoms around carbon atoms.
- In hydrocarbons, dispersion forces are the only intermolecular forces. The forces are weak but increase with increasing molecular mass.
- The physical properties of hydrocarbons include high volatility, low melting and boiling points, high solubility in non-polar solvents and low solubility in water. These are due to the relatively weak dispersion forces between hydrocarbon molecules.

- Evaporation is the change from liquid to gas at a temperature below the boiling point. Evaporation occurs at the surface of a liquid.
- Vapour pressure is the pressure exerted by a vapour in equilibrium with the liquid from which it was derived.
- The vapour pressure of liquids is inversely related to the strength of the intermolecular forces.
- The vapour pressure of a liquid increases with temperature.
- Boiling is the change from liquid to gas at the boiling point. Boiling occurs throughout the liquid.
- The boiling point is the temperature at which the vapour pressure of a liquid equals atmospheric pressure.
- The ignition temperature of a fuel is the temperature at which the fuel/air mixture spontaneously ignites.
- The flash point of a fuel is the lowest temperature at which the fuel produces enough vapour to form an explosive mixture when it comes in contact with a flame.
- The flash point and volatility of a fuel are determinants of its flammability.
- Special safety precautions must be adopted when using, storing and transporting flammable fuels.

* APPLICATION AND INVESTIGATION

1 **Recall** the major sources of organic compounds used as fuels.

2 **Classify** the following straight chain hydrocarbons as alkanes, alkenes or alkynes.

$C_{12}H_{26}$, C_9H_{16}, C_7H_{14}, $C_{32}H_{62}$, $C_{12}H_{22}$,
C_5H_{10}, C_8H_{18}, C_6H_{12}, $C_{20}H_{42}$, $C_{15}H_{28}$

3 **Identify** the following compounds by their systematic (IUPAC) names.

a $CH_3CH_2CH{=}CH_2$
b $CH_3CH{=}CHCH_2CH_3$
c $CH_3CH_2CH_2CH_2CH_2CH_3$
d $CH_3CH_2CH_2CH{=}CHCH_2CH_3$

4 **Assess** the benefits of using the condensed structural formula $CH_3CHCHCH_3$ in preference to a molecular formula such as C_4H_8.

5 Draw structural formulas for the following:

a heptane
b 2-pentene
c 1-butyne
d propene.

6 Write the molecular formula, condensed structural formula and structural formula, showing all bonds, for the following:

- **a** the fifth member of the alkanes
- **b** the third member (four carbon atoms) of the alkenes.

7 Write the structural formulas and names for the position structural isomers for all straight chain alkynes containing seven carbon atoms.

8 **Compare** the bonding present in C_2H_6, C_2H_4 and C_2H_2.

➲ **Investigation**

9 The term 'polyunsaturated' is often used to advertise foodstuffs. **Clarify** what is meant by this term.

10 a **Identify** the physical property used to separate the various fractions in crude oil.

- **b** In the refining of petroleum, **explain** why the lower molecular mass hydrocarbons rise to the top of the fractionating column.

➲ **Investigation**

11 a Apart from oil refineries, **identify** where else fractional distillation is used in industry.

- **b** For one of the industries named in part **a**, **describe** the separation process, including the names of the various components separated.

12 **Account** for the extensive use of hydrocarbons as fuels.

13 a Using the data in Table 17.6, plot a graph of melting point against the number of carbon atoms for the first 10 members of the alkanes.

- **b** On the same graph, plot the boiling points as a function of the number of carbon atoms.
- **c** **Account** for the shape of each graph.

14 **Explain** in terms of intermolecular forces why petrol would be a more effective solvent than water in removing oil or grease from clothing.

15 **Explain** why a sealed can partly filled with petrol may begin to bulge in hot weather.

16 **Explain** how the volatility and boiling point of a liquid are related to the strength of the intermolecular forces in liquid.

17 Consider the vapour pressures at 20°C of the following compounds: pentane 55.6 kPa, acetone 24.7 kPa, ethanol 5.87 kPa, and ethanoic acid 1.60 kPa.

- **a** Rank the compounds in order of increasing volatility (ease of evaporation).
- **b** Rank the compounds in order of increasing boiling point.
- **c** **Discuss** the strength of the intermolecular forces present in the four liquids.
- **d** The following table shows the variation in vapour pressure with increasing temperature for carbon tetrachloride. Plot this data, then **predict** the boiling point of carbon tetrachloride at standard pressure (100 kPa).

Temperature (°C)	20	30	40	50	60	70	80	90
Vapour pressure (kPa)	12.1	19.0	28.6	42.2	60.0	82.7	112.1	149.2

18 The flash points for pentane, octane and decane are –49°C, 14°C and 46°C respectively.

a **Assess** the relative risk of explosive combustion associated with the storage or transportation of each of these fuels.

b **Compare** the relative vapour pressures and boiling points of these three liquids.

c **Predict** the relative strengths of the intermolecular forces in pentane, octane and decane.

CHAPTER 18

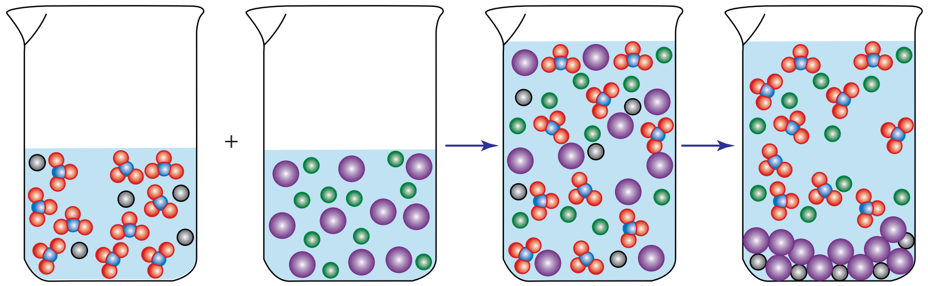
COMBUSTION OF HYDROCARBONS

18.1 Combustion reactions

Chemical changes are those in which new substances with different compositions and properties are formed. The combustion of petrol in car engines and methane in gas ovens and stoves are examples of chemical changes. In both cases the new substances carbon dioxide and water are produced. Evidence that a chemical reaction has taken place includes the following:

- a permanent change in colour
- a change in odour
- production of gas bubbles
- the formation of a precipitate
- release or absorption of energy.

There are many types of reactions and different ways to classify them. Some of the important classes of chemical reactions include decomposition reactions, precipitation reactions, acid–base reactions and oxidation–reduction reactions.
In this chapter we will investigate an important group of oxidation–reduction reactions called *combustion reactions*.
Combustion reactions involve the burning of a substance, usually in air, to produce heat and light energy. The oxidising agent, usually oxygen, reacts with another reactant, resulting in the release of chemical energy in the form of heat. Combustion reactions are exothermic.



Aqueous lead(II) nitrate

Aqueous potassium iodide

A solution of lead(II) nitrate and potassium iodide immediately after mixing but before precipitation

As soon as the solutions are mixed, solid lead(II) iodide precipitates, leaving potassium cations and nitrate anions in the solution.

Figure 18.1 The chemical reaction between lead(II) nitrate and potassium iodide

The burning of magnesium ribbon or butane from a cigarette lighter are examples of combustion.

magnesium + oxygen → magnesium oxide + energy

butane + oxygen → carbon dioxide + water + energy

Figure 18.2 Combustion of butane from a lighter

Combustion of hydrocarbons

Complete combustion

When ignited with a plentiful supply of oxygen, hydrocarbons undergo complete combustion to produce water, carbon dioxide and a large quantity of heat. This makes hydrocarbons very useful as fuels.

The general equation for the reaction of an alkane with oxygen can be represented as:

$$C_nH_{2n+2} + \frac{3n+1}{2}O_2 \rightarrow nCO_2 + (n+1)H_2O + \text{heat}$$

The following equations represent the complete combustion of methane (natural gas) and butane.

$$\begin{array}{ccccccccccc}
\text{methane} & + & \text{oxygen} & \rightarrow & \text{carbon dioxide} & + & \text{water} & + & \text{energy} \\
CH_4(g) & + & 2O_2(g) & \rightarrow & CO_2(g) & + & 2H_2O(g) & + & \text{energy} \\
\text{butane} & + & \text{oxygen} & \rightarrow & \text{carbon dioxide} & + & \text{water} & + & \text{energy} \\
C_4H_{10}(g) & + & \frac{13}{2}O_2(g) & \rightarrow & 4CO_2(g) & + & 5H_2O(g) & + & \text{energy}
\end{array}$$

Incomplete combustion

The equation for the combustion of butane indicates that for every one mole of butane, 6.5 moles of oxygen are required to ensure that all the hydrocarbon is converted into carbon dioxide and water. If excess oxygen is present, complete combustion occurs. If there is insufficient oxygen to ensure complete combustion, incomplete combustion occurs. During incomplete combustion, the products carbon monoxide (CO) and carbon (soot) may be produced as well as water.

Consider the combustion of one mole of methane (natural gas) in decreasing amounts of oxygen.

$$2CH_4(g) + 4O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$$

$$2CH_4(g) + \frac{7}{2}O_2(g) \rightarrow CO_2(g) + CO(g) + 4H_2O(g)$$

$$2CH_4(g) + \frac{5}{2}O_2(g) \rightarrow CO(g) + C(s) + 4H_2O(g)$$

Most school science laboratories use methane as a fuel for Bunsen burners. In a Bunsen burner, methane gas supplied from the gas mains or a cylinder enters at the base of the burner. Air is drawn through an adjustable air hole and the gas mixture burns at the top of the barrel. When the air hole at the base of a Bunsen burner is fully open, complete combustion occurs, carbon dioxide and water are produced, and the flame has a blue, luminous appearance. When the air hole is closed, less oxygen mixes with the methane and incomplete combustion occurs. Consequently the methane burns, producing carbon in the form of soot, and water. In these conditions the flame has a characteristic yellow colour.

Incomplete combustion is not only inefficient, as the full energy content of the fuel is not obtained, but it is also harmful to the environment. Carbon monoxide, carbon and unburnt fuel all contribute to pollution. Carbon monoxide is a colourless, odourless and toxic gas that is produced by the incomplete combustion of organic fuels. It interferes with the functioning of haemoglobin as an oxygen carrier in the blood. Idling motor vehicles produce particularly large quantities of carbon monoxide. Where cars and trucks may be idling for long periods in poorly ventilated spaces such as tunnels and underground car parks, warning signs are often posted advising motorists to switch off their engines if traffic is delayed. A poorly tuned engine or one in which the fuel/air mixture is too rich (that is, too much fuel and not enough oxygen) contributes to incomplete combustion and consequently poor performance and increased pollution.

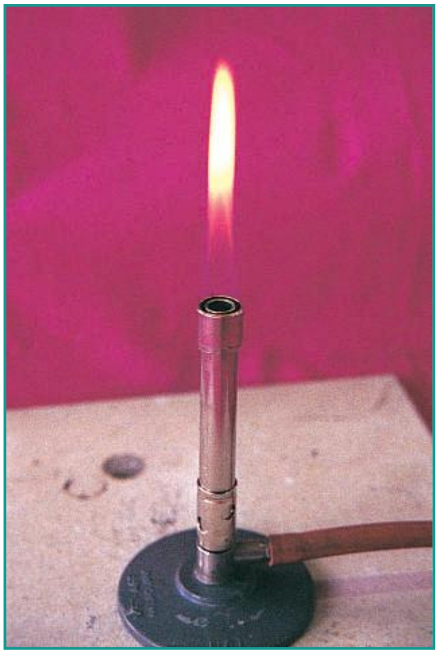


Figure 18.3 Incomplete combustion occurs when the air hole on a Bunsen burner is closed.

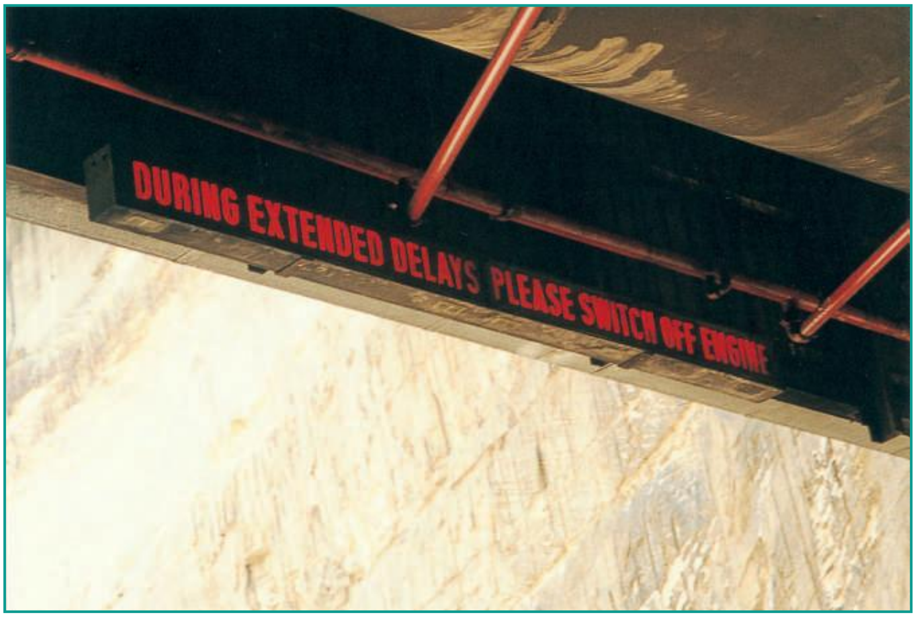


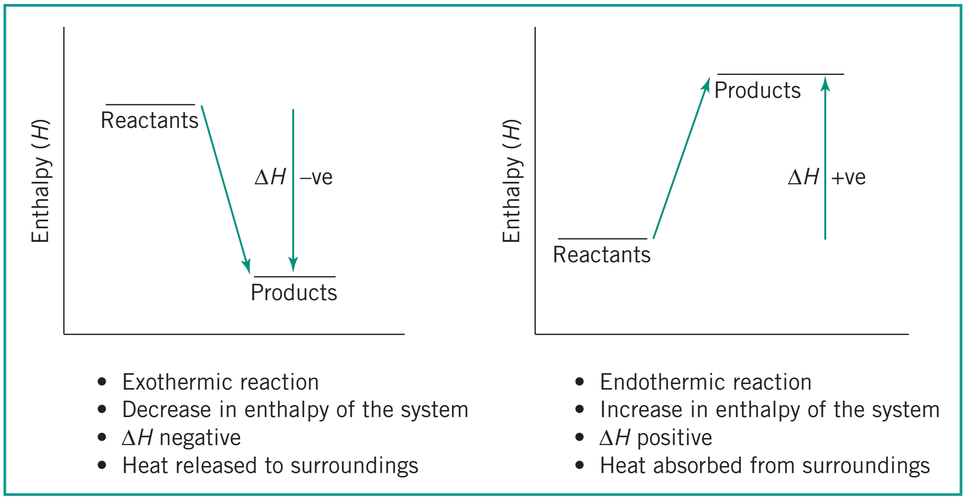
Figure 18.4 Sign warning motorists to switch off car engine when delayed

❇ Review exercise 18.1

1. Some organic compounds burn with an almost invisible flame. **Describe** some observations that could be made that would indicate a chemical reaction was taking place.
2. **Construct** a balanced chemical equation for the complete combustion of pentane.
3. Kerosene lamps often leave a dirty black deposit on the ceiling above the lamp. **Account** for this observation.
4. **Justify** the recommendation that adequate cross-ventilation should be provided (for example, by opening windows) when using gas heaters.

18.2 Energy changes in chemical reactions

In Units 14.2 and 14.3, energy changes in chemical reactions were introduced in terms of enthalpy changes in the reacting system. The enthalpy (*H*) of a substance represents the stored chemical potential energy and depends on the chemical bonding present in the substance. Exothermic reactions are associated with a decrease in the enthalpy of a system, while endothermic reactions are associated with an increase in the enthalpy. Therefore the change in enthalpy (ΔH) for an exothermic reaction is negative and the enthalpy change for an endothermic reaction is positive. This is illustrated in Figure 18.5.



- Exothermic reaction
- Decrease in enthalpy of the system
- ΔH negative
- Heat released to surroundings

- Endothermic reaction
- Increase in enthalpy of the system
- ΔH positive
- Heat absorbed from surroundings

Figure 18.5 Enthalpy changes for exothermic and endothermic reactions

The energy effects associated with chemical reactions can be considered to result from the breaking of some bonds and the formation of others. For example, the breaking of the covalent bond in a HCl molecule is a process that absorbs energy. Conversely, the formation of a H–Cl bond releases energy. From the law of conservation of energy, the quantity of energy released when a H–Cl bond forms is the same as that absorbed when such a bond is broken. The energy absorbed when a chemical bond is broken leads to an increase in the enthalpy of the system. The individual atoms that result represent a higher enthalpy state than when they were combined in the molecule. Alternatively, if the same bond is re-formed, the same amount of energy is released as the system changes back to a lower enthalpy state.

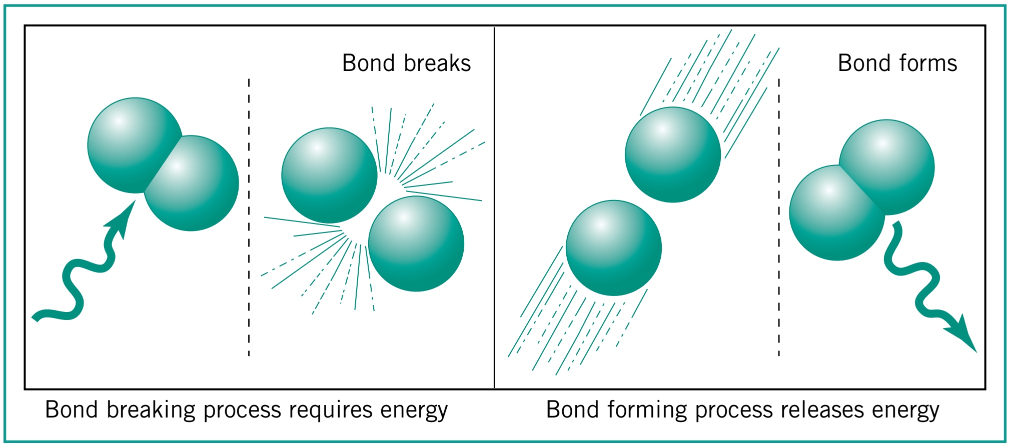


Figure 18.6 The energy required to break a chemical bond equals the energy released when the bond forms.

All chemical reactions involve the breaking and making of chemical bonds. If the energy required to break bonds in the reactants is greater than the energy released when new bonds are formed to make products, then the reaction will be endothermic. If, on the other hand, the energy absorbed to break bonds is less than the energy released when bonds formed, the reaction will be exothermic.

Consider the reaction between hydrogen and oxygen.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) + \text{energy}$$

This reaction can be considered to involve the breaking of two H–H bonds and one O=O bond and the formation of four O–H bonds. The overall reaction involves the release of heat energy, so the energy released from forming the four O–H bonds must be greater than that needed to break the H–H and O=O bonds. The product molecules therefore have a lower enthalpy than the reactants.

Heat of combustion of fuels

The combustion reactions of hydrocarbons are strongly exothermic, indicating that the enthalpy of the products, usually carbon dioxide and water, is much less than that of the reactants. In the combustion of methane, for example,

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) + 890\text{ kJ}$$

there is a decrease in enthalpy of the system of 890 kJ for every mole of methane that burns. For every methane molecule that burns, four C–H and two O=O bonds are broken, and two C=O and four O–H bonds are formed. The large decrease in enthalpy indicates that much less energy is needed to break the bonds in the reactants than is released when the product molecules are formed.

The *molar heat of combustion* ($-\Delta H_c^\theta$) of a substance is the heat released when one mole of a substance undergoes complete combustion with oxygen at a constant pressure of one atmosphere (or 100 kPa). For hydrocarbons, it is the heat released when one mole of the hydrocarbon is burned in oxygen to produce carbon dioxide and water. For example, the heat of combustion of butane, $-\Delta H_c^\theta$, is 2877 kJ mol^{-1}. Since the heat of combustion is defined in terms of the heat released it has by definition a positive value. This can be a source of confusion because the change in enthalpy (ΔH) has a negative value. Note that the heat of combustion has the symbol $-\Delta H_c^\theta$. The minus sign at the front of the symbol ensures that the value is always positive, as all combustion reactions release energy and are therefore exothermic. Thus, in the combustion of one mole of butane, 2877 kJ of energy is released.

The heats of combustion for some common fuels are given in Table 18.1.

Table 18.1 Heats of combustion of some common fuels

Substance	Heat of combustion $-\Delta H_c^\theta$ (kJ mol^{-1})	Substance	Heat of combustion $-\Delta H_c^\theta$ (kJ mol^{-1})
Hydrogen	285.8	Butane	2877
Carbon	393.5	Octane	5470
Methane	890	Ethene	1411
Ethane	1560	Ethyne	1301
Propane	2220	Ethanol	1367

Activation energy

All reactions, even exothermic reactions, require an initial input of energy to start the reaction. For example, the combustion of methane requires an *ignition temperature* of 630°C, or a flame or spark to initiate the reaction. The minimum energy required by reacting molecules before they will react is known as the *activation energy* (E_A). The activation energy overcomes an energy barrier for the reaction and varies from one reaction to another. If the activation energy for a combustion reaction is relatively low, the ignition temperature will also be low. Combustion reactions with higher activation energies will have higher ignition temperatures. The activation energy of both endothermic and exothermic reactions can be shown on an energy profile diagram. Activation energy and energy profile diagrams are discussed in greater detail in the next chapter.

❄ Review exercise 18.2

1 **Compare** the relative enthalpies of the following:
  a a hydrogen molecule and two separate hydrogen atoms
  b a hydrogen fluoride molecule and separate hydrogen and fluorine atoms.

2 **Identify** the bonds that are broken and those that are formed in the following reactions:
  a $C_2H_2 + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$
  b $NH_4NO_2(s) \rightarrow N_2(g) + 2H_2O(g)$

3 The reaction between hydrogen gas and chlorine gas to form hydrogen chloride is exothermic. **Compare** the relative energy needed to decompose hydrogen and chlorine molecules with that released when an HCl molecule is formed between hydrogen and chlorine atoms.

4 **Define** the term ‘activation energy’.

18.3 Pollution caused by burning fossil fuels

The burning of fossil fuels, particularly coal, oil and petrol, is responsible for much of the air pollution produced by humans. The products of combustion include particulate matter (ash and soot), unburnt hydrocarbons, carbon dioxide, carbon monoxide, water, sulfur dioxide and nitrogen oxides. The main producers of this pollution are power stations, factories, motor vehicles and domestic heaters.

Carbon dioxide

In previous sections, carbon dioxide was identified as one of the products of complete combustion of hydrocarbon fuels. Increasing demands for energy have resulted in higher levels of consumption of fossil fuels. Also, the clearing of vast areas of forests is contributing to increasing levels of carbon dioxide in the atmosphere as less photosynthesis is occurring. Carbon dioxide is one of the gases known to play a major role in global warming or the greenhouse effect (see Chemistry Context, page 330).

CHEMISTRY CONTEXT

❄ GLOBAL WARMING

The Earth receives energy from incoming sunlight and radiates some of this energy back into space. Some of the energy radiated back into space as infra-red radiation is trapped in the atmosphere, resulting in the Earth being warmer than it would be if it had no atmosphere of its own. Thus the Earth has a natural greenhouse effect, due to the presence of water and carbon dioxide molecules in the atmosphere. These are the molecules in the atmosphere that are most responsible for trapping the infra-red radiation.

Within the Earth's atmosphere, the increasing concentrations of greenhouse gases have the potential to increase the Earth's natural greenhouse effect and produce global warming. Apart from carbon dioxide and water vapour, other gases known to contribute to the greenhouse effect include methane (CH_4) and nitrous oxide (N_2O).

Table 18.2 shows the changes in concentrations of some major greenhouse gases from pre-industrial times to the present, and projected to the year 2050, assuming continued commitment to the use of fossil fuels.

Table 18.2 Concentrations of some major greenhouse gases

Gas	Pre-industrial level	Present level	Predicted (2050) levels
CO_2 (ppm)	275	375	400–600
CH_4 (ppb)*	750	1650	2100–4000
N_2O (ppb)*	285	305	330–450

*ppb means parts per billion.

The evidence is clear that human activities are changing the composition of the atmosphere. Changes to the major atmospheric components, nitrogen and oxygen, are insignificant. However, the relative changes in the concentrations of the minor atmospheric constituents are marked. For example, carbon dioxide levels are projected to increase to about 600 ppm by about 2050.

The effect of these changes in levels of the minor atmospheric components is difficult to predict. Scientists are using computer models called General Circulation Models (GCMs). These consist of extremely complicated mathematical equations used to predict winds, temperatures, pressures, cloud cover and precipitation as the concentration of greenhouse gases increases.

Using these models, scientists are attempting to predict the effect that increasing levels of greenhouse gases may have on the Earth's climate by the middle of the twenty-first century. The models, at this stage of their development, suggest the following:

- temperature increases of 2–4°C
- increased rainfall of about 10%, but unevenly distributed; some regions are likely to be drier, others wetter
- rising sea levels (10–80 cm) as a result of thermal expansion of the oceans
- poleward shift of climatic zones
- increased frequency of extreme weather events such as hurricanes and heatwaves
- threat to some ecosystems due to the rapidity of climatic change.

While there is no doubt that the atmosphere's composition is changing, there is considerable debate over the extent to which climatic change is taking place. It has been suggested that the Earth's temperature has increased by about 0.5°C and sea levels have risen by 10–20 cm over the past century. It will probably be several more years before the likely extent of climate change can be predicted more accurately. In the meantime, attempts are being made to reduce greenhouse gas emissions. These include the development of renewable energy sources, more efficient energy use, the preferred use of natural gas and better land management practices.

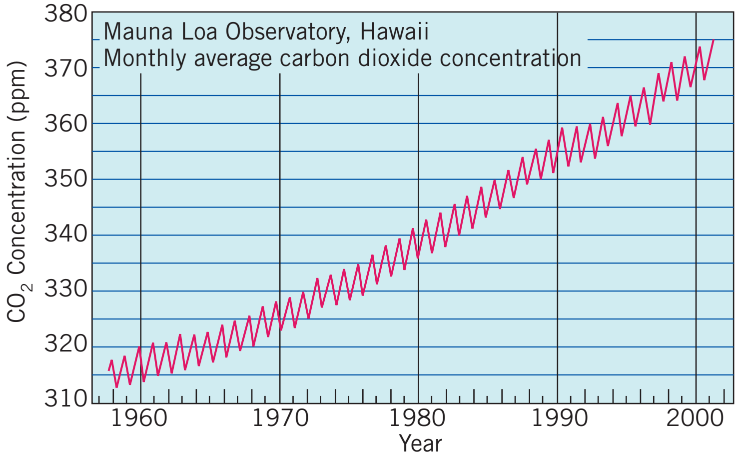


Figure 18.7 **The concentration of carbon dioxide has been rising steadily over the past century.**

Carbon monoxide

The formation of carbon monoxide when fossil fuels are burnt under conditions favouring incomplete combustion was discussed in Unit 18.1. Carbon monoxide interferes with the functioning of haemoglobin as an oxygen carrier in the blood. Carbon monoxide oxidises to carbon dioxide in the environment fairly readily, so the main problem arises in areas of high traffic density such as city centres, tunnels and carparks.

Particulate matter

Fine particles of ash and soot are produced during the combustion of wood, coal and diesel fuel, particularly in conditions that favour incomplete combustion. This particulate matter, which may enter the atmosphere as smoke, can settle on buildings, leaving a dirty, grimy film and is known to cause damage to human lungs and to plants. These particles can be removed from the emissions of power stations using electrostatic separators.

Sulfur dioxide

One of the major gaseous pollutants is sulfur dioxide, which is being released into the atmosphere by humans at the rate of 200 million tonnes per year. Over two-thirds of this sulfur dioxide is produced by the burning of coal and oil, which may contain up to 5% sulfur. During the combustion process, sulfur is converted to sulfur dioxide.

$$S(\text{in fuel}) + O_2(g) \rightarrow SO_2(g)$$

The sulfur dioxide produced is readily oxidised in the air to form sulfur trioxide.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

The sulfur oxides formed can dissolve in atmospheric water to form an acid haze of sulfurous and sulfuric acids. In very severe cases, particularly if high smoke levels are present, a most unpleasant smog can develop. This was the nature of the so-called London smog, which resulted in many deaths in the early 1950s. Another problem with high levels of sulfur oxides in the atmosphere is that they can result in acid rain. The worst examples of acid rain are probably those in Europe and the north-east of North America, where it has caused significant damage to natural ecosystems and stone buildings and structures. The formation of acid rain and the damage it may cause are discussed in detail in Module 2 of *Chemistry Contexts 2*.

Figure 18.8 Damage caused by acid rain

Much research is being undertaken into measures aimed at reducing the emissions of sulfur oxides into the atmosphere. These include:

- use of low-sulfur fuels (fortunately, Australian coal and oil are relatively low in sulfur content compared with other parts of the world)
- reducing the sulfur content of fuels before combustion
- removing sulfur oxides from atmospheric emissions.

Photochemical smog

The formation of photochemical smog occurs mainly in large modern cities such as Los Angeles, Sydney and Melbourne. Such smog occurs as a brown haze and causes reduced visibility, eye and bronchial irritation, damage to plants and animals, and deterioration of materials.

Photochemical smog is most likely to occur on warm, sunny days when the air is very still. It occurs through a complicated series of reactions involving unburned hydrocarbons and nitrogen oxides. Motor vehicles are mainly responsible for the formation of photochemical smog.

Unburned hydrocarbons in petrol are released into the atmosphere as part of motor vehicle emissions. Nitrogen oxides are formed in car engines because the high temperatures cause nitrogen and oxygen to react. The reactions can be represented as:

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

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

It is the brown nitrogen dioxide that gives photochemical smog its characteristic brown colour.

The release of hydrocarbons and initial formation of NO and NO_2 is followed later in the day by increasing levels of ozone and other pollutants. The nitrogen dioxide absorbs ultraviolet radiation from the sun, to form nitric oxide and oxygen atoms. The oxygen atoms combine with molecular oxygen to form ozone.

$$NO_2(g) + \text{ultraviolet radiation} \rightarrow NO(g) + O(g)$$

$$O_2(g) + O(g) \rightarrow O_3(g)$$

Additional reactions between unburned hydrocarbons and ozone or oxygen atoms produce a range of organic compounds. These include aldehydes such as ethanal, CH_3CHO, and peroxyacetyl nitrate or PAN, $CH_3CO–OO–NO_2$.

The increasing occurrence of photochemical smog in Australian cities is quite apparent. This is mainly the result of the high level of car use by people living in these cities. Reducing photochemical smog will depend on improving technology and changing public attitudes towards the use of motor vehicles. Improved engine design and the use of catalytic convertors are reducing the emissions of unburned hydrocarbons and nitrogen oxides. In large cities, however, it will also be necessary to reduce the use of petrol-fuelled motor vehicles as the main method of transport.

Figure 18.9 Photochemical smog over Melbourne

❊ Review exercise 18.3

1 In one or two sentences, **summarise** what is meant by the following terms:
  - **a** global warming
  - **b** acid rain
  - **c** photochemical smog.

2 **Identify** the origin and the effect of the following substances produced in the burning of fossil fuels:
  - **a** carbon monoxide
  - **b** carbon dioxide
  - **c** particulates
  - **d** sulfur oxides
  - **e** nitrogen oxides
  - **f** hydrocarbons.

*KEY POINTS

- Indications that a chemical reaction has taken place include:
  - a change in colour
  - a change in odour
  - production of gas bubbles
  - the formation of a precipitate
  - release or absorption of energy.
- Most of the world's energy demands are met by the combustion of fossil fuels.
- The complete combustion of hydrocarbons produces water and carbon dioxide as products. For example:

  $$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$
- The incomplete combustion of hydrocarbons produces water with carbon monoxide and or carbon (soot) as products. For example:

  $$2CH_4(g) + \frac{5}{2}O_2(g) \rightarrow CO(g) + C(s) + 4H_2O(g)$$
- Incomplete combustion is inefficient and causes pollution.
- The enthalpy of a substance is mainly a function of the bonding in the substance. The formation of a bond is an exothermic process and is associated with a decrease in the enthalpy of a system. The breaking of a bond is an endothermic process and is associated with an increase in the enthalpy of a system.
- In a chemical reaction, if more or stronger chemical bonds are formed, the reaction will be exothermic. If less or weaker chemical bonds are formed, the reaction will be endothermic.
- The molar heat of combustion ($-\Delta H_c^\theta$) of a substance is the enthalpy change when one mole of the substance reacts with oxygen in a combustion reaction. For hydrocarbons, it is the enthalpy change when one mole of the hydrocarbon is burned in oxygen to produce carbon dioxide and water.
- The combustion of fossil fuels produces the following pollutants:
  - carbon dioxide, which contributes to global warming (greenhouse effect)
  - carbon monoxide, which is highly toxic
  - particulates, which make the environment grimy and are harmful to health
  - sulfur oxides, which contribute to smog formation and acid rain
  - nitrogen oxides and unburnt hydrocarbons, which form photochemical smog.

∗ APPLICATION AND INVESTIGATION

1 **Construct** balanced chemical equations for the combustion of hexane under the following conditions:

- **a** a plentiful supply of oxygen
- **b** a limited supply of oxygen.

2 Gather information from secondary sources to **investigate** how carbon monoxide affects the ability of haemoglobin to act as an oxygen carrier within the blood. **Describe** the symptoms of carbon monoxide poisoning. **⊂ Investigation**

3 For the reaction:

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

- **a** **Identify** which bonds are broken.
- **b** **Identify** which bonds are formed.
- **c** Given that $\Delta H = -184$ kJ for this reaction, is more energy involved in bond breaking or bond forming?

4 **Explain** why much more energy is required to decompose liquid water into hydrogen and oxygen gas than is needed to vaporise liquid water.

5 A lighted match held above a beaker of kerosene will not cause it to ignite. However, if the same beaker of kerosene is heated to 80°C and the experiment repeated, the kerosene will catch alight. **Explain** these observations, given that the ignition temperature of kerosene is 380°C and the flash point is 48°C.

6 **Assess** the link between the ignition temperature of a fuel and the activation energy required for its combustion.

7 Gather information from secondary internet sources to **investigate** and obtain the latest available information on one of the following: **⊂ Investigation**

- **a** the current levels of important greenhouse gases in the atmosphere and their major sources
- **b** the state of current Global Circulation Models and their accuracy in predicting current global climate
- **c** recommendations of the Intergovernmental Panel on Global Change (IPCC).

8 **a** **Outline** alternatives to our current dependence on fossil fuels to meet our energy demands. **⊂ Investigation**

- **b** **Discuss** the advantages and disadvantages of these alternatives.

9 **Propose** a set of recommendations for our state environment minister aimed at reducing photochemical smog levels in Sydney. **⊂ Investigation**

CHAPTER 19

RATES OF CHEMICAL REACTIONS

19.1 Chemical reactions occur at different rates

Not all chemical reactions occur at the same rate. Some reactions, such as the rusting of iron, are very slow, taking months or years to reach completion. Other reactions, such as the combustion of petrol, are so rapid that they may result in an explosion.

Figure 19.1 Reactions occur at different rates.

Expressing reaction rates

The two reactions mentioned above are said to have different *reaction rates*. In general, reaction rate can be determined in one of the following ways:

- the rate of disappearance of reactants, for example, how rapidly the iron disappears during rusting
- the rate of appearance of products, for example, how rapidly the rust is formed during rusting.

Consider the reaction of an acid with marble chips.

$$CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(l)$$

During the reaction, several changes take place.

- The mass of $CaCO_3(s)$ decreases.
- The concentration of $H^+(aq)$ decreases.
- The concentration of $Ca^{2+}(aq)$ increases.
- The volume of $CO_2(g)$ produced increases.

The rate of this reaction can be followed by observing the rate of any of these changes. The usual way of establishing reaction rate is to make a series of suitable measurements over known time intervals. For example, the volume of CO_2 produced in a particular time interval could be recorded at various times as the reaction progressed. The rate of reaction at the various times could then be determined using the following formula:

$$\text{reaction rate} = \frac{\text{volume of } CO_2 \text{ produced in time interval}}{\text{time interval}}$$

Alternatively, if measurements of the mass of $CaCO_3$ had been used to determine the rate, the following expression would be used:

$$\text{reaction rate} = \frac{\text{mass of } CaCO_3 \text{ consumed in time interval}}{\text{time interval}}$$

The rate of a reaction, at any particular time, is defined as the change in concentration of a substance in a short interval of time divided by that time interval.

❈ Review exercise 19.1

1 When sulfuric acid is added to zinc, hydrogen gas is produced. **Construct** a balanced chemical equation for the reaction and **describe** two observations that could be used to measure the rate of the reaction.

2 When liquid heptane is burnt completely in air, carbon dioxide and water vapour are produced. **Construct** a balanced chemical equation for the reaction and **describe** two observations that could be used to measure the rate of the reaction.

19.2 Factors affecting the rate of reactions

The nature of the reactants

The type of reactants involved in a chemical reaction can influence the rate of reaction. However, it is not easy to make accurate predictions about the rate of a particular reaction simply from a consideration of the reactants involved. The only sure way to find out about the rate of a reaction is to measure it in an experiment. Nevertheless, some very rough predictions can be made by closely examining the way the reactant species are bonded and what changes they must undergo during reaction.

Consider the oxidation of methane in the following equation:

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

At room temperature, the rate of this reaction is insignificant. If natural gas is allowed to mix with air at room temperature, virtually none of the methane will be converted to $CO_2(g)$ and $H_2O(g)$. Contrast this with the reaction that occurs between solutions of silver nitrate and sodium chloride. When $AgNO_3(aq)$ and NaCl(aq) solutions are mixed, a white precipitate of AgCl(s) forms almost instantaneously.

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

A range of reaction rates lies between very rapid reactions such as this and very slow reactions such as the oxidation of methane at room temperature. For example, the reaction between hydrochloric acid and calcium carbonate described previously has a reaction rate between these extremes.

By examining many different reactions, chemists have produced some guidelines that are sometimes useful in helping to predict reaction rates. These are as follows:

- If a reaction does not involve bonding rearrangements, it is likely to be rapid at room temperature. For example, the reaction between $Ag^+(aq)$ and $Cl^-(aq)$ occurs as a result of simple collisions between these two types of ions. No complex bond-breaking and bond-forming processes are required.
- If a reaction involves the breaking of bonds, it is likely to be slow at room temperature. For example, the reaction between methane and oxygen involves the breaking of bonds in both the $CH_4(g)$ and the $O_2(g)$ molecules. These processes will only take place if the collisions between molecules occur with sufficient energy and have suitable orientation.

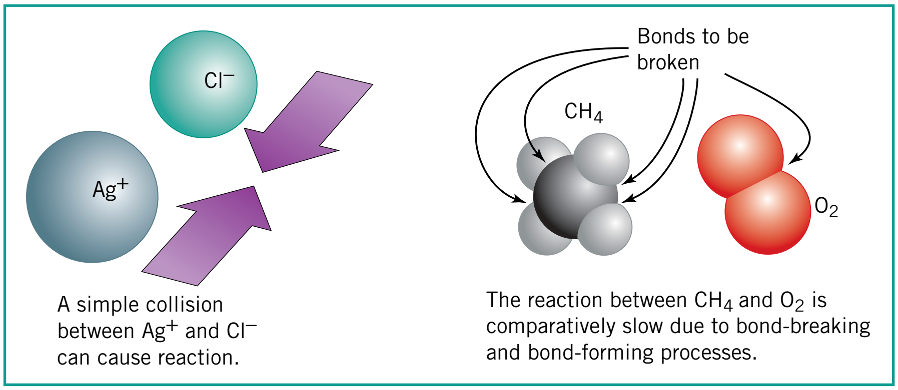


Figure 19.2 Reactions that involve complex bond-breaking and bond-forming processes are likely to be slower than reactions that involve only bond formation.

The concentrations of the reactants

The rate of reaction between $HCl(aq)$ and $CaCO_3(s)$ can be varied by altering the concentration of the hydrochloric acid solution. If a very dilute acid solution such as 0.01 mol L^{-1} HCl is used, the reaction is quite slow. However, with a more concentrated solution such as 2 mol L^{-1} HCl, the reaction rate is much greater. As the concentration of the HCl increases, the reaction rate increases.

A similar effect is observed when a gas is involved in a reaction. This is illustrated by the 'glowing splint' test for oxygen gas. In this test, a splint of wood is ignited in air and then blown out so that it is only glowing. While the splint will not relight in air that contains approximately 20% oxygen, it will relight if exposed to a high concentration of oxygen. This test can therefore be used to identify the presence of high concentrations of oxygen because of the increase in reaction rate that results.

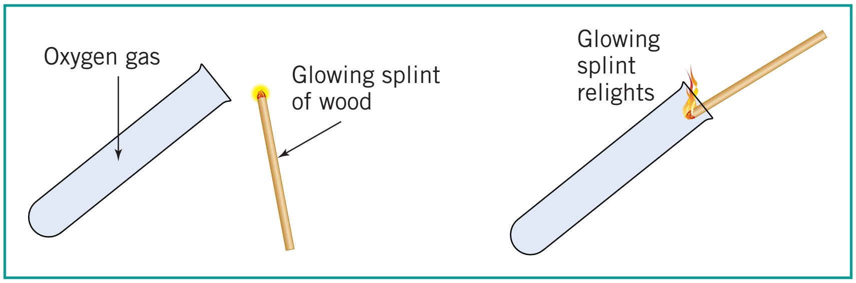


Figure 19.3 A glowing splint relights if placed in a test tube of pure oxygen.

The two reactions discussed previously were heterogeneous systems, as the reactants were in different states. The first reaction involved a solid and a solution, while the second reaction was between a solid and a gas. Increasing the concentration can also increase the reaction rate in homogeneous systems in which the reactants are in the same state. For example, hydrogen gas and gaseous iodine can react to form hydrogen iodide according to the following equation:

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

Increasing the concentration of $H_2(g)$ and/or $I_2(g)$ results in an increased reaction rate.

Similarly, in the reaction between hydrochloric acid and sodium thiosulfate solution,

$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow S(s) + SO_2(aq) + H_2O(l)$$

increasing the concentration of thiosulfate ions increases the reaction rate.

The surface area of the reactants

In heterogeneous systems, the surface area of the solid or liquid can affect the reaction rate. For example, a log of wood cut into smaller pieces burns far more rapidly than if it were in one piece. The effect of cutting the log into pieces is to expose more of the wood to the oxygen that it needs for combustion.

Coal can be quite difficult to burn in air when it is in large pieces. However, fine coal dust particles suspended in air form an explosive mixture. Explosions caused by the ignition of coal dust are one of the main dangers to underground coal miners. Many lives have been lost as a result of explosions caused by an accumulation of coal dust. Similar explosions have occurred in other dusty environments such as grain silos.

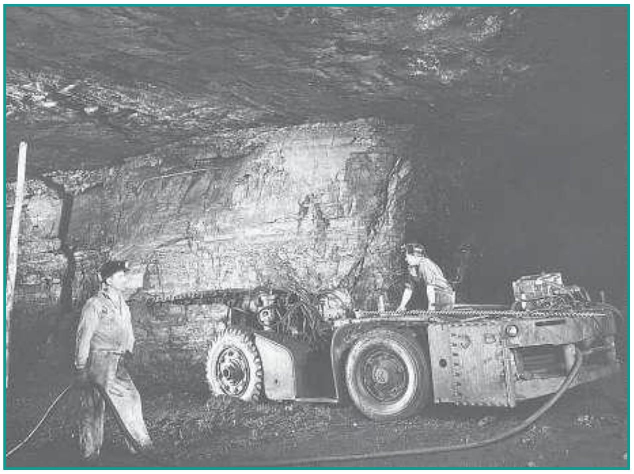


Figure 19.4 Underground coal mining in the 1950s. Coal dust can oxidise explosively in air. Increased surface area increases the rate of a chemical reaction.

Temperature

A mixture of adhesive and hardener in a two-component epoxy glue such as Araldite sets more quickly in hot weather than in cold. If 'extra fast' setting is required, the glue mixture can be heated artificially. Such two-component glues set because of a chemical reaction between the two components. Raising the temperature increases the rate of this chemical reaction. Another example of the effect of temperature on reaction rates is the rate of rusting in the Antarctic. Exposed steel rusts extremely slowly in this region because of the very low temperatures.

Catalysts

A dramatic increase in the rate of certain chemical reactions can be produced by the use of substances known as *catalysts*. A catalyst is a substance, or mixture of substances, that increases the rate of a chemical reaction without being permanently consumed in the reaction. For example, manganese(IV) oxide (MnO_2) acts as a catalyst to increase the rate of decomposition of hydrogen peroxide (H_2O_2). In the absence of a catalyst, H_2O_2 decomposes into oxygen and water at a very slow rate.

$$2H_2O_2(aq) \rightarrow O_2(g) + 2H_2O(l) \text{ (very slow)}$$

The addition of a small amount of MnO_2 causes the H_2O_2 to bubble vigorously due to the rapid production of $O_2(g)$. The mass of MnO_2 is the same before and after the reaction, showing that the catalyst is not consumed.

$$2H_2O_2(aq) \xrightarrow{MnO_2} O_2(g) + 2H_2O(1) \text{ (fast)}$$

Notice that in this equation, the catalyst is written above the arrow to show that although it is not consumed, it plays an essential role in the reaction.

In industry, a wide variety of processes employ catalysts to increase the rates of reactions that would be uneconomically slow without them. For example, the oxidation of sulfur dioxide to sulfur trioxide in the manufacture of sulfuric acid uses a platinum (Pt) or vanadium pentoxide (V_2O_5) catalyst. Many chemical processes that occur in nature, such as photosynthesis and digestion, only proceed at a significant rate because of the action of catalysts. In many of these processes, *enzymes* are involved. Enzymes are biochemical catalysts that are usually highly specific in their function. This means that they act to catalyse one type of chemical reaction but have no influence on other reactions.

Review exercise 19.2

1 Based on bonding rearrangements only, **predict** which of the following reactions are likely to be rapid at room temperature. Support your prediction with an **explanation**.

- **a** $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$
- **b** $C_2H_6(g) + Br_2(g) \rightarrow C_2H_5Br(l) + HBr(g)$
- **c** $C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$
- **d** $Ce^{4+}(aq) + Fe^{2+}(aq) \rightarrow Ce^{3+}(aq) + Fe^{3+}(aq)$

2 **Explain** why the rate of the reaction between $H_2(g)$ and $I_2(g)$ to form HI(g) is found to increase when the volume of the system is decreased.

3 **Account** for the fact that many metal catalysts are used in the form of fine wire mesh.

4 **Explain** the following observations.

- **a** Although wheat is usually slow to burn, wheat silos have been known to explode.
- **b** Food products are often stored in refrigerators.
- **c** Liquid hydrogen, used as a fuel to launch the space shuttle, is reacted with pure liquid oxygen rather than air.

5 In the manufacture of nitric acid, nitric oxide is produced by the oxidation of ammonia according to the following equation:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

Under standard conditions of temperature and pressure, the rate of this reaction is very slow. **Propose** three ways in which the rate of the reaction might be increased.

19.3 Collision theory and activation energy

The chemical equation for a reaction indicates the nature of the reactants and products but provides no information about the way in which the reactants are converted to products. For example, the decomposition of hydrogen iodide is represented by the equation:

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

This equation indicates that for every two molecules of HI(g) that decompose, one molecule of $H_2(g)$ and one molecule of $I_2(g)$ are produced. However, the equation does not indicate how HI molecules are converted to H_2 and I_2. The first step in a chemical reaction is thought to involve a collision between the reactant particles. This idea is part of the collision theory of reaction rates. The collision theory assumes that if particles are to react, they must first undergo an appropriate collision.

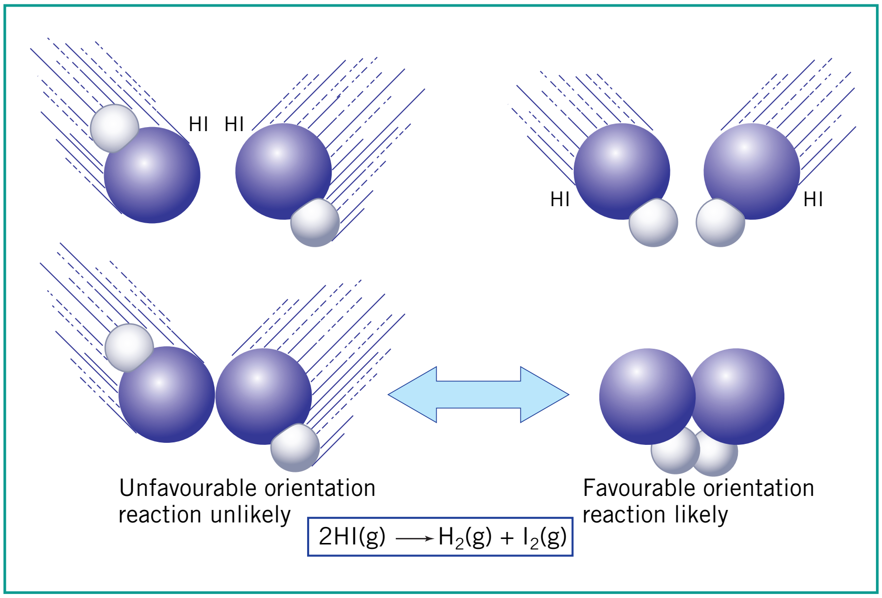
According to the kinetic theory (discussed in Chapter 1), the particles in a gas are in a continuous state of random straight-line motion. While most of the particles have energies that are close to the average for all the particles in the system, a small number have energies much lower or much higher than the average. Because of this range of kinetic energies, collisions between HI molecules will occur with differing energies. A collision between reactant molecules does not necessarily mean that a reaction will take place. In fact, most collisions do not bring about a reaction. The collision theory requires that for a collision between reactant particles to lead to a chemical reaction, the following conditions must be fulfilled:

- The molecules must collide with sufficient energy to disrupt the bonds of the reactant molecules.
- The molecules must collide with an orientation that is suitable for the breaking of some bonds and the formation of others.

For a reaction to occur between reactant molecules, they must collide with a certain minimum energy. Unless this minimum collision energy is exceeded, the colliding molecules will simply rebound and move away from each other. The minimum energy that is required for a collision to result in a reaction is known as the *activation energy* for the particular reaction. Some reactions have relatively low activation energies and so react at a significant rate at room temperature. For these reactions, a noticeable reaction occurs as soon as the reactants are mixed. For example, a piece of sodium metal added to water at room temperature produces a violent reaction almost instantaneously. Other reactions occur to an almost insignificant extent at room temperature. In such reactions the activation energy is so high that it is very unlikely that reactant molecules will collide with sufficient energy to undergo reaction. For example, methane will not react with oxygen unless the mixture is ignited. There is a relatively high activation energy for the reaction between methane and oxygen. Despite the fact that under standard conditions there would be in the order of 10^{10} collisions per second between reactant molecules, virtually none of these would have sufficient energy for a reaction to take place.

In Unit 17.6, the ignition temperature was defined as the minimum temperature at which a fuel/air mixture spontaneously ignites. If a combustion reaction has a relatively low activation energy it is more likely that collisions between the reactant particles will have sufficient energy to undergo reaction. The ignition temperatures of these combustion reactions will be relatively low. Combustion reactions with higher activation energies will have higher ignition temperatures.

As well as needing a minimum amount of energy, successful collisions also often have an orientational requirement. The relative orientations of the reactant molecules during a collision must be favourable—that is, they must collide with each other at the correct angle and in the correct position, for the breaking of particular bonds in the reactants and the formation of new bonds in the products. This factor also contributes to the fact that many collisions between reactants are unsuccessful in producing a reaction.



$2HI(g) \longrightarrow H_2(g) + I_2(g)$

Figure 19.5 Reaction between colliding molecules is more likely to occur if the orientation of the collision is favourable.

Energy profile diagrams

An *energy profile diagram* is a way of representing the enthalpy (energy) changes that occur during a chemical reaction. A typical example of an energy profile diagram is shown in Figure 19.6.

The enthalpies (chemical potential energies) of the reactants (a) and products (c) are identified in Figure 19.6. The energy difference (ΔH) between the reactants and products represents the heat of reaction. Between the reactant and product states is a very high energy state (b) known as the *transition state* or activated complex. The transition state represents the highest energy state for the reacting system and corresponds to some stage in the reaction at which bond-breaking and bond-formation are taking place. The transition state is an unstable state and cannot have any more than a very temporary existence. Once formed it will

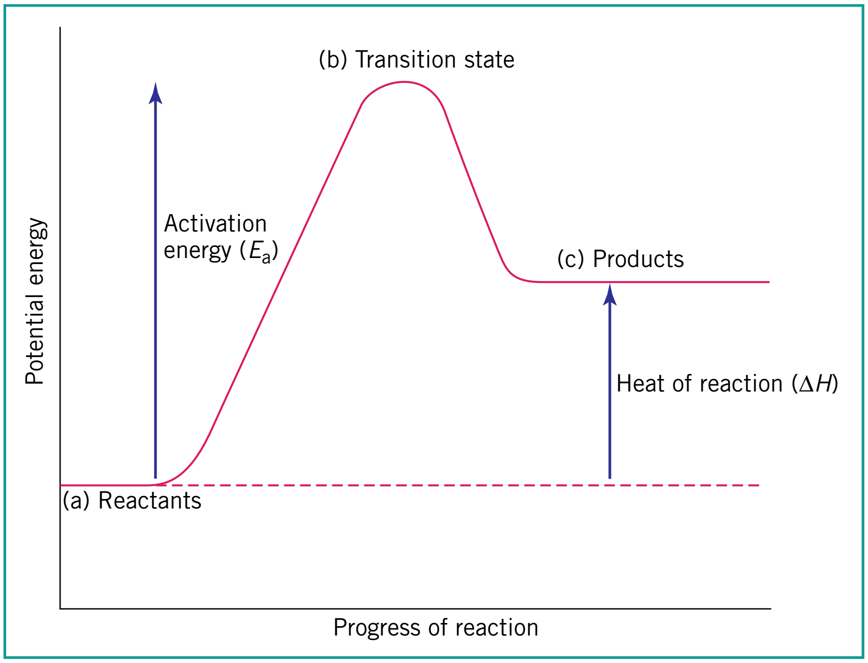


Figure 19.6 A typical energy profile diagram

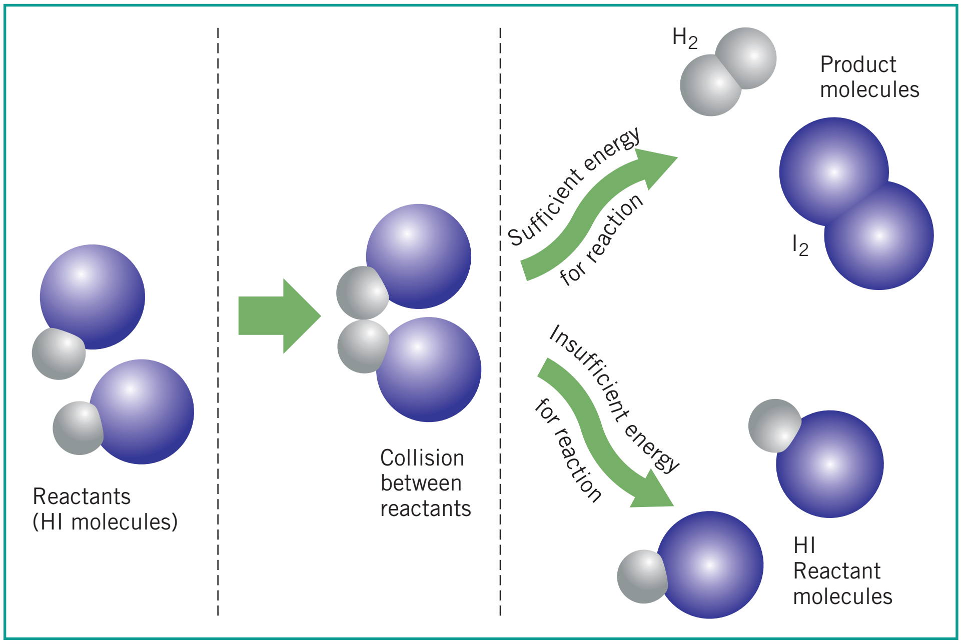


Figure 19.7 For reaction to occur, a collision between reactant molecules must have sufficient energy to reach the transition state.

quickly convert to products or return to reactants. The activation energy (E_a) for the reaction is the difference in the enthalpies of the reactants and the transition state. Because the activation energy can be thought of as a barrier that must be overcome for a reaction to take place, it is sometimes referred to as the *activation energy barrier*.

When reactant molecules collide, a reaction may only occur if the energy of collision is sufficient to supply the activation energy needed for the reactants to reach the transition state and the orientation is correct. If the energy is sufficient to reach the transition state, a collision can be successful and the reactant molecules will be converted to products. If the collision energy is insufficient to reach the transition state, the collision will be unsuccessful and reaction will not take place.

The energy profile diagram can be related to the kinetic energy distribution diagram for a reaction at some particular temperature, as shown in Figure 19.8. The graphs in Figure 19.8 indicate that only a relatively small proportion of molecules in this system have energies greater than that of the activation energy barrier. In this system it would therefore be expected that few collisions would have sufficient energy to be successful in bringing about a reaction. As a result, the reaction rate would be slow.

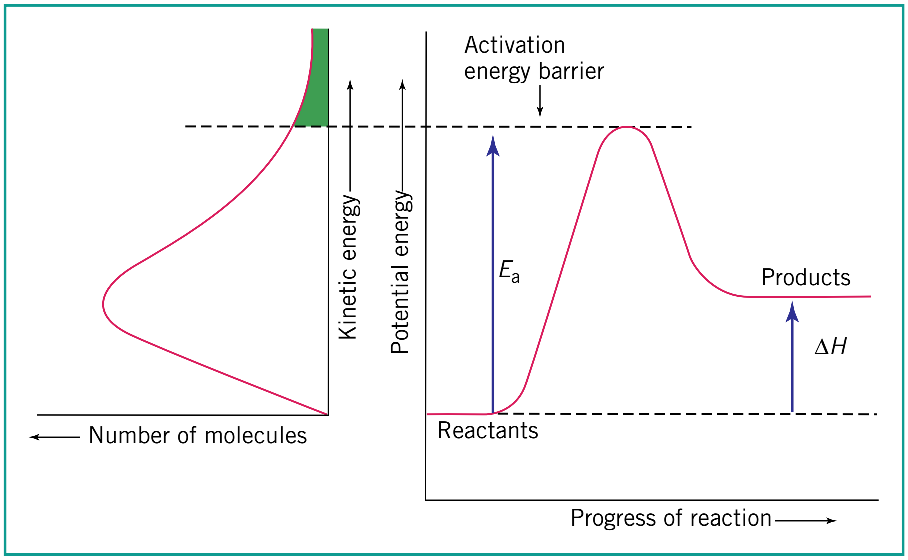


Figure 19.8 The rate of reaction depends on the proportion of molecular collisions with enough energy to overcome the activation energy barrier.

Energy profile diagrams for exothermic and endothermic processes are shown in Figure 19.9. These indicate that an activation energy exists for both exothermic and endothermic reactions.

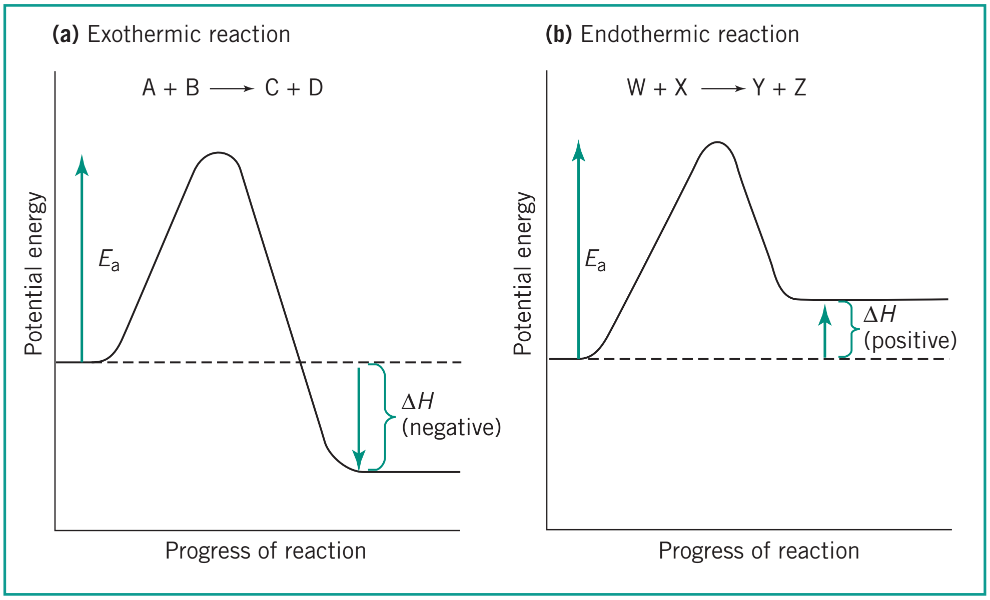


Figure 19.9 Energy profile diagrams for exothermic and endothermic reactions

In these particular examples, both reactions are depicted as having the same activation energy. This means that the same amount of energy is needed for a molecular collision to be successful in either reaction.

Reversibility of reactions

In Unit 13.2 the concept of reversible reactions was introduced, using the following reaction as an example:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

The double arrow is used as a way of indicating significant reversibility of a reaction. This indicates that the reaction can proceed in either direction. It is customary, in such systems, to use the terms 'forward reaction' and 'reverse reaction'.

The energy profile diagrams in Figure 19.9 indicate that an activation energy barrier exists for both the forward and reverse reactions. The activation energies for the reverse reactions are shown in Figure 19.10. In these particular systems, the activation energy for the reverse reaction is considerably higher for reaction (a) than for reaction (b). This means that more energetic collisions would be needed for C and D to react to produce A and B than for Y and Z to react to form W and X.

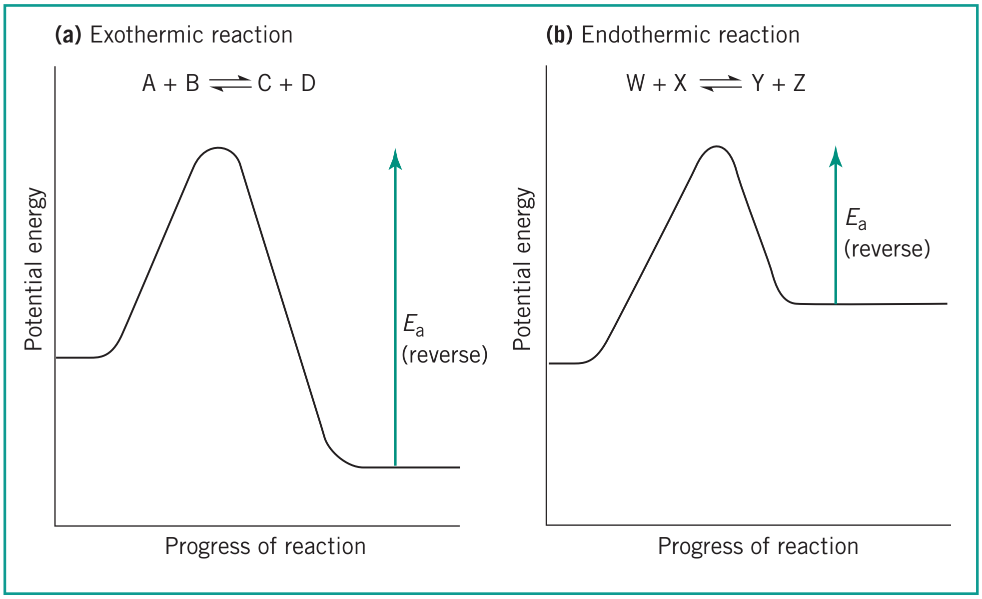


Figure 19.10 Activation energies for reverse reactions

❊ Review exercise 19.3

1 **Identify** two factors that determine whether a particular collision between reactant molecules will lead to a reaction.

2 **Describe** what happens if molecules collide with less than the activation energy for a reaction.

3 A piece of white phosphorus left in the open air at room temperature spontaneously ignites and burns to form P_4O_{10}. In contrast, a piece of iron rusts very slowly when exposed to the atmosphere. **Account** for these observations in terms of the activation energies for these reactions.

4 The ignition temperature for the combustion of kerosene is 220°C, while that of natural gas is 540°C. What does this suggest about the relative activation energies for the combustion reactions of natural gas and kerosene?

5 a **Construct** an energy profile diagram for each of the reactions (X, Y, Z), which have activation energies and heats of reaction as shown in the table.

	X	Y	Z
Activation energy (kJ)	100	50	120
Heat of reaction (kJ)	–50	–80	50

b Assuming all the other factors affecting the rates of these reactions are equal, **identify** the following:

i the fastest and slowest forward reaction

ii the fastest and slowest reverse reaction.

6 When nitrogen (N_2) and hydrogen (H_2) react under conditions of high temperature and pressure, ammonia (NH_3) is formed. However, a sample of ammonia when heated produces nitrogen and hydrogen. **Construct** an appropriate balanced chemical equation to represent this reversible system.

19.4 Applying collision theory

In this section the factors affecting reaction rate will be reconsidered in terms of collision theory and energy profile diagrams.

Nature of the reactants

In general, if other factors affecting reaction rates are equal, slower reactions will have higher activation energies than faster reactions. The different activation energies for different reactions are related to the ease with which bond-breaking and re-forming processes occur. High activation energies are often associated with reactions in which strong bonds have to be broken. For example, the low reactivity of nitrogen gas (N_2) is related to the large amount of energy needed to break the N≡N triple bond.

Concentration

One of the major assumptions of the collision theory is that molecules must collide before they react. The effect of increasing the concentration of a reactant in solution is to increase the rate at which reactant molecules collide with one another. If a greater number of collisions occur per unit of time, the reaction rate will increase. Although the same proportion of these collisions will be successful, the greater rate of collisions results in a greater number of successful collisions. The same argument can be applied to reactions involving gases. Increasing the pressure of reactant gases increases the rate of collisions between the molecules and hence the rate of reaction.

The extent of the increase in reaction rate which occurs when the concentration of reactants is increased depends on the reaction involved. Often the relationship is a fairly simple one. For example, in the reaction

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

doubling the pressure of $H_2(g)$ doubles the rate of reaction. For the reaction

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

doubling the pressure of HI(g) quadruples the rate.

Surface area

If the surface area of a solid or liquid reactant is increased, more of the reactant molecules are exposed to collision. Figure 19.11 indicates how subdividing a piece of solid reactant increases its surface area. Since molecules must collide before they react, increasing the surface area can lead to an increased rate of reaction. Solid reactants are often powdered to increase the rate of reaction. When liquid reactants are used, the liquids are frequently used as sprays or subjected to vigorous agitation to ensure that a large surface area is available for reaction.

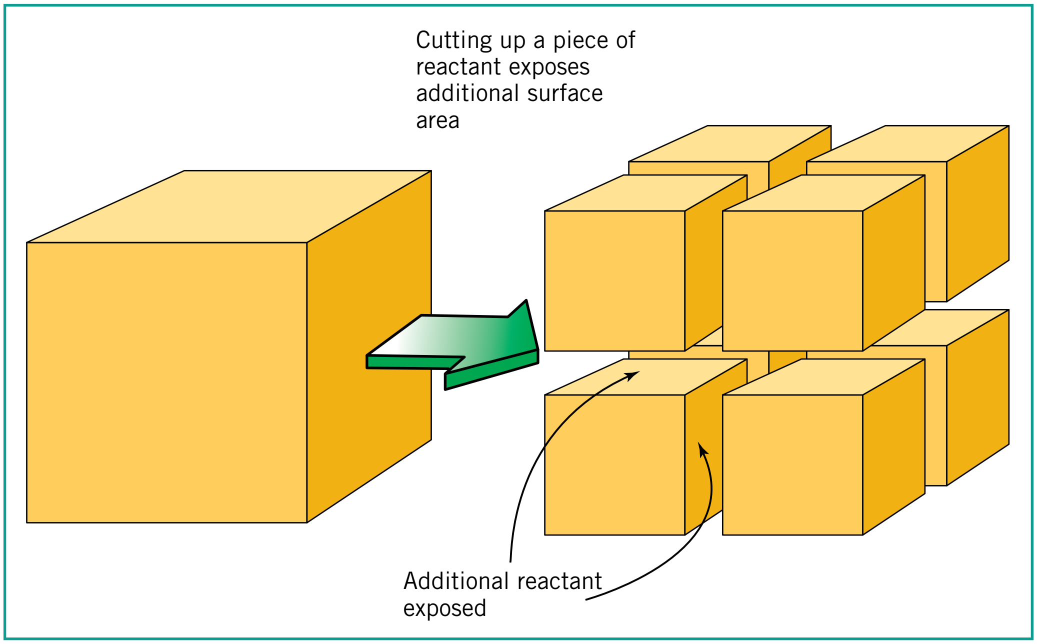


Figure 19.11 Increasing the surface area of a solid or a liquid can increase the rate of a reaction.

Temperature

The temperature of a reacting system has a significant effect on the rate of reaction. An increase of 10°C above room temperature can lead to a two- or three-fold increase in the rate of solution reactions. In gaseous systems, there is often an even greater increase in reaction rate. An increase in temperature increases the average kinetic energy of the reacting molecules and, more importantly, changes the distribution of molecular kinetic energies.

The increased velocities of the molecules lead to a greater rate of collision and hence a greater rate of reaction. However, the increase in reaction rate due to the increased rate of collision is fairly small.

The main reason that an increase in temperature increases reaction rate is because of its effect on the distribution of molecular kinetic energies, as shown in Figure 19.12. As the temperature is raised, a greater proportion of reactant molecules have sufficient kinetic energy to supply the activation energy needed for reaction. This means that a greater proportion of molecular collisions will be successful collisions. As a result, the rate of the reaction is increased.

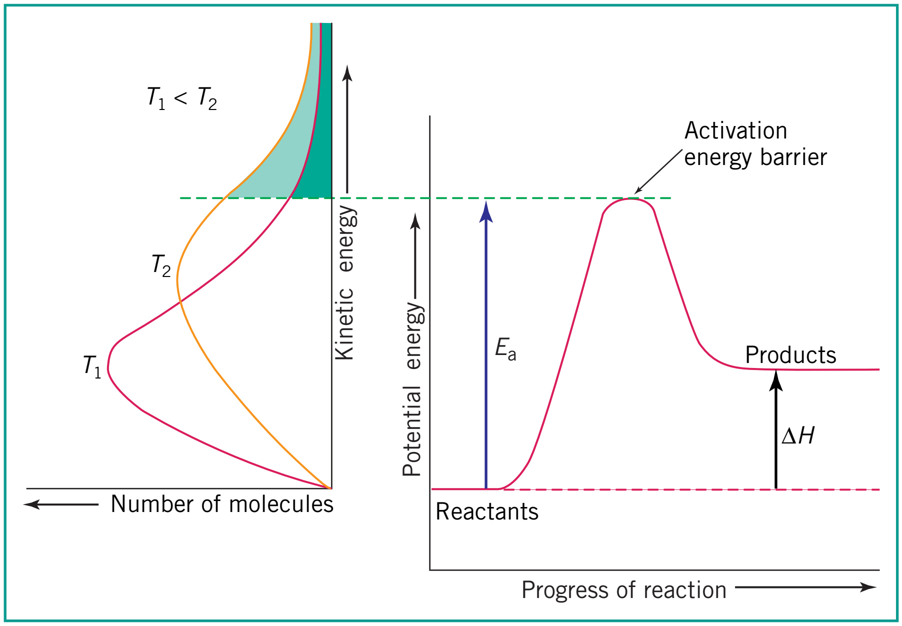


Figure 19.12 Increasing the temperature increases the proportion of reactant molecules with enough kinetic energy to overcome the activation energy barrier.

Catalysts

A catalyst provides an alternative reaction pathway to that available when the reactants alone are used. This different pathway has a lower activation energy, as shown in Figure 19.13. The catalyst allows the reaction to occur in such a way that less collision energy is required for reaction to take place. As a result, a greater proportion of reactant collisions will be successful and the reaction rate will be greater than without a catalyst. Figure 19.14 illustrates how a greater proportion of reactant molecules have sufficient energy to overcome the activation energy barrier in a catalysed reaction.

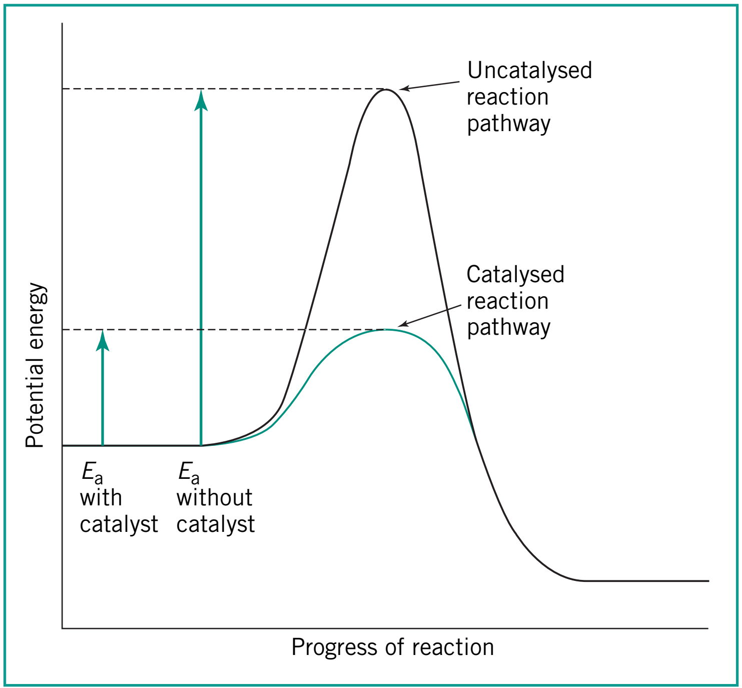


Figure 19.13 A catalyst provides an alternative reaction pathway with a lower activation energy.

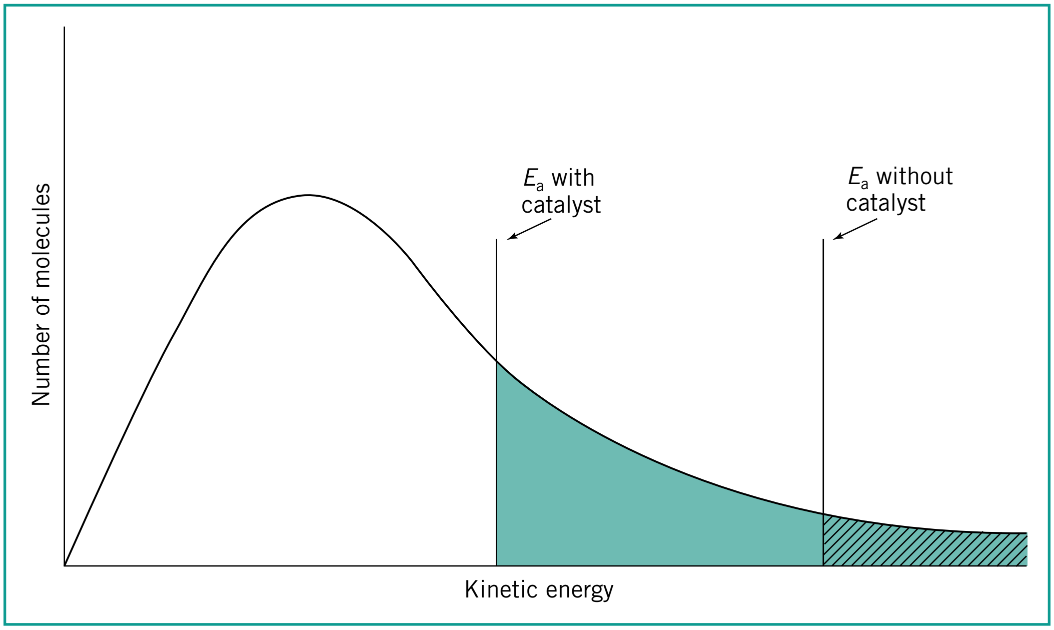


Figure 19.14 A catalyst provides an alternative reaction pathway. This results in a greater proportion of molecular collisions having sufficient energy to reach the transition state.

It is important to note that the activation energies for both the forward and reverse reactions are decreased by the action of a catalyst. The rates of both the forward and reverse reactions are therefore increased by the use of a catalyst.

Catalysts are extremely important in industry because they help make reactions possible that would normally be slow or require large amounts of heating to achieve. The use of catalysts often allows reactions to be carried out at much lower temperatures, thereby using less energy and reducing costs. Examples of industrially important catalysts are listed in Table 19.1.

Table 19.1 Some industrially important catalysts

Product	Process	Catalyst
Ammonia	Haber	Iron
Nitric acid	Ostwald	Platinum/rhodium
Sulfuric acid	Contact	Vanadium(V) oxide
Petroleum	Catalytic cracking	Zeolite
Margarine	Hydrogenation	Nickel or platinum
Wine	Fermentation	Enzymes in yeast

Catalysts generally operate by forming intermediate compounds in which the bond-breaking and rearrangement processes require less energy than if the reactants alone were involved. For example, with metal catalysts, reactants molecules that collide with the metal surface may become attached to the metal. The molecular rearrangements that occur during this process make it more likely that subsequent reactant collisions will be successful. For example, in the manufacture of ammonia using an iron catalyst, it appears that the N_2 and H_2 reactants are bound to the surface as separate atoms. These atoms are reactive and combine to form NH_3 molecules, as shown in Figure 19.15.

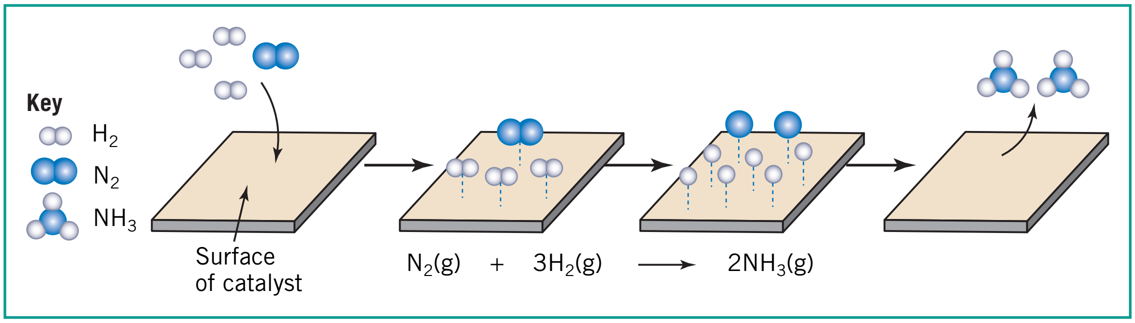


Figure 19.15 The iron catalyst in the manufacture of ammonia allows the bonds in the nitrogen and hydrogen molecules to be broken more easily.

Another example is the use of nickel or platinum as a catalyst in the manufacture of margarine. Solid margarine is made from liquid vegetable oils. In this process the vegetable oil reacts with hydrogen gas in the presence of a catalyst. Hydrogenation reduces the number of carbon–carbon double bonds, thereby improving the consistency of the margarine.

Increasingly, catalysts are being used in controlling the emission of pollutants, from cars and power plants. An example is the use of catalytic converters in cars sold in Australia since 1986. The catalytic converter is located between the engine and the exhaust pipe. Its function is to catalyse reactions that remove pollutants, leaving the engine, including unburnt petrol (mostly octane), carbon monoxide and nitrogen oxides. Catalytic converters typically contain platinum and rhodium. The catalyst serves to catalyse the following reactions:

$$2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$$

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

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

In the first reaction, carbon monoxide and nitrogen oxide react to produce nitrogen and carbon dioxide. The second and third reactions remove carbon monoxide and unburnt petrol respectively by oxidising these substances to carbon dioxide and water. The lower emissions of NO and unburnt hydrocarbon (petrol) help to reduce photochemical smog formation, and the quantity of the highly poisonous gas, carbon monoxide, in exhaust emissions is also reduced.

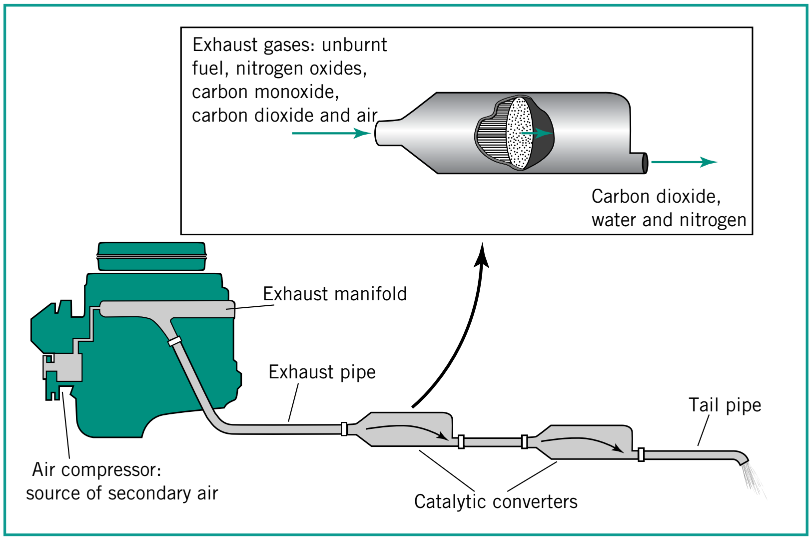


Figure 19.16 Catalytic converters reduce the emission of unburnt hydrocarbons, nitrogen oxides and carbon monoxide from motor vehicles.

CHEMISTRY CONTEXT

❇ ENZYMES, BIOLOGICAL CATALYSTS

Another important group of catalysts are the biological catalysts called *enzymes*. Enzymes are proteins that catalyse the thousands of chemical reactions involved in sustaining life.

Plants and animals can only survive within a limited temperature range. All chemical reactions that occur in them must take place within this temperature range. However, many of these reactions involve large and complex molecules that would normally react very slowly. The rates of these reactions are increased by enzymes, which help the complex bond-breaking and molecular rearrangements to occur more readily. These natural catalysts are highly specific in their activity; each enzyme catalyses a particular type of reaction. For example, the enzyme carboxypepsidase-A helps the human digestive system break down large protein molecules in food into small amino acid units. These are then used to build the body's own proteins.

Combustion reactions and explosions: energy and rate factors

Combustion reactions are those in which a substance reacts with oxygen, releasing heat and light energy, and are usually accompanied by a flame. We usually think of combustion reactions involving hydrocarbon fuels such as methane, petrol or coal but other examples are the combustion of ethanol, metals such as magnesium and iron, and non-metals such as phosphorus, sulfur and carbon (in the form of coke).

Combustion reactions are always exothermic. The decrease in enthalpy of the reacting system is accompanied by the release of heat and sometimes light energy to the surroundings. The actual rate at which combustion reactions take place depends on the many factors that influence reaction rates. These include: the nature of the reactants (affects activation energy); the surface area, concentration and pressure of the reactants; temperature; and the use of catalysts.

Some combustion reactions occur spontaneously under normal conditions. For example, white phosphorus reacts spontaneously with oxygen in the air to form phosphorus(V) oxide.

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

Because of the spontaneous nature of this reaction, white phosphorus is stored under water to prevent it coming into contact with air. Phosphorus has been responsible for many fires when its storage under water has not been carefully controlled and monitored.

Hydrocarbon fuels do not undergo spontaneous combustion at normal temperatures. This is due to the high activation energy of these reactions. However, at temperatures above their ignition temperatures, hydrocarbons and other fuels will undergo spontaneous combustion. Fortunately the ignition temperatures for most fuels are reasonably high, as described in Unit 17.6. As a result they do not spontaneously react with oxygen in the air unless heated to high temperatures or a flame or spark is present that can initiate the reaction. The presence of a flame or spark can provide the activation energy required for some molecules to react. The release of heat energy that accompanies the reaction of these molecules is then sufficient to maintain a high enough temperature for the reaction to continue. For this reason, the flash point for fuels is much lower than the ignition temperature. This is clearly illustrated by the burning of wood, coal, natural gas, sulfur and magnesium. Once a flame has provided the activation energy for some of the molecules to react, these reactions becomes self-sustaining.

If a combustion reaction has a low activation energy or is initiated by a flame or spark, the rate of the reaction depends mainly on the availability of fuel molecules for collision with oxygen molecules. This is often a function of the surface area of the fuel. In coal and wood fires, the solid fuel is usually present in ‘lumps’ and has a relatively small surface area. The combustion is slow as a result. The reaction rate can be increased by increasing the surface area of the fuel, by chopping the wood or breaking the coal into smaller pieces. If the fuel is very finely divided, as in coal dust, the collision rate of fuel and oxygen molecules is much greater. This can increase the rate of reaction to such an extent that an explosion may occur. In liquids, too, the rate of combustion depends on the state of subdivision of the fuel. To increase the rate of combustion in some furnaces, liquid fuels are injected as a spray. Where the rate of combustion needs to be controlled, the supply of fuel is often limited. For gases this is achieved by varying the rate of inflow of gas, as in a stove or oven. In liquids a wick is sometimes used to provide a steady supply of fuel. Explosive chemical reactions are those that result in a rapid increase in pressure, often in a confined space. These are always exothermic reactions and often involve the release of large volumes of gas. Many hydrocarbons have the ability to react explosively under certain conditions. For example, the combustion reaction of propane is exothermic and releases large quantities of gas.

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

Hydrogen, nitroglycerine ($C_3H_5(NO_3)_3$), TNT ($C_7H_5(NO_2)_3$) and ammonium nitrate (NH_4NO_3) also have the capacity to react explosively.

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

$$2C_3H_5(NO_3)_3(s) \rightarrow 3N_2(g) + 6CO_2(g) + 5H_2O(g) + \tfrac{1}{2}O_2(g)$$

Nitroglycerine reacts so rapidly that it is usually mixed with a clay material to reduce the rate of decomposition and make the material easier to handle. This mixture, dynamite, is often about a 75:25 mix of nitroglycerine and clay material.

In explosive chemical reactions, the reaction must occur at a very rapid rate so that the heat and gas products are released over a short period of time. Explosive reactions may have high activation energies. However, once a reaction has been initiated by a flame or spark, the exothermic nature of the process maintains a rapid reaction rate. Other important factors that can affect the rate are those that influence the rate of collision between the reacting species, such as the surface area of the fuel and the pressure of oxygen. In most explosive reactions, the reactants are finely divided, existing as vapour, powder or dust, which increases the rate of collision between reactant particles and therefore favours a rapid reaction rate.

From a safety point of view it is important to control or eliminate those conditions that favour explosive combustion. Naked flames and sparks that can initiate chemical reactions must be avoided in high-risk environments such as oil refineries and petrol stations. In other situations such as homes, boats and caravans, as well as high-risk locations, care must be exercised to maintain equipment so that accumulations of vapour, finely divided coal and cereal dust are avoided.

❇ Review exercise 19.4

1 Sulfur burns in air to form sulfur dioxide. If sulfur is burnt in pure oxygen at the same temperature, the rate of reaction is much greater despite the fact that the fraction of successful collisions is the same as before. **Explain**.

2 Milk kept at room temperature can sour in as little as a day, but can keep for a week in a refrigerator. Use energy profile and molecular kinetic energy distribution diagrams to **explain** these observations.

3 **Explain** why many liquid fuels are vaporised before being used in a combustion chamber.

4 Glucose is quite stable in aqueous solution but in the human body is converted fairly rapidly into CO_2 and H_2O by the catalytic effect of certain enzymes. **Explain** how a catalyst can increase the fraction of successful collisions between reactant molecules.

5 **a** **Explain** why the flash point for pentane (–49°C) is much lower than its ignition temperature (260°C).

b **Account** for the explosive risks in small motor boats, wheat storage silos and underground coal mines.

c **Explain** how white phosphorus, which has a much lower ignition temperature than butane, can have a lower risk of explosive combustion.

*KEY POINTS

- The rate of a chemical reaction is the speed at which reactants are converted to products.
- Chemical reactions display a great range of reaction rates, from very fast, occurring in a fraction of a second, to very slow, taking place over months or years.
- The rate of a chemical reaction can be expressed in terms of the rate of removal of reactants or the rate of formation of products.
- Factors that affect the rate of a reaction are: the nature of the reactants; the concentration or pressure of the reactants; the surface area of the reactants; the temperature of the system; and the presence of a catalyst.
- The collision theory of reaction rates is based on the idea that if particles are to react they must first undergo a collision. For a collision to bring about a change from reactants to products, it must have the following:
  - sufficient energy to disrupt the bonds in the reactant molecules
  - an orientation that is suitable for the breaking of some bonds and the formation of new bonds.
- Activation energy (E_a) is the minimum energy that must be supplied by the reactant particles in a chemical reaction if they are to react to form products.
- An energy profile diagram represents the energy changes that occur in a chemical reaction.
- The transition state or activated complex is the highest energy state in a chemical reaction. The difference in energy between the reactants and the transition state is the activation energy for the reaction.
- A successful collision is a collision between reactant particles that leads to the formation of products.
- A reversible reaction is one in which the formation of products from reactants and the formation of reactants from products are both significant. Double arrows ($\rightleftharpoons$) in the chemical equation represent a reversible reaction.
- The nature of the reactants affects the rate of reactions because different reactions have different activation energies. Reactions that involve the breaking of many bonds tend to have higher activation energies and consequently slower rates.
- Increasing the concentrations or gas pressures of reactants increases the rate of collisions and hence the rate of reaction.
- Increasing the surface area of solids and liquids in heterogeneous systems increases the rate of collisions between reactants and hence the rate of reaction.
- Increasing the temperature increases the fraction of molecular collisions with sufficient energy to overcome the activation energy barrier. This leads to an increased rate of reaction.
- A catalyst increases the rate of a reaction by providing an alternative reaction pathway with a lower activation energy.

- Catalysts have important roles in the following:
  - the industrial manufacture of many chemical substances
  - the removal of pollutants from combustion processes
  - life-sustaining processes in plants and animals.
- Explosive chemical reactions are those that result in a rapid increase in pressure, often in a confined space. These are always exothermic reactions and often involve the release of large volumes of gas.

* APPLICATION AND INVESTIGATION

1 **Describe** two ways of measuring the rate of the following reaction.

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

2 In the reaction

$$C_4H_9Cl(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + H^+(aq) + Cl^-(aq)$$

the concentration of C_4H_9Cl decreases with time, as shown below.

Time (s)	0	100	200	300	400	500	600	800
Concentration (mol L^{-1})	0.100	0.082	0.067	0.055	0.045	0.037	0.030	0.020

a **Construct** a graph of concentration versus time.
b **Describe** how the rate of this reaction changes as the reaction proceeds.
c **Explain** why this change in reaction rate occurs.

3 **Suggest** reasons for the difference in rate of the following reactions at room temperature.

fast $Cu^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CuCO_3(s)$

slow $C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

4 **Predict** the effect of increasing the pressure of oxygen on the rates of the following reactions.

a $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
b $2Na(s) + O_2(g) \rightarrow Na_2O_2(s)$
c $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
d $2H_2O_2(aq) \rightleftharpoons O_2(g) + 2H_2O(l)$

5 **Account** for the fact that when hydrogen gas is prepared in the laboratory, hydrochloric acid is usually added to granulated rather than powdered zinc.

6 When dilute acid is added to sodium thiosulfate solution, a precipitate of sulfur is formed.

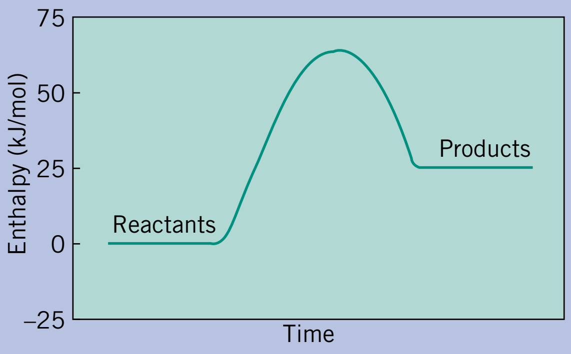
$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow S(s) + SO_2(aq) + H_2O(l)$$

If it takes 30 seconds for a precipitate to appear using 0.05 mol L^{-1} $Na_2S_2O_3$ solution, **predict** how long it might take if the $Na_2S_2O_3$ solution was 0.10 mol L^{-1}.

7 a **Explain** why reactant molecules must collide with an energy greater than a certain minimum value for reaction to occur.

b **Explain** why not all collisions with this minimum energy result in the formation of products.

8 Use the energy profile diagram below to answer the questions that follow.



a **Identify** whether the reaction is exothermic or endothermic.

b **Deduce** the value of ΔH for the forward reaction.

c **Identify** the activation energy for both the forward and reverse reactions.

d A catalyst for the reaction lowers the activation energy by 10 kJ mol^{-1}. **Calculate** the activation energy of the forward and reverse reactions in the presence of the catalyst.

e **Explain** how the catalyst affects the rate of the forward and reverse reactions.

9 a **Construct** energy profile diagrams for the following reactions.

i $2H_2O_2(aq) \rightarrow O_2(g) + 2H_2O(l)$ $E_a = 75$ kJ; $\Delta H = -98$ kJ

ii $O_2(g) + NO_2(g) \rightarrow NO(g) + O_3(g)$ $E_a = 210$ kJ; $\Delta H = +200$ kJ

b **Deduce** the activation energies for the reverse reactions.

10 For the following reactions, **sketch** energy profile diagrams, indicating the relative potential energies of the reactants and products and the activation energy for the reaction.

a A piece of sodium added to water reacts rapidly to produce hydrogen and sodium hydroxide solution. The reaction is accompanied by the release of considerable quantities of heat.

b A mixture of $N_2(g)$ and $O_2(g)$ when heated very strongly is converted to NO(g). The reaction is endothermic.

11 Using the collision theory and energy profile diagrams, **explain** at a molecular level how the following factors can affect the rate of a chemical reaction:

- **a** reactant concentration or pressure
- **b** state of sub-division of a reactant
- **c** temperature of the reactants.

12 Hydrogen and oxygen ignite spontaneously at room temperature if passed through platinum gauze. Without the gauze, no reaction occurs. **Outline** the role of the platinum gauze and **explain** its action using an energy profile diagram.

13 A common misunderstanding regarding catalysts is that ‘they speed up a reaction but take no part in the reaction’. Critically **evaluate** this statement.

14 a **Identify** three industrial processes that use transition metals as catalysts.

b The following sequence of reactions has been proposed as contributing to ozone depletion in the stratosphere.

$$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$$

$$ClO(g) + O(g) \rightarrow Cl(g) + O_2(g)$$

Justify the assertion that chlorine atoms act as a catalyst in this sequence of reactions.

15 **Investigate** and report on the use of a catalyst in a named industrial process.

Investigation

16 **Investigate**, using secondary sources, two incidents involving explosive combustion reactions: one in a high-risk environment such as an oil refinery or other industrial plant, the other relating to an explosion in a boating, camping or home accident. **Identify** the cause of the explosion and how it might have been avoided.

Investigation

*MODULE 4 REVIEW

MULTIPLE-CHOICE QUESTIONS

1 The combustion of 2 moles of hydrogen with 1 mole of oxygen produces 2 moles of water. During this reaction there is an increase in temperature, because

A more energy is released when four O–H bonds are formed than is required to break two H–H bonds and one O=O bond.
B there is an increase in volume.
C energy is absorbed from the surroundings.
D the reactants have less energy than the products.

2 Buckminsterfullerene is

A a mixture of elements.
B an isotope of carbon.
C an allotrope of carbon.
D a hydrocarbon.

3 Within a homologous series such as the alkanes, the boiling points

A decrease as the molecular weights increase because molecules become more non-polar.
B increase as the size of the molecule increases as a result of increased dispersion forces.
C remain fairly constant.
D show no particular trend.

4 Petrol should not be stored in open containers because

A it may undergo spontaneous combustion.
B it has a large heat of combustion.
C it is extremely volatile and flammable.
D it can react with oxygen in the air to form toxic carbon monoxide gas.

5 A catalyst increases the rate of a reaction because it

A increases the enthalpy of the reaction.
B absorbs energy from the reactants.
C increases the average kinetic energy of the system.
D provides an alternative pathway for the reaction with a lower activation energy.

6 A reaction is exothermic if

A the energy of the products is less than the energy of the reactants.
B heat energy is absorbed during the course of the reaction.
C ΔH is positive.
D the energy of the products is greater than the energy of the reactants.

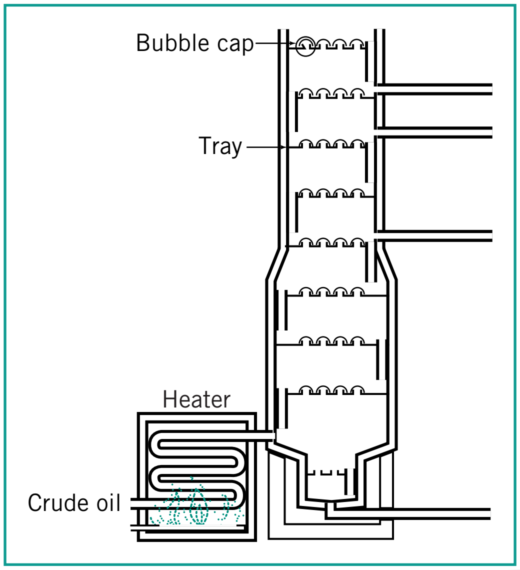
7 Underground coal mines are especially susceptible to explosions unless suitable precautions are taken. The best explanation for this is that the fine particles of coal dust

A can produce a chain reaction by collision of one particle with another.
B rub against each other and the resulting heat provides the activation energy required to initiate the reaction.
C have a very large surface area, causing combustion reactions to proceed much faster.
D react to form methane gas, which is highly flammable.

8 The petrol in a car engine requires a spark from the spark plugs to start the combustion. This is because

A ΔH is negative for this reaction.
B an energy barrier must be overcome before the reaction can proceed.
C the reaction is endothermic and requires an external source of energy.
D the petrol needs to be vaporised before the reaction can proceed.

9 The diagram below represents a fractionating tower, which is used in the refining of petroleum. Hydrocarbon fractions are removed from outlets on the right-hand side of the tower.



Which of the following compounds is most likely to be obtained from an upper level of the fractionation tower?

A $CH_3CH_2CH_3$
B $CH_3(CH_2)_{10}CH_3$
C $CH_3CH_2CH{=}CH_2$
D $CH_3(CH_2)_{25}CH_3$

10 A homologous series is a group of compounds in which the

A compounds have the same molecular formula but different structural formulas.
B compounds have the same physical and chemical properties but different formulas.
C successive members differ a by CH_2 group.
D successive members differ by one methyl group (CH_3).

SHORT-ANSWER QUESTIONS

11 One method for increasing the rate of a reaction is to increase the temperature of the system. For example, magnesium reacts more rapidly with hydrochloric acid when it is warmed.

Each of the following methods can also be used to increase the rate of some reactions:

i increasing the surface area of one of the reactants
ii the addition of a catalyst
iii the absorption of light.

Using word equations, recall an example of a reaction whose rate could be increased by each of the methods described above. Choose a different reaction for each example and **identify** the catalyst in **ii**.

12 The following equations describe the combustion of some common fuels. The molar heat of combustion ($-\Delta H_c^\theta$) is also given.

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad -\Delta H_c^\theta = 393 \text{ kJ mol}^{-1}$$

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) \qquad -\Delta H_c^\theta = 2220 \text{ kJ mol}^{-1}$$

$$C_9H_{20}(s) + 14O_2(g) \rightarrow 9CO_2(g) + 10H_2O(l) \qquad -\Delta H_c^\theta = 6125 \text{ kJ mol}^{-1}$$

a **Calculate** which of these fuels provides more energy per gram of fuel on combustion. Show your working.
b **Describe** a safe method of transporting each of these three fuels. **Justify** your answer by giving reasons for each method of transport.

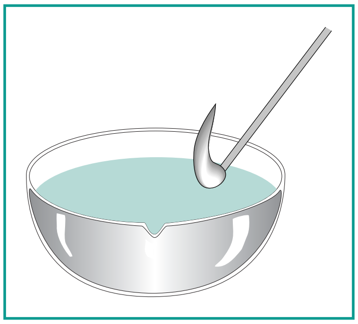
13 A student investigated the combustion of hexane (C_6H_{14}) and hexadecane ($C_{16}H_{34}$). Her results are given below.

Experiment 1

The hexane (C_6H_{14}) ignited immediately. It burned with a yellow sooty flame. When a white tile was held above the flame, a black deposit formed.

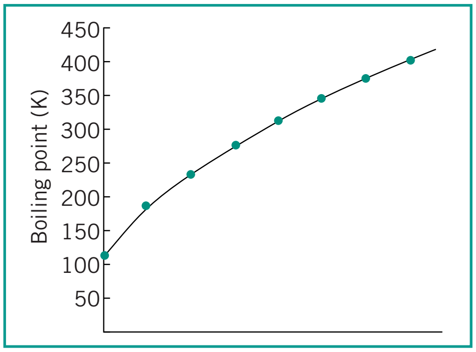
Experiment 2

The hexadecane ($C_{16}H_{34}$) did not ignite.



a **Explain** why the hexane in experiment 1 ignited but the hexadecane in experiment 2 did not.
b **Account** for the fact that the hexane in experiment 1 burnt with a sooty, yellow flame. Use an equation to support your answer.

14 The graph below shows the boiling points of the first eight alkanes.



Explain why the boiling points increase as the length of the carbon chain increases.

15 Petrol is the most common fuel used in motor vehicles.

- **a** **Describe** how the energy used to drive the car can be traced back to the sun. Use an equation(s) to support your answer.
- **b** **Outline** the process by which petrol is obtained from petroleum (crude oil).
- **c** **Explain** the importance of each of the following properties of petrol in relation to its use as a fuel:
  - **i** activation energy
  - **ii** volatility.

16 At high temperatures, dinitrogen tetroxide (N_2O_4) decomposes to nitrogen dioxide (NO_2). 12 kJ of energy are produced for each mole of NO_2 that forms. The activation energy for this process is 55 kJ for each mole of N_2O_4 that is decomposed.

- **a** **Construct** a balanced chemical equation for this reaction, including the value and sign of ΔH.
- **b** **Construct** an energy profile diagram for this reaction. Label the activation energy and ΔH on your profile. Your graph should show the relative magnitudes of these values.
- **c** **Deduce** the activation energy for the formation of one mole of N_2O_4 from NO_2.

17 The Bunsen burners found in most schools burn natural gas (mostly methane gas). Different flames indicate different combustion products and heats of combustion, as shown in the table below.

Flame colour	**Main combustion products**	**$-\Delta H_c^\theta$ (kJ mol^{-1})**
Blue	Carbon dioxide and water	804
Mauve	Carbon monoxide and water	521
Yellow	Carbon and water	410

- **a** **Construct** balanced chemical equations, including the energy term, for methane burning in each of these three ways.
- **b** **Identify** the most efficient flame for heating water and **justify** your answer.

18 The following table lists some of the properties of four liquid hydrocarbons.

Hydrocarbon	**Molecular formula**	**Boiling point (°C)**	**Heat of combustion (kJ g^{-1})**
Hexane	C_6H_{12}	68.7	48.3
Octane	C_8H_{18}	125.7	47.9
Dodecane	$C_{12}H_{26}$	216.3	47.5
Hexadecane	$C_{16}H_{34}$	286.8	47.3

- **a** **Construct** a balanced chemical equation for the complete combustion of octane.
- **b** **Draw** and **name** one structural isomer of octane.
- **c** **Calculate** the molar heat of combustion for hexadecane in kJ mol^{-1}.
- **d** **Explain** the trend in boiling points shown by this data.

19 **a** **Identify** the sources of pollution that accompany the combustion of coal.

- **b** **Explain** how these can be avoided.

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