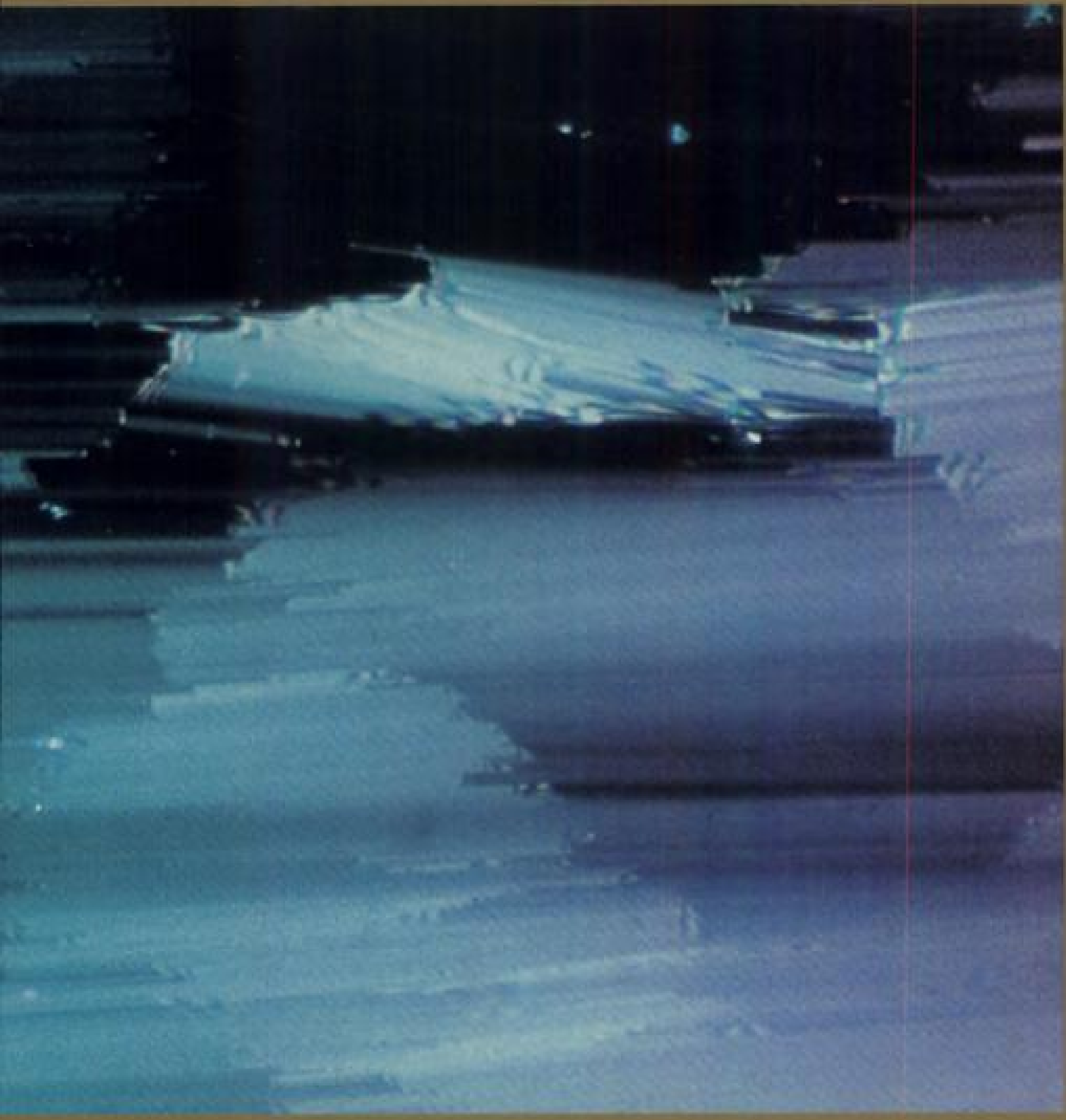
A-Level CHEMISTRY

FOURTH EDITION



**E.N.
Ramsden**

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E N Ramsden
1999

PREFACE TO FOURTH EDITION

This text prepares students for AS-level and A-level (A2) examinations in Chemistry. It is assumed that students are approaching AS-level from a study of *GCSE Science: Double Award*. The third edition included additional material to help the student to make the transition from *GCSE Science: Double-Award* to *A-level Chemistry*. The fourth edition takes this approach further. 'Summary boxes' have been added to encourage readers to take stock of what they have learned. 'Concept maps' have been added to help with revision. The introductions to some topics have been rewritten to be more accessible to students with a background of *GCSE Science: Double-Award*.

Each chapter starts with a topic of general interest related to some aspect of the chemistry of that chapter. This may be a famous scientist, a historical anecdote, a contribution of chemistry to medicine or industry or an interesting application. In addition there are topics in many chapters covering environmental concerns (e.g. acid rain, the greenhouse effect and the ozone layer), medicine (e.g. drugs and anaesthetics), agriculture (e.g. fertilisers and pesticides) and industrial accidents.

It is difficult to read a chapter and take in all the information and retain it! To make readers pause for thought, the margin carries a summary of the text. On reaching the end of a section or chapter, a reader can glance back through the summary to see whether he or she has assimilated all the material. If the reader notes any points which need further study, he or she has only to glance at the text alongside the summary to find the relevant passage.

I hope that students like the technique I have devised for integrating descriptive material with diagrams, so that the reader's eye does not have to travel constantly to and fro between a diagram and the text which describes it. I have used this technique largely in the physical chemistry section of the book. The annotated diagrams were consumer-tested and approved by sixth formers in my own school.

At intervals in each chapter 'Checkpoints' are included so that students can pause and test their understanding and, if necessary, revise a section before they pass on to new material. The AS-level and A-level specifications cover so much ground that many teachers find it difficult to take their classes through all the material, while still leaving time for practical work. I hope that teachers will be able to allow students to cover parts of the specification on their own from this text, assisted by the checkpoints, thus reducing the amount of note-taking which needs to be done in class and releasing time for discussion, reinforcement and practical work. Each chapter ends with a searching set of questions, including questions from past examination papers.

Much of the inorganic chemistry is summarised in the form of tables and reaction schemes. Students find these helpful for revision. My preference is to take the s block metals first, follow them with the halogens, and then work through the relevant sections of Groups 6 and 5 to arrive at Group 4 with its interesting gradation from non-metallic to metallic behaviour and end with the transition metals. Teachers whose specifications require a different order will find no difficulty in taking the inorganic chapters in a different sequence.

Some students are preparing for staged assessments, while others are preparing for terminal assessments. Some are preparing for AS-level examinations and others for A2-level examinations. Consequently, changes have been made in the structure of certain chapters to make it easier for students to select text relevant to the modules or units which they are studying. Some topics are present in the core specifications of all Awarding Bodies, and no changes have been made in the structure of these chapters. Some topics are present in optional units, and no changes have been made in the structure of these chapters. Other topics appear in specifications at two levels: a foundation coverage in an AS unit and a more advanced coverage in an A2 unit to be taken in the second year of the course. To meet this development, in the fourth edition some topics are divided into AS-level material and 'Further study' which covers more advanced work for A-level (A2) topics. Options which are not covered in the text but are available separately are *Biochemistry and Food Science*, *Materials Science*, *Detection and Analysis*, *Chemistry of the Environment* and *Chemistry and Society for Hong Kong* by E N Ramsden (Stanley Thornes Publishers).

Some topics are not common to all Awarding Bodies. These topics are marked with asterisks so that students can check their own specification and omit these topics if they wish. I envisage teachers and students selecting the material they require for the unit or module they are studying. Each topic is treated from the beginning without assuming that GCSE work has been remembered.

In the fourth edition, there has been some pruning of topics which are no longer included in specifications and the addition of some new topics. I have divided Chapter 18 into Group 1 and Group 2 so that students who require both groups and those who require Group 2 only will both be able to find their way through it. The coverage of polymers and instrumental analysis is more extensive than in previous editions, in response to the popularity of these topics in the Awarding Bodies' specifications.

In my experience, even students with a fair knowledge of the various series of organic compounds find difficulty in tackling problems which require a knowledge of several series of compounds. The method of converting **A** into **D** by the route

$$\mathbf{A} \longrightarrow \mathbf{B} \longrightarrow \mathbf{C} \longrightarrow \mathbf{D}$$

may well be difficult to formulate. I have tackled this problem in stages by summarising at the end of a chapter the relationship between the series of compounds covered in that chapter and those considered in previous chapters. At the end of the section on organic chemistry all the synthetic routes are summarised in a few reaction schemes. A number of threads which run through the separate chapters on organic chemistry are also drawn together at the end of this section.

New to the fourth edition is the Appendix: Mathematics. It reminds students of the mathematics which they need in order to tackle the calculations in the book. This Appendix will help students with the physical chemistry and inorganic chemistry. Further help and practice is available in *Calculations for A-level Chemistry* by E N Ramsden (Stanley Thornes Publishers).

The fourth edition contains new questions from past examination papers at the ends of the chapters. These are designated (AS/AL) or (AL). These correspond approximately to the standard required for the AS and A2 examinations which will begin in the year 2001. When AS-level and A2-level questions become available, new questions will be substituted.

Answers to numerical questions and selected questions are given. These are not model answers, and the Awarding Bodies take no responsibility whatsoever for the accuracy or method of working in the answers which I give to questions from past papers.

New to this edition is the supporting *Answers Key*. This separate booklet gives outline answers to the questions in the Checkpoints and at the ends of chapters. It also contains a selection of synoptic examination questions with outline answers.

The key skills of communication, application of number, information technology, working with others, improving own learning and performance and problem solving can all be exercised as part of a Chemistry course. During his or her course a student can work towards the Key Skills Qualification. He or she can carry out activities which provide evidence of the key skills of communication, application of number and information technology and build up a portfolio of evidence which can contribute towards the Key Skills Qualification.

There is more to chemistry than the content of any AS- and A-level specification. I assume that all students will be following a course of practical work, but I have not found room for instructions for experiments. I would also like to think that students are reading outside the confines of their specifications. At this level their understanding is sufficiently advanced to open the door to many fascinating topics. Many chapters include examples of the impact of chemistry on medicine, agriculture and the environment and the problems faced by the chemical industry. To keep up to date with developments in chemistry, students will have to read newspapers and periodicals. Their advanced chemistry course equips them to understand many of the scientific issues which they will see reported. I hope they will continue to take an interest in scientific topics long after their examinations are behind them.

E N Ramsden
Oxford 1999

Part 1

The Foundation

1.2 THE ATOMIC THEORY

The main points in Daltons's theory can be summarised as follows.

1. Matter is composed of tiny particles called atoms, which cannot be created or destroyed or split.
2. All the atoms of any one element are identical: they have the same mass and the same chemical properties. They differ from the atoms of all other elements.
3. A chemical reaction consists of rearranging atoms from one combination into another. The individual atoms remain intact. When elements combine to form compounds, small whole numbers of atoms combine to form compound atoms (as Dalton called them or **molecules** as we call them).

Some points in the atomic theory have been modified since Dalton's time. The atoms of some elements, e.g. uranium, can be split [see § 1.10.8]. Some elements have atoms of more than one kind, which differ slightly in mass; we call these atoms **isotopes** [see § 1.8].

Evidence for the particulate nature of matter

You will be familiar from your earlier work with evidence to support the atomic theory. Checkpoint 1.2 will allow you to check up on how much you remember.

CHECKPOINT 1.2: PARTICLES

1. A purple crystal is dropped into a beaker full of water. After a time, a pink solution has formed. Explain, on the basis of the particle theory of matter, how this happens.

2. Chlorine is denser than air. Yet when air and chlorine are mixed, a homogeneous mixture is obtained [see Figure 1.2A]. Explain, on the basis of the particulate theory of matter, how this happens.

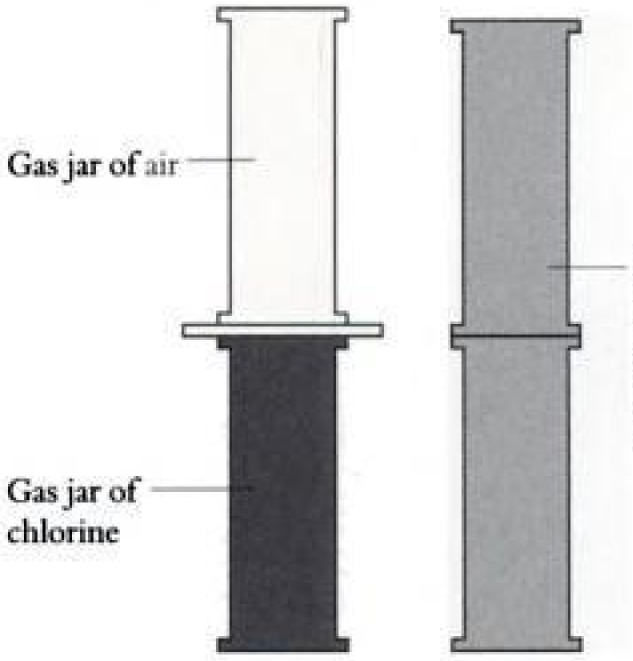


Figure 1.2A
Diffusion of chlorine and air

3. A smoke cell enables one to view the paths of particles of smoke. Figure 1.2B shows the path of a single particle. Explain, on the basis of the particle theory of matter, why the particle moves in this way, constantly changing direction.

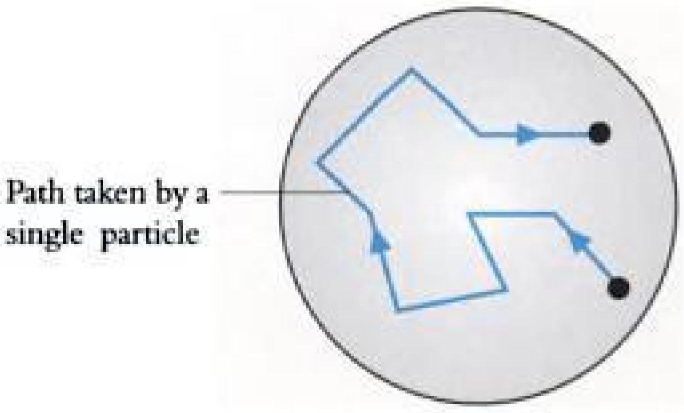


Figure 1.2B
A smoke cell

4. When ice is heated, it melts to form water. When water is heated, is forms water vapour. Explain what happens to particles in the transition (*a*) solid ⟶ liquid and (*b*) liquid ⟶ gas.

5. What has happened to make us disagree with Dalton on the question of whether atoms can be created or destroyed or split?

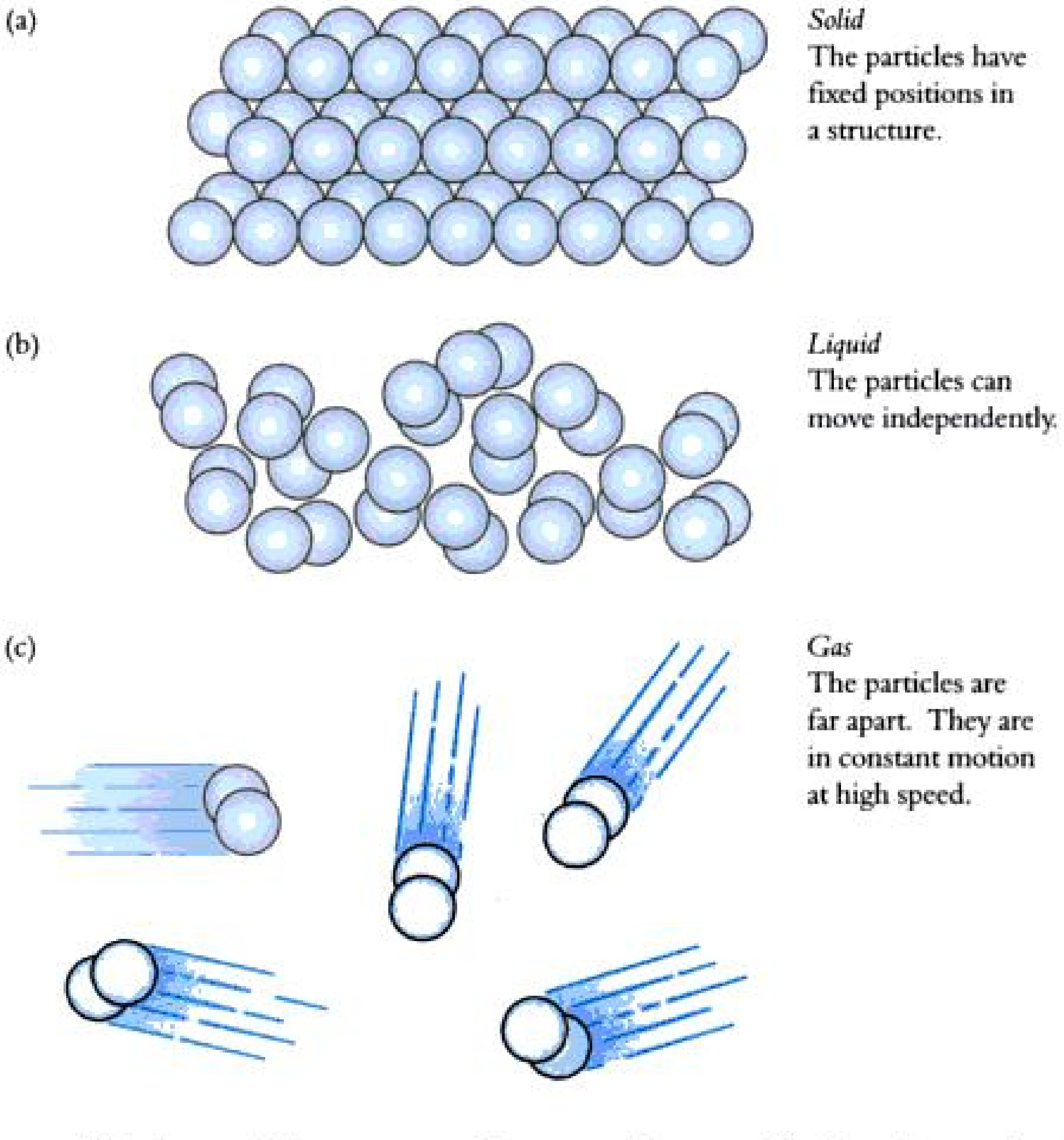
Evidence from X ray diffraction and electron microscope studies

You know from your previous studies that different kinds of matter consist of different kinds of particles. An element is a substance which cannot be split into simpler substances. Some elements consist of single atoms, e.g. helium consists of helium atoms, He. Other elements consist of molecules, particles which are composed of two or more atoms of the same kind, e.g. nitrogen consists of N_2 molecules, phosphorus consists of P_4 molecules and sulphur consists of S_8 molecules. A compound is a substance which is composed of two or more elements, chemically combined. Some compounds consist of molecules; these particles consist of two or more atoms bonded together. Other compounds consist of charged particles called ions. The numbers of positive and negative charges in a compound are equal. This topic is taken further in Chapters 4 and 6.

1.2.1 PARTICLES IN MOTION

The particulate theory of matter explains the difference in behaviour between solids, liquids and gases.

Figure 1.2C
Particles in a solid, a liquid and a gas



Particles in solids, liquids and gases

In a solid, the particles are very close together, and their only motion is vibration about a mean position [Figure 1.2C(a)]. In a liquid the particles are further apart than in a solid. The particles move slowly until they collide with another particle or with the container [Figure 1.2C(b)]. In a gas the particles are far apart. They move in straight lines, changing direction when they collide with another particle or with the walls of the container [see Figure 1.2C(c)]. Particles of a gas move at speeds of the order of 1000 km h^{-1}. The changes in energy that accompany changes of state are defined in § 10.7.2.

1.3 THE SIZE OF THE ATOM

Twentieth-century X ray work [§ 6.2] has shown that the diameters of atoms are of the order of 2×10^{-10} m, which is 0.2 nm (1 nm = 1 nanometre = 10^{-9} m).

The masses of atoms [§ 1.9] range from 10^{-27} to 10^{-25} kg. They are often stated in atomic mass units, u (where 1 u = 1.661×10^{-27} kg).

1.4 THE ELECTRON

Crookes detected cathode rays

Around the year 1900, physicists began to find evidence that atoms are made up of smaller particles. Sir William Crookes was experimenting in 1895 on the discharge of electricity through gases at low pressure. He discovered that a beam of rays was given off by the cathode (the negative electrode). Crookes called the rays **cathode rays**.

The rays also have the properties of particles

Crookes showed that cathode rays also behave like negatively charge particles.

The ratio e/m for cathode ray particles

Sir J J Thomson studied the deflection of cathode rays in electric and magnetic fields. From his measurements he calculated that the ratio of charge/mass, *e/m*, was -1.76×10^{11} C kg^{-1} (C = coulomb, the SI unit of charge). Since he obtained the same value, regardless of what gas was used or what kind of electrodes were used, he deduced that these negatively charged particles are present in all matter. They were named **electrons**, and were recognised as the particles of which an electric current is composed.

The charge on an electron and its mass

R A Millikan found the value of the electric charge carried by an electron. His 'oil drop' experiments, carried out from 1909 to 1917, are described in many physics books*. From his experiments, he obtained the value of -1.60×10^{-19} C. This amount of charge is called 1 elementary charge unit. Combining this value of charge with Thomson's value of charge/mass gave a value of 9.11×10^{-31} kg for the mass of an electron. This is 5×10^{-4} times the mass of a hydrogen atom.

1.5 THE ATOMIC NUCLEUS

The Thomson model of the atom

In 1898, Thomson surveyed all the evidence that atoms consist of charged particles. He described an atom as a sphere of positive electricity, in which negative electrons are embedded. Other people described this as the 'plum pudding' picture of the atom!

Geiger and Marsden tested the model ...

If this model of the atom is correct, then a metal foil is a film of positive electricity containing electrons. A beam of α particles (helium nuclei, see § 1.8) fired at it should pass straight through. In 1909, Lord Rutherford's colleagues, Geiger and Marsden, tested this prediction [see Figure 1.5A].

... their results ...

They found, as they expected, that α particles penetrated the gold foil. They also found, to their amazement, that a small fraction (about 1 in 8000) of the α particles were deflected through large angles and even turned back on their tracks. Rutherford described this as 'about as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you'.

... Rutherford's explanation

Rutherford deduced that the mass and the positive charge must be concentrated in a tiny fraction of the atom, called the **nucleus**. Figure 1.5B shows his interpretation of the results.

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* See, e.g., R Muncaster, *A-Level Physics* (Stanley Thornes).

Figure 1.5A
Illustration of Geiger–Marsden experiment

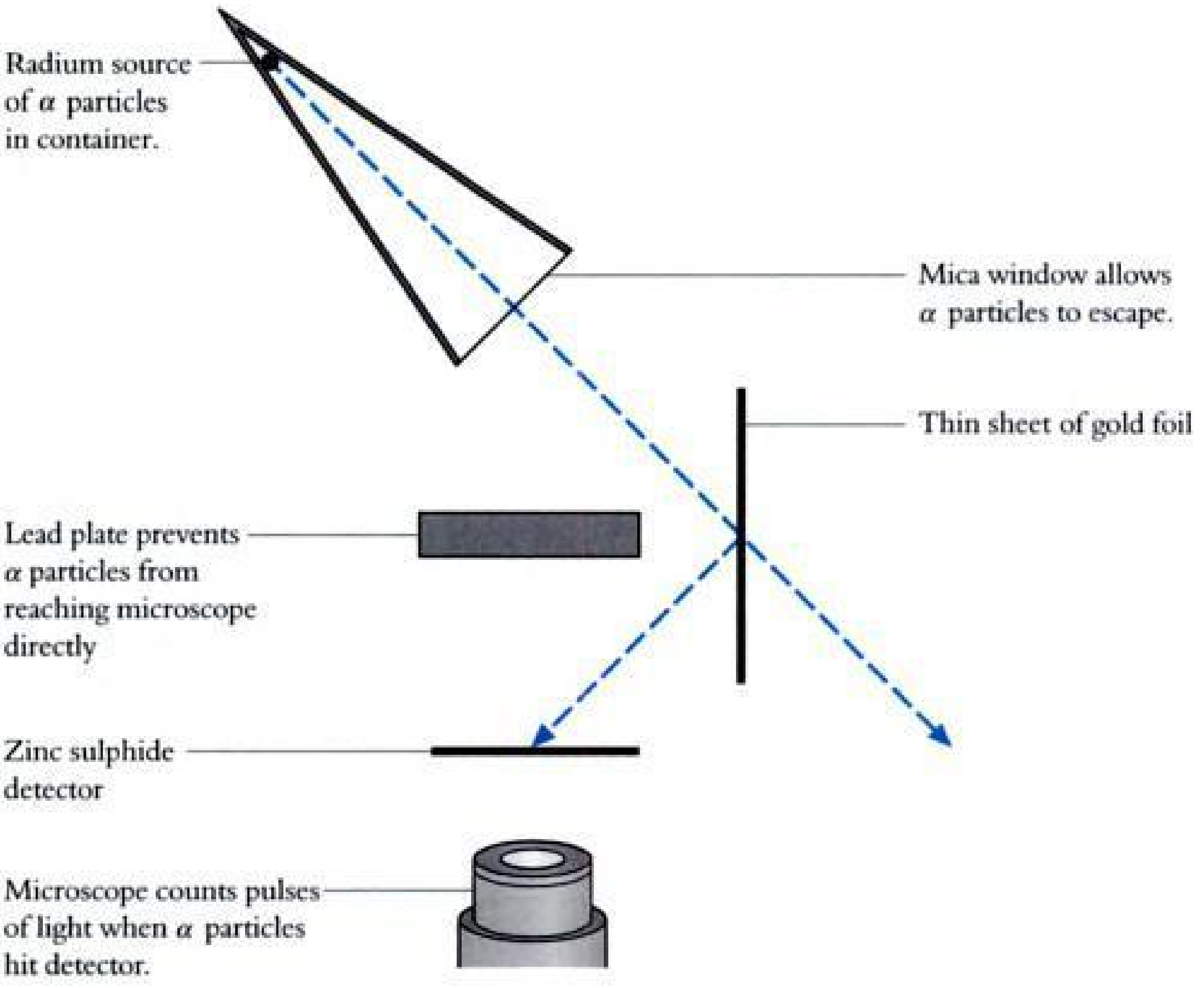
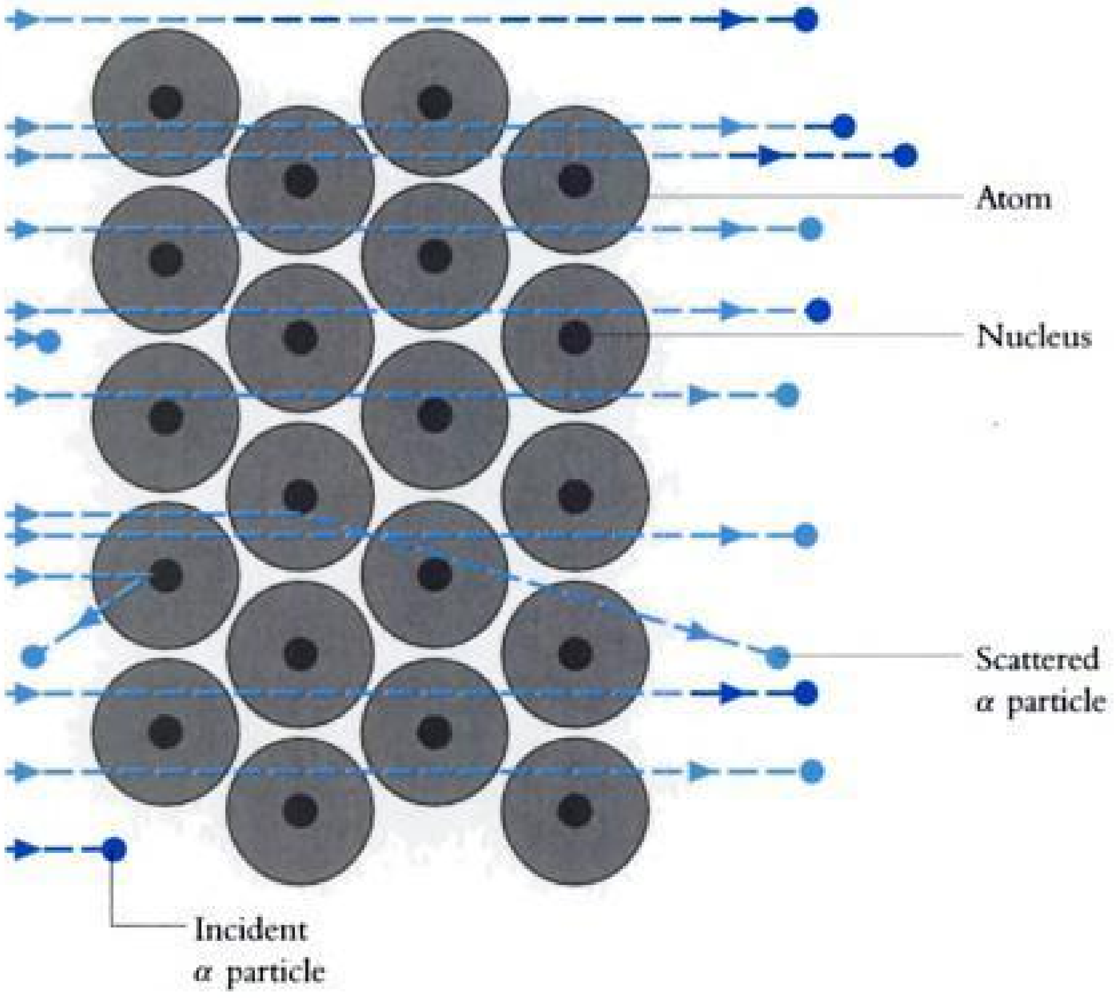


Figure 1.5B
Scattering of α particles by the nuclei of metal atoms

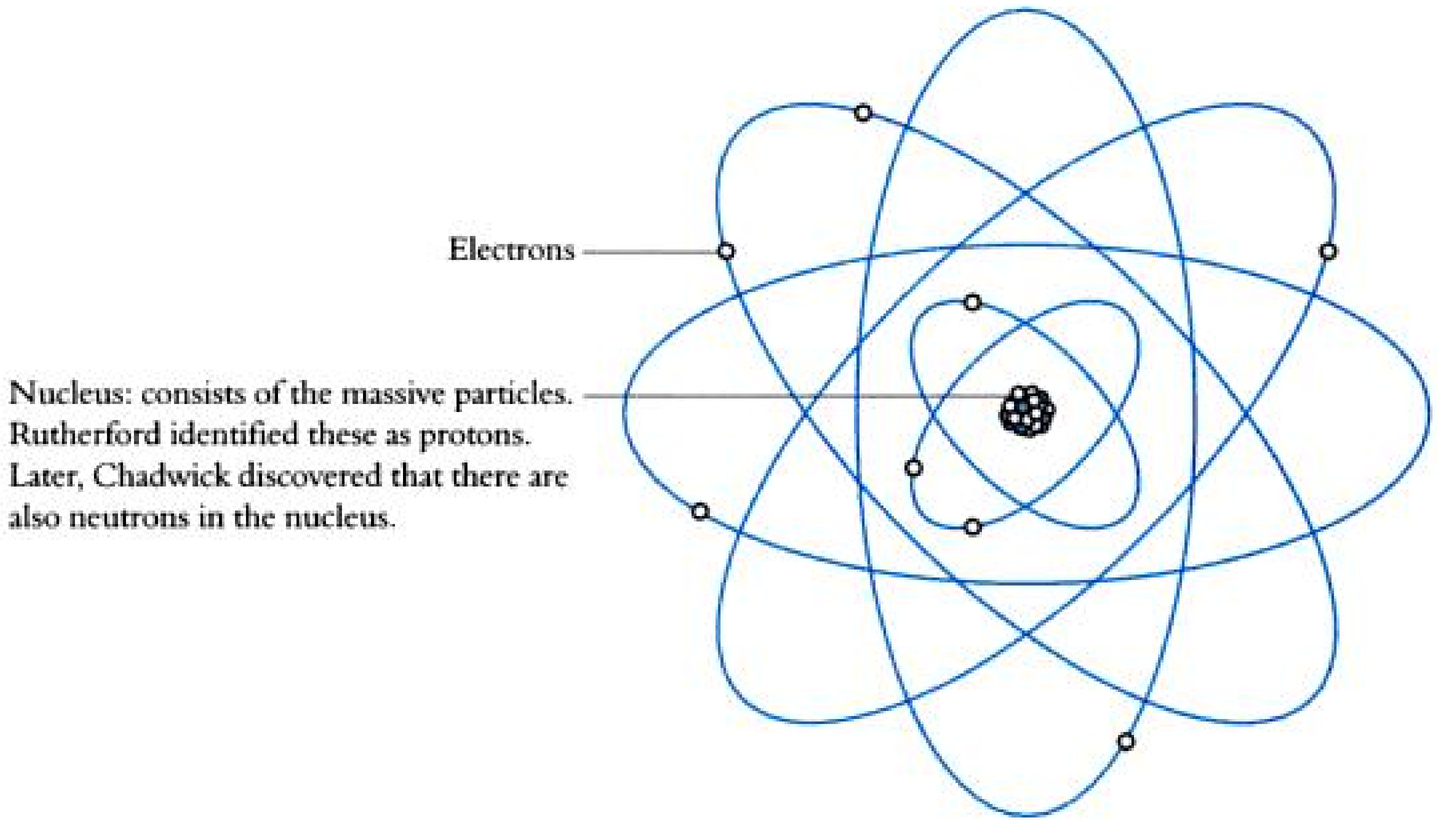


The mass of an atom is concentrated in its nucleus

Only the α particles which collide with the nuclei are deflected; the vast majority pass through the spaces in between the nuclei. The figure is not drawn to scale: a nucleus of the size shown here would belong to an atom the size of your classroom. An atom of diameter 10^{-10} m has a nucleus of diameter 10^{-15} m.

The model of the atom which Rutherford put forward in 1911 was like the solar system [see Figure 1.5C].

Figure 1.5C
The Rutherford atom



Rutherford's model of the atom

The electrons are present in the space surrounding the nucleus. The electrons inhabit a region with a radius one hundred thousand times greater than that of the nucleus. They occupy this space by repelling the electrons of neighbouring atoms. Since electrons are negatively charged, repulsion occurs between the like charges on two electrons if they come close enough together. If another atom approaches too closely, its electrons are repelled by the electrons of the first atom.

1.5.1 THE ARRANGEMENT OF ELECTRONS IN THE ATOM

The electrons are negatively charged; the nucleus is positively charged. What stops the electrons from being pulled into the nucleus by electrostatic attraction? The electrons are in constant motion. They move round and round the nucleus in circular paths called orbits [see Figure 1.5C]. It was suggested that the movement of electrons in orbits round the nucleus would prevent their being pulled in. However, according to the laws of classical physics, an electron moving in a circle round a positive nucleus would gradually lose energy and the electron would spiral into the nucleus. In this way, the Rutherford model of the atom was unsatisfactory. In § 2.3.1, you will see what solution was proposed for this problem.

1.6 THE NEUTRON

The atomic number is the number of protons in the nucleus which equals the number of electrons in the atom

Neutrons have mass but no charge

H G Moseley suggested in 1913 that the multiple charge on the nucleus arose from the presence of **protons**, which contribute the charge. Since atoms are uncharged, the number of electrons must be the same as the number of protons. Atomic masses are greater than the mass of the protons in the atom. To make up the extra mass, the existence of **neutrons** was postulated. These particles should have the same mass as a proton and zero charge. The search for the neutron began. Many years later it was a member of Rutherford's team, J Chadwick, who established the existence of the neutron in 1934.

1.7 THE FUNDAMENTAL PARTICLES

Proton number or atomic number

Nucleon number or mass number

The nucleus was thus shown to consist of protons and neutrons. The number of protons is called the **atomic number** or **proton number**. Protons and neutrons are both **nucleons**. The number of protons and neutrons is called the **nucleon number**, or, alternatively, the **mass number**.

Table 1.1
The mass and charge of sub-atomic particles

Particle	Charge/C	Relative charge	Mass/kg	Mass/u
Proton	$+1.6022 \times 10^{-19}$	+1	1.6726×10^{-27}	1.0073
Neutron	0	0	1.6750×10^{-27}	1.0087
Electron	-1.6022×10^{-19}	−1	9.1095×10^{-31}	5.4858×10^{-4}

1.8 NUCLIDES AND ISOTOPES

Notation for nuclides

The word **nuclide** is used to describe any atomic species of which the proton number and the nucleon number are specified. Nuclides are written as ${}^{\text{nucleon number}}_{\text{proton number}}\text{Symbol}$ (i.e. ${}^{\text{mass number}}_{\text{atomic number}}\text{Symbol}$). The species ${}^{12}_{6}\text{C}$ and ${}^{9}_{4}\text{Be}$ are nuclides. Protons are represented as ${}^{1}_{1}\text{H}$, neutrons as ${}^{1}_{0}\text{n}$, α particles as ${}^{4}_{2}\text{He}$ and electrons as ${}^{0}_{-1}\text{e}$.

Isotopes contain the same number of protons and different numbers of neutrons

When an element has a relative atomic mass [§ 3.4] which is not a whole number, it is because it consists of a mixture of **isotopes**. Isotopes are nuclides of the same element. They have the same atomic number but different mass numbers, i.e. they differ in the number of neutrons in the nucleus. Since chemical properties depend upon the nuclear charge and electronic structure of an atom, with mass having little effect, isotopes show the same chemical behaviour. The isotopes of chlorine, ${}^{35}_{17}\text{Cl}$ and ${}^{37}_{17}\text{Cl}$, have the same atomic number, 17. The difference between the mass numbers shows that one isotope has 18 neutrons and the other has 20 neutrons. The chemical reactions of the two isotopes are identical. Their names can be written as chlorine-35 and chlorine-37.

CHECKPOINT 1.8: ATOMS

1. State the number of protons, neutrons and electrons in the following atoms:

   (*a*) ${}^{39}_{19}\text{K}$ (*b*) ${}^{27}_{13}\text{Al}$ (*c*) ${}^{137}_{56}\text{Ba}$ (*d*) ${}^{226}_{88}\text{Ra}$

2. State the number of protons, neutrons and electrons in the following atoms:

   (*a*) ${}^{12}_{6}\text{C}$ (*b*) ${}^{14}_{6}\text{C}$ (*c*) ${}^{1}_{1}\text{H}$ (*d*) ${}^{2}_{1}\text{H}$ (*e*) ${}^{3}_{1}\text{H}$

   (*f*) ${}^{87}_{38}\text{Sr}$ (*g*) ${}^{90}_{38}\text{Sr}$ (*h*) ${}^{235}_{92}\text{U}$ (*i*) ${}^{238}_{92}\text{U}$

   What is the relationship between the different atoms of strontium?

3. 'Dalton was incorrect in saying that all the atoms of a particular element are identical.' Discuss this statement.

4. Why did Chadwick look for the neutron? Why was it hard to find?

1.9 MASS SPECTROMETRY

In mass spectrometry …

… ions are deflected in a magnetic field

Atomic masses are determined by **mass spectrometry**. In the mass spectrometer, atoms and molecules are converted into ions. The ions are separated as a result of the deflection which occurs in a magnetic field. Figure 1.9B shows how a mass spectrometer operates, and Figure 1.9A is a photograph of an instrument. Figure 1.9C shows a mass spectrometer trace for copper(II) nitrate.

Figure 1.9A
A mass spectrometer

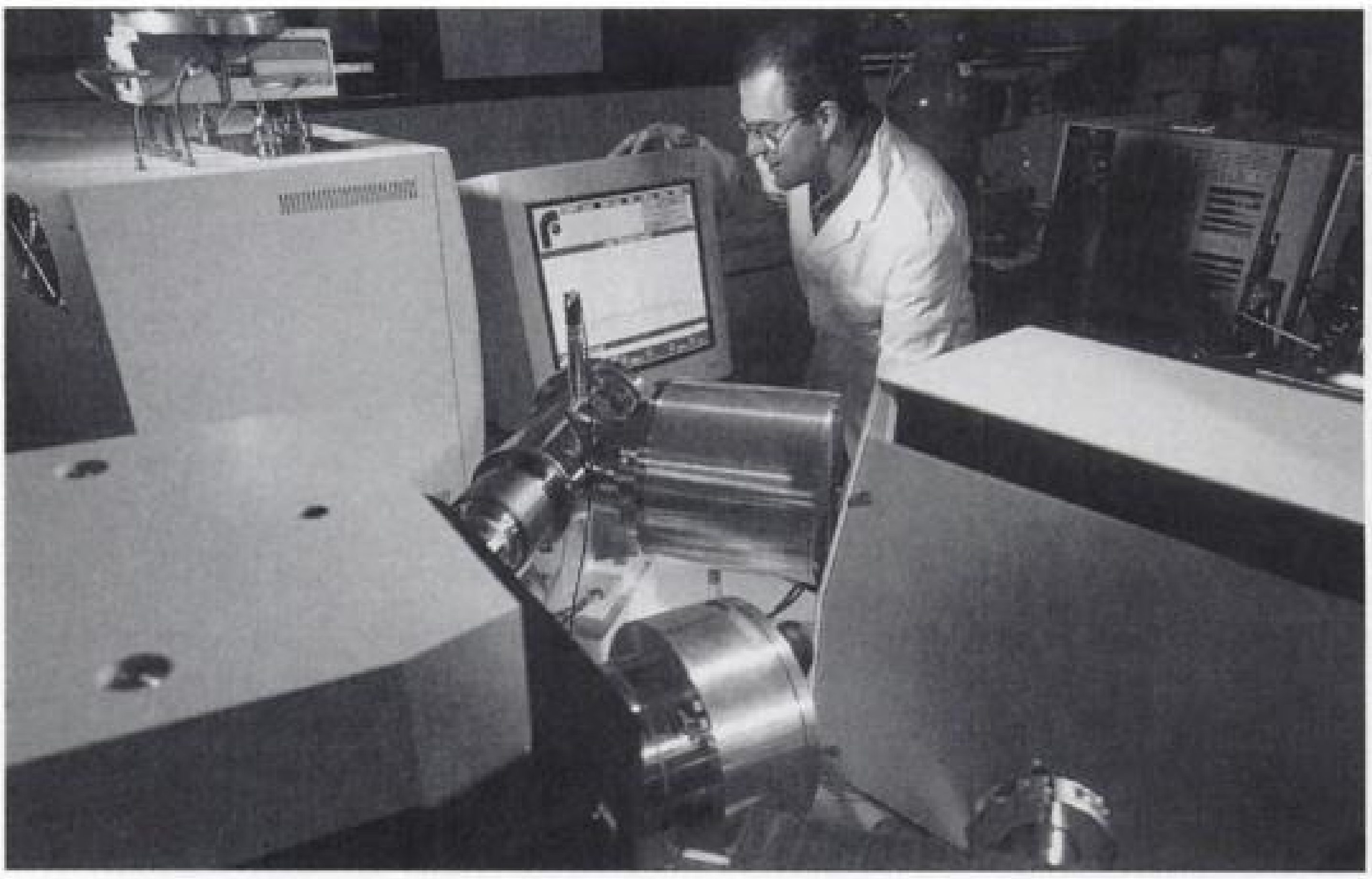
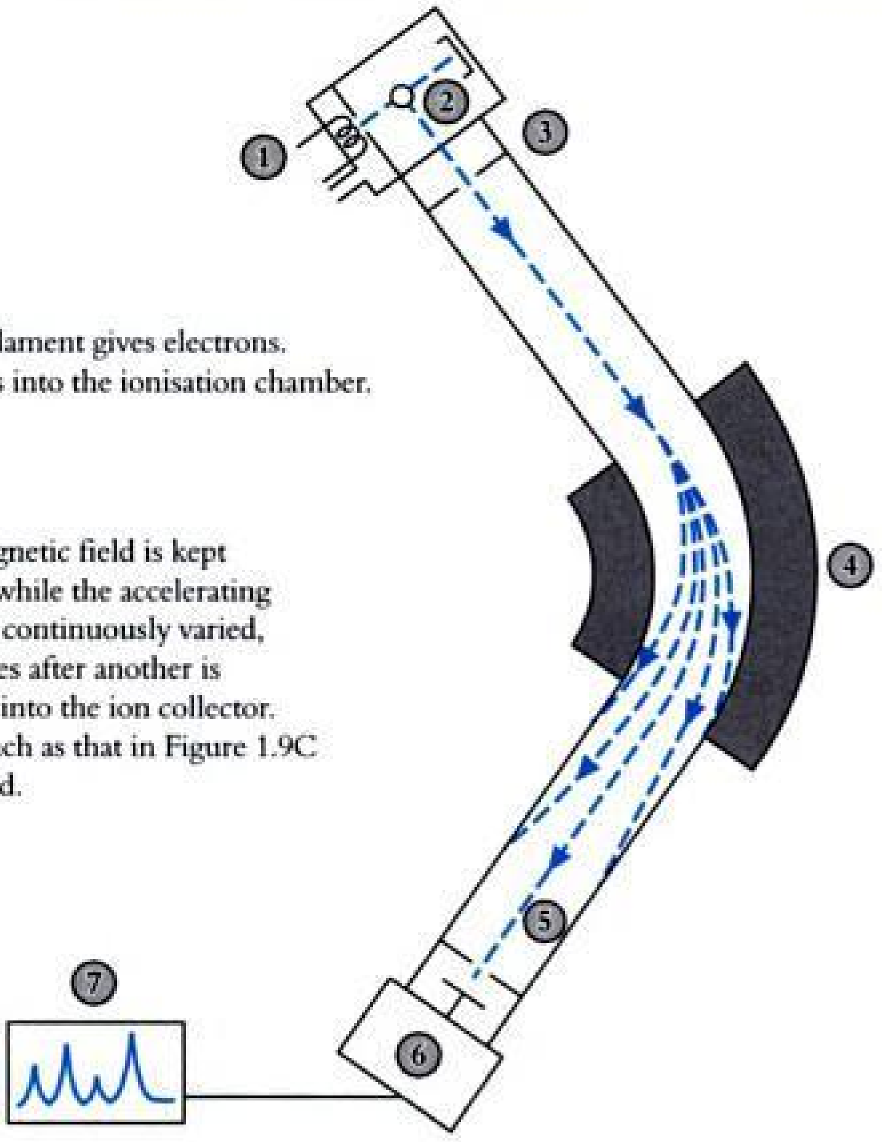


Figure 1.9B
A mass spectrometer: how it works



1 Heated filament gives electrons. They pass into the ionisation chamber.

2 The sample is injected as a gas into the ionisation chamber. Electrons collide with molecules of the sample and remove electrons to give positive ions. Some molecules break into fragments. The largest ion is the molecular ion.

3 To this plate, a negative potential is applied (above 8000 V). The electric field accelerates the positive ions.

4 An electromagnet produces a magnetic field. The field deflects the beam of ions into circular paths. Ions with a high ratio of mass/charge are deflected less than those with a low ratio of mass/charge.

5 These ions have the correct ratio of mass/charge to pass through the slit and arrive at the collector.

6 Amplifier. Here the charge received by the collector is turned into a sizeable electric current.

7 Recorder. The electric current operates a pen which traces a peak on a recording.

8 If the magnetic field is kept constant while the accelerating voltage is continuously varied, one species after another is deflected into the ion collector. A trace such as that in Figure 1.9C is obtained.

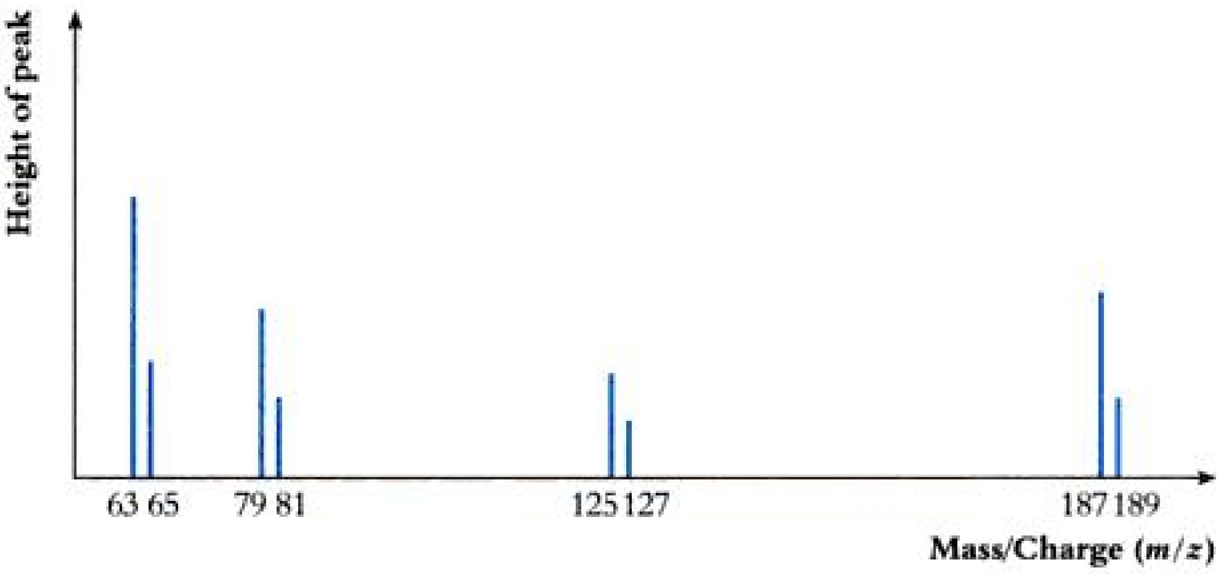
Notes

(1) The height of each peak measures the relative abundance of the ion which gives rise to that peak.

(2) The ratio of mass/charge for each species is found from the value of the accelerating voltage associated with a particular peak. Many ions have a charge of $+1$ **elementary charge unit**, and the ratio m/z is numerically equal to m, the mass of the ion (1 elementary charge unit = 1.60×10^{-19} C).

... deflection of ion depends on ratio m/z

Figure 1.9C
The mass spectrum of copper(II) nitrate



(*3*) The peaks on this trace correspond to the ions

$63 = {}^{63}Cu^+$, $65 = {}^{65}Cu^+$, $79 = {}^{63}CuO^+$, $81 = {}^{65}CuO^+$,
$125 = {}^{63}CuNO_3{}^+$, $127 = {}^{65}CuNO_3{}^+$, $187 = {}^{63}Cu(NO_3)_2{}^+$,
$189 = {}^{65}Cu(NO_3)_2{}^+$

1.9.1 USES OF MASS SPECTROMETRY

Determination of the relative atomic mass of an element

Mass spectrometry is used for the determination of relative atomic mass

Figure 1.9D shows the mass spectrum of neon.

The calculation of the average atomic mass of neon ...

The average atomic mass of neon is calculated as follows. Multiply the relative abundance (the height of the peak) by the mass number to find the total mass of each isotope present:

Mass of ^{22}Ne = 11.2 × 22.0 = 246.4 u
Mass of ^{21}Ne = 0.2 × 21.0 = 4.2 u
Mass of ^{20}Ne = 114 × 20.0 = 2280.0 u
Total = 125.4 = 2530.6 u
Average mass of Ne = 2530.6/125.4 u
= 20.18 u

... and the relative atomic mass

The average atomic mass of neon is 20.2 u, and the relative atomic mass is 20.2.

Determination of the relative molecular mass of a compound

Mass spectrometry also gives the relative molecular masses of compounds ...

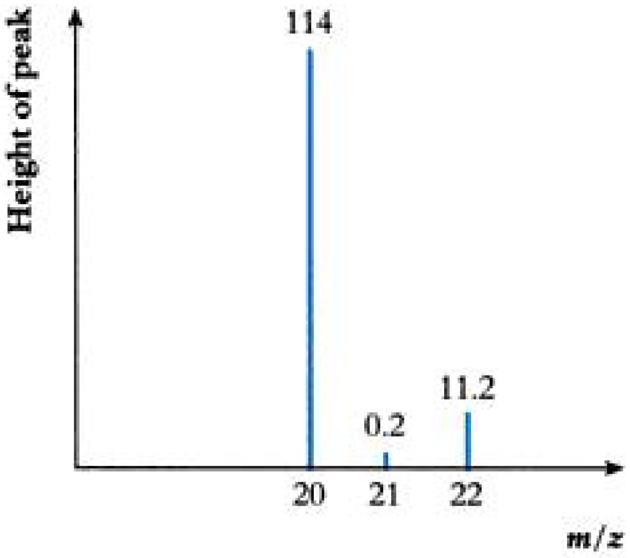
The ion with the highest value of m/z is the molecular ion, and its mass gives the molecular mass of the compound. If isotopes are present, the average molecular mass and the relative molecular mass are found as in the neon example. Some large molecules (e.g. polymers) are fragmented, and do not give molecular ions.

Identification of compounds

... and can be used for the identification of compounds ...

A mass spectrum is obtained, and information about the peak heights and m/z values is fed into a computer. The computer compares the spectrum of the unknown compound with those in its data bank, and thus identifies the compound.

Figure 1.9D
The mass spectrum of neon



Forensic science

... and in forensic science where it is useful as a small sample is enough to give results – see also § 35.9.4

The sensitivity of the mass spectrometer makes it an admirable tool for forensic scientists. The size of sample which they receive for analysis is often very small. A mass spectrum can be obtained on as little as 10^{-12} g. Small amounts of drugs can be identified by mass spectrometry. A fibre left at the scene of a crime can be compared by mass spectrometry with a fibre from a suspect's clothing.

CHECKPOINT 1.9: MASS SPECTROMETRY

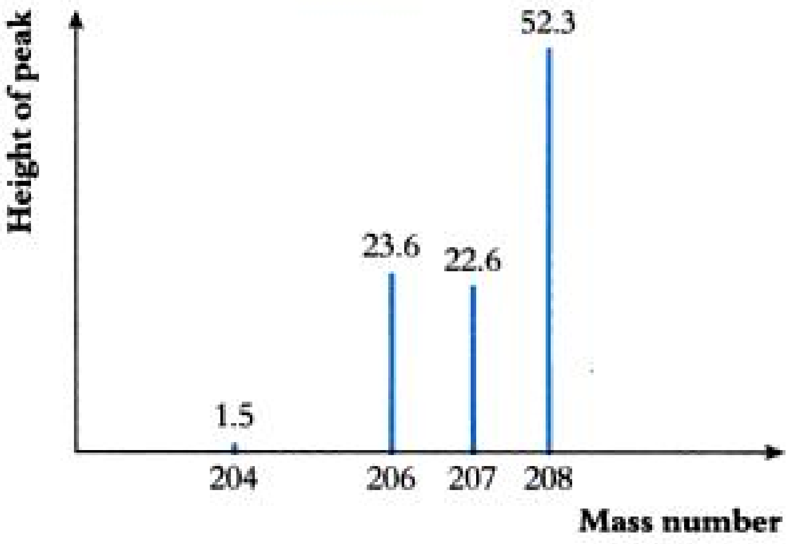
1. Describe how, in a mass spectometer, ions are *(a)* formed, *(b)* accelerated, *(c)* separated and *(d)* detected.

2. Define the terms mass number, isotope, relative atomic mass.
Chlorine has two isotopes of relative atomic masses 34.97 and 36.96 and relative abundance 75.77% and 24.23% respectively.
Calculate the mean relative atomic mass of naturally occurring chlorine.

3. The mass spectrum of dichloromethane shows peaks at 84, 86 and 88. The intensities of the lines at 84, 86 and 88 u are in the ratio 9 : 6 : 1. What species give rise to these lines? How do you account for the relative intensities of the lines?

4. Figure 1.9E shows the mass spectrum of lead. The heights of the peaks and the mass numbers of the isotopes are shown on the figure. Calculate the average atomic mass of lead.

Figure 1.9E
The mass spectrum of lead



1.10 NUCLEAR REACTIONS

In nuclear reactions new elements are formed

A nuclear reaction is different from a chemical reaction. In a chemical reaction, the atoms which make up the reactants enter into different combinations to form the products, but the nuclei of the atoms are unchanged. In a nuclear reaction, a rearrangement of the protons and neutrons in the nucleus of the atom takes place, and new elements are formed.

1.10.1 RADIOACTIVITY

Discovery

Becquerel discovered a new type of radiation

In 1896, a French physicist called A H Becquerel was experimenting on salts which fluoresced (glowed in the dark). One day he developed a photographic plate which had been left wrapped in a drawer and found to his surprise that the plate had been exposed. He knew that no light could penetrate the wrapping, so Becquerel concluded that the uranium salts in the drawer were to blame. Perhaps the plate had been fogged by some rays coming from the uranium salt. However, there was no known type of radiation that had this effect. Becquerel's instinct told him that it would be worth while investigating this mysterious radiation. He gave the problem to a young research worker called Marie Curie.

Marie Curie found that the radiation was a property of uranium atoms, which she named radioactivity

Marie Curie soon found that the strange effect happened with all uranium salts. It depended on the amount of uranium present but not on the type of compound. She realised that the ability to give off the radiation must be a property of the *atoms* of uranium, and was independent of any chemical bonds which they formed. She realised that this was a completely new type of property, quite different from a chemical reaction. Marie Curie called this property of the uranium atom **radioactivity**.

Marie's husband, Pierre, left his own research work to help her with her exciting new discovery of radioactivity. In 1898 they discovered two new radioactive elements. They called one **polonium** after Marie's native country, Poland. The other element they named **radium**, meaning 'giver of rays'.

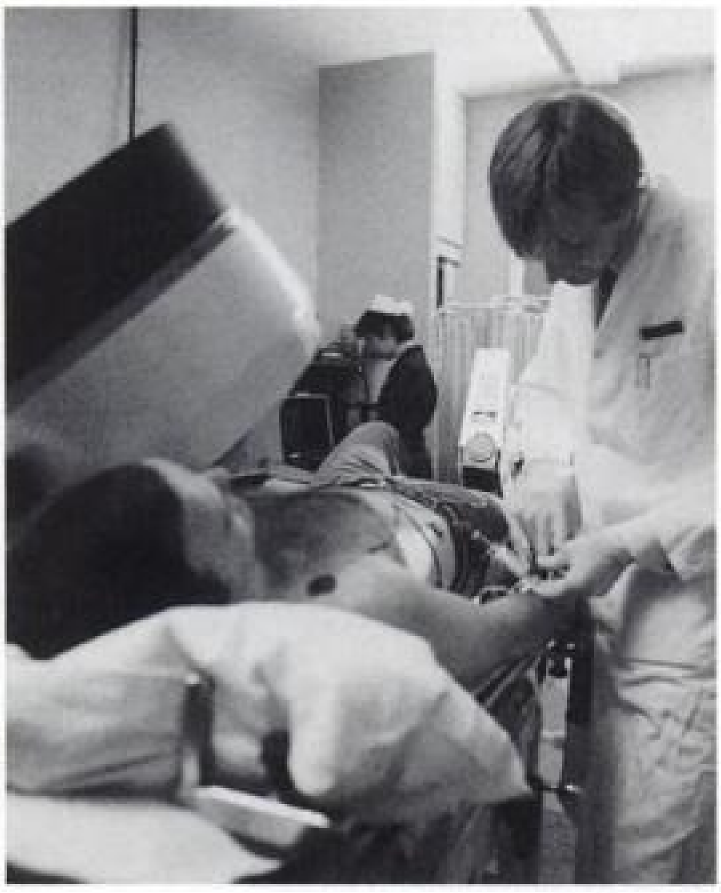
Madame Curie is often praised for the arduous work she did in isolating a small quantity of radium from a tonne of the uranium ore **pitchblende**. The work involved back-breaking handling of the ore, crushing it and stirring it with reagents to remove the large mass of unwanted substances. Her real claim to fame, however, is the insight she showed in realising that she was dealing with a new phenomenon which was completely uncharted in either physics or chemistry.

Figure 1.10A
Marie Curie in her laboratory

... in medicine ...

5. **Tracer studies** use radioactive isotopes to track the path of an element through the body. Radioactive iodine (iodine-131) is administered to patients with defective thyroids to enable doctors to follow the path of iodine through the body. As the half-life is only 8 days, the radioactivity soon falls to a low level. [See Figure 1.10D.]

Figure 1.10D
Medical uses of radioisotopes. Injection of a short half-life radioactive isotope and a miniature nuclear battery for a heart pacemaker



6. Mechanistic studies sometimes employ radioisotopes. The path of a labelled atom in a molecule can be followed through a sequence of reactions [see esterification, § 33.8.2].

... and in studies of reaction mechanism

7. People who work with radioactive materials take precautions to ensure that they do not receive a high dose of radiation. A radioactive source is surrounded by a wall of lead bricks, except for an outlet through which a beam of radiation can emerge. To handle a powerful source of radiation, people use long-handled tongs. Since radioactivity fogs photographic film, workers exposed to radioactivity wear badges containing film, which is examined periodically so that the dose of radiation they are receiving can be monitored.

CHECKPOINT 1.10: NUCLEAR REACTIONS

1. Write the symbols for the isotopes of chlorine (proton number 17, nucleon numbers 35 and 37).
2. If 8 g of a radioactive isotope decay in a year to 4 g, will 6 g of the same isotope decay to 2 g in the same time? Explain your answer.
3. Supply the missing proton numbers and nucleon numbers:

(a) $^{14}_{6}\mathrm{C} \longrightarrow \mathrm{N} + {}^{0}_{-1}\mathrm{e}$

(b) $^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \longrightarrow \mathrm{O} + {}^{1}_{1}\mathrm{H}$

(c) ${}_{88}\mathrm{Ra} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{222}\mathrm{Rn}$

(d) ${}^{73}\mathrm{As} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}_{32}\mathrm{Ge}$

(e) ${}^{24}_{12}\mathrm{Mg} + {}^{4}_{2}\mathrm{He} \longrightarrow \mathrm{Si} + {}^{1}_{0}\mathrm{n}$

(f) ${}^{19}_{9}\mathrm{F} + \longrightarrow {}^{16}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He}$

*1.10.6 NUCLEAR FISSION

The mass of the nucleus is less than the sum of the nucleon masses ...

The mass of a nucleus is slightly less than the sum of the masses of the protons and neutrons of which it is composed. The difference in mass is transformed into the **binding energy** of the nucleus. The connection between mass and energy is given in Einstein's equation

$$E = mc^2$$

The mass defect is the source of the binding energy of the nucleus

where E = energy released, m = loss in mass, and c = velocity of light. Since the constant c^2 has a large numerical value, even a very small loss in mass is equivalent to the loss (or release) of a large amount of energy. This is the origin of the substantial quantity of energy released in the **fission** of atomic nuclei.

The first person to obtain energy from **'splitting the atom'** was O Hahn, in 1937. He bombarded uranium-235 with neutrons. Atoms of ^{235}U split into two smaller atoms and two neutrons, with the release of energy:

Splitting the atom of $^{235}_{92}U$

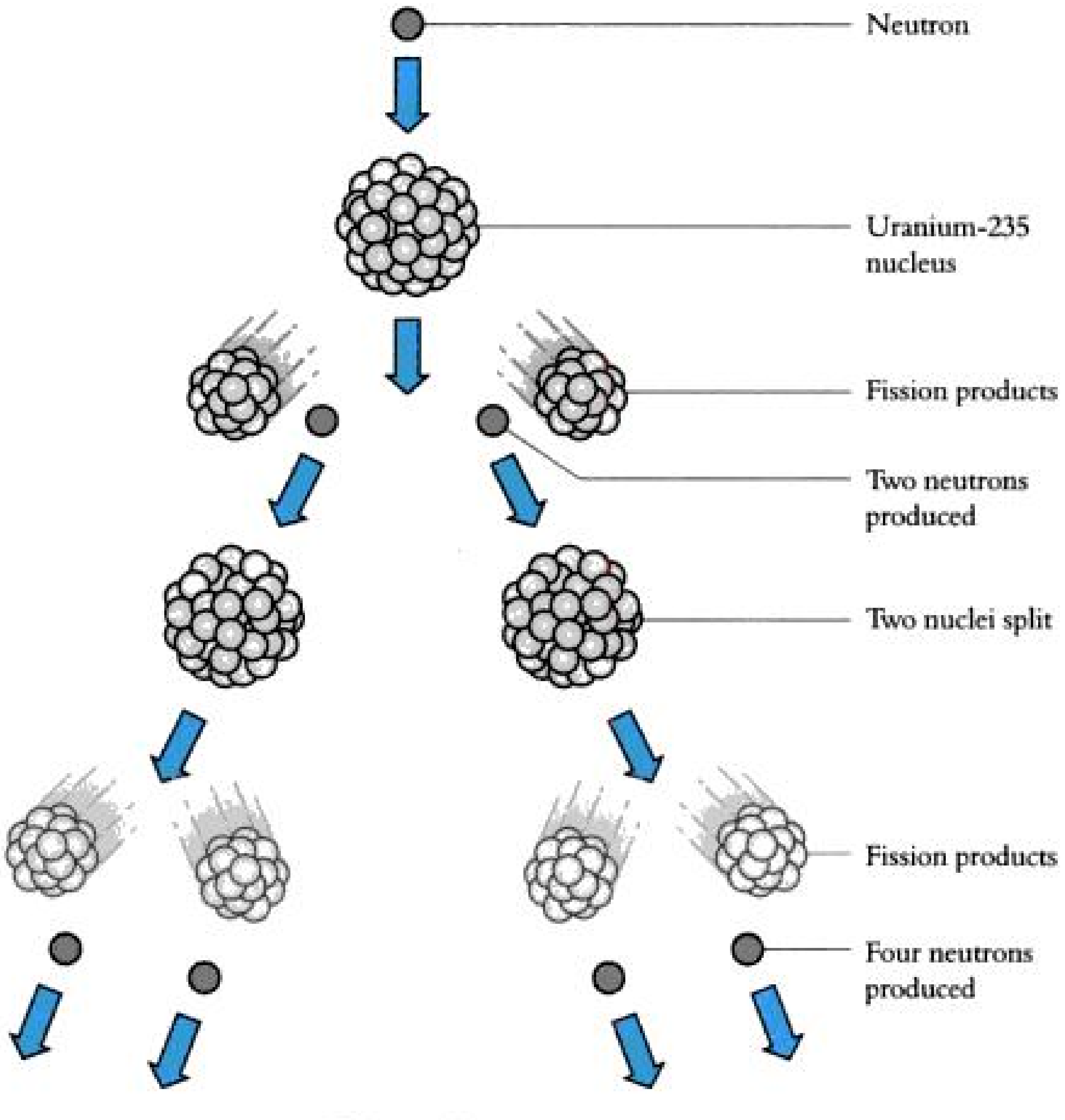
$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{144}_{56}\mathrm{Ba} + {}^{90}_{36}\mathrm{Kr} + 2{}^{1}_{0}\mathrm{n}$$

Mass is converted into energy

The sum of the masses of the fission products is less than the mass of the $^{235}_{92}U$ atom

If the sample of uranium-235 is smaller than a certain size, called the **critical mass**, neutrons will escape from the surface. In a large block of uranium-235, neutrons are more likely to meet uranium-235 atoms and produce fission than to escape. Since each nuclear fission produces two neutrons, as shown in Figure 1.10E, a chain reaction is set up. Each time an atom of uranium-235 is split, the mass of the atoms produced is 0.2 u less than the mass of an atom of $^{235}_{92}U$. The lost mass is converted into energy. This is where the energy of the atomic bomb comes from. The atomic bomb consists of two blocks of uranium-235, each smaller than the critical mass. On detonating the bomb, one mass is fired into the other to make a single block larger than the critical mass. The detonation is followed by an **atomic explosion**.

Figure 1.10E
The chain reaction in fission of uranium-235



Atomic bombs

The only time atomic bombs have been used in warfare was when two cities in Japan, Hiroshima and Nagasaki, were destroyed in 1945. The death and destruction which followed were on such a terrible scale that nations fighting subsequent wars have avoided using atomic weapons.

In a nuclear reactor ...

... the release of nuclear energy is controlled ...

... boron is used to absorb neutrons

Energy from **nuclear reactors** is obtained by fission of ^{235}U, carried out in a controlled way. The method of controlling the rate of fission to avoid an atomic explosion is to insert rods of boron, an element which is a very good neutron-absorber, into the reactor. If the fission process speeds up, the rods are pushed further into the reactor; if the chain reaction slows down, the rods are pulled out to allow the number of neutrons to increase and speed up the reaction.

QUESTIONS ON CHAPTER 1

1. Explain how a mass spectrometer is used to measure molecular mass.

2. The mass spectrum of C_2H_5Cl shows peaks corresponding to ^{1}H, ^{2}H, ^{12}C, ^{13}C, ^{35}Cl and ^{37}Cl. Calculate the mass numbers of the most abundant molecular ion and the heaviest molecular ion. Write the formulae of all the possible ions that contribute to the peak at a mass number of 66.

3. Imagine you have a mixture of hydrogen-1, hydrogen-2 and hydrogen-3, (hydrogen, deuterium and tritium) present as diatomic molecules and that the numbers of atoms of the three species are the same. Sketch the mass spectrum.

4. In 1909, Geiger and Marsden reported the amazing results of their experiments on α particles and thin metal foils.

(a) What is an α particle?
(b) Why did most α particles pass through the foils?
(c) Why were some α particles scattered backwards?
(d) What did they infer from their results about the structure of metal atoms?

5. When chlorine is bubbled through a concentrated aqueous solution of ammonium chloride, a yellow oily liquid, nitrogen trichloride, NCl_3, is formed, together with a solution of hydrochloric acid. Apart from peaks associated with solitary nitrogen atoms (at $m/z = 14$) and chlorine atoms (at $m/z = 35$ and $m/z = 37$), the mass spectrum of nitrogen trichloride contains 9 peaks arranged in 3 groups, ranging from $m/z = 49$ to $m/z = 125$. Predict the m/z values of all 9 peaks, and suggest a formula for the species responsible for each one.

***6.** A series of radioactive decays can be represented

$${}^{232}_{90}\mathrm{Th} \xrightarrow{\alpha\text{ emission}} \mathbf{X} \xrightarrow{\beta\text{ emission}} \mathbf{Y} \xrightarrow{\beta\text{ emission}} \mathbf{Z}$$

State the mass number and atomic number of the element **Z**.

***7.** Identify the emitted particles (1) and (2), and state in which groups of the Periodic Table the elements Pb, **X**, **Y** and **Z** occur.

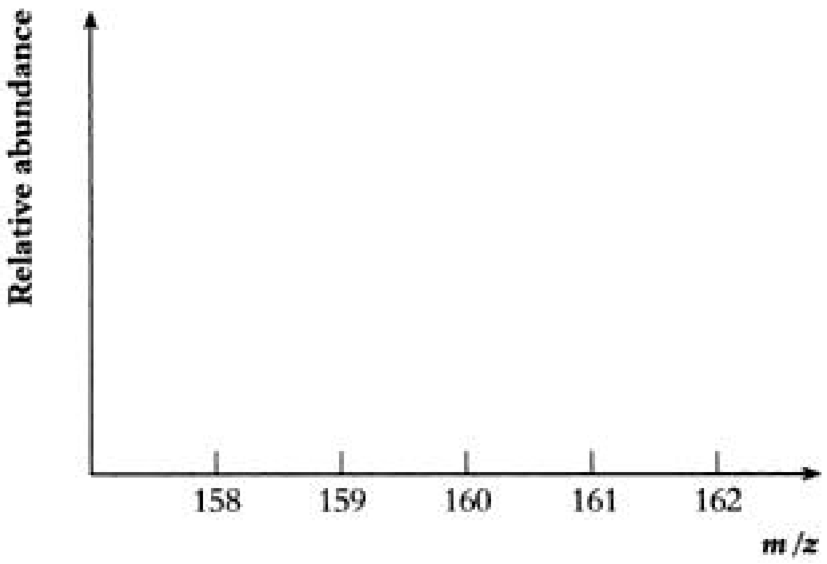
$${}^{212}_{82}\mathrm{Pb} \xrightarrow{(1)} {}^{212}_{83}\mathbf{X} \xrightarrow{(2)} {}^{208}_{81}\mathbf{Y} \xrightarrow{\beta\text{ particle}} \mathbf{Z}$$

***8.** Give values for *a*, *b*, *c* and *d*, and the symbols for **X** and **Y** in the equations

(a) ${}^{35}_{17}\mathrm{Cl} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{a}_{b}\mathbf{X} + {}^{1}_{1}\mathrm{H}$
(b) ${}^{7}_{3}\mathrm{Li} + {}^{2}_{1}\mathrm{H} \longrightarrow 2\,{}^{c}_{d}\mathbf{Y} + {}^{1}_{0}\mathrm{n}$

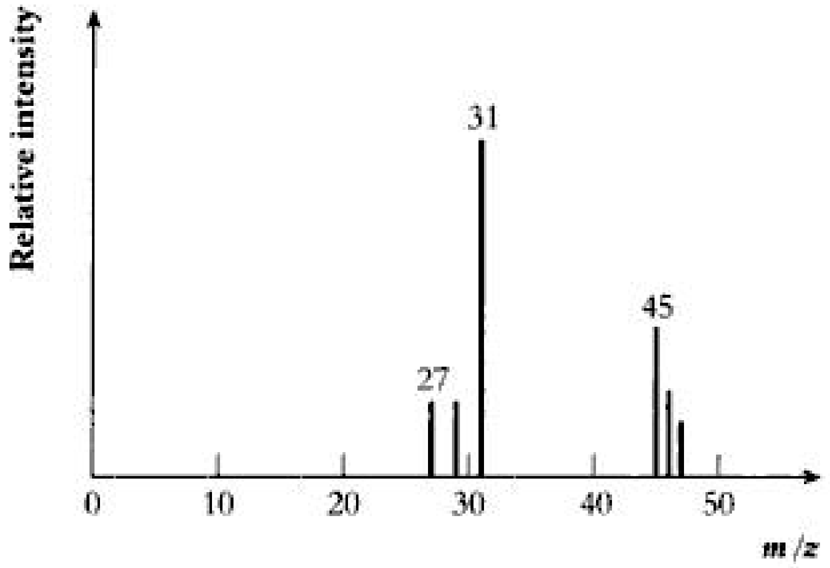
9. Bromine consists of two isotopes, ^{79}Br (relative abundance 50.5%) and ^{81}Br (relative abundance 49.5%).

(a) Calculate the relative atomic mass to three significant figures.
(b) Copy the figure shown below and sketch on it the peaks you would expect in the mass spectrum of bromine vapour.



10. The figure below shows a simplified version of the mass spectrum of ethanol, C_2H_5OH. Explain the origin of the six peaks.

Note An asterisk means that the topic is not included in **all** the examination specifications.

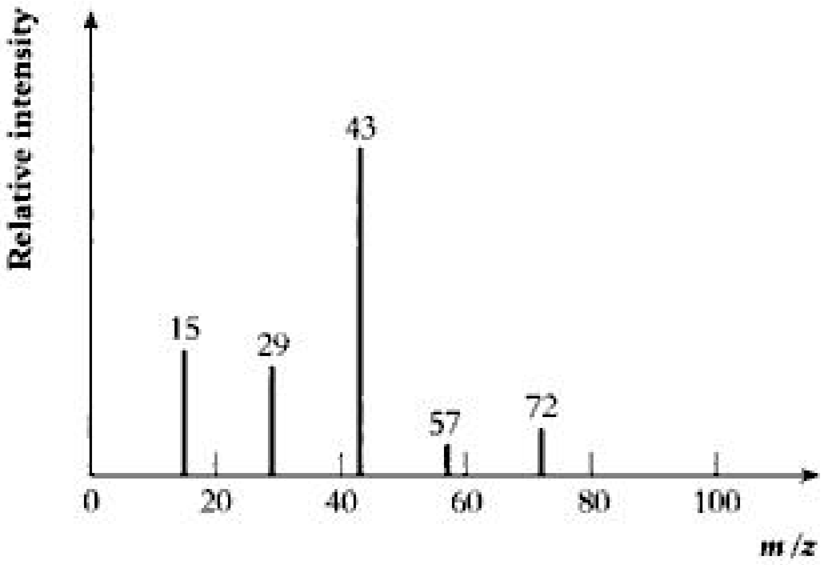


11. A sample of carbon dioxide was prepared from carbon (^{12}C) and oxygen enriched with oxygen-18 and containing $^{16}O_2$ and $^{18}O_2$ in the molar ratio 4 : 1. The mass spectrum of the carbon dioxide contained three peaks, each due to a singly charged molecular ion. What are the relative molecular masses of the three species? Deduce the relative intensities of the three peaks.

12. An organic compound has the composition by mass C 66.7%, H 11.1%, O 22.2%. Its mass spectrum is shown below. The compound is obtained by the oxidation of an alcohol so it is thought to be an aldehyde (with a —CHO group) or a ketone (with a >C=O group).

(a) Calculate the empirical formula of the compound.

(b) Interpret the peaks of the mass spectrum to give the molecular formula of the compound.



13. *(a)* How is the mass spectrum of an element produced? In your answer explain how the following processes are involved:
- (i) ionisation,
- (ii) acceleration,
- (iii) deflection,
- (iv) detection. **12**

(b) The mass spectrum of a sample of magnesium contains three peaks with mass/charge ratios and relative intensities shown below.
- (i) Explain why magnesium gives three peaks in its mass spectrum.

m/z	24	25	26
Relative intensity	1	0.127	0.139

- (ii) Use the information in the table to calculate an accurate value for the relative atomic mass of magnesium **6**

18 *NEAB (AS/AL)*

14. *(a)* State the meaning of the term *mass number* of an isotope. **1**

(b) Define the term *relative atomic mass* of an element. **2**

(c) A mass spectrometer measures the relative abundance of ions with different values of *m/z*. Explain the meaning of the symbols *m* and *z*. **2**

(d) A sample of nickel was analysed in a mass spectrometer. Three peaks were observed with the properties shown in the following table

Relative abundance/%	69	27	4
m/z	58	60	62

- (i) Give the symbol, including the mass number and the atomic number, for the ion which was responsible for the peak with *m/z* = 58.
- (ii) Calculate the relative atomic mass of this sample of nickel. **4**

(e) Complete the electronic configurations for Ni and Ni^{2+}:

Ni [Ar] ..., Ni^{2+} [Ar] ... **2**

11 *NEAB (AS/AL)*

15. The table below shows some accurate relative atomic masses.

Atom	^{1}H	^{12}C	^{6}Li
Relative atomic mass	1.0078	12.0000	6.0149

(a) Why is ^{12}C the only atom with a relative atomic mass which is an exact whole number? **1**

(b) Calculate the mass of 1 mol of $^{1}H^{+}$ ions. The mass of a single electron is 9.1091×10^{-28} g. (Avogadro's number, *L*, is 6.0225×10^{23}) **2**

(c) (i) Explain briefly the process by which a sample is ionised in a mass spectrometer.
- (ii) Give **one** reason why it is important to use the minimum possible energy to ionise a sample in a mass spectrometer.
- (iii) After ionisation and before deflection, what happens to the ions in a mass spectrometer; how is this achieved? **5**

(d) Why is it a good approximation to consider that the relative atomic mass of the $^{6}Li^{+}$ ion, determined in a mass spectrometer, is the same as that of ^{6}Li? **1**

9 *NEAB (AS/AL)*

16. *(a)* A proton, a neutron and an electron all travelling at the same velocity enter a magnetic field. State which particle is deflected the most and explain your answer. **2**

(b) Give two reasons why particles must be ionised before being analysed in a mass spectrometer. **2**

(c) A sample of boron with a relative atomic mass of 10.8 gives a mass spectrum with two peaks, one at $m/z = 10$ and one at $m/z = 11$. Calculate the ratio of the heights of the two peaks. **2**

(d) Compound **X** contains only boron and hydrogen. The percentage by mass of boron in **X** is 81.2%. In the mass spectrum of **X** the peak at the largest value of m/z occurs at 54.

(i) Use the percentage by mass data to calculate the empirical formula of **X**.

(ii) Deduce the molecular formula of **X**. **4**

10 *NEAB (AS/AL)*

17. *(a)* Complete the following equations for nuclear reactions:

(i) $^{226}_{88}\text{Ra} \longrightarrow {}^{4}_{2}\text{He} +$

(ii) $^{14}_{6}\text{C} \longrightarrow {}^{0}_{-1}\beta +$

(iii) $^{60}_{27}\text{Co} \longrightarrow {}^{0}_{-1}\beta +$ **3**

(b) (i) Suggest a medical application for any named isotope of your own choice. **2**

(ii) Why is the knowledge of the half-life of this isotope essential to its application? **1**

(c) Write equations for a decay scheme whereby $^{241}_{95}$Am could emit three particles and become an isotope of americium. **3**

(d) Mass spectrometry can be used to determine isotopic abundances in elements, and fragmentation patterns which are useful in structure determination of organic molecules.

(i) The mass spectrum of magnesium gives peaks at m/e 24 (78.99%), 25 (10.00%) and 26 (11.01%). Calculate the relative atomic mass of naturally-occurring magnesium. Give your answer to 4 significant figures. **2**

(ii) The compounds propanone, CH_3COCH_3, and propanal CH_3CH_2CHO, both have the molecular formula C_3H_6O. The mass spectrum of propanone shows large peaks at m/e 15 and 43, amongst others. Suggest the identity of the species producing these peaks. **2**

(iii) A compound known to have the molecular formula C_3H_6O gives, in its mass spectrum, a large peak at m/e 29. Suggest the identity of a species which could give this peak, and hence identify the compound. **2**

15 *L (AS/AL)*

18. *(a)* State the meaning of the term ***atomic number***. **1**

(b) What is the function of the electron gun and the magnet in a mass spectrometer? **2**

(c) The mass spectrum of a pure sample of a noble gas has peaks at the following m/z values.

m/z	10	11	20	22
Relative intensity	2.0	0.2	17.8	1.7

(i) Give the complete symbol, including mass number and atomic number for one isotope of this noble gas.

(ii) Give the species which is responsible for the peak at $m/z = 11$.

(iii) Use appropriate values from the data above to calculate the relative atomic mass of this sample of noble gas. **6**

9 *NEAB (AS/AL)*

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Through a spectrometer, the hydrogen emission spectrum is seen to consist of series of lines

Viewed through a spectrometer, the emission spectrum of hydrogen is seen to be a number of separate sets of lines or **series** of lines. These series of lines are named after their discoverers, as shown in Figure 2.2C. The Balmer series, in the visible part of the spectrum, is shown in Figure 2.2D.

Figure 2.2C
The hydrogen spectrum

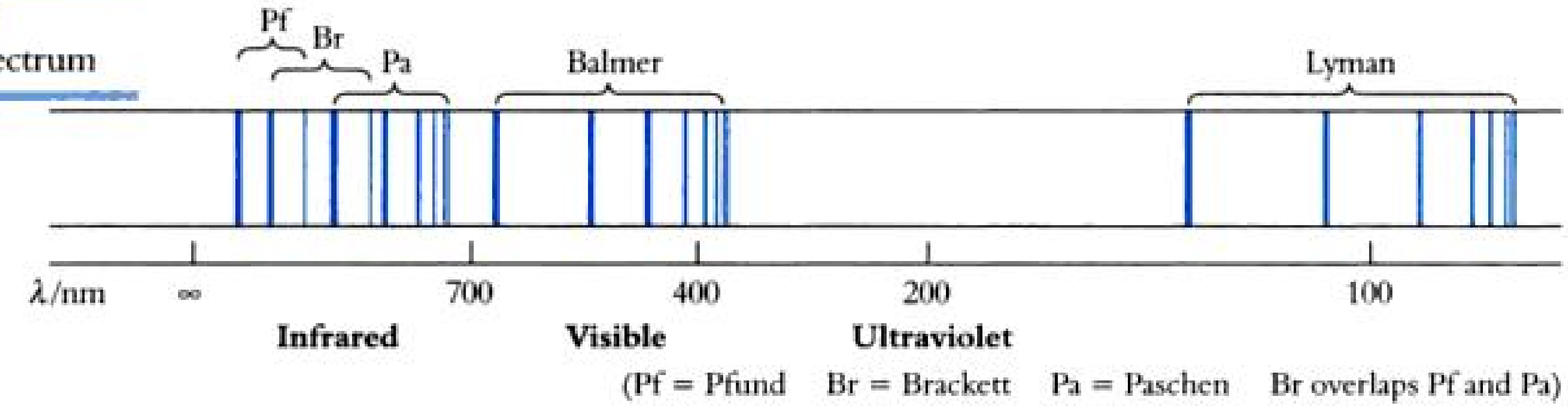
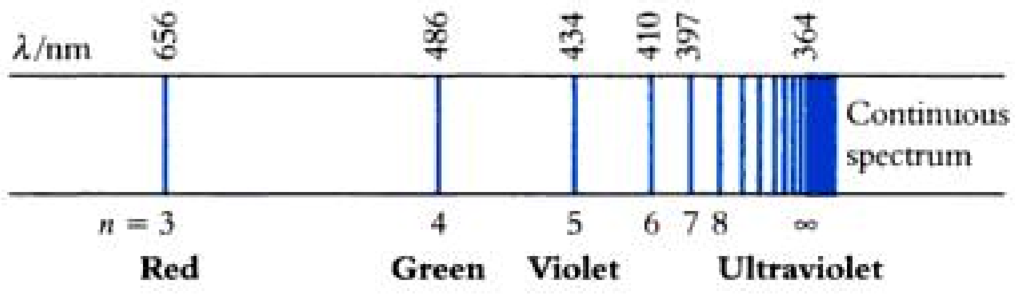


Figure 2.2D
The Balmer series of hydrogen



In each series, the lines become closer together as the frequency increases until at high frequency the lines coalesce

In each series, the intervals between the frequencies of the lines become smaller and smaller towards the high frequency end of the spectrum until the lines run together or **converge** to form a **continuum** of light.

The Rutherford model of the atom does not explain spectral lines

Why do atomic spectra consist of **discrete** (separate) lines? Why do atoms absorb or emit light of certain frequencies? Why do the spectral lines converge to form a continuum? The Rutherford picture of the atom offers no explanation.

2.3 ELECTRONS IN ORBITS

2.3.1 THE BOHR MODEL

Planck theorised that energy is quantised. Bohr suggested that electrons can have only certain amounts of energy ...

In 1913, Niels Bohr (1885–1962) put forward his picture of the atom to answer these questions. Bohr referred to Max Planck's recently developed **quantum theory**, according to which energy can be absorbed or emitted in certain amounts, like separate packets of energy, called **quanta**. Bohr suggested:

1. An electron moving in an orbit can have only certain amounts of energy, not an infinite number of values: its energy is **quantised**.

... and their orbits can have only certain radii

2. The energy that an electron needs in order to move in a particular orbit depends on the radius of the orbit. An electron in an orbit distant from the nucleus requires higher energy than an electron in an orbit near the nucleus.
3. If the energy of the electron is quantised, the radius of the orbit also must be quantised. There is a restricted number of orbits with certain radii, not an infinite number of orbits.

Electrons which absorb photons move to higher orbits

4. An electron moving in one of these orbits does not emit energy. In order to move to an orbit farther away from the nucleus, the electron must absorb energy to do work against the attraction of the nucleus. If an atom absorbs a **photon** (a quantum of light energy), it can promote an electron from an inner orbit to an outer orbit. If sufficient photons are absorbed, a black line appears in the absorption spectrum.

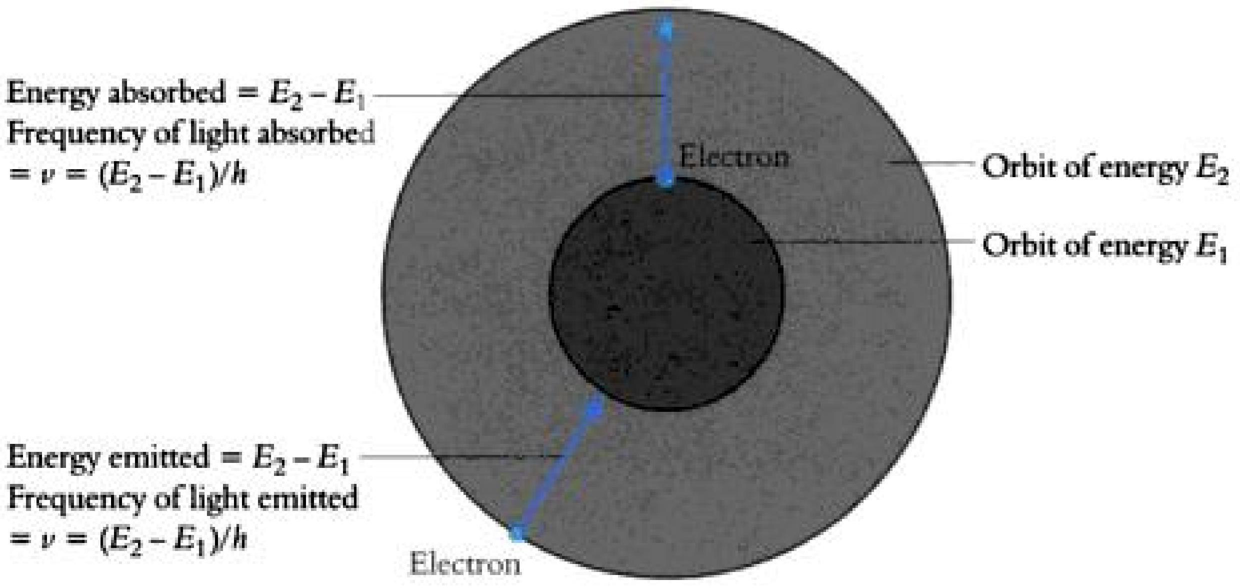
Electrons which fall to lower orbits emit photons of light ...

For an electron to move from an orbit of energy E_1 to one of energy E_2, the light absorbed must have a frequency given by **Planck's equation**:

$$h\nu = E_2 - E_1 \qquad \text{where } \nu = \text{frequency}, \quad h = \text{Planck's constant}$$

The emission spectrum arises when electrons which have been excited (raised to orbits of high energy) drop back to orbits of lower energy. They emit energy as light with a frequency given by Planck's equation [see Figure 2.3A].

Figure 2.3A
The origin of spectral lines

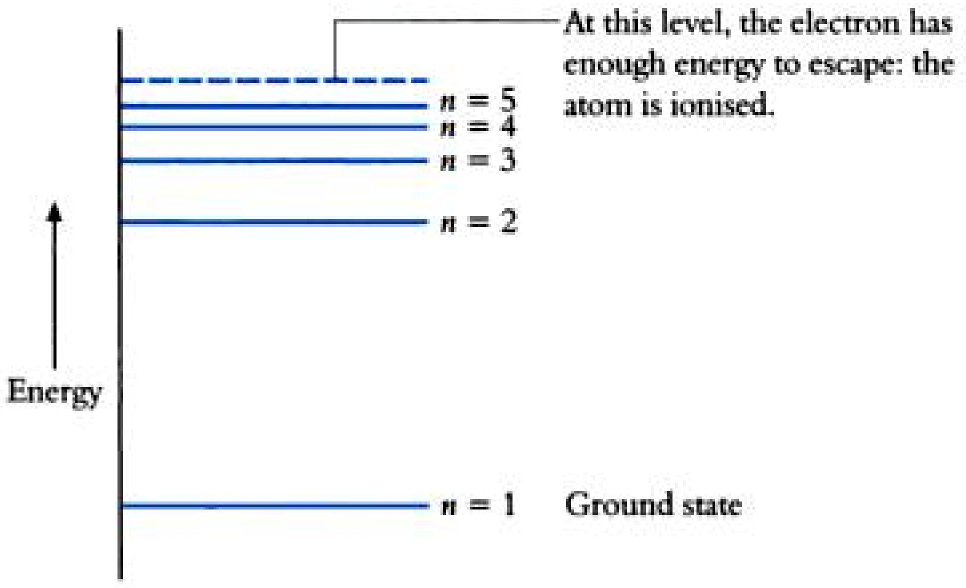


Planck's equation gives the frequencies of light emitted

Bohr gave orbits of different energy different quantum numbers

Bohr assigned **quantum numbers** to the orbits. He gave the orbit of lowest energy (nearest to the nucleus) the quantum number 1. An electron in this orbit is in its **ground state**. The next energy level has quantum number 2 and so on [see Figure 2.3B]. If the electron receives enough energy to remove it from the attraction of the nucleus completely, the atom is **ionised**.

Figure 2.3B
The energy levels at various values of the quantum number, n



The hydrogen emission spectrum arises as electrons move from orbits of high quantum number to orbits of lower quantum number

Figure 2.3C shows how the lines in the hydrogen emission spectrum arise from transitions between orbits. The Lyman series in the emission spectrum arises when the electron moves to the $n = 1$ orbit (the ground state) from any of the other orbits. The Balmer series arises from transitions to the $n = 2$ orbit from the $n = 3$, $n = 4$ etc. orbits. The Paschen, Brackett and Pfund series arise from transitions to the $n = 3$, $n = 4$ and $n = 5$ orbits from higher orbits.

The frequency of the convergence of spectral lines can be used to give the ionisation energy

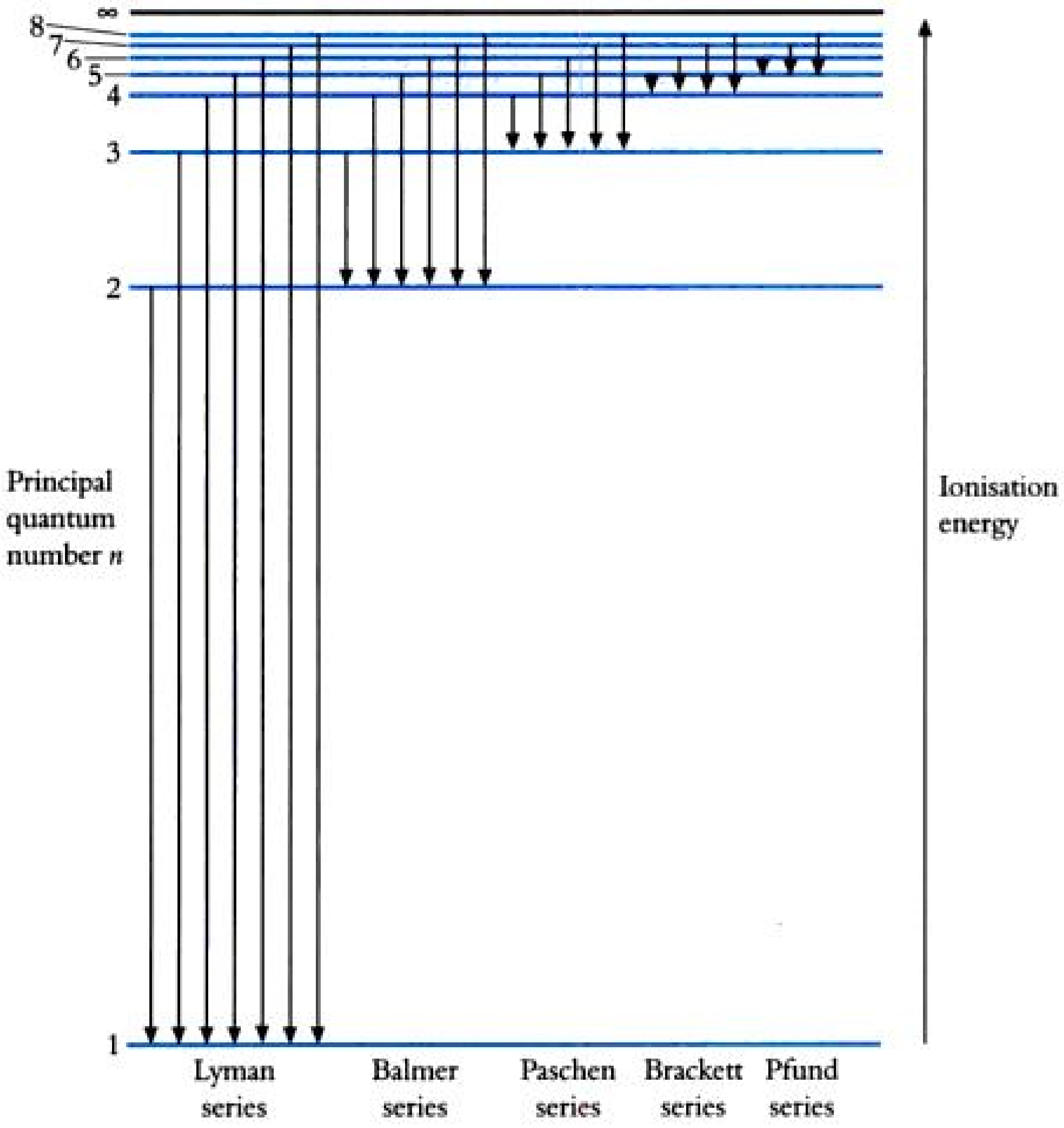


Figure 2.3C Energy transitions in the hydrogen atom

SUMMARY

Absorption spectra arise when electrons move to higher energy levels. Emission spectra arise when excited electrons move to lower energy levels.

When the lines in the spectrum converge it means that the atom has ionised

In each series of lines, as the frequency increases, each line becomes closer to the previous line until the lines converge, and the spectrum becomes continuous. The Lyman series arises from transitions to the ground state from higher energy levels. The highest frequency lines relate to the highest energy levels. The limit of the Lyman series (the convergence of the lines) corresponds to a transition from the $n = \infty$ orbit (i.e. from an energy level where the electron has escaped from the atom, and the atom has ionised) to the $n = 1$ orbit (the ground state):

$$\mathbf{A}^+ + e^- \longrightarrow \mathbf{A}$$

This transition happens when an electron collides with an ion and returns to the ground state. The convergence frequency can be used to find the **ionisation energy** of the atom.

2.3.2 DETERMINATION OF IONISATION ENERGY

The definition of the first ionisation energy ...

The first ionisation energy of an element is the energy required to remove one electron from each of one mole of atoms in the gas phase to form one mole of cations in the gas phase:

$$\mathbf{A}(g) \longrightarrow \mathbf{A}^+(g) + e^-$$

... and using the emission spectrum to find it ...

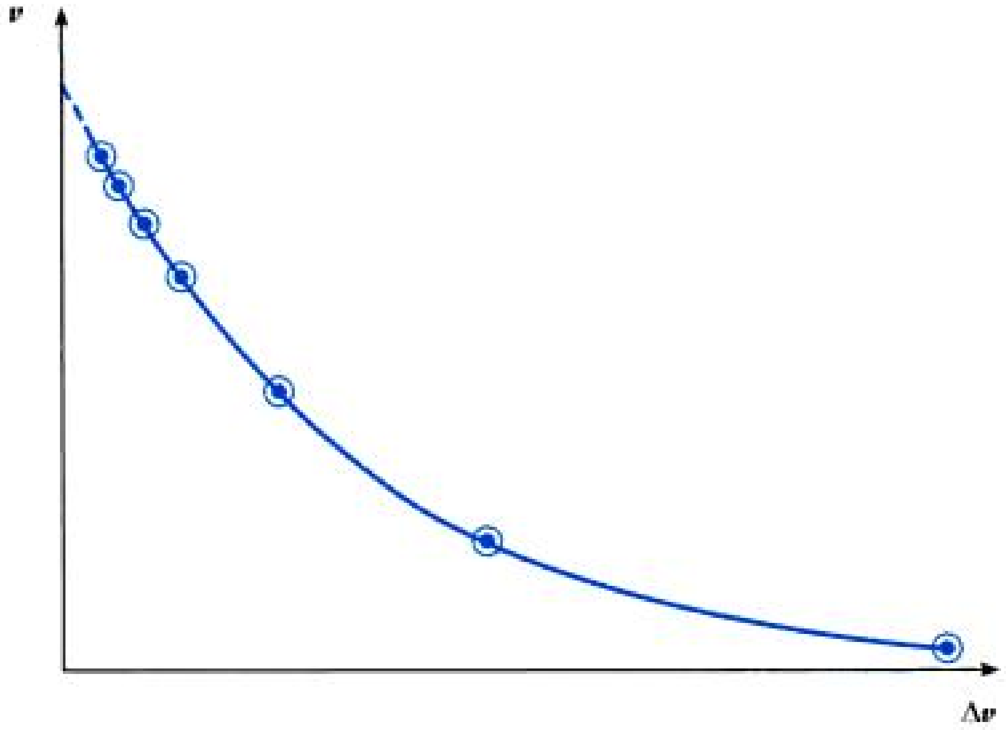
A graphical method can be used to find the value of the ionisation energy from the emission spectrum. The interval between the frequencies of spectral lines becomes smaller and smaller as they approach the continuum.

(a) The frequencies of the first lines in the Lyman series are measured. If these are $\nu_1, \nu_2, \nu_3, \nu_4$, etc., the intervals $\Delta\nu = (\nu_2 - \nu_1), (\nu_3 - \nu_2), (\nu_4 - \nu_3)$, etc., can be calculated.

... by a graphical method ...

(b) A graph of ν (the lower frequency) against $\Delta\nu$ is shown in Figure 2.3D. It can be extrapolated back to $\Delta\nu = 0$. If there is no interval between lines, this is the beginning of the continuum.

Figure 2.3D
Finding the convergence frequency by a graphical method



SUMMARY

If an electron gains so much energy that it leaves the outermost orbit, the atom has ionised.

(c) The value of ν at $\Delta\nu = 0$ is read off and inserted in Planck's equation

$$\Delta E = h\nu$$

(d) The value of ΔE is multiplied by Avogadro's constant to give the first ionisation energy for a mole of atoms.

For example, the value of the wavelength at the start of the continuum in the sodium emission spectrum is 242 nm. From this the first ionisation energy of sodium can be calculated. The value is 494 kJ mol^{-1}.

2.3.3 ELECTRON AFFINITY

Energy is given out when an atom gains one electron

When an electron is acquired by an atom, energy is given out, e.g.

$$Cl(g) + e^- \longrightarrow Cl^-(g)$$

The **first electron affinity** is the energy taken in when 1 mole of gaseous atoms accept 1 mole of electrons to become ions. It has a negative value, showing that in fact energy is given out.

Electron affinity is defined ...

The **second electron affinity** of an element is the energy taken in when 1 mole of gaseous ions with a single negative charge accept 1 mole of electrons, e.g.

$$O^-(g) + e^- \longrightarrow O^{2-}(g)$$

It has a positive value because energy is required for the introduction of an electron against the repulsion between e$^-$ and O$^-$. There is more information about electron affinity in § 10.12.

2.3.4 SOMMERFELD'S QUANTUM NUMBERS

Sommerfeld's second quantum number

Sommerfeld elaborated Bohr's theory in 1916. He proposed that each quantum number governed the energy of a circular orbit and also a set of elliptical orbits of similar energy. He called n the **principal quantum number** and introduced a second quantum number which describes the shape of the elliptical orbits. The **second quantum number**, l, can have values from $(n - 1)$ down to 0. If $n = 4$, $l = 3, 2, 1$ and 0.

2.4 THE WAVE THEORY OF THE ATOM

2.4.1 PARTICLES AND WAVES

The Schrödinger wave equation

According to the wave theory of light, refraction* and diffraction* can be explained by the properties of waves. Other properties of light, such as the origin of line spectra and the photoelectric effect*, need a particle or photon theory for their explanation. The success of the dual theory of light led Louis de Broglie to speculate in 1924 on whether particles might have wave properties. He made the bold suggestion that electrons have wave properties as well as the properties of particles. Erwin Schrödinger used this model to work out a wave theory of the atom. Solutions to the wave equation can only be obtained under certain conditions. An integral number of wavelengths must be fitted into one orbit of the electron round the nucleus.

... Its solution gives the probability of finding the electron at any distance from the nucleus

The solution of the wave equation give the **probability density** of the electron. This is the probability that the electron is present in a given small region of space. The probability that the electron is at a distance, r, from the nucleus is plotted against r for the hydrogen atom in its ground state in Figure 2.4A. The maximum probability of finding the electron is at a distance of 0.053 nm. This is the same as the radius of the orbit occupied by the electron in its ground state according to the Bohr–Sommerfeld model of the atom.

SUMMARY

The wave theory of the electron replaces the idea of finding the electron in a certain position in its orbit with the idea of the probability of finding the electron in a certain volume: the orbital.

The volume of space in which there is a 95% chance of finding the electron is called the atomic orbital

There is a possibility that the electron will be either closer to the nucleus or outside the radius of 0.053 nm. The probability of finding the electron decreases sharply, however, as the distance from the nucleus increases beyond $3r$. The volume of space in which there is a 95% chance of finding the electron is called the **atomic orbital**. There is a 5% probability that the electron will be outside this volume of space at a given instant. On this model, the electron is not described as revolving in an orbit. The electron is said to occupy a three-dimensional space around the nucleus called an atomic orbital. The nucleus is described as being surrounded by a three-dimensional 'cloud of charge' or 'electron cloud'.

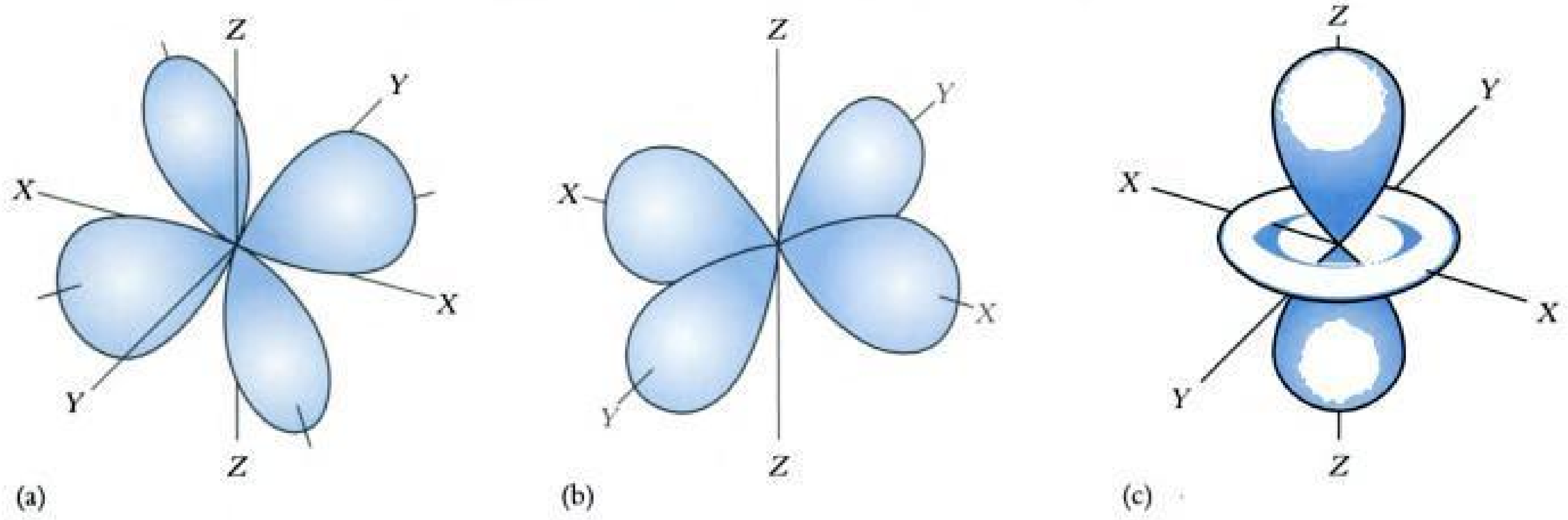
The four quantum numbers

Solutions of the wave equation can be obtained if the orbitals are described by four quantum numbers. The first is Bohr's quantum number, n. The second

Figure 2.4D

The shape and orientation of d orbitals

There are four d orbitals of shape (a). The lobes lie between the X–Y axes as shown in (a), between the X–Z axes, between the Y–Z axes and, in the fourth case, along the axes X and Y as shown in (b). The fifth orbital has the shape shown in (c).



2.5 ELECTRONIC CONFIGURATIONS OF ATOMS

In atoms with more than one electron, there are shells of orbitals with the same principal quantum number

The energy levels of the orbitals of the hydrogen atom are illustrated in Figure 2.3C [§ 2.3.1]. For atoms with more than one electron, the energy levels for each value of n are split between orbitals with different values of l. The relative energy levels of the orbitals are shown in Figure 2.5A. The term **shell** is used for a group of orbitals with the same principal quantum number. A **subshell** is a group of orbitals with the same principal and second quantum numbers, e.g. the 3p subshell.

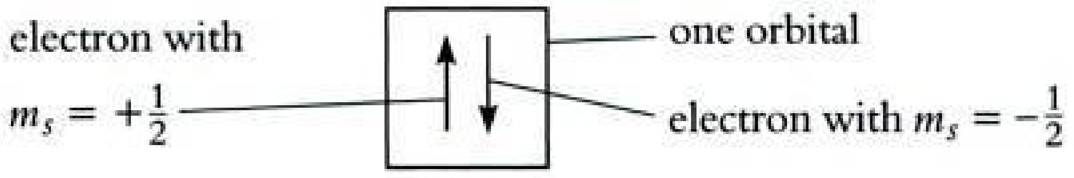
The arrangement of electrons in atomic orbitals is governed by two factors.

The orbitals of lowest energy are filled first

1. In a normal atom the electrons are arranged so that the energy is at a minimum. Any other arrangement would make the atom an excited atom, which could emit energy and pass to its ground state.
2. The Pauli Exclusion Principle: no two electrons can have the same four quantum numbers.

It is convenient to draw an 'electrons-in-boxes' diagram to show the arrangement of electrons in orbitals.

'Electrons-in-boxes'

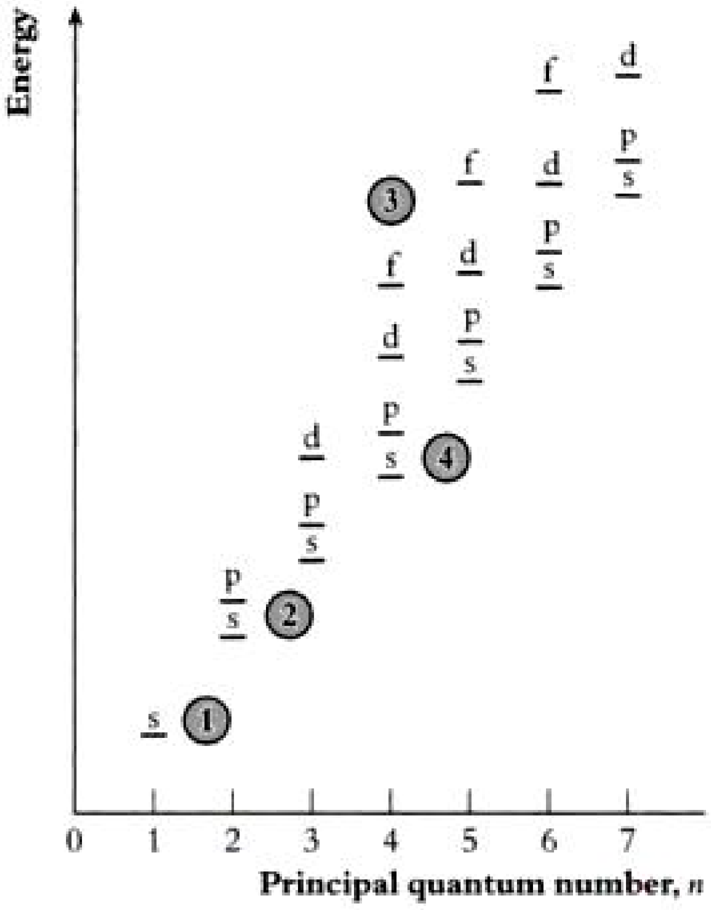


An s subshell consists of one box, a p subshell of *three* boxes, a d subshell of *five* boxes and an f subshell of *seven* boxes. The boxes are arranged in order of energy in Figure 2.5B.

Electrons occupy lowest energy 'boxes' first

To work out the arrangement of electrons in an atom with 12 electrons, the electrons must be put into the lowest energy boxes first, two to a box, until all the electrons are accommodated [see Figure 2.5B]. It is interesting to do this for the elements in order of atomic number, the order in which they appear in the Periodic Table [p. 732].

Figure 2.5A
The relative energy levels of atomic orbitals (not to scale)



3 Note 4f > 4d > 4p > 4s in energy.

4 Note 4s < 3d in energy. The orbitals of n = 4 overlap those with n = 3.

2 Note 2p electrons have more energy than 2s.

1 Lowest energy: n = 1.

Figure 2.5B
'Electrons-in-boxes', diagram for an atom with 12 electrons

Shells of electrons have the same principal quantum number ...

... and subshells also have the same second quantum number ...

... and are called s, p, d or f subshells

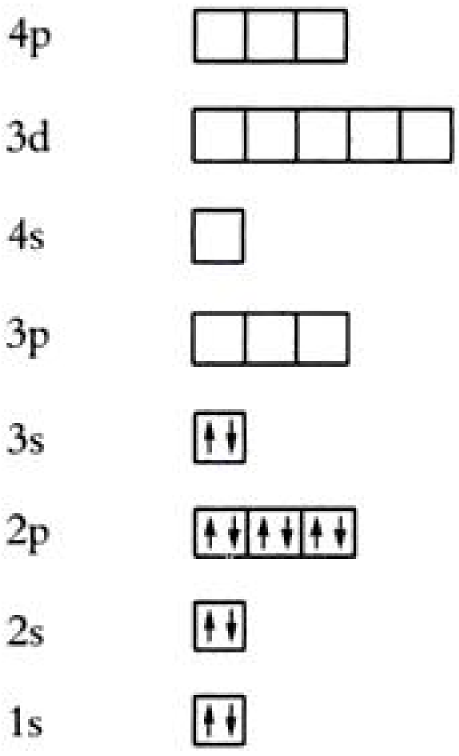
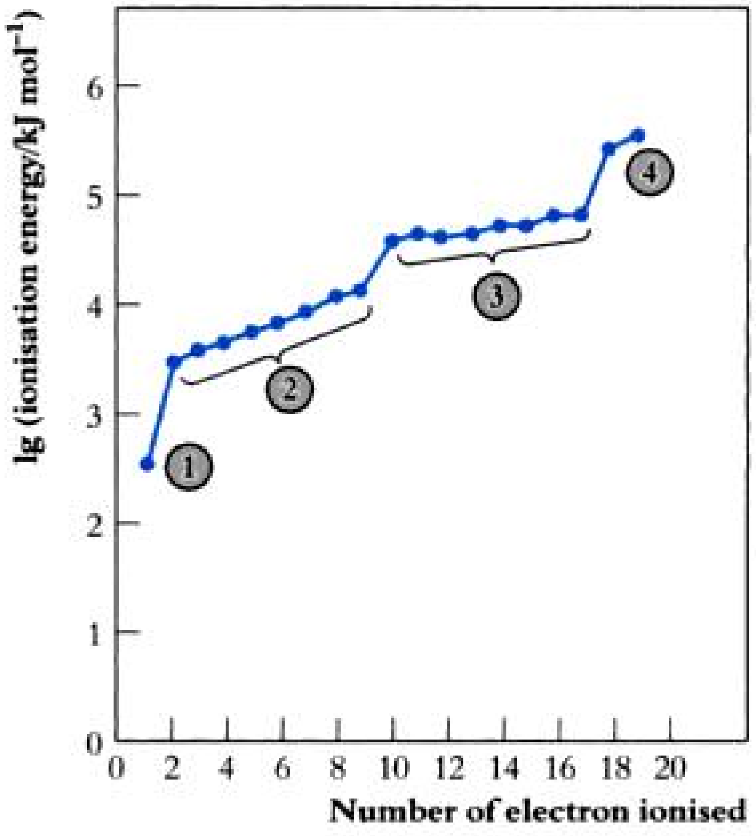


Figure 2.5C
Graph of lg (ionisation energy) against number of electron removed for the potassium atom

The electrons closest to the nucleus require the most energy to remove them



4 The two electrons with the highest ionisation energies are closest to the nucleus, and form the n = 1 shell.

3 These eight electrons are in the next shell, the n = 2 shell.

2 These eight electrons are in the n= 3 shell.

1 This electron has the lowest ionisation energy. It is the easiest to remove. It is in the n = 4 shell.

Measurements of successive ionisation energies support the idea of shells

Evidence for the arrangement of electrons in shells of different energies is provided by values of successive **ionisation energies** for elements. Figure 2.5C shows a graph of the logarithm of the ionisation energy required for the removal of one electron after another from a potassium atom. (A logarithmic plot is used in order to give a condensed graph.) You can see that the electrons fall into four groups. The higher the ionisation energy, the more difficult the electrons are to remove and the nearer they must be to the nucleus.

2.6 THE HISTORY OF THE PERIODIC TABLE

There are over 70 metallic elements, and over 20 non-metallic elements. As you know, elements are classified as metallic and non-metallic elements.

Table 2.6
Properties of metallic and non-metallic elements

Metallic elements	Non-metallic elements
Solids (except mercury, a liquid).	Solids or gases (except bromine, a liquid).
A fresh surface is shiny; corrosion can occur.	Have no one characteristic appearance.
Malleable (can be hammered) and ductile (can be drawn into wire).	Shatter when attempts are made to change the shape.
Conduct heat and electricity.	Are poor thermal conductors and electrical conductors, with exceptions.
The oxides are basic.	The oxides are acidic or neutral.

Classification of elements ...

... as metallic and non-metallic ...

... and metalloid

For a long time chemists look at ways of dividing up the two big groups, metallic and non-metallic elements, into smaller sub-groups. They drew up groups of similar elements, such as the very reactive metals lithium, sodium and potassium. They grouped together a set of slightly less reactive metals, calcium, strontium and barium. Another such group was the very reactive non-metals, chlorine, bromine and iodine. Some elements were discovered which had properties in between metallic and non-metallic. These elements, e.g. silicon, were described as **metalloids**.

Newlands arranged the elements in order of relative atomic mass

In 1866, a British chemist called John Newlands had the idea of arranging the elements in order of their relative atomic masses:

H Li Be B C N O F Na Mg Al Si P S Cl K Ca

[For the symbols of elements see p. 732.]

Newlands noticed that similar elements appeared at regular intervals in the list. He arranged the elements in columns [Figure 2.6A].

Figure 2.6A
Newland's octaves of elements

H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe

He drew up a Law of Octaves ...

In the first column were hydrogen and the very reactive non-metallic elements fluorine and chlorine. In the second column were the very reactive metals sodium, lithium and potassium. In the third column were the metals beryllium, magnesium and calcium. Carbon and silicon both fell into the fifth column, and oxygen and sulphur both fell into the sixth column.

... but his ideas were scorned

Newlands compared his chemical 'octaves' with musical octaves, and called the resemblance the **Law of Octaves**. The comparison was unfortunate: people poured scorn on his ideas.

Mendeleev carried on the work on classification ...

... and drew up his Periodic Table

It was a Russian chemist, Dimitri Mendeleev, who developed Newlands' idea and persuaded chemists to use it. In 1869, Mendeleev summarised his **periodic law** in the statement: *The properties of chemical elements are not arbitrary, but vary with their relative atomic masses in a systematic way*. He arranged the elements in order of increasing relative atomic mass [see Figure 2.6B]. A modern version of his classification, which we call the Periodic Table, is shown on p. 732. You will notice that Mendeleev's Periodic Table lacks the noble gases (helium, neon, argon, etc. in Group 0) because they had not yet been discovered! A vertical row of elements is called a **group** and a horizontal row is called a **period**.

Figure 2.6B
Part of Mendeleev's Periodic Table of 1871

	Gp 1	Gp 2	Gp 3	Gp 4	Gp 5	Gp 6	Gp 7	Gp 8
Row 1	H							
Row 2	Li	Be	B	C	N	O	F	
Row 3	Na	Mg	Al	Si	P	S	Cl	
Row 4	K	Ca	–	–	–	–	–	Ti V Cr Mn Fe Co Ni
Row 5	Cu	Zn	–	–	As	Se	Br	

For the full Periodic Table, see p. 732

Mendeleev made various improvements on Newlands' system.

Mendeleev's improvements included long periods to accommodate transition metals ...

1. Mendeleev introduced long rows or **periods** for the elements we now call **transition metals**. This meant that the metals Ti, Mn, Fe were no longer placed under the non-metals Si, P, S [see Figure 2.6A].

... spaces ...

2. He left spaces. When he saw that arsenic fitted naturally into Group 5 he left two spaces between zinc and arsenic.

... new values of relative atomic mass ...

3. When elements did not fit comfortably into the slots in the Periodic Table dictated by their relative atomic masses, Mendeleev made new measurements of relative atomic mass. In each case (Cr, In, Pt, Au) the new value justified the arrangement in Mendeleev's Periodic Table.

... predictions about undiscovered elements

4. Where he had left gaps in the Periodic Table, Mendeleev predicted that new elements would be discovered to fill the gaps. He had some outstanding successes in predicting the properties of elements. When elements were discovered and found to have the relative atomic mass and the physical and chemical properties Mendeleev had predicted, faith in the Periodic Table soared.

The Periodic Table helped chemists in their search for the elements which were still to be discovered. For example, Mendeleev predicted that an element would be discovered to fill the space under silicon and above tin. His predictions for the element which he called ekasilicon (below silicon) were fulfilled by the properties of the element germanium, which was discovered in 1886 by Winkler.

Similar agreement was found between the predicted properties of eka-aluminium and gallium, which was discovered in 1875 and between ekaboron and scandium, discovered in 1879.

The noble gases were discovered and found to fit into a new group of the Periodic Table ...

The **noble gases** had not been discovered when the Periodic Table was drawn up. As they were discovered one by one, they were found to fit in between the halogens in Group 7 and the alkali metals in Group 1. A separate Group 0 was added to the right-hand side of the table. Argon, however, has a higher relative atomic mass than potassium ($A_r(Ar) = 40; A_r(K) = 39$) [§ 3.4]. It made more sense chemically to put potassium with the alkali metals, rather than keep to the order of relative atomic masses. Another example of this kind was the positions of tellurium and iodine. Relative atomic masses placed tellurium under bromine, and iodine under sulphur and selenium; chemical properties placed them in the reverse order.

... Discrepancies were resolved by arranging elements in order of atomic number

Moseley's work on X rays in 1914, solved this problem. He showed that the atomic numbers (proton numbers) of elements are more significant than their relative atomic masses. This discovery was the final step in the validation of the Periodic Table. In the modern Periodic Table elements are arranged in order of proton number (atomic number).

2.7 FEATURES OF THE PERIODIC TABLE

The Periodic Table is divided into the s block, the d block and the p block

What patterns can be seen in the arrangement of the elements in the Periodic Table? First, note the positions occupied by metallic and non-metallic elements. The reactive metals are at the left-hand side of the table, less reactive metallic elements in the middle block and non-metallic elements at the right-hand side.

The metals in Groups 1 and 2 are described as **s block elements** because their outer electron subshells contain s electrons. The metals in the block between Group 2 and Group 3 are called **transition metals**. They are described as **d block elements** because they have incomplete d subshells. Groups 3 to 7 form the **p block** of the Periodic Table [see § 15.5]. As you have seen, their outer electrons are p electrons.

2.7.1 LOOKING AT THE GROUPS

The very reactive alkali metals of Group 1 ...

From the summary in Table 2.7A, you can see how the Periodic Table makes it easier to learn about all the elements. Look at the elements in Group 1: lithium, sodium, potassium, rubidium and caesium. They are all very reactive metals. Their oxides and hydroxides have the general formulae $\mathbf{M}_2\mathrm{O}$ and **M**OH (where **M** is the symbol for the metallic element) and are strongly basic. The oxides and hydroxides dissolve in water to give strongly alkaline solutions. The metals in Group 1 are called the **alkali metals**. Their reactivity increases as you pass down the group. If you know these fact, you do not need to learn the properties of all the metals separately. If you know the properties of sodium, you can predict those of potassium and lithium. Think of having to learn the properties of 106 elements separately! The Periodic Table saves you from this.

The metals in Group 2 are less reactive than those in Group 1. They form basic oxides and hydroxides with the general formulae **M**O and $\mathbf{M}(\mathrm{OH})_2$. Their oxides and hydroxides are either sparingly soluble or insoluble. These elements

2.7.2 LOOKING AT THE PERIODS

Period 1 contains hydrogen and helium. Period 2 contains the elements from lithium to neon. Table 2.7C shows some of the patterns which are seen in passing across Period 3. The properties shown are metallic and non-metallic character, the charge on the ions which the element forms, and the structure of the element and its oxide. You will be learning more about structure in Chapters 4 and 6. This table simply tells whether the substance consists of

1. individual atoms, e.g. argon which consists of Ar atoms
2. individual molecules, e.g. sulphur dioxide which consists of SO_2 molecules
3. a giant ionic structure containing millions of ions bonded together, e.g. sodium chloride which consists of Na^+ ions and Cl^- ions in equal numbers
4. a giant covalent structure containing millions of atoms bonded together, e.g. silicon(IV) oxide, SiO_2 which contains silicon atoms and oxygen atoms in the ratio of 2 atoms of oxygen for every silicon atom
5. a giant metallic structure, which consists of millions of atoms of a metallic element bonded together by the metallic bond [see § 6.3].

SUMMARY

Across a period, there is a transition in properties, structure, reactivity and the nature of compounds.

Table 2.7C
Trends across Period 3

Group	**1** **Na**	**2** **Mg**	**3** **Al**	**4** **Si**	**5** **P**	**6** **S**	**7** **Cl**	**0** **Ar**
Character	Metallic			Metalloid	Non-metallic			Noble gas
Reactivity	— Decreases →			–	← Decreases —			–
Structure of element	Giant metallic			Giant covalent	Molecular			Atomic
Ion	Na^+	Mg^{2+}	Al^{3+}	None	P^{3-}	S^{2-}	Cl^-	None
Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5 P_2O_3	SO_2 SO_3	Cl_2O Cl_2O_7 etc.	None
Type of oxide	Strongly basic		Some acidic and some basic character		Acidic			None
Structure of oxide	Giant ionic			Giant covalent	Molecular			None
T_m/°C	97.8	650	660	1410	44 (wh) 590 (red)	113 (rh)	−101	−189
T_b/°C	890	1110	2470	2360	280 (wh)	445	−34.7	−186
Electric conductivity/ $\mu\Omega^{-1}$ cm^{-1}	0.218	0.224	0.382	0.10	10^{-7}	10^{-23}	---	---
First ionisation energy/ kJ mol^{-1}	494	736	577	786	1060	1000	1260	1520

(Note: wh = white, rh = rhombic, T_m = melting temperature, T_b = boiling temperature)

From left to right across a period, there is a transition

- *from metals to non-metals*
- *from elements which form positive ions to elements which form negative ions*
- *from giant structures to molecular structures*
- *from basic, ionic oxides to acidic, molecular oxides*

... then the 2s subshell, followed by the 2p subshell ...

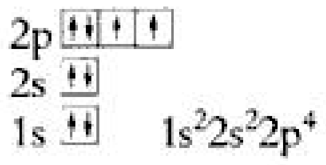
... then the 3s subshell, followed by the 3p subshell

The 4s subshell is filled and followed by the 3d subshell ...

... before the 4p subshell is filled

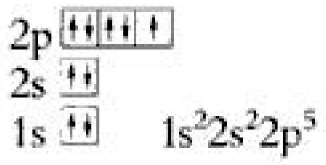
Oxygen ($Z = 8$). The fourth 2p electron pairs with one of the other three 2p electrons.

O



Fluorine ($Z = 9$) has the arrangement $1s^22s^22p^5$

F



Neon ($Z = 10$) $1s^22s^22p^6$, has a full 2p subshell, thus completing the $n = 2$ shell. The next element, **sodium** ($Z = 11$) has to utilise the $n = 3$ shell, starting with the 3s subshell. The diagrams for sodium and the twelfth element, **magnesium**, are

Na

Mg

The following six elements have electrons in the 3p subshell. The configurations of the next six elements are (writing (Ne) for $1s^22s^22p^6$)

Al	($Z = 13$)	(Ne)$3s^23p$
Si	($Z = 14$)	(Ne)$3s^23p^2$
P	($Z = 15$)	(Ne)$3s^23p^3$
S	($Z = 16$)	(Ne)$3s^23p^4$
Cl	($Z = 17$)	(Ne)$3s^23p^5$
Ar	($Z = 18$)	(Ne)$3s^23p^6$

Electron configuration and the Periodic Table

How do the elements fit into the Periodic Table? So far we have:

Filling the $n = 1$ shell: H and He: First period

Filling the $n = 2$ shell: Li to Ne: Second period

Filling the $n = 3$ shell: Na to Ar: Third period

The next elements start the fourth period. They are

K ($Z = 19$) (Ar)4s

Ca ($Z = 20$) (Ar)$4s^2$

Once the 4s subshell is full, the 3d orbitals are filled [see Figure 2.5B, § 2.5]. Over the next 10 elements, electrons enter the 3d subshell. These elements are

The fourth period

Sc ($Z = 21$) (Ar)$4s^23d$

to Zn ($Z = 30$) (Ar)$4s^23d^{10}$

Filling the d subshell ...

While the d subshell fills, the chemistry of the elements is not greatly affected. The metals scandium to zinc are a very similar set of metals, called **transition metals** [Chapter 24]. The elements gallium ($Z = 31$) to krypton ($Z = 36$) complete the $n = 3$ shell by filling the 4p orbitals. The 18 elements from potassium to krypton comprise the **first long period**.

Electronic configurations can be written as e.g. B(2.3), C(2.4), N(2.5), O(2.6), F(2.7), Mg(2.8.2), where the numbers give the numbers of electrons in the $n = 1$, $n = 2$ and $n = 3$ shells.

Table 2.8
Electronic configurations of the atoms of the first 36 elements

	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	6f	7s
H	1	1																		
He	2	2																		
Li	3	2	1																	
Be	4	2	2																	
B	5	2	2	1																
C	6	2	2	2																
N	7	2	2	3																
O	8	2	2	4																
F	9	2	2	5																
Ne	10	2	2	6																
Na	11	2	2	6	1															
Mg	12	10 electrons			2															
Al	13				2	1														
Si	14				2	2														
P	15				2	3														
S	16				2	4														
Cl	17				2	5														
Ar	18	2	2	6	2	6														
K	19	2	2	6	2	6		1												
Ca	20	18 electrons						2												
Sc	21						1	2												
Ti	22						2	2												
V	23						3	2												
Cr	24						5	1												
Mn	25						5	2												
Fe	26						6	2												
Co	27						7	2												
Ni	28						8	2												
Cu	29						10	1												
Zn	30						10	2												
Ga	31						10	2	1											
Ge	32						10	2	2											
As	33						10	2	3											
Se	34						10	2	4											
Br	35						10	2	5											
Kr	36	2	2	6	2	6	10	2	6											

CHECKPOINT 2.8: ELECTRONIC CONFIGURATIONS

1. There are six calcium isotopes, of nucleon number 40, 42, 43, 44, 46 and 48. How many protons and neutrons are there in the nuclei?

2. Draw 'electrons-in-boxes' diagrams of the electronic configuration of the following atoms, given the proton number (*Z*): boron (5), fluorine (9), aluminium (13) and potassium (19).

3. Draw diagrams to show the electronic configurations of the ions: K^+, Cl^-, Ca^{2+}, O^{2-}, Al^{3+}, H^-.
(Proton numbers are K = 19, Cl = 17, Ca = 20, O = 8, Al = 13 and H = 1.)

4. Write down the electronic configurations of the atoms with the proton numbers 4, 7, 18, 27, 37. State to which Group of the Periodic Table each element belongs.

5. Write the electronic configurations of the following species (e.g., Li = $1s^2 2s$). Their proton numbers range from Na = 11 to Ar = 18.

   Na^+, Mg^{2+}, Al, Si, P, S, S^{2-}, Cl, Cl^-, Ar

2.9 THE REPEATING PATTERN OF THE ELEMENTS

We have spent time looking at the structure of the atom [Chapter 1] and the electron configurations of the elements [§§ 2.5 and 2.8]. How does this study fit in with the Periodic Table? If you look at the electron configurations of the atoms, some interesting points strike you.

The noble gases have a full outer shell of electrons (helium 2; the other gases 8)

First, notice the elements with a full outer shell of electrons. These are helium (2), neon (2.8), argon (2.8.8), krypton and xenon. These elements are the noble gases (Group 0). Their lack of chemical reactivity has been mentioned. They exist as single atoms. Their atoms do not combine in pairs to form molecules as do the atoms of most gaseous elements (e.g. O_2, H_2). It seems only logical to suppose that it is the full outer shell of electrons that makes the noble gases chemically unreactive.

For members of other groups, the number of electrons in the outermost shell equals the group number

Following each noble gas (that is, with atomic number 1 greater than each noble gas) is an alkali metal [see Table 2.9]. These elements are lithium (2.1), sodium (2.8.1), potassium (2.8.8.1), rubidium and caesium. We can infer that it is because the alkali metals all have a single electron in the outer shell that they all behave in a very similar way.

Following each alkali metal is an alkaline earth metal [see Table 2.9]. The alkaline earths, beryllium (2.2), magnesium (2.8.2), calcium (2.8.8.2), strontium and barium all have two electrons in the outer shell. It seems logical to suppose that it is the similar configuration of electrons that gives the elements similar properties.

Preceding each noble gas (with atomic number 1 less than the noble gas) are the halogens of Group 7: fluorine (2.7), chlorine (2.8.7), bromine and iodine [see Table 2.7B]. We can infer that the halogens all have similar chemical reactions because they all have the same number of electrons in the outer shell.

Table 2.9
A section of the Periodic Table

	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 0
Period 1	H (1)							He (2)
Period 2	Li (2.1)	Be (2.2)	B (2.3)	C (2.4)	N (2.5)	O (2.6)	F (2.7)	Ne (2.8)
Period 3	Na (2.8.1)	Mg (2.8.2)	Al (2.8.3)	Si (2.8.4)	P (2.8.5)	S (2.8.6)	Cl (2.8.7)	Ar (2.8.8)
Period 4	K (2.8.8.1)	Ca (2.8.2)						

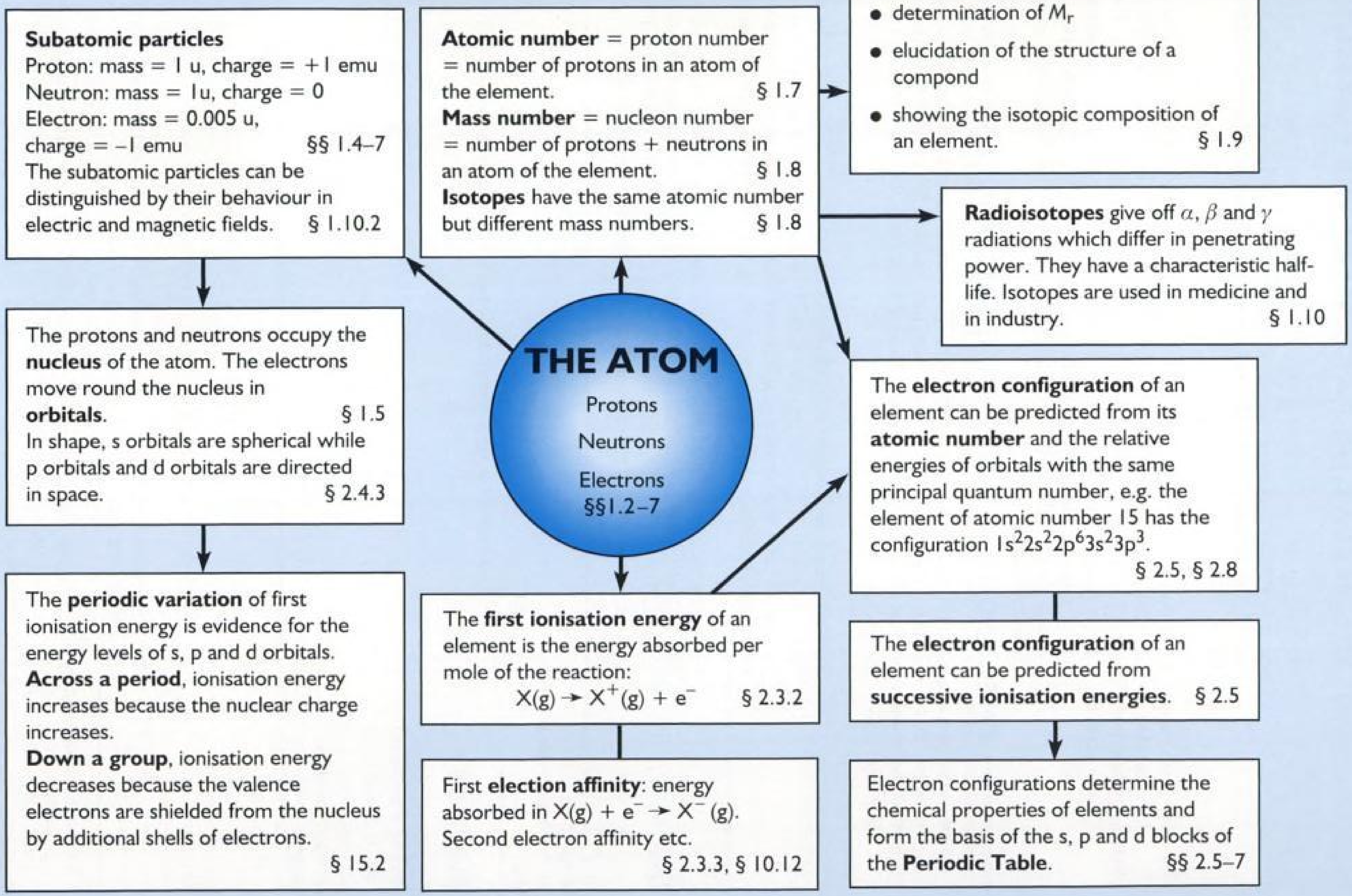
SUMMARY

The position of an element in the Periodic Table is related to the electronic configuration of its atoms.

You can see the following features:

1. The elements are listed in order of increasing atomic number.
2. Elements which have the same number of electrons in the outermost shell fall into the same group of the Periodic Table.
3. The first period contains only hydrogen and helium. The second period contains the elements lithium to neon. The third period contains the elements sodium to argon.

ATOMIC STRUCTURE



Subatomic particles
Proton: mass = 1 u, charge = +1 emu
Neutron: mass = 1u, charge = 0
Electron: mass = 0.005 u,
charge = −1 emu §§ 1.4–7
The subatomic particles can be distinguished by their behaviour in electric and magnetic fields. § 1.10.2

The protons and neutrons occupy the **nucleus** of the atom. The electrons move round the nucleus in **orbitals**. § 1.5
In shape, s orbitals are spherical while p orbitals and d orbitals are directed in space. § 2.4.3

The **periodic variation** of first ionisation energy is evidence for the energy levels of s, p and d orbitals.
Across a period, ionisation energy increases because the nuclear charge increases.
Down a group, ionisation energy decreases because the valence electrons are shielded from the nucleus by additional shells of electrons. § 15.2

Atomic number = proton number = number of protons in an atom of the element. § 1.7
Mass number = nucleon number = number of protons + neutrons in an atom of the element. § 1.8
Isotopes have the same atomic number but different mass numbers. § 1.8

THE ATOM
Protons
Neutrons
Electrons
§§1.2–7

The **first ionisation energy** of an element is the energy absorbed per mole of the reaction:

$$X(g) \rightarrow X^+(g) + e^- \qquad § 2.3.2$$

First **election affinity**: energy absorbed in $X(g) + e^- \rightarrow X^-(g)$.
Second electron affinity etc.
§ 2.3.3, § 10.12

Mass spectrometry is used for

- determination of M_r
- elucidation of the structure of a compond
- showing the isotopic composition of an element. § 1.9

Radioisotopes give off α, β and γ radiations which differ in penetrating power. They have a characteristic half-life. Isotopes are used in medicine and in industry. § 1.10

The **electron configuration** of an element can be predicted from its **atomic number** and the relative energies of orbitals with the same principal quantum number, e.g. the element of atomic number 15 has the configuration $1s^22s^22p^63s^23p^3$.
§ 2.5, § 2.8

The **electron configuration** of an element can be predicted from **successive ionisation energies**. § 2.5

Electron configurations determine the chemical properties of elements and form the basis of the s, p and d blocks of the **Periodic Table**. §§ 2.5–7

6\. *(a)* In terms of the numbers of sub-atomic particles, state **one** difference and **two** similarities between two isotopes of the same element. **3**

(b) Give the chemical symbol, including its mass number, for an atom which has 3 electrons and 4 neutrons **1**

(c) (i) An element has an atomic number of 23. Its ion has a charge of 3+. Complete the electronic configuration of this ion: [Ar] ...

(ii) To which block in the Periodic Table does this element belong? **2**

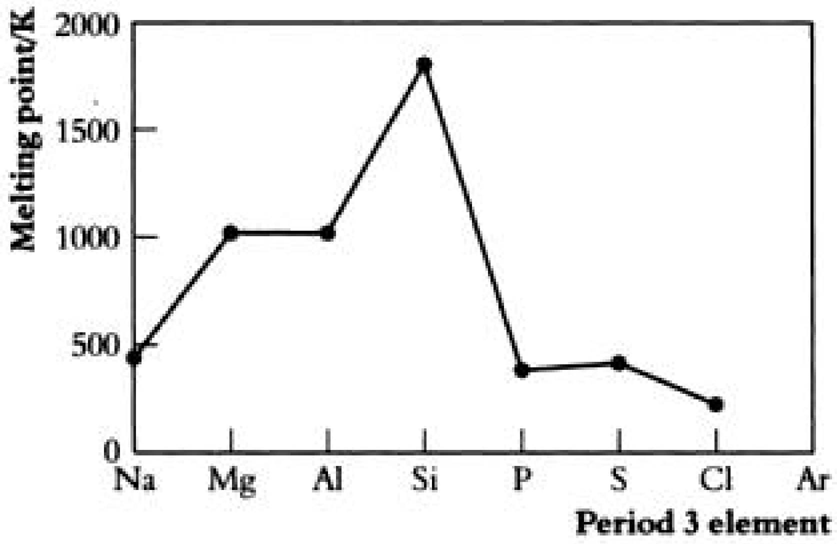
(d) (i) Write an equation for the process involved in the first ionisation energy of boron.

(ii) Explain why the second ionisation energy of boron is greater than the first.

(iii) Explain why the fourth ionisation energy of boron is much greater than the third. **6**

12 *NEAB (AS/AL)*

7\. *(a)* The graph below shows how the melting points of the elements vary across Period 3.



(i) Explain why magnesium has a higher melting point than sodium. **2**

(ii) Copy and complete the graph to show the likely melting point of argon. **1**

(iii) Explain why argon has the melting point which you have shown. **2**

(b) Write an equation for the formation of phosphorus(V) oxide from phosphorus and oxygen. **1**

(c) Write equations to show how sodium oxide and sulphur trioxide react with water and in **each case** predict the approximate pH of the resulting solution. **4**

10 *NEAB (AS/AL)*

8\. *(a)* Figure 1 shows the mass spectrum of neon (Ne). Use the isotopic abundances (given in brackets) to calculate the relative atomic mass of neon. **$1\frac{1}{2}$**

(b) (i) Neon is a monatomic gas. Using your value for the relative atomic mass of neon obtained in part *(a)*, calculate the volume occupied by 3.03 g of neon at 298 K and 1.01×10^5 Pa pressure. **$2\frac{1}{2}$**

[1 mole of ideal gas occupies 22.4 dm^3 at 273 K and 1.01×10^5 Pa.]

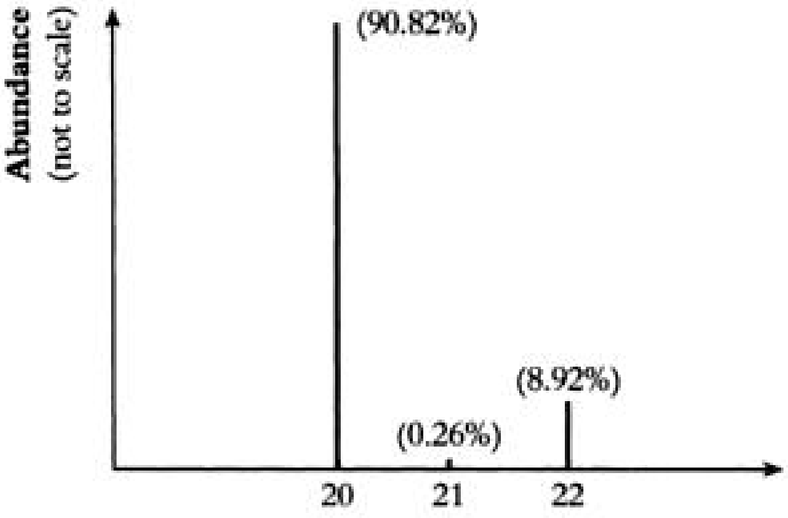


Figure 1

(ii) Calculate the volume which 3.03 g of neon would occupy at 298 K and 5.05×10^5 Pa pressure. **1**

(c) Figure 2 shows a plot of first ionisation energy against atomic number for the first thirteen elements of the Periodic Table.

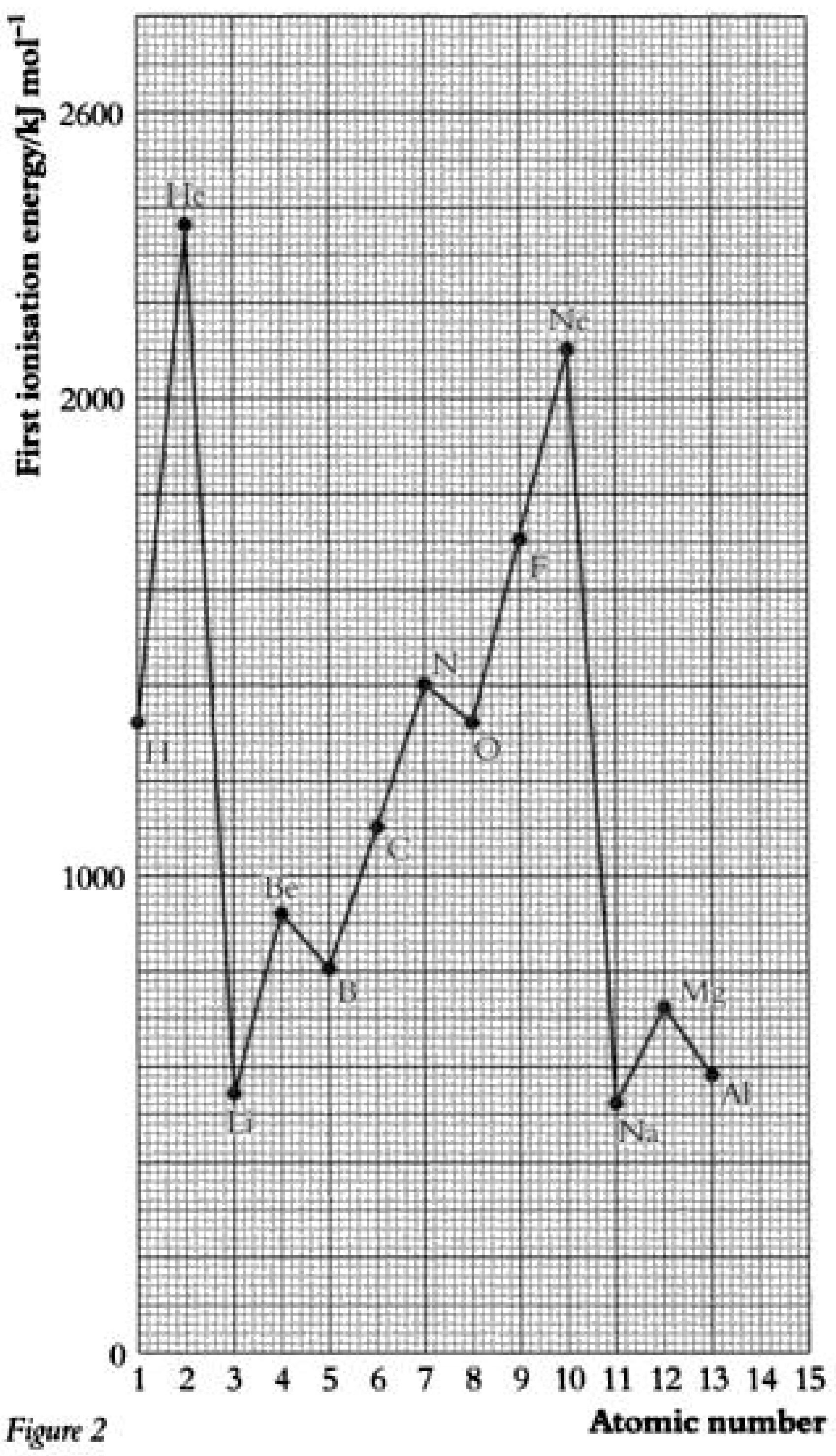


Figure 2

With reference to the *electronic configuration* of the elements explain why:

(i) the first ionisation energy for neon (Ne) is lower than that for helium (He); **$1\frac{1}{2}$**

(ii) the first ionisation energy for beryllium (Be) is greater than those for lithium (Li) **and** boron (B): **2**

3

EQUATIONS AND EQUILIBRIA

In this chapter we begin to see how equations, a knowledge of equilibria and calculations help chemical industry.

3.1 EQUATIONS, EQUILIBRIA AND CALCULATIONS – WHO NEEDS THEM?

Many cars have air bags which inflate if the car is involved in a collision and cushion the driver. A manufacturer has an order for gas generators for car air bags. How much sodium azide shall the manufacturer put into the gas generator? The bag must generate enough nitrogen to cushion the driver if there is a crash but not enough to push him into the back seat. To find the answer to this question, he has to know the equation for the reaction and he has to be able to relate the mass of solid sodium azide to the volume of nitrogen produced.

How much dynamite shall a miner use for blasting a rock face? He wants enough explosive to bring down enough rock salt to fill fifty trucks but not enough to blast him into the next world. To answer the question, he has to know the chemical composition of dynamite and the equation for the reaction and he has to be able to calculate the force produced from a mass of dynamite detonated.

Smith Brothers have an order for 1000 tonnes of fertiliser. What mass of ammonia do they need to buy so that they can fill the order? It's easy to work out if they know the equation. The manufacturer of ammonia will have to know about systems reaching equilibrium and how to use the best conditions to give the maximum yield of ammonia.

Brown Brothers have an order for 1000 tonnes of concrete. What mass of limestone do they need to buy so that they can fill the order? They can work it out in an instant if they know the equation for the decomposition of limestone. They will also need to know about the best conditions for ensuring that the decomposition of limestone carries on without reaching equilibrium.

3.2 FORMULAE

Every element has a symbol [see Periodic Table, p. 732]. A symbol is a letter or two letters which stand for one atom of the element. Formulae are written for compounds. The formula of a compound consists of the symbols of the elements present and the numbers which show the ratio in which the atoms are present. The compound sulphur dioxide has the formula SO_2. The compound sulphur trioxide has the formula SO_3. The formulae tell you the difference between them. Sulphur dioxide contains 2 oxygen atoms for every sulphur atom: the 2 below the line multiplies the O in front of it. Sulphur trioxide consist of molecules [see Figure 3.2A]. To show three molecules of sulphur dioxide, you write $3SO_2$.

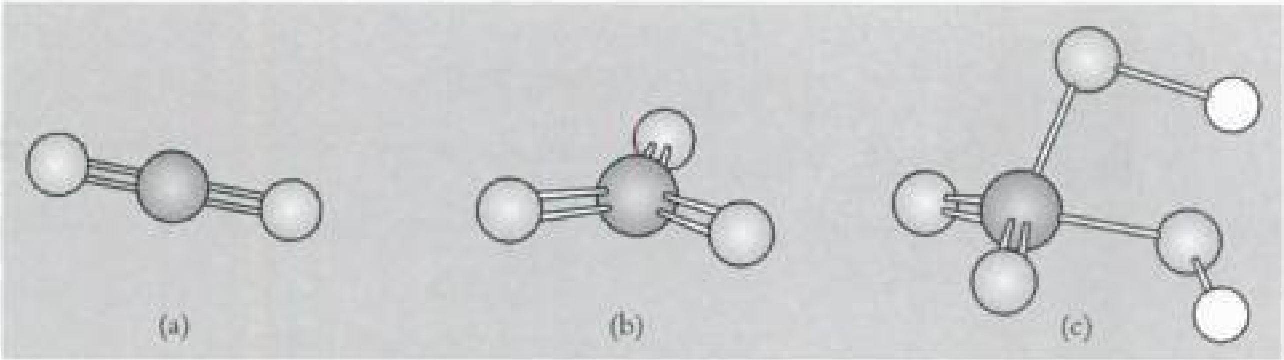


Figure 3.2A
Models of molecules of
(a) sulphur dioxide,
(b) sulphur trioxide,
(c) sulphuric acid

The formula of a compound is a set of symbols and numbers. The symbols say what elements are present in the compound. The numbers give the ratio of the numbers of atoms of the different elements in the compound

The formula of sulphuric acid is H_2SO_4. The compound contains two hydrogen atoms and four oxygen atoms for every sulphur atom; to write three molecules, you write $3H_2SO_4$. The 3 in front of the formula multiplies everything after it. In $3H_2SO_4$, there are 6 H, 3 S and 12 O atoms, a total of 21 atoms.

Many compounds do not consist of molecules; they consist of ions. The compound calcium hydroxide is composed of calcium ions, Ca^{2+}, and hydroxide ions, OH^-. There are twice as many hydroxide ions as calcium ions, so the formula for calcium hydroxide is $Ca(OH)_2$. The 2 multiplies the symbols in the brackets. There are 2 oxygen atoms, 2 hydrogen atoms and 1 calcium atom. This is not a molecule of calcium hydroxide; it is a formula unit of calcium hydroxide: one calcium ion and 2 hydroxide ions. A piece of calcium hydroxide contains this formula unit repeated many times. To write $4Ca(OH)_2$ means that the whole of the formula is multiplied by 4. It means 4 Ca, 8 O and 8 H atoms. § 4.3.7 deals with how to work out the formula of a compound. Table 3.2 lists the formulae of some common compounds.

Table 3.2
The formulae of some compounds

Water	H_2O	Aluminium chloride	$AlCl_3$
Sodium hydroxide	$NaOH$	Aluminium oxide	Al_2O_3
Sodium chloride	$NaCl$	Carbon monoxide	CO
Sodium sulphate	Na_2SO_4	Carbon dioxide	CO_2
Sodium nitrate	$NaNO_3$	Sulphur dioxide	SO_2
Sodium carbonate	Na_2CO_3	Ammonia	NH_3
Sodium hydrogencarbonate	$NaHCO_3$	Ammonium chloride	NH_4Cl
Calcium oxide	CaO	Hydrogen chloride	HCl
Calcium hydroxide	$Ca(OH)_2$	Hydrochloric acid	$HCl(aq)$
Calcium chloride	$CaCl_2$	Sulphuric acid	$H_2SO_4(aq)$
Calcium sulphate	$CaSO_4$	Nitric acid	$HNO_3(aq)$
Calcium carbonate	$CaCO_3$	Copper(II) oxide	CuO
		Copper(II) sulphate	$CuSO_4$

CHECKPOINT 3.2: FORMULAE

1. How many atoms are present in the following?

   (a) C_6H_6 *(b)* P_4O_{10} *(c)* SO_2Cl_2
   (d) $C_2H_4Cl_2$ *(e)* $2ZnSO_4$ *(f)* $5CuSO_4$
   (g) $Al(NO_3)_3$ *(h)* $2Al(OH)_3$ *(i)* $Fe_2(SO_4)_3$
   (j) $3Fe(NO_3)_3$

2. Give the formula of:

   (a) sodium hydroxide, *(b)* hydrochloric acid,
   (c) ammonia, *(d)* sodium chloride,
   (e) calcium oxide, *(f)* calcium hydroxide,
   (g) calcium carbonate, *(h)* sulphuric acid,
   (i) nitric acid.

3.3 EQUATIONS

You have studied symbols for elements and formulae for compounds [§ 3.2]. These enable you to write equations for chemical reactions.

Example (a) Calcium carbonate decomposes to give calcium oxide and carbon dioxide.

Calcium carbonate ⟶ Calcium oxide + Carbon dioxide

Writing an equation ...

Replacing names with formulae, you can write the chemical equation for the reaction:

$$CaCO_3 \longrightarrow CaO + CO_2$$

On the left-hand side, you have 1 atom of calcium, 1 atom of carbon and 3 atoms of oxygen combined as calcium carbonate. On the right-hand side, you have 1 atom of calcium and 1 atom of oxygen combined as calcium oxide and 1 atom of carbon and 2 atoms of oxygen combined as carbon dioxide. The two sides are equal, and this is why the expression is called an equation.

... adding state symbols

You can give more information if you include state symbols in the equation. These are (s) = solid, (l) = liquid, (g) = gas, and (aq) = in aqueous (water) solution. Putting in the state symbols,

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

tells you that solid calcium carbonate decomposes to form solid calcium oxide and carbon dioxide gas.

Example (b) Magnesium reacts with sulphuric acid to give hydrogen and a solution of magnesium sulphate.

Magnesium + Sulphuric acid ⟶ Hydrogen + Magnesium sulphate

The chemical equation is

$$Mg(s) + H_2SO_4(aq) \longrightarrow H_2(g) + MgSO_4(aq)$$

Hydrogen is written as H_2 because hydrogen gas consists of molecules containing two atoms.

Example (c) Hydrogen and oxygen combine to form water. The word equation is

Hydrogen + Oxygen ⟶ Water

The chemical equation could be

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

This equation is not balanced. There are 2 oxygen atoms on the left-hand side (LHS) and only 1 oxygen atom on the right-hand side (RHS). To balance the O atoms, multiply H_2O on the RHS by 2.

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

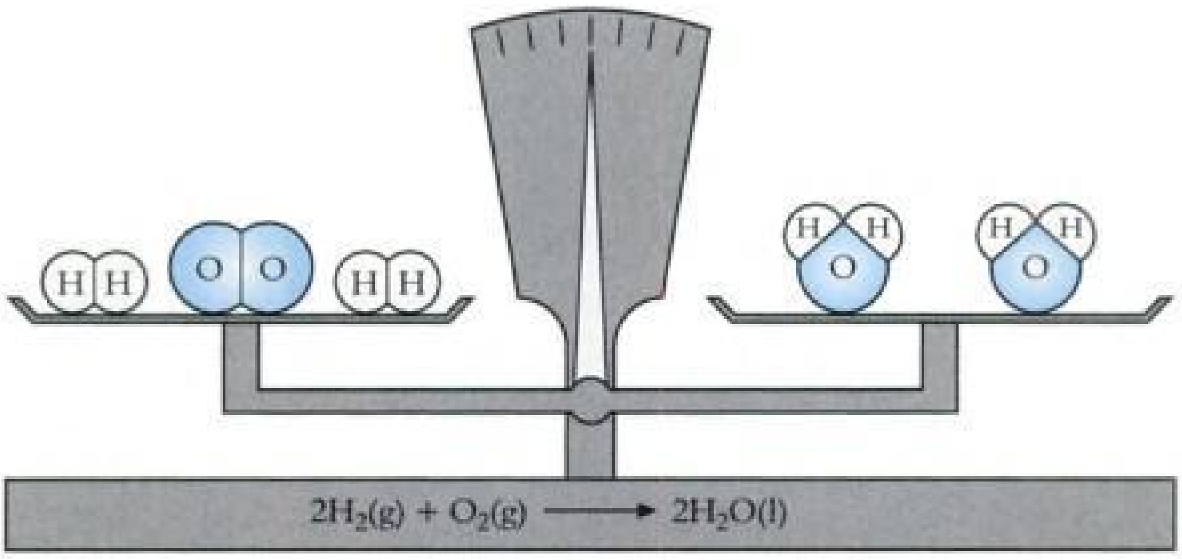
The O atoms are now balanced, but there are 4H atoms on the RHS and only 2H on the LHS. Multiplying H on the LHS by 2,

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

The equation is now balanced.

Number of atoms on LHS = 4H + 2O
Number of atoms on RHS = 4H + 2O
Number of atoms of each element on LHS = Number of atoms of each element on RHS
The total mass of the reactants = The total mass of the products [see Figure 3.3A]

Figure 3.3A
A balanced equation (Example (c))



Example (d) Sulphur dioxide is oxidised by oxygen to sulphur trioxide.

Sulphur dioxide + Oxygen ⟶ Sulphur trioxide

$$SO_2(g) + O_2(g) \longrightarrow SO_3(g)$$

Balancing an equation ...

... by multiplying a formula or formulae ...

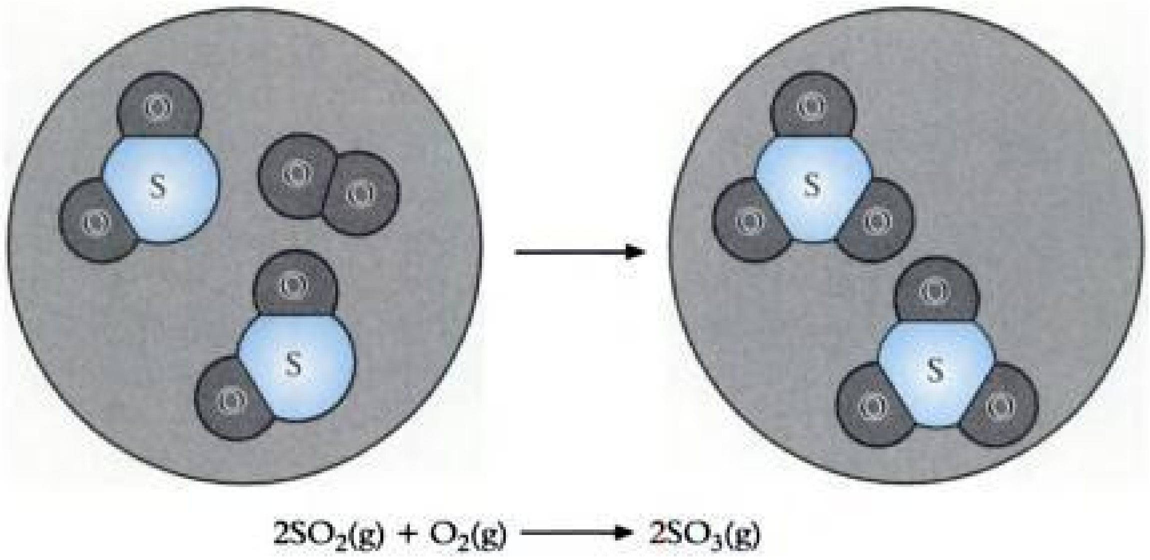
You can see that the equation is not balanced. There are 4O on the LHS and 3O on the RHS. It is tempting to write O for oxygen on the LHS. You must not do this. Never change a formula. All you can do to balance an equation is to multiply formulae. Instead of changing O_2 to O, multiply SO_2 and SO_3 by 2.

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

The equation is now balanced: 2S + 6O on the LHS; 2S + 6O on the RHS [see Figure 3.3B].

Figure 3.3B
A balanced equation (Example (d))

... never by changing a formula



Example (e) Sodium carbonate reacts with dilute hydrochloric acid to give carbon dioxide and a solution of sodium chloride.

Sodium carbonate + Hydrochloric acid ⟶ Carbon dioxide + Sodium chloride + Water

The chemical equation could be

$$Na_2CO_3(s) + HCl(aq) \longrightarrow CO_2(g) + NaCl(aq) + H_2O(l)$$

... and omits spectator ions

The other method is to write an equation showing which ions take part in the reaction and ignoring the ions which do not change their bonding during the reaction, e.g.

$$\text{Sulphate ion} + \text{Barium ion} \longrightarrow \text{Barium sulphate}$$
$$SO_4^{2-}(aq) + Ba^{2+}(a) \longrightarrow BaSO_4(s)$$

The other ions present, in this case the sodium ions and chloride ions, pass through the reaction unchanged; they are described as **spectator ions**.

CHECKPOINT 3.3: EQUATIONS

1. Copy these equations, and balance them.
   - *(a)* $Fe_2O_3(s) + C(s) \longrightarrow Fe(s) + CO(g)$
   - *(b)* $Fe_2O_3(s) + CO(g) \longrightarrow Fe(s) + CO_2(g)$
   - *(c)* $NH_3(g) + O_2(g) \longrightarrow NO(g) + H_2O(l)$
   - *(d)* $Cr(s) + HCl(aq) \longrightarrow CrCl_3(aq) + H_2(g)$
   - *(e)* $Fe_3O_4(s) + H_2(g) \longrightarrow Fe(s) + H_2O(l)$
   - *(f)* $C_3H_8(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(l)$
2. Try writing equations for the reactions:
   - *(a)* Hydrogen + Copper(II) oxide ⟶ Copper + Water
   - *(b)* Carbon + Carbon dioxide ⟶ Carbon monoxide
   - *(c)* Magnesium + Sulphuric acid ⟶ Hydrogen + Magnesium sulphate
   - *(d)* Copper + Chlorine ⟶ Copper(II) chloride
   - *(e)* Mercury + Oxygen ⟶ Mercury(II) oxide
   - *(f)* Iron + Sulphur ⟶ Iron(II) sulphide
3. Write balanced chemical equations for the reactions:
   - *(a)* Calcium + Water ⟶ Hydrogen + Calcium hydroxide solution
   - *(b)* Iron + Hydrochloric acid ⟶ Iron(II) chloride solution + Hydrogen
   - *(c)* Iron + Chlorine ⟶ Iron(III) chloride
   - *(d)* Aluminium + Chlorine ⟶ Aluminium chloride
   - *(e)* Zinc + Steam ⟶ Zinc oxide + Hydrogen
   - *(f)* Sodium + Oxygen ⟶ Sodium oxide
4. Write the full equation and the ionic equation for each of the following reactions.
   - *(a)* Iron(II) sulphate + Sodium hydroxide ⟶ Iron(II) hydroxide + Sodium sulphate
   - *(b)* Silver nitrate + Sodium bromide ⟶ Silver bromide + Sodium nitrate
   - *(c)* Lead(II) nitrate + Sodium iodide ⟶ Lead(II) iodide + Sodium nitrate

3.4 RELATIVE ATOMIC MASS

The masses of atoms are very small, from 10^{-24} to 10^{-22} grams. Instead of using the actual masses of atoms, **relative atomic masses (A_r)** are used. Originally, they were defined as

Atoms range in mass from 10^{-24} g to 10^{-22} g

$$\text{Original relative atomic mass} = \frac{\text{Mass of one atom of an element}}{\text{Mass of one atom of hydrogen}}$$

Since relative atomic masses are now determined by mass spectrometry, and since volatile carbon compounds are much used in mass spectrometry, the mass of an atom of $^{12}_{6}C$ is now taken as the standard of reference:

The definition of relative atomic mass...

$$\boxed{\text{Relative atomic mass} = \frac{\text{Mass of one atom of an element}}{1/12 \text{ the mass of one atom of carbon-12}}}$$

The difference between the two scales is small. On the carbon-12 scale, the relative atomic mass of $^{12}_{6}C$ is 12.0000, and the relative atomic mass of $^{1}_{1}H$ is 1.0078. The mass of a $^{12}_{6}C$ atom is 12.0000 u, and the mass of a $^{1}_{1}H$ atom is 1.0078 u [§ 1.3].

and it follows that, if we have a piece of magnesium which has twice the mass of a piece of carbon, the two masses must contain equal numbers of atoms.
2 grams of magnesium and 1 gram of carbon contain the same number of atoms; 10 tonnes of magnesium and 5 tonnes of carbon contain the same number of atoms.

The same argument applies to the other elements. Take the relative atomic mass in grams of any element:

12 g	24 g	56 g	40 g	108 g	238 g	207 g
Carbon	Magnesium	Iron	Calcium	Silver	Uranium	Lead

All these masses contain the same number of atoms. The number is 6.022×10^{23}.

> The amount of an element that contains 6.022×10^{23} atoms (the same number of atoms as 12 g of carbon-12) is called **one mole** of that element.

The symbol for mole is **mol**. The ratio $6.022 \times 10^{23}\ \text{mol}^{-1}$ is called the **Avogadro constant**. When you weigh out 12 g of carbon, you are counting out 6×10^{23} atoms of carbon. This amount of carbon is one mole (1 mol) of carbon atoms. Similarly, 48 g of magnesium is two moles (2 mol) of magnesium atoms. You can say that the **amount** of magnesium is two moles (2 mol).

You can have a mole of magnesium atoms, Mg, a mole of magnesium ions, Mg^{2+}, a mole of sulphuric acid molecules, H_2SO_4. One mole of sulphuric acid contains 6×10^{23} molecules of H_2SO_4, that is, 98 g of H_2SO_4 (the molar mass in grams). To write 'one mole of nitrogen' is imprecise: one mole of nitrogen atoms, N, has a mass of 14 grams; one mole of nitrogen molecules, N_2, has a mass of 28 grams.

CHECKPOINT 3.6: THE AVOGADRO CONSTANT

(Take the Avogadro constant to be $6 \times 10^{23}\ \text{mol}^{-1}$.)

1. There are 4 billion people in the world. If you had one mole of £1 coins to distribute equally between them, how much would each person receive?
2. What mass of potassium contains *(a)* 6×10^{23} atoms, *(b)* 2×10^{25} atoms?
3. The price of gold is £8.20 per gram; $A_r(\text{Au}) = 198$. Calculate the price of 1 million million atoms of gold.

3.7 MOLAR MASS

Molar mass is defined

The unit is g mol^{-1}

The mass of one mole of a substance is called the **molar mass**, symbol M, unit g mol^{-1}. The molar mass of carbon is $12\ \text{g mol}^{-1}$; that is the relative atomic mass expressed in grams per mole. The term molar mass applies to compounds as well as elements. The molar mass of a compound is the relative molecular mass expressed in grams per mole. Sulphuric acid, H_2SO_4, has a relative molecular mass of 98; its molar mass is $98\ \text{g mol}^{-1}$. Notice the units: relative molecular mass has no unit; molar mass has the unit g mol^{-1}.

$$\text{Amount (in moles) of substance} = \frac{\text{Mass of substance}}{\text{Molar mass of substance}}$$

Molar mass of element = Relative atomic mass in grams per mole

Molar mass of compound = Relative molecular mass in grams per mole

Sample calculations of amount of substance

Example (a) What is the amount of calcium present in 120 g of calcium?

Method A_r of calcium = 40

Molar mass of calcium = 40 g mol^{-1}

Amount of substance = Mass / Molar mass

$$\text{Amount of calcium} = \frac{\text{Mass of calcium}}{\text{Molar mass of calcium}} = \frac{120\text{ g}}{40\text{ g mol}^{-1}}$$
$$= 3.0\text{ mol}$$

The amount (number of moles) of calcium is 3.0 mol.

Example (b) If you need 2.50 mol of sodium hydrogencarbonate, what mass of the substance do you have to weigh out?

Method Relative molecular mass of $NaHCO_3 = 23 + 1 + 12 + (3 \times 16) = 84$

Molar mass of $NaHCO_3$ = 84 g mol^{-1}

$$\text{Amount of substance} = \frac{\text{Mass of substance}}{\text{Molar mass of substance}}$$

$$2.50\text{ mol} = \frac{\text{Mass}}{84\text{ g mol}^{-1}}$$

$$\text{Mass} = 84\text{ g mol}^{-1} \times 2.50\text{ mol}$$
$$= 210\text{ g}$$

You need to weigh out 210 g of sodium hydrogencarbonate.

CHECKPOINT 3.7: THE MOLE

1. State the mass of:
   - *(a)* 3 mol of magnesium ions, Mg^{2+}
   - *(b)* 0.50 mol of oxygen atoms, O
   - *(c)* 0.50 mol of oxygen molecules, O_2
   - *(d)* 0.25 mol of sulphur atoms, S
   - *(e)* 0.25 mol of sulphur molecules, S_8
2. Find the amount (moles) of each element present in:
   - *(a)* 69 g of lead, Pb
   - *(b)* 14 g of iron, Fe
   - *(c)* 56 g of nitrogen, N_2
   - *(d)* 2.0 g of mercury, Hg
   - *(e)* 9.0 g of aluminium, Al
3. State the mass of
   - *(a)* 2.0 mol of carbon dioxide molecules, CO_2
   - *(b)* 10 mol of sulphuric acid, H_2SO_4
   - *(c)* 2.0 mol of sodium chloride, NaCl
   - *(d)* 0.50 mol of calcium hydroxide, $Ca(OH)_2$
4. Calculate the molar masses of the following:
   - *(a)* $NH_4Fe(SO_4)_2 \cdot 12H_2O$
   - *(b)* $Al_2(SO_4)_3$
   - *(c)* $K_4Fe(CN)_6$
5. How many moles of substance are present in the following?
   - *(a)* 0.250 g of calcium carbonate
   - *(b)* 5.30 g of anhydrous sodium carbonate
   - *(c)* 5.72 g of sodium carbonate-10-water crystals
6. Use the value of 6.0×10^{23} mol^{-1} for the Avogadro constant to find the number of atoms in
   - *(a)* 2.0×10^{-3} g of calcium
   - *(b)* 5.0×10^{-6} g of argon
   - *(c)* 1.00×10^{-10} g of mercury

3.8 EMPIRICAL FORMULAE

The **empirical formula** of a compound is the simplest formula which represents its composition.

It shows the elements present and the ratio of the amounts of elements present.

Finding an empirical formula ...

To find an empirical formula, you need to work out the ratio of the amounts of the elements present.

Example A 0.4764 g sample of an oxide of iron was reduced by a stream of carbon monoxide. The mass of iron that remained was 0.3450 g. Find the empirical formula of the oxide.

Method

...A worked example ...

...composition by mass ...

... composition by amount (moles) ...

Elements present	*Iron*		*Oxygen*
Mass/g	0.3450		0.1314
A_r	56		16
Amount/mol	0.3450/56 $= 6.16 \times 10^{-3}$		0.1314/16 $= 8.21 \times 10^{-3}$
Ratio of amounts	1	:	$\dfrac{8.21 \times 10^{-3}}{6.16 \times 10^{-3}}$
	1	:	1.33
	3	:	4

...empirical formula

Empirical formula is Fe_3O_4.

3.9 MOLECULAR FORMULAE

Finding a molecular formula ...

The **molecular formula** is a simple multiple of the empirical formula.

... a multiple of the empirical formula

If the empirical formula is CH_2O, the molecular formula may be CH_2O, $C_2H_4O_2$, $C_3H_6O_3$ and so on.

The way to find out which molecular formula is correct is to find out which gives the correct molar mass.

Example A polymer of empirical formula CH_2 has a molar mass of 28 000 g mol^{-1}. What is its molecular formula?

... A worked example

Method

Empirical formula mass = 14 g mol^{-1}

Molar mass = 28 000 g mol^{-1}

The molar mass is 2000 times the empirical formula mass; therefore the molecular formula is $(CH_2)_{2000}$.

3.10 CALCULATION OF PERCENTAGE COMPOSITION

The empirical formula shows percentage by mass composition ...

From the formula of a compound and the relative atomic masses of the elements in it, the percentage of each element in the compound can be calculated. This is called the **percentage composition by mass**.

Example Calculate the percentage mass of water of crystallisation in copper(II) sulphate-5-water.

Method

... A worked example

Formula is $CuSO_4 \cdot 5H_2O$

Relative atomic masses are Cu = 63.5 S = 32 O = 16 H = 1

$$\text{Molar mass} = 63.5 + 32 + (4 \times 16) + (5 \times 18)$$
$$= 249.5 \text{ g mol}^{-1}$$
$$\text{Percentage of water} = \frac{90}{249.5} \times 100$$
$$= 36\%$$

CHECKPOINT 3.10: FORMULAE AND PERCENTAGE COMPOSITION

1. Calculate the percentage by mass of the named element in the compound listed:

   (a) Mg in Mg_3N_2, *(b)* Na in NaCl, *(c)* Br in $CaBr_2$

2. Calculate the empirical formulae of the compounds for which the following analytical results were obtained:

   (a) 27.3% C, 72.7% O
   (b) 53.0% C, 47.0% O
   (c) 29.1% Na, 40.5% S, 30.4% O
   (d) 32.4% Na, 22.6% S, 45.0% O

3. Find the empirical formulae of the compounds formed in the reactions described below:

   (a) 10.800 g magnesium form 18.000 g of an oxide
   (b) 3.400 g calcium form 9.435 g of a chloride
   (c) 3.528 g iron form 10.237 g of a chloride

4. Weighed samples of the following crystals were heated to drive off the water of crystallisation. When they reached constant mass, the following masses were recorded. Deduce the empirical formulae of the hydrates:

   (a) 0.942 g of $MgSO_4 \cdot a\, H_2O$ gave 0.461 g of residue
   (b) 1.124 g of $CaSO_4 \cdot b\, H_2O$ gave 0.889 g of residue
   (c) 1.203 g of $Hg(NO_3)_2 \cdot c\, H_2O$ gave 1.172 g of residue

3.11 EQUATIONS FOR REACTIONS OF SOLIDS

Equations give us much information ...

Equations tell us not only what substances react together but also what amounts of substances react together.

The equation for the action of heat on sodium hydrogencarbonate

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

tells us that 2 moles of sodium hydrogencarbonate give 1 mole of sodium carbonate. Since the molar masses are $NaHCO_3 = 84$ g mol^{-1} and $Na_2CO_3 = 106$ g mol^{-1}, it follows that 168 g of sodium hydrogencarbonate give 106 g of sodium carbonate.

... about the relationship between the amounts of reactants and products

The amounts of substances undergoing reaction, as given by the balanced chemical equation, are called the **stoichiometric** amounts. **Stoichiometry** is the relationship between the amounts of reactants and products in a chemical reaction. If one reactant is present in excess of the stoichiometric amount required to react with another of the reactants, then the excess of one reactant will be left unused at the end of the reaction.

Method From the equation you can see that

2 mol of $KClO_3$ give 3 mol of O_2

Molar mass of $KClO_3 = 92.5\ \text{g mol}^{-1}$

Therefore $2 \times 92.5\ \text{g}\ KClO_3 \longrightarrow 3 \times 22.4\ \text{dm}^3\ O_2$

To supply $200\ \text{cm}^3$ O_2 you need $\dfrac{2 \times 92.5}{3 \times 22.4} \times 200 \times 10^{-3}\ \text{g}\ KClO_3$

Mass of $KClO_3$ decomposed = 0.551 g

CHECKPOINT 3.12: REACTING VOLUMES OF GASES

1. What volume of hydrogen is formed when 3.00 g of magnesium react with an excess of dilute sulphuric acid?
2. Carbon dioxide is obtained by the fermentation of glucose:

   $$C_6H_{12}O_6(aq) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

   If 20.0 dm^3 of carbon dioxide (at stp) are collected, what mass of glucose has reacted?
3. In the preparation of hydrogen chloride by the reaction

   $$NaCl(s) + H_2SO_4(l) \longrightarrow HCl(g) + NaHSO_4(s)$$

   what masses of sodium chloride and sulphuric acid are required for the production of 10.0 dm^3 of hydrogen chloride (at stp)?

3.13 CONCENTRATION

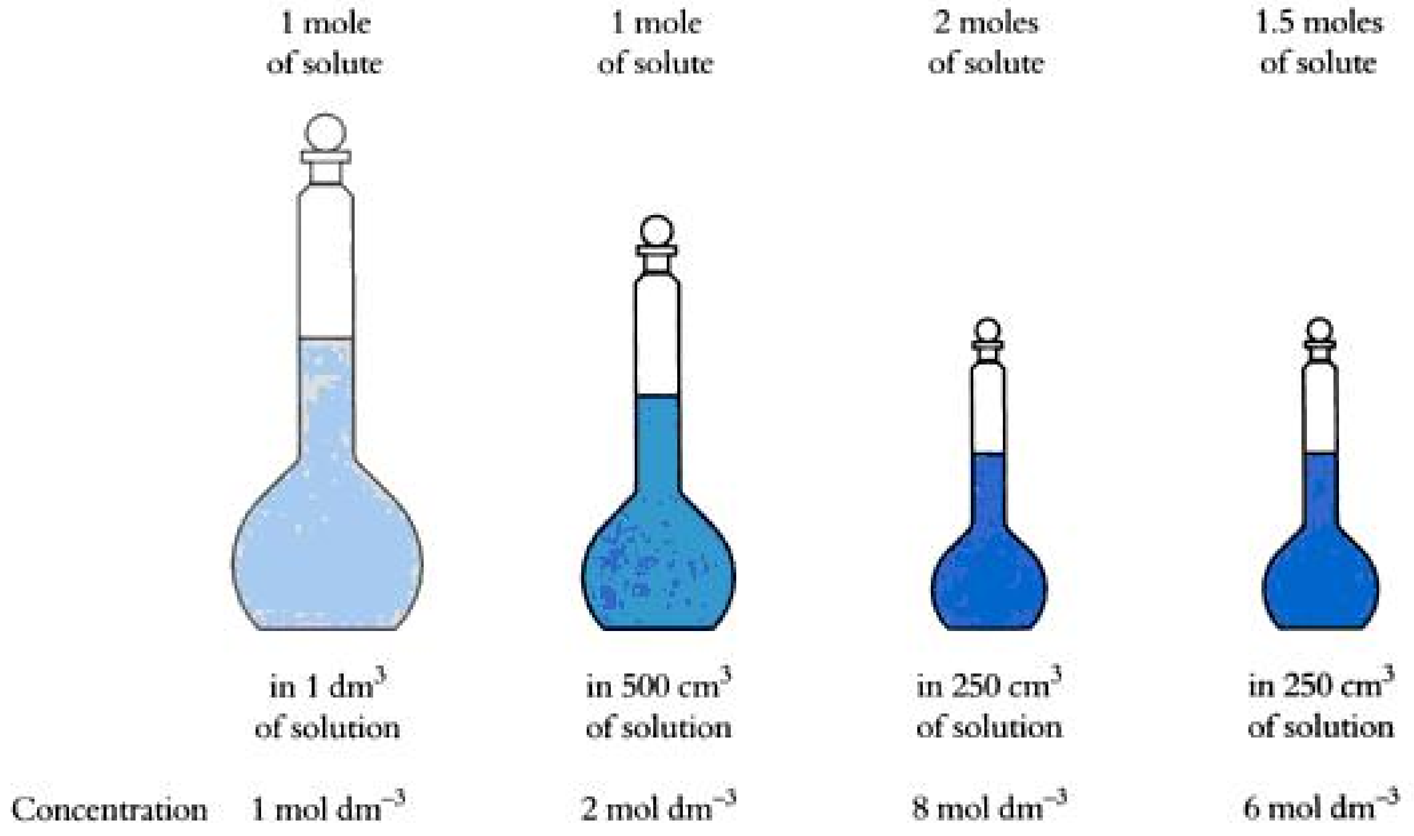
The concentration of a solution can be stated ...

One way of stating the concentration of a solution is to state the **mass** of solute present in 1 cubic decimetre of solution, e.g. grams per cubic decimetre (g dm^{-3}). There is another method which is more convenient when it comes to chemical reactions. This is to state the **amount** in moles of a solute present in 1 dm^3 of solution.

... either in grams of solute per cubic decimetre of solution (g dm^{-3}) ...

If 1 mole of solute is present in 1 dm^3 of solution, the concentration of solute is 1 mole per dm^3 (1 mol dm^{-3}). The solution is a 1 mol dm^{-3} solution or, for short, a 1 M solution [see Figure 3.13A].

Figure 3.13A Solutions of known concentration



CHECKPOINT 3.13A: CONCENTRATION

1. Calculate the concentrations of the following solutions:

   (a) 4.0 g of sodium hydroxide in 500 cm^3 of solution
   (b) 7.4 g of calcium hydroxide in 5.0 dm^3 of solution
   (c) 49.0 g of sulphuric acid in 2.5 dm^3 of solution
   (d) 73 g of hydrogen chloride in 250 cm^3 of solution

2. Find the amount of solute present in the following solutions:

   (a) 1.00 dm^3 of a solution of sodium hydroxide of concentration 0.25 mol dm^{-3}
   (b) 500 cm^3 of hydrochloric acid of concentration 0.020 mol dm^{-3}
   (c) 250 cm^3 of 0.20 mol dm^{-3} sulphuric acid
   (d) 10 cm^3 of a 0.25 mol dm^{-3} solution of potassium hydroxide

3.13.1 PREPARING A STANDARD SOLUTION BY WEIGHING

A standard solution is made from a primary standard

Now you know how to calculate the mass of solid which you need to make a standard solution. A standard solution can only be made from a solid which can be obtained 100% (almost) pure. Anhydrous sodium carbonate and sodium hydrogencarbonate can be used to make standard solutions. They are called **primary standards**. Ethanedioic acid, $C_2H_2O_4$, and butanedioic acid, $C_4H_6O_4$, are primary standards which can be used to make standard acid solutions. For other substances, a solution of approximately known concentration is made and then the solution is standardised against a primary standard. You could not make a standard solution of sodium hydroxide. As you were weighing it out, it would absorb water vapour from the air and react with carbon dioxide in the air. You would have to make a solution of approximately known concentration and titrate it against, for example, a standard solution of ethanedioic acid to find its exact concentration.

Method of preparing a standard solution of sodium carbonate

A known mass of the primary standard is dissolved in distilled water ...

1. Calculate the mass of sodium carbonate needed, m_1.

2. Weigh a clean weighing bottle, and record its mass, m_2. [See Figure 3.13B(a).] With a clean spatula, add pure anhydrous sodium carbonate until the combined mass of weighing bottle and sodium carbonate is $m_1 + m_2$.

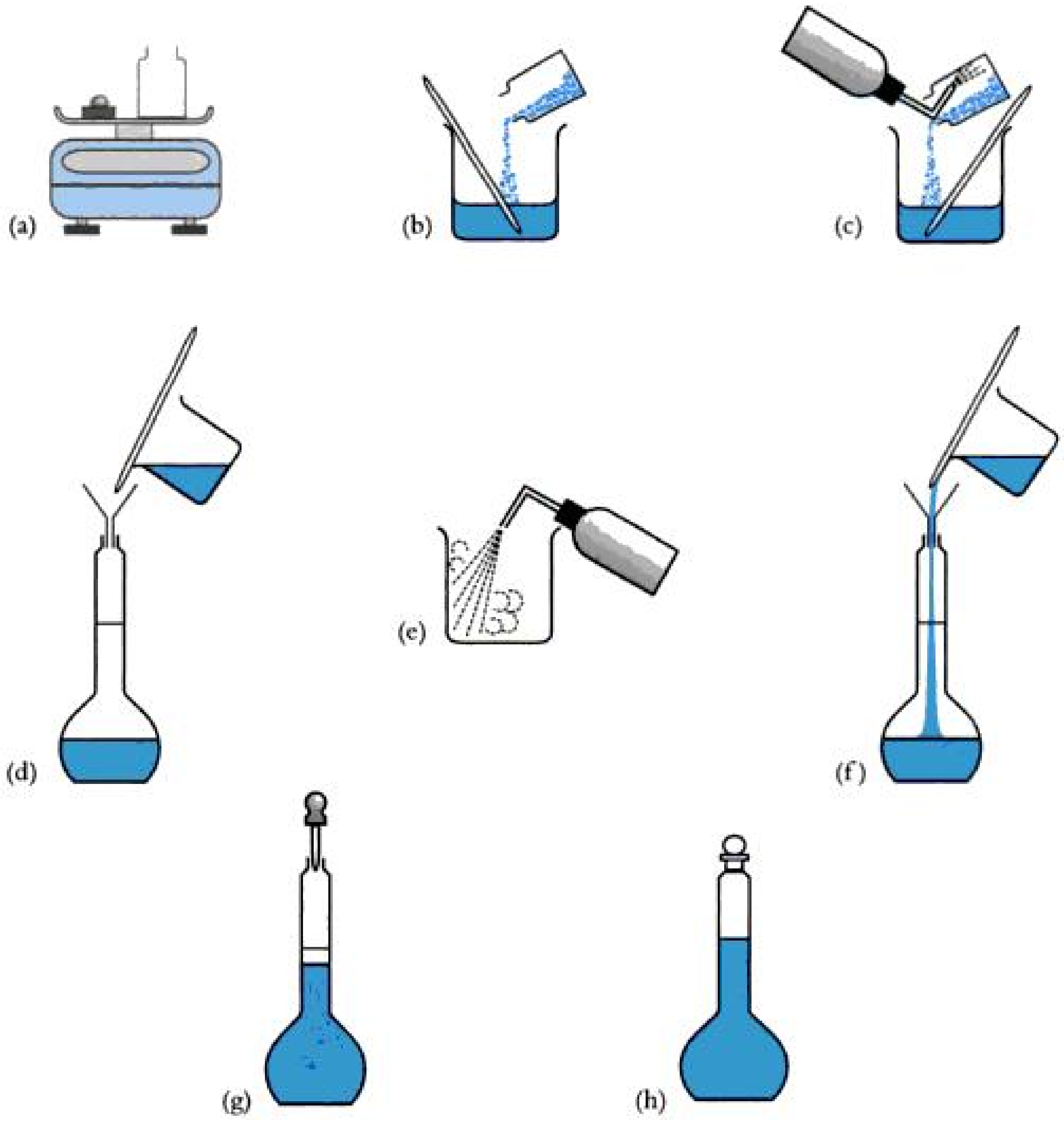
3. Transfer the sodium carbonate carefully into a clean beaker. [See Figure 3.13B(b).] Use a wash bottle of distilled water so that all the washings run into the beaker. Add about 100 cm^3 of distilled water. Stir with a glass rod until all the solid has dissolved [Figure 3.13B(c)].

4. Pour all the solution carefully through a filter funnel into a graduated flask [Figure 3.13B(d)]. Wash all the solution out of the beaker and off the glass rod [Figure 3.13B(e), (f)].

... and the volume of the solution is made up to a known volume

5. Add distilled water until the level is about 2 cm below the graduation mark on the graduated flask. Add the rest of the distilled water drop by drop from a dropping pipette until the bottom of the meniscus is level with the graduation mark when viewed at eye level [Figure 3.13B(g)]. Insert the stopper of the flask and invert the flask several times to mix the solution [Figure 3.13B(h)].

Figure 3.13B
Preparing a standard solution



3.13.2 PREPARING A STANDARD SOLUTION BY DILUTION

A standard solution can be made by diluting a more concentrated standard solution

You can prepare a dilute standard solution by diluting a more concentrated standard solution in a measured way.

... either accurately, using a burette and volumetric flask ...

If you want to know the concentration accurately, you use a burette and a volumetric flask. You would not be able to do this with a very concentrated solution, e.g. concentrated sulphuric acid or glacial ethanoic acid. You could use the method to prepare, for instance, a 0.1 mol dm^{-3} solution from a 2 mol dm^{-3} solution. The steps you would follow are:

1. Fill a clean, dry burette with the more concentrated standard solution.
2. Run the calculated volume of the more concentrated solution into a volumetric flask.
3. Make the solution up to the mark with distilled water. Shake.

(*Note* You cannot use very concentrated acids and alkalis in burettes.)

... or approximately using a measuring cylinder and a graduated beaker

If you do not need to know the concentration accurately, the steps to follow are:

1. Use a measuring cylinder to measure the volume of the concentrated solution.
2. Transfer the solution to a graduated beaker.
3. Make up to the mark with distilled water. Stir.

CHECKPOINT 3.13B: SOLUTIONS

1. (a) On Monday, Jerry's teacher gives him some 1.00 mol dm^{-3} acid and instructs him to make a solution which is exactly 0.100 mol dm^{-3}. Say what apparatus Jerry should use and describe what he should do.
   (b) On Tuesday, Jerry is given the same 1.00 mol dm^{-3} acid. This time he is asked to prepare quickly a solution which is between 0.09 mol dm^{-3} and 0.11 mol dm^{-3}. Say what apparatus he should use and what he should do.

2. Explain what dangers you would risk by using a very concentrated acid in a burette.

3. The concentrated hydrochloric acid in the store has a concentration of 12 mol dm^{-3}. The college technician has to fill all the reagent bottles in the lab with approximately 2 mol dm^{-3} hydrochloric acid. There are 24 bottles, each of which holds 250 cm^3.

   Describe how the technician should prepare the solution of dilute hydrochloric acid.

4. Ammonia is bought as '880 ammonia' (a solution of density 0.880 g cm^{-3}), which contains 245 g ammonia per dm^3 of solution. What volume of the concentrated solution would you need to prepare 1.0 dm^3 of 2.0 mol dm^{-3} ammonia solution?

5. (a) Why can sodium hydrogencarbonate be used to prepare standard solutions?
   (b) What mass of sodium hydrogencarbonate would you weigh out to prepare 500 cm^3 of a 0.0100 M solution?
   (c) Describe how you would make up the solution as accurately as possible.

6. You have a large stock bottle of ethanoic acid of concentration 4.00 mol dm^{-3}. You also have a large bottle of 'glacial' ethanoic acid. This is the name given to a concentrated solution of ethanoic acid which freezes at 10 °C. It has a concentration of about 17 mol dm^{-3}.

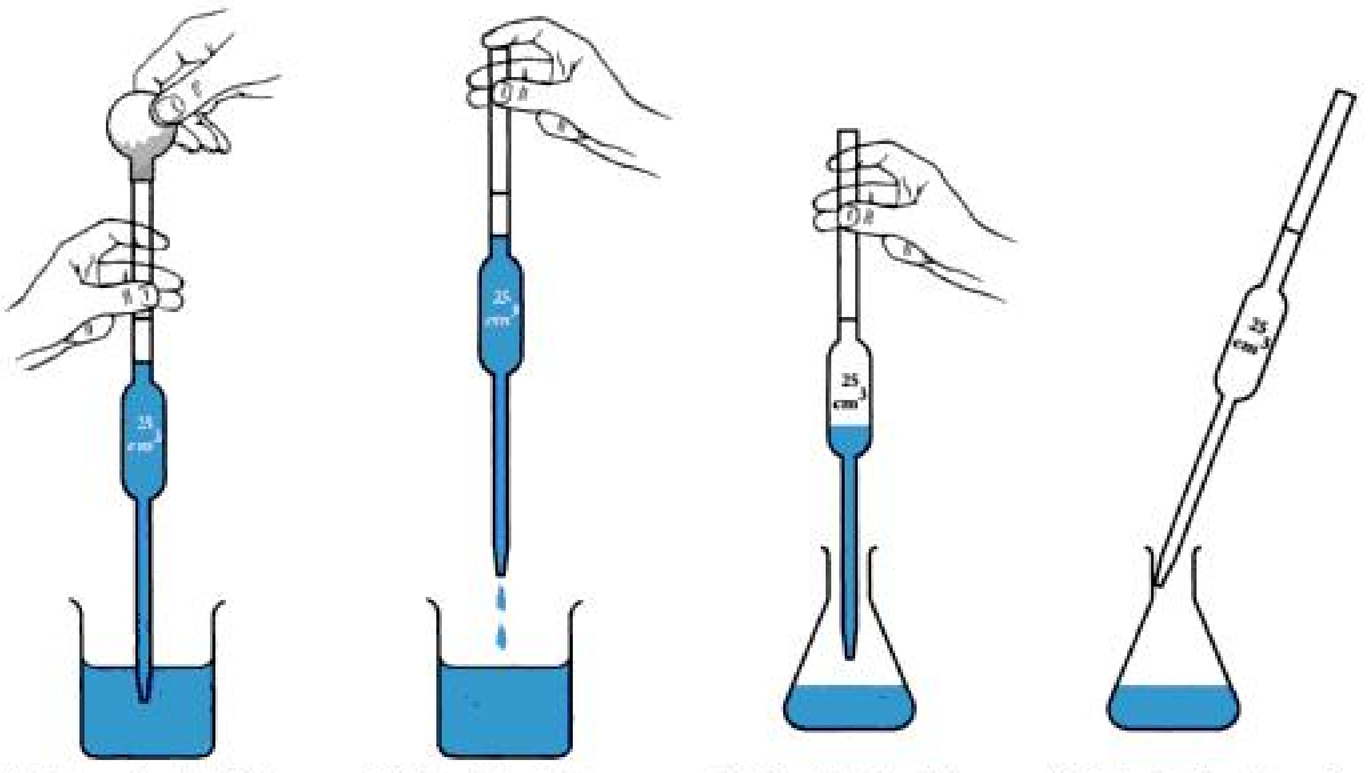
   (a) How can you make up 1.00 dm^3 of a 0.250 mol dm^{-3} solution of the acid? Say what quantities you would measure and what apparatus you would use.
   (b) Explain how you would prepare 2 dm^3 of 2 mol dm^{-3} ethanoic acid.

3.14 VOLUMETRIC ANALYSIS

The concentration of a solution can be found by volumetric analysis

Volumetric analysis is a means of finding the concentration of a solution. The method is to add a solution of, say, an acid to a solution of, say, a base, in a measured way until there is just enough of the acid to neutralise the base. This method is called **titration** [see Figures 3.14A and 3.14B].

Figure 3.14A
Using a pipette



1 Use a pipette filler to suck up the liquid into the pipette.

2 Allow liquid to run slowly down to the graduation mark.

3 Run the liquid into a conical flask.

4 Touch the side of the flask with the tip of the pipette.

The method of titration is used ...

... for example an acid of unknown concentration is titrated against a measured volume of a standard solution of a base

The concentration of one of the two solutions must be known, and the volumes of both must be measured. You can use a standard solution of a base to find out the concentration of a solution of an acid. You have to find out what volume of the acid solution of unknown concentration is needed to neutralise a known volume, usually 25.0 cm^3, of the standard solution of a base. An indicator tells when exactly the right volume of solution has been added to achieve neutralisation. You will learn titration in your laboratory periods. Here is a reminder of the practical details:

1. Use a pipette to deliver 25.0 cm^3 of the alkali solution into a clean conical flask [see Figure 3.14A]. Add a few drops of indicator.

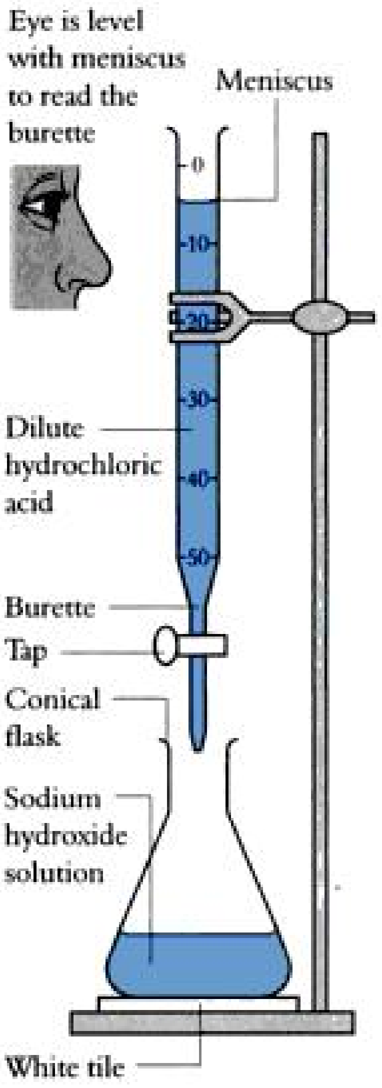
2. Wash the burette with a little of the acid solution. Allow the solution to run into the tip of the burette. Read the burette (V_1 cm^3, the bottom of the meniscus) [see Figure 3.14B].

3. Arrange the apparatus as shown in Figure 3.14B. Run the acid solution from the burette dropwise. Use your left hand to open the tap and your right hand to swirl the conical flask (unless you are left-handed). Stop when the indicator just changes colour. This is the 'end-point' of the titration.

4. Read the burette again (V_2 cm^3). Subtract to find the volume of acid used, $(V_2 - V_1)$ cm^3. This 'titre' is the volume of acid needed to neutralise 25.0 cm^3 of alkali.

5. Repeat the titration. Obtain an average titre. From this volume, you can calculate the unknown concentration.

Figure 3.14B
Titration



Example (a) By titration, you find that 15.0 cm^3 of hydrochloric acid neutralise 25.0 cm^3 of a 0.100 mol dm^{-3} solution of sodium hydroxide. What is the concentration of hydrochloric acid?

Method

The method of calculating concentration from the results of titration

1. The equation for the reaction,

$$\text{Hydrochloric acid} + \text{Sodium hydroxide} \longrightarrow \text{Sodium chloride} + \text{Water}$$
$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

tells you that 1 mole of HCl neutralises 1 mole of NaOH.

Where to start? Start with the substance for which you know both the volume of the solution and the concentration. Work out the amount (moles) of that substance

2. Now work out the amount (mol) of base. You must start with the base because you know the concentration of base, and you do not know the concentration of acid.

$$\text{Amount (mol)} = \text{Volume (dm}^3) \times \text{Concentration (mol dm}^{-3})$$
$$\begin{aligned}\text{Amount (mol) NaOH} &= \text{Volume (25.0 cm}^3) \\ &\quad \times \text{Concentration (0.100 mol dm}^{-3}) \\ &= 25.0 \times 10^{-3}\ \text{dm}^3 \times 0.100\ \text{mol dm}^{-3} \\ &= 2.50 \times 10^{-3}\ \text{mol}\end{aligned}$$

CHECKPOINT 3.14: TITRATION

1. 25.0 cm^3 of sodium hydroxide solution are neutralised by 15.0 cm^3 of a solution of hydrochloric acid of concentration 0.25 mol dm^{-3}. Find the concentration of the sodium hydroxide solution.

2. A solution of sodium hydroxide contains 10 g dm^{-3}.
   (a) What is the concentration of the solution in mol dm^{-3}?
   (b) What volume of this solution would be needed to neutralise 25.0 cm^3 of 0.10 mol dm^{-3} hydrochloric acid?

3. 25.0 cm^3 of hydrochloric acid are neutralised by 20.0 cm^3 of a solution of 0.15 mol dm^{-3} sodium carbonate solution.
   (a) How many moles of sodium carbonate are neutralised by 1 mol HCl?
   (b) What is the concentration of the hydrochloric acid?

4. The sixth form decide to test some antacid indigestion tablets. They obtain the results shown in the table by dissolving tablets and titrating the alkali in them against a standard acid.

Brand	**Price (£) of 100 tablets**	**Volume (cm^3) of 0.01 mol dm^{-3} acid required to neutralise 1 tablet**
Stopit	0.91	2.8
Setlit	1.04	3.0
Mendit	1.30	3.3
Basit	1.56	3.6

   (a) Which antacid tablets offer the best value for money?
   (b) What other factors would you consider before choosing a brand?

5. A tanker of acid is emptied into a water supply by mistake. A water company chemist titrates the water and finds that 10.0 dm^3 of water are needed to neutralise 10.0 cm^3 of a 0.010 mol dm^{-3} solution of sodium hydroxide. What is the concentration of hydrogen ions in the water?

6. A solution is made by dissolving 5.00 g of impure sodium hydroxide in water and making it up to 1.00 dm^3 of solution. 25.0 cm^3 of this solution is neutralised by 30.3 cm^3 of hydrochloric acid, of concentration 0.102 mol dm^{-3}. Calculate the percentage purity of the sodium hydroxide.

7. Sodium carbonate crystals (27.8230 g) were dissolved in water and made up to 1.00 dm^3. 25.0 cm^3 of the solution were neutralised by 48.8 cm^3 of hydrochloric acid of concentration 0.100 mol dm^{-3}. Find *n* in the formula $Na_2CO_3 \cdot nH_2O$.

8. A fertiliser contains ammonium sulphate. A sample of 0.500 g of fertiliser was warmed with sodium hydroxide solution. The ammonia evolved neutralised 44.1 cm^3 of 0.100 mol dm^{-3} hydrochloric acid. Calculate the percentage of ammonium sulphate in the sample.

3.15 EQUATIONS FOR OXIDATION–REDUCTION REACTIONS

3.15.1 REDOX REACTIONS

Oxidising agents accept electrons ...

Oxidising agents are substances which can accept electrons from other substances. **Reducing agents** are substances which can give electrons to other substances.

... reducing agents donate electrons

Oxidation and **reduction** occur together. In an **oxidation–reduction** reaction or **redox** reaction, electrons pass from the reducing agent to the oxidising agent.

Iron(II) ions are reducing agents, losing electrons to form iron(III) ions:

$$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^- \qquad [1]$$

Write the half-reaction equation for the oxidant

Chlorine is an oxidising agent, accepting electrons to form chloride ions:

$$Cl_2(aq) + 2e^- \longrightarrow 2Cl^-(aq) \qquad [2]$$

To obtain the equation for the redox reaction between acidified potassium dichromate and sodium ethanedioate, equation [5] is multiplied by 3 and added to equation [4]:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 3C_2O_4^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6CO_2(g)$$

Reaction between iodine and sodium thiosulphate

Obtaining the equation for the reaction between I_2 and $S_2O_3^{2-}$

... by combining half-reaction equations ...

Sodium thiosulphate(VI), $Na_2S_2O_3$, is a reducing agent. It is most often used in titrimetric analysis for reducing iodine to iodide ions, being oxidised in the process to sodium tetrathionate, $Na_2S_4O_6$. When the brown colour of iodine fades as the end-point approaches, a little starch solution is added. This gives an intense blue colour with even a trace of iodine. At the end-point the blue colour vanishes. The two half-reaction equations are

... so that the electrons on the RHS cancel the electrons on the LHS of the overall equation

$$2S_2O_3^{2-}(aq) \longrightarrow S_4O_6^{2-}(aq) + 2e^- \qquad [6]$$

$$I_2(aq) + 2e^- \longrightarrow 2I^-(aq) \qquad [7]$$

Combining the two half-reaction equations gives

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

CHECKPOINT 3.15: REDOX REACTIONS

1. Write balanced half-reaction equations for the oxidation of each of the following:

   (a) $Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq)$
   (b) $Cl^-(aq) \longrightarrow Cl_2(aq)$
   (c) $H_2S(aq) \longrightarrow S(s) + H^+(aq)$
   (d) $SO_3^{2-}(aq) \longrightarrow SO_4^{2-}(aq) + H^+(aq)$
   (e) $H_2O_2(aq) \longrightarrow O_2(g) + H^+(aq)$

   Check that the equations are balanced with respect to charge as well as mass. Remember that H_2O is present in all solutions; you will need it to balance some of the equations.

2. Write balanced half-reaction equations for the following reductions:

   (a) $Br_2(aq) \longrightarrow Br^-(aq)$
   (b) $MnO_2(s) + H^+(aq) \longrightarrow Mn^{2+}(aq)$
   (c) $PbO_2(s) + H^+(aq) \longrightarrow Pb^{2+}(aq)$
   (d) $IO^-(aq) + H^+(aq) \longrightarrow I_2(aq)$
   (e) $ClO_3^-(aq) + H^+(aq) \longrightarrow Cl_2(aq)$

   Balance the equations for mass, using H_2O from the solution if needed, and then balance with respect to charge.

3. By combining half-reaction equations, write balanced equations for the following reactions:

   (a) $Fe^{3+}(aq) + I^-(aq) \longrightarrow$
   (b) $Fe^{3+}(aq) + Sn^{2+}(aq) \longrightarrow$
   (c) $MnO_4^-(aq) + Cl^-(aq) + H^+(aq) \longrightarrow$
   (d) $MnO_4^-(aq) + H_2O_2(aq) + H^+(aq) \longrightarrow$
   (e) $MnO_4^-(aq) + H^+(aq) + I^-(aq) \longrightarrow$
   (f) $Cr_2O_7^{2-}(aq) + H^+(aq) + I^-(aq) \longrightarrow$
   (g) $Cr_2O_7^{2-}(aq) + H^+(aq) + Fe^{2+}(aq) \longrightarrow$
   (h) $MnO_4^-(aq) + H^+(aq) + Sn^{2+}(aq) \longrightarrow$
   (i) $Cr_2O_7^{2-}(aq) + H^+(aq) + SO_3^{2-}(aq) \longrightarrow$
   (j) $MnO_4^-(aq) + H^+(aq) + SO_3^{2-}(aq) \longrightarrow$
   (k) $MnO_4^-(aq) + H^+(aq) + Fe^{2+}(aq) \longrightarrow$
   (l) $Cr_2O_7^{2-}(aq) + H^+(aq) + Sn^{2+}(aq) \longrightarrow$
   (m) $PbO_2(s) + H^+(aq) + Cl^-(aq) \longrightarrow$
   (n) $ClO_3^-(aq) + H^+(aq) + I^-(aq) \longrightarrow$
   (o) $Br_2(aq) + I^-(aq) \longrightarrow$
   (p) $Cl_2(g) + H^+(aq) + IO^-(aq) \longrightarrow$
   (q) $Br_2(g) + H_2S(g) \longrightarrow$

3.16 OXIDATION NUMBER

A method of expressing the combining power of elements is the idea of **oxidation number** or **oxidation state**.

Examples are:

- The oxidation number of sodium in Na^+ is +1.
- The oxidation number of aluminium in Al^{3+} is +3.
- The oxidation number of iodine in I^- is −1.
- The oxidation number of oxygen in O^{2-} is −2.

The use of oxidation numbers is extended to covalent compounds. Some elements are assigned positive oxidation numbers and others are assigned negative oxidation numbers in accordance with certain rules.

3.16.1 RULES FOR ASSIGNING OXIDATION NUMBERS

The oxidation number of an element in the uncombined state is zero ...

1. The oxidation numbers of elements in their uncombined states, such as Na, Ca, Al, are zero. Similarly the oxidation numbers of iodine in I_2, oxygen in O_2 and sulphur in S_8 are zero.

... The oxidation number of an element in an ionic compound is equal to the charge on its ions, e.g. +1, +2, −1, −2 ...

2. In ionic compounds the oxidation number is equal to the charge on the ion. The oxidation number of an element is not always the same. Iron has an oxidation number of +2 in Fe^{2+} and an oxidation number of +3 in Fe^{3+}.

... The oxidation numbers of the elements in a compound add up to zero

3. The sum of the oxidation numbers of all the atoms or ions in a compound is zero.

   In NaCl,

   $$(\text{Ox. No. of Na}) + (\text{Ox. No. of Cl}) = 0$$
   $$(+1) + (-1) = 0$$

   In Na_2O,

   $$2(\text{Ox. No. of Na}) + (\text{Ox. No. of O}) = 0$$
   $$2(+1) + (-2) = 0$$

   In CuS,

   $$(\text{Ox. No. of Cu}) + (\text{Ox. No. of S}) = 0$$
   $$(+2) + (-2) = 0$$

   In $CaBr_2$,

   $$(\text{Ox. No. of Ca}) + 2(\text{Ox. No. of Br}) = 0$$
   $$(+2) + 2(-1) = 0$$

The oxidation numbers of the elements in an ion add up to the charge on the ion

4. The sum of the oxidation numbers of all the atoms in an ion is equal to the charge on the ion. In SO_4^{2-}, the sum of the oxidation numbers (S = +6, O = −2) is

   $$+6 + 4(-2) = -2$$

   which is the charge on the ion.

Reference elements ...

5. Some elements nearly always employ the same oxidation number in their compounds. They are used as reference points in assigning oxidation numbers to other elements. The reference elements are

... which nearly always have the same oxidation number in their compounds

K	Na	+1	H	+1	except in metal hydrides
Mg	Ca	+2	F	−1	
Al		+3	Cl	−1	except in compounds with O and F
			O	−2	except in peroxides, superoxides, fluorides

... Some worked examples

Example (a) What is the oxidation number of thallium in $TlCl_3$?

Method Chlorine always has the oxidation number −1.

Therefore (Ox. No. of Tl) + 3(−1) = 0

and the oxidation number of thallium is +3.

Example (b) What is the oxidation number of Cl in Cl_2O_7?

Method The exceptions to the rule that the oxidation number of Cl equals −1 are compounds with O and F. Oxygen is the reference point with the oxidation number −2.

Therefore 2 (Ox. No. of Cl) + 7(−2) = 0

and the oxidation number of chlorine is +7.

Example (c) What is the oxidation number of Cr in $Cr(CN)_6^{3-}$?

Method The cyanide ion, CN^-, has a charge of −1.

Therefore (Ox. No. of Cr) + 6(−1) = −3

and the oxidation number of chromium is +3.

CHECKPOINT 3.16A: OXIDATION NUMBER

1. State the oxidation numbers of the elements in following atoms or ions:

   Na, Na^+, Ba, Ba^{2+}, Rb^+, Rb, Ga, As, As^{3-}, Br^-, H_2, H^+, F_2, F^-

2. Give the oxidation numbers of the first element in each of the following compounds. Remember the oxidation numbers of the elements in a compound add up to zero. Take oxidation numbers for hydrogen (+1), oxygen (−2), fluorine (−1) and chlorine (−1) as reference points.

   CuO, Cu_2O, H_2S, SO_2, SO_3, PbO, PbO_2, $AlCl_3$, SF_6, SCl_2, $TiCl_4$, V_2O_5

3. What is the oxidation number of the named element in the following species (ions or molecules)?

   (a) N in NO, NO_2, N_2O_4, N_2O, NO_2^-, NO_3^-, N_2O_5
   (b) Mn in $MnSO_4$, Mn_2O_3, MnO_2, MnO_4^-, MnO_4^{2-}
   (c) As in As_2O_3, AsO_2^-, AsO_4^{3-}, AsH_3
   (d) Cr in CrO_4^{2-}, $Cr_2O_7^{2-}$, CrO_3
   (e) I in I^-, IO^-, IO_3^-, I_2, ICl_3, ICl_2^-

3.16.2 CHANGES IN OXIDATION NUMBER

Oxidation–reduction reactions are often discussed in terms of the change in oxidation number of each reactant. In the redox reaction,

$$2Fe^{2+}(aq) + I_2(aq) \longrightarrow 2Fe^{3+}(aq) + 2I^-(aq)$$

When an element is oxidised, its oxidation number increases

When Fe^{2+} is converted into Fe^{3+}, the oxidation number increases from +2 to +3, and we say that Fe^{2+} has been oxidised to Fe^{3+}. When I_2 is converted into I^-, the oxidation number decreases from 0 in I_2 to −1 in I^-, and we say that I_2 has been reduced to I^-.

Change in Ox. No. of iron = No. of atoms × Change in Ox. No.
$= 2(+1) = +2$

Change in Ox. No. of iodine = No. of atoms × Change in Ox. No.
$= 2(-1) = -2$

Sum of changes in Ox. No. $= +2 - 2 = 0$

When an element is reduced, its oxidation number decreases

In general, when an element is **oxidised**, its oxidation number increases; when an element is **reduced**, its oxidation number decreases. In a redox reaction

$$x\mathbf{A} + y\mathbf{B} \longrightarrow$$

if the oxidation number of **A** changes by $+a$ units, and the oxidation number of **B** changes by $-b$ units

then $x(+a) + y(-b) = 0$

... Some worked examples

Example (a) Consider the reduction of iron(III) ions by a tin(II) salt:

$$Sn^{2+}(aq) + 2Fe^{3+}(aq) \longrightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$$

For tin, change in Ox. No. = +2

For iron, change in Ox. No. = −1

And $1(+2) + 2(-1) = 0$

In disproportionation part of a substance is oxidised and part is reduced

Example (b) $3I_2(aq) + 3OH^-(aq) \longrightarrow IO_3^-(aq) + 5I^-(aq) + 3H^+(aq)$

The only element which changes its oxidation number is iodine.

On the LHS, in I_2 Ox. No. of I = 0

On the RHS, in IO_3^- (Ox. No. of I) $+ 3(-2) = -1$

and the Ox. No. of I = +5

In I^-, Ox. No. of I = −1

Iodine has changed from oxidation number zero on the LHS to a combination of Ox. No. +5 and Ox. No. −1 on the RHS. Part of the iodine has been oxidised and part has been reduced. A reaction of this kind is termed a **disproportionation reaction**.

3.16.3 BALANCING EQUATIONS BY THE OXIDATION NUMBER METHOD

Balancing equations ...

The oxidation number method of balancing equations is best explained through an example.

Sum of increases in oxidation number = sum of decreases in oxidation number ...

... a worked example

Example Balance the equation

$$aKIO_3(aq) + bNa_2SO_3(aq) \longrightarrow cKIO(aq) + dNa_2SO_4(aq)$$

Iodine changes from Ox. No. +5 in KIO_3 to +1 in KIO.

Change in Ox. No. of I = −4

Sulphur changes from Ox. No. +4 in Na_2SO_3 to +6 in Na_2SO_4.

Change in Ox. No. of S = +2

Therefore $a(-4) + b(+2) = 0$

3.17.3 ANIONS

Elemental **anions** (negative ions) are named after the element, with the ending *-ide*:

e.g. H^- hydride N^{3-} nitride

Compound anions have names ending in *-ide*, *-ite* or *-ate*:

e.g. OH^- hydroxide NO_2^- nitrite NO_3^- nitrate

Many elements form more than one **oxoanion**, using more than one oxidation state (e.g., NO_2^-, NO_3^-). The names are derived from the name of the element which is combined with oxygen and the ending *-ate*:

e.g. SO_4^{2-} sulphate ion HCO_3^- hydrogencarbonate ion

Both ClO^- and ClO_3^- are chlorate ions. To distinguish between them, the oxidation number of chlorine is added:

Names of anions

e.g.	ClO^-	chlorate(I)	ClO_3^-	chlorate(V)
also	CrO_4^{2-}	chromate(VI)	$Cr_2O_7^{2-}$	dichromate(VI)
	MnO_4^{2-}	manganate(VI)	MnO_4^-	manganate(VII)
	NO_3^-	nitrate(V) or nitrate	NO_2^-	nitrate(III) or nitrite
	SO_4^{2-}	sulphate(VI) or sulphate	SO_3^{2-}	sulphate(IV) or sulphite

The Stock names for the last four examples have not been widely adopted, and people prefer to use nitrate, nitrite, sulphate and sulphite. These names date back to their usage before the changes in nomenclature of 1970.

3.17.4 ACIDS

Acids are named after their anions:

Names of acids

e.g. $HClO$ chloric(I) acid
$HClO_2$ chloric(III) acid
$HClO_3$ chloric(V) acid

Again, the names nitrous acid and sulphurous acid are preferred to the Stock names (nitric(III) and sulphuric(IV)) for the acids HNO_2 and H_2SO_3.

3.17.5 SALTS

Salts are named by combining the names of the cation, with its oxidation number if that is variable, and the anion:

Names of salts

e.g. $FeSO_4$ iron(II) sulphate $NaClO$ sodium chlorate(I)

When a salt is hydrated, the number of water molecules per formula unit is stated:

e.g. $CuSO_4 \cdot 5H_2O$ copper(II) sulphate-5-water

3.17.6 STOICHIOMETRIC FORMULAE

The oxides, sulphides and halides of non-metallic elements are usually named, not by the Stock system but according to their stoichiometry:

Some compounds are named by stoichiometry

e.g.	NO	nitrogen oxide	CS_2	carbon disulphide
	N_2O	dinitrogen oxide	$SiCl_4$	silicon tetrachloride
	NO_2	nitrogen dioxide	$POCl_3$	phosphorus trichloride oxide
	N_2O_4	dinitrogen tetraoxide	$SOCl_2$	sulphur dichloride oxide

$$\text{Concentration of thiosulphate} = (2.416 \times 10^{-3})/(17.5 \times 10^{-3}) \text{ mol dm}^{-3}$$
$$= 0.138 \text{ mol dm}^{-3}$$

CHECKPOINT 3.18: REDOX TITRATIONS

1. A 0.1576 g piece of iron wire was converted into Fe^{2+} ions and then titrated against potassium dichromate solution of concentration 1.64×10^{-2} mol dm^{-3}. From the fact that 27.3 cm^3 of the oxidant were required, calculate the percentage purity of the iron wire.

2. A volume of 27.5 cm^3 of a 0.0200 mol dm^{-3} solution of potassium manganate(VII) was required to oxidise 25.0 cm^3 of a solution of hydrogen peroxide. Calculate the concentration of hydrogen peroxide and the volume of oxygen (at stp) evolved during the titration.

3. Calculate the percentage purity of an impure sample of sodium thiosulphate from the following data. A 0.2368 g sample of the sodium thiosulphate was added to 25.0 cm^3 of 0.0400 mol dm^{-3} iodine solution. The excess of iodine that remained after reaction needed 27.8 cm^3 of 0.0400 mol dm^{-3} thiosulphate solution in a titration.

4. What volume of potassium manganate(VII) solution of concentration 0.0100 mol dm^{-3} will oxidise 50.0 cm^3 of iron(II) ethanedioate solution of concentration 0.0200 mol dm^{-3} in acid conditions?

* See Footnote.

3.19 EQUILIBRIUM

An equilibrium is a state of balance ...

... either static ...

... or dynamic

Imagine that you are looking through the window of a popular restaurant during a busy lunchtime. You can see that all of the restaurant's 200 seats are taken. You come back 30 minutes later, and you see that all the seats are still occupied. However, you can see that people are entering the restaurant and other people are leaving the restaurant. The same situation continues over the next 2 hours. The population remains constant at 200 people while all the time people are entering and leaving the restaurant. There is a balance between the number leaving and the number arriving. This state of balance can be described as a state of **equilibrium**. If the same 200 people sat at the tables all the time, one would say that the situation was **static** (unchanging). However, in the restaurant you are observing, there is motion as some customers arrive and others leave. The thing that remains constant is the balance between the number arriving and the number leaving. This is a **dynamic** (moving) equilibrium.

The restaurant you have been observing can be described as a system. The word **system** is used to describe a part of the universe which one wants to study in isolation from the rest of the universe. There are two kinds of systems: systems in a state of change and systems at equilibrium. A system in which a change in the properties of the system is occurring is described as 'a system in a state of change'. A system in which no change in its properties is occurring is described as 'a system at equilibrium'. An equilibrium may be a **static equilibrium** or a **dynamic equilibrium**.

Consider a system in which a physical change, vaporisation, occurs. Consider what happens when you drop 5 cm^3 of the brown liquid, bromine, into a gas jar and replace the lid [see Figure 3.19A].

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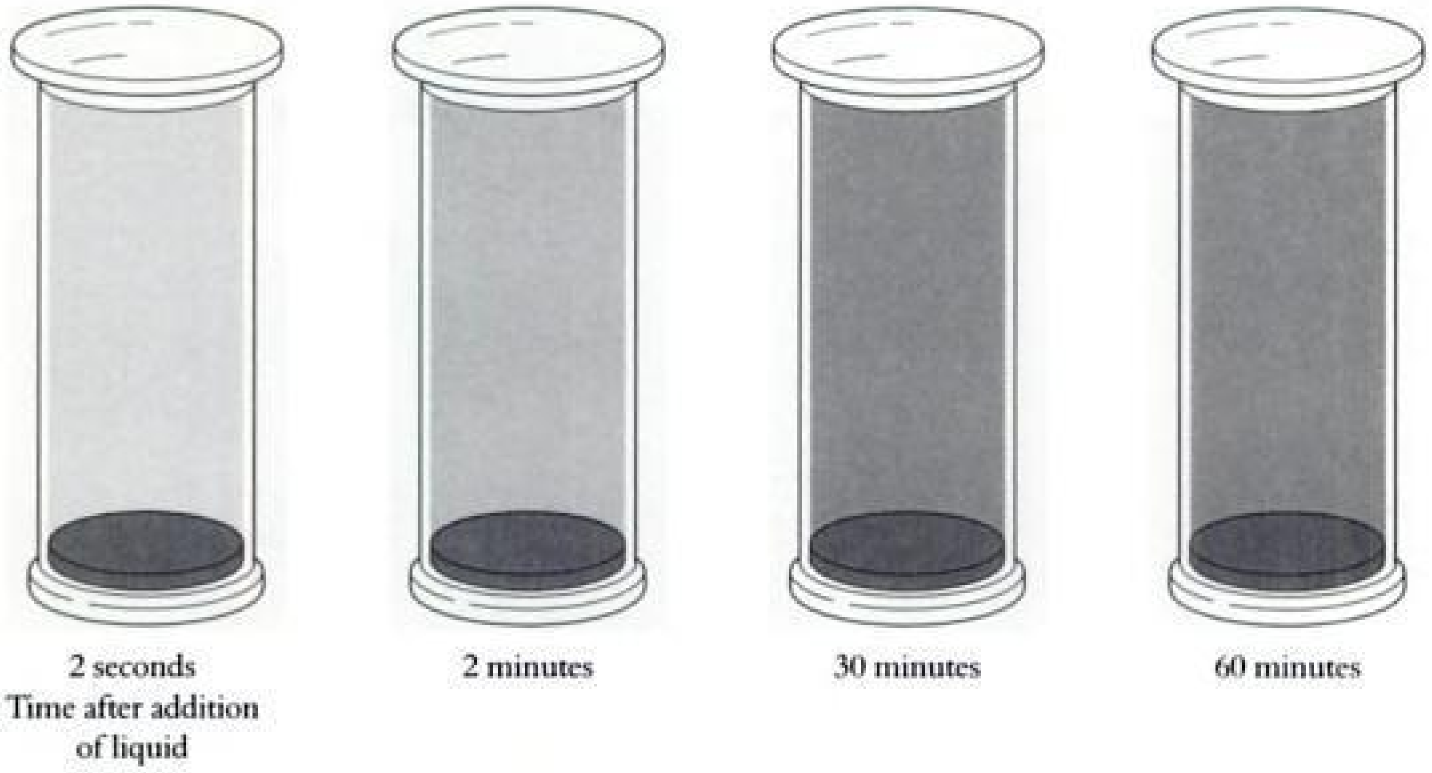
* For further practice, see E N Ramsden, *Calculations for A-Level Chemistry* (Stanley Thornes).

Figure 3.19A
Vaporisation of liquid bromine



A phase is a physically distinct part of a system

As soon as the liquid enters the gas jar, it begins to **vaporise**: some molecules leave the liquid phase and enter the vapour phase. A **phase** is a part of a system which is physically distinct from other parts of the system. The system we are considering is the contents of the closed gas jar. Two phases are present: liquid (bromine) and gas (bromine vapour and air).

A physical change can reach equilibrium ...

After 2 minutes, the gas in the gas jar is brown because it contains bromine molecules as well as air. Vaporisation (or **evaporation**) continues, and after 30 minutes the brown colour of bromine vapour is even more intense. The colour does not continue to deepen for ever. After 60 minutes, it is no more intense than after 30 minutes. It looks as though vaporisation has ceased, and the system is at equilibrium.

... $Br_2(l)$ and $Br_2(g)$ reach equilibrium in a closed system ...

If you could see individual molecules of bromine, however, you would see that the population of bromine molecules in the gas phase is constantly changing. Molecules of bromine are still passing from the liquid to the gas phase but, as fast as they do this, molecules of bromine pass from the gas phase to the liquid phase, that is, they **condense**. The system is at equilibrium because

Rate of vaporisation = Rate of condensation

... and the equilibrium is dynamic

This kind of system is described as being in **dynamic equilibrium**. Dynamic means *moving*, and, at a molecular level, the system is in motion. The properties of the system in bulk are unchanging; the volume of liquid bromine and the concentration of bromine in the gas phase are no longer changing:

$$Br_2(l) \rightleftharpoons Br_2(g)$$

Only a closed system reaches equilibrium

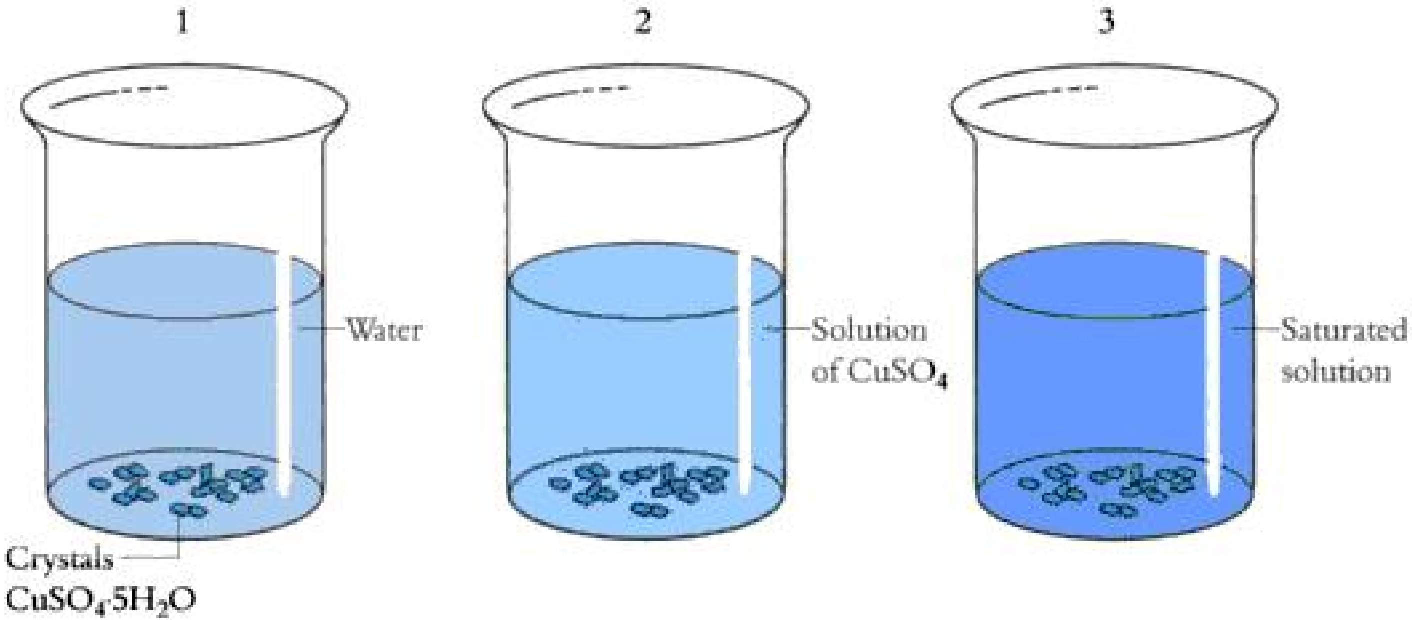
If the system were not closed, it would not come to equilibrium. If the gas jar were open, bromine would continue to vaporise until there was no liquid bromine left.

Another physical change is dissolution (dissolving). Consider what happens when you stir a scoopful of copper(II) sulphate crystals in a beaker of water. As the salt dissolves, the solution becomes a more and more intense blue colour. [See Figure 3.19B.]

A saturated solution is in a state of dynamic equilibrium

After a while, the intensity of the blue colour remains constant, although (provided you have used an excess of crystals) undissolved copper(II) sulphate remains at the bottom of the beaker. The saturated solution is a system at equilibrium. Although nothing more seems to be happening, in fact copper(II)

Figure 3.19B
Dissolution



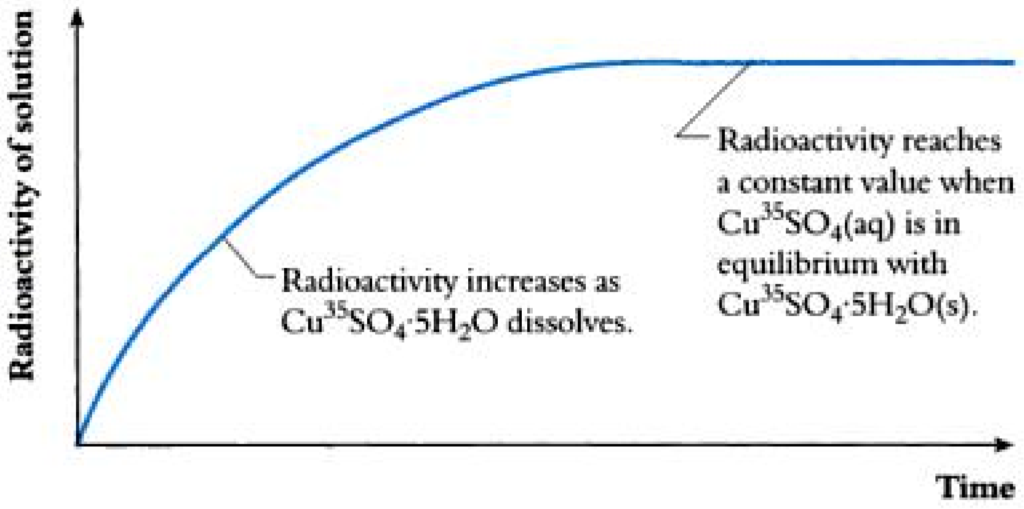
sulphate is still dissolving but, as fast as it does so, copper(II) sulphate is crystallising from solution:

$$CuSO_4\cdot 5H_2O(s) + aq \rightleftharpoons Cu^{2+}(aq) + SO_4^{2-}(aq) + 5H_2O(l)$$

A radioactive tracer can be used to demonstrate the dynamic nature of the equilibrium

There is a way of demonstrating that this system is in dynamic equilibrium. It involves the use of a radioactive **tracer**. If some crystals of $Cu^{35}SO_4\cdot 5H_2O$, which contain radioactive ^{35}S, are added, you might expect that none would dissolve because the solution is already saturated. After a time, however, it is found that the radioactivity is divided between the solution and the undissolved crystals. The reason is that undissolved solid is constantly dissolving, while solute crystallises from the solution at the same rate. [See Figure 3.19C.]

Figure 3.19C
An experiment using a radioactive tracer



3.20 CHEMICAL EQUILIBRIA

The dynamic equilibria described above are physical changes. Chemical reactions can also come to equilibrium.

Chemical reactions, like physical changes, can reach a state of equilibrium

Some chemical reactions take place in one direction almost exclusively. For example, magnesium burns to form magnesium oxide:

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

The tendency for magnesium oxide to split up to form magnesium and oxygen is negligible at normal temperatures.

Other chemical reactions take place in both directions at comparable rates. For example, when calcium carbonate is heated strongly, it decomposes:

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

The products formed are the base, calcium oxide, and the acid gas, carbon dioxide. They recombine to form calcium carbonate:

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

In the thermal dissociation of $CaCO_3$ …

… CaO(s) + CO_2(g) are in equilibrium with $CaCO_3$(s) in a closed system …

When calcium carbonate is heated at a fixed temperature in a closed container, at first calcium carbonate decomposes faster than the products recombine. After a while the amounts of calcium oxide and carbon dioxide build up to a level at which the rate of combination of calcium oxide and carbon dioxide is equal to the rate at which calcium carbonate dissociates. The system has reached a state of dynamic equilibrium:

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

… if one of the products is removed the equilibrium is disturbed …

… because the system is no longer closed

Equilibrium is reached in a closed system. If the container is open, carbon dioxide can escape. The equilibrium is disturbed, and more calcium carbonate dissociates to try to restore the equilibrium. When limestone is heated in a lime kiln, as the aim is to make plenty of quicklime, the carbon dioxide formed is removed by a powerful through draft of air in order to stop the system coming to equilibrium.

The pressure, the temperature and other external factors affect systems in equilibrium. H L Le Chatelier made a study of the way in which systems at equilibrium adjust when external factors are changed. His work is covered in Chapter 11.

3.20.1 CATALYSTS AND EQUILIBRIUM

Catalysts increase the speed with which the equilibrium conditions are reached

Catalysts alter the rates of chemical reactions. In the case of a reaction which reaches a state of dynamic equilibrium, a catalyst increases the rates of both the forward reaction and the reverse reaction by the same ratio. The position of equilibrium is therefore unchanged. What the catalyst does is to decrease the time needed for the system to reach a state of equilibrium. In industrial processes, a catalyst can make a valuable contribution to the economy of the process. In the Haber process, the percentage conversion of nitrogen and hydrogen to ammonia at the temperatures at which plants operate is small. The use of a catalyst to achieve the same percentage conversion in a shorter time increases the productivity of the plant.

CHECKPOINT 3.20: EQUILIBRIUM

1. An aqueous solution of bromine is called 'bromine water'. Some bromine molecules react with water molecules:

$$Br_2(aq) + H_2O(l) \rightleftharpoons \underset{\text{Hydrobromic acid}}{HBr(aq)} + \underset{\text{Bromic(I) acid}}{HBrO(aq)}$$

The products, hydrobromic acid and bromic(I) acid are both strong acids. The reaction is reversible, and a solution of bromine in water reaches an equilibrium state in which the concentrations of all the species are constant.

Predict what change in the equilibrium will happen as the result of the addition of a small amount of sodium hydroxide. In which direction will the equilibrium be displaced, from left to right or from right to left? Predict what colour change you will see. How could you reverse the colour change?

Do an experiment to check your predictions.

2. A solution of bismuth trichloride in concentrated hydrochloric acid contains four substances: bismuth trichloride, $BiCl_3$, bismuth chloride oxide, BiOCl, hydrochloric acid and water. All four substances are in equilibrium:

$$BiCl_3(aq) + H_2O(l) \rightleftharpoons BiOCl(s) + 2HCl(aq)$$

Bismuth chloride oxide is a white solid which is insoluble in water.

(a) Explain why adding water makes the solution change from clear to cloudy.

(b) Suggest how you could make the solution clear again.

$$I_2(aq) + 2Na_2S_2O_3(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

(a) Which of the two reactions for which equations are given above are redox reactions?

(b) Which indicator could be used in the titration?

(c) (i) What amount (in moles) of sodium thiosulphate was used in the titration?
  (ii) What amount of iodine was titrated?
  (iii) What mass of copper was present in the coin?
  (iv) What is the percentage of copper in the coin?

11. Bronze is an alloy of copper and tin. The problem is to find the percentage by mass of tin in the alloy. Potassium manganate(VII) oxidises tin(II) ions to tin(IV) ions.

A 9.40 g sample of powdered bronze was warmed with an excess of dilute sulphuric acid to convert the tin into tin(II) sulphate. After filtration, the solution was made up to 250 cm^3.

In a titration, 25.0 cm^3 of the solution of tin(II) sulphate required 19.0 cm^3 of 0.0200 mol dm^{-3} potassium manganate(VII) solution for oxidation.

(a) Why was the solution obtained from bronze filtered?

(b) What conditions were employed for the titration?

(c) How was the end-point of the titration spotted?

(d) Write the half-equations for (i) the oxidation of tin(II) to tin(IV) (ii) the reduction of manganate(VII) to manganese(II).

(e) Combine the half-equations to give the equation for the reaction.

(f) Calculate the percentage by mass of tin in the alloy.

12. *(a)* The first ionisation energy of sodium is +500 kJ mol^{-1}. Write an equation to show this change. 2

(b) (i) What type of bonding is present in sodium oxide, Na_2O? 1
  (ii) What type of oxide is Na_2O? 1
  (iii) Write an equation for the reaction of Na_2O with water. 1

(c) Sodium also forms sodium peroxide, Na_2O_2. Treatment of this with dilute sulphuric acid gives hydrogen peroxide, H_2O_2, and sodium sulphate.
  (i) What is the oxidation number of oxygen in sodium peroxide? 1
  (ii) Write an equation for the conversion of sodium peroxide to hydrogen peroxide. 1

(d) Hydrogen peroxide reacts with acidified potassium dichromate(VI) as follows:

$$Cr_2O_7^{2-}(aq) + 3H_2O_2(aq) + 8H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3O_2(g)$$

A solution containing 14.7 g dm^{-3} of potassium dichromate(VI), $K_2Cr_2O_7$, is reacted with 20.0 cm^3 of a 0.100 mol dm^{-3} solution of hydrogen peroxide. Calculate the volume of potassium dichromate(VI) solution required. 4

(e) When dilute aqueous ammonia is added to a solution of nickel(II) sulphate, a green precipitate **B** is formed which dissolves in excess of the same ammonia solution to give a blue solution **C**.
  (i) Give the formula of the green precipitate **B**. 1
  (ii) Suggest a formula for the ion responsible for the blue colour in **C**. 1
  (iii) Write an equation for the conversion of **B** to **C**. 1
  (iv) What type of reaction is this? 1

15 *L (AS/AL)*

13. Silver used to be alloyed with copper to make coins. Before 1921 **silver** coinage in the UK was mostly silver (composition by mass: Ag 92.5%, Cu 7.5%). After 1927, until World War II, coins were **half-silver** (composition by mass: Ag 50%, Cu 40%, Ni 5%, Zn 5%). Today, silver is not used in UK coins.

(a) Silver is one of the best metallic conductors. Explain electronic conduction in silver. 2

(b) Calculate the percentage molar composition of a UK **silver** coin before 1921. 2

(c) The percentage of silver in an alloy may be found by dissolving the alloy in nitric acid and reacting the silver nitrate produced with a solution of sodium chloride to give a precipitate of silver chloride. After purification the precipitate is dried and weighed.
  (i) Write a balanced equation for the reaction of silver nitrate with sodium chloride.
  (ii) Find the percentage by mass of silver in an alloy from the following information:

  A sample of 1.245 g of the alloy was dissolved in nitric acid and reacted with an excess of sodium chloride. The purified silver chloride had a mass of 1.519 g. 4

(Relative atomic masses: Ag = 107.868; Cl = 35.453)

CCEA (AS/AL)

14. When burnt in oxygen, 24.00 g of magnesium produces 40.00 g of magnesium oxide, MgO. When burnt in nitrogen, 24.00 g of magnesium would produce 33.33 g of magnesium nitride, Mg_3N_2. When magnesium is burnt in air it produces both magnesium oxide and magnesium nitride.

The following experimental results were obtained when a sample of magnesium ribbon was burnt in air. [A_r (Mg) 24.0; A_r (O) 16.0; A_r (N) 14.0]

Mass of test-tube	= 12.20 g
Mass of test-tube + magnesium ribbon	= 18.20 g
Mass of test-tube after burning	= 21.70 g

(a) What do you understand by the chemical term *mole*? 3

(b) Use the numerical data to confirm that one mole of magnesium nitride is obtained from three moles of magnesium. **2**

(c) Write balanced chemical equations for the formation of:

(i) *magnesium oxide* (ii) *magnesium nitride* **2**

(d) (i) Calculate the total mass of product formed when 1.0 mol of magnesium is burnt in air. **2**

(ii) Calculate the mass of magnesium oxide formed when 1.0 mol of magnesium is burnt in air.

[Hint: let x = mass of magnesium oxide formed] **4**

(iii) What is the molar ratio of MgO to Mg_3N_2 formed in the reaction? **1**

(iv) Suggest a reason for the amount of Mg_3N_2 formed being small. **1**

15 *O&C (AS/AL)*

15. *(a)* The concentration of sulphur dioxide in air can be measured using an acidified solution of potassium manganate(VII) which oxidises sulphur dioxide to sulphate ions, SO_4^{2-}.

(i) State, in terms of electrons, what happens to a species when it is oxidised.

(ii) State the oxidation states of sulphur in SO_2 and in SO_4^{2-}

(iii) Deduce the half equation for the oxidation of sulphur dioxide to sulphate ions in the presence of water.

(iv) Write the half equation for the reduction of manganate(VII) ions in acid solution. **6**

(b) Air, contaminated with sulphur dioxide, was bubbled through an acidified solution of potassium manganate(VII). It was found that 0.5 m^3 of air decolorised 100 cm^3 of 0.01 M $KMnO_4$.

(i) Calculate the number of moles of $KMnO_4$ which were decolorised.

(ii) In this analysis, $KMnO_4$ reacts with SO_2 in the ratio 2 : 5.

Use this information to calculate the number of moles of SO_2 in 0.5 m^3 of air and hence the mass of SO_2 per m^3 of this sample of air. **4**

10 *NEAB (AS/AL)*

16. *(a)* Use the concept of oxidation states to deduce whether either of the reactions given below involves redox processes. Explain your answers and, where appropriate, identify the element which is being oxidised.

(i) $2NH_3 + 3Cl_2 \longrightarrow N_2 + 6HCl$

(ii) $CuO + 2HCl \longrightarrow CuCl_2 + H_2O$ **5**

(b) (i) Potassium manganate(VII), $KMnO_4$, can be used in the quantitative estimation of ethanedioate ions, $C_2O_4^{2-}$, in an acidified aqueous solution. In this reaction, ethanedioate ions are converted into carbon dioxide. Deduce half equations for the redox processes involved and hence derive an equation for the overall reaction. **3**

(ii) A 1.93 g sample of a crystalline ethanedioate salt was dissolved in water and made up to 250 cm^3. 25.0 cm^3 of this solution, after acidification, was found to react with 30.4 cm^3 of 0.0200 M $KMnO_4$. Calculate the percentage by mass of ethanedioate ions in the original salt.

NB If you are unable to deduce the overall ratio $C_2O_4^{2-}$: MnO_4^- for this reaction you may assume the ratio 5 : 3 (This is not the correct ratio). **6**

14 *NEAB (AS/AL)*

17. Antimony, symbol Sb, proton (atomic) number 51, has been known since about 4000 BC. Nowadays, its main use is to harden and to strengthen lead alloys.

(a) A typical sample of antimony consists of two isotopes and has the following composition, by mass: ^{121}Sb, 57.25%; ^{123}Sb, 42.75%.

(i) How could this information be obtained experimentally? **1**

(ii) What can be deduced about the atomic structure of these two isotopes? **2**

(iii) Calculate the relative atomic mass of the antimony sample. **2**

(b) Antimony is produced in a two-stage process from the sulphide ore, Sb_2S_3.

The ore is first roasted in oxygen to form the oxide.

$$2Sb_2S_3(s) + 9O_2(g) \longrightarrow Sb_4O_6(s) + 6SO_2(g)$$

The oxide is then reduced with carbon.

$$Sb_4O_6(s) + 3C(s) \longrightarrow 4Sb(s) + 3CO_2(g)$$

(i) State the oxidation state of antimony in its oxide. **1**

(ii) Showing each stage of your working clearly, calculate the volume of carbon dioxide that would be produced by the processing of 10 moles of Sb_2S_3. [Assume that 1 mole of a gas occupies 24 dm^3 under the experimental conditions.] **3**

9 *C (AS/AL)*

18. When potassium nitrate, KNO_3, is heated, it decomposes according to the equation given below.

$$2KNO_3(s) \longrightarrow 2KNO_2(s) + O_2(g)$$

(a) Deduce the oxidation state of nitrogen in (i) KNO_3 (ii) KNO_2 **2**

(b) Calculate the maximum mass of KNO_2 which could be obtained if 1.55 g KNO_3 were fully decomposed by heat. **4**

(c) Another 1.55 g sample of KNO_3 was partly decomposed by heating. The residue was dissolved in water and the volume of the solution made up to 250 cm^3. A 25.0 cm^3 portion of this solution was found to react, in acid solution, with 28.9 cm^3 of 0.0150 M $KMnO_4$. The reaction can be represented by the equation

$$2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

- (i) Calculate the number of moles of $KMnO_4$ which reacted with 25.0 cm^3 of the solution.
- (ii) Calculate the total number of moles of KNO_2 present in the residue.
- (iii) Calculate the mass of KNO_2 present in the residue.
- (iv) Use the result obtained in parts *(b)* and *(c)*(iii) to calculate the percentage conversion of KNO_3 to KNO_2 in this experiment. **7**

13 *NEAB (AS/AL)*

19. The concentration of hydrochloric acid in the human stomach is approximately 0.1 mol dm^{-3}. Excess of this acid causes discomfort referred to as 'heartburn' or 'acid indigestion'. Remedies designed to neutralize some of this excess acid often contain compounds such as magnesium hydroxide, $Mg(OH)_2$, and sodium hydrogencarbonate, $NaHCO_3$.

(a) The hydrogencarbonate ion, HCO_3^-, is capable of behaving as either an acid or a base. Write equations, with state symbols, to show the hydrogencarbonate ion acting as

- (i) an acid by reacting with water **2**
- (ii) a base by reacting with hydroxonium ions, H_3O^+(aq), and giving off a gas. **2**

(b) Magnesium hydroxide reacts with hydrochloric acid according to the equation

$$Mg(OH)_2(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + 2H_2O(l)$$

- (i) The molar mass of magnesium hydroxide is 58.0 g mol^{-1}. Calculate the number of moles of hydrochloric acid which can be neutralized by 1.00 g of magnesium hydroxide. **2**
- (ii) Calculate the volume of 0.100 M HCl which can be neutralized by 1.00 g of magnesium hydroxide, giving your answer to 3 significant figures. **2**

8 *L(N) (AS/AL)*

20. The concentration of hydrogen peroxide in a solution can be determined by titrating an acidified solution against aqueous potassium manganate(VII) added from a burette. The potassium manganate(VII) reacts with the colourless aqueous solution of hydrogen peroxide as shown in the equation given below.

$$5H_2O_2 + 2MnO_4^- + 6H^+ \longrightarrow 5O_2 + 8H_2O + 2Mn^{2+}$$

(a) State the role of hydrogen peroxide in this reaction. **1**

(b) Identify a suitable acid for use in this titration. **1**

(c) State the colour change at the end-point of this reaction. **1**

(d) After acidification with a suitable acid, 25.0 cm^3 of a dilute aqueous solution of hydrogen peroxide were found to react with 18.1 cm^3 of 0.0200 M $KMnO_4$. Calculate the molar concentration of hydrogen peroxide in the solution. **4**

7 *NEAB (AS/AL)*

21. Standard solutions containing thiosulphate ions are used to measure the amount of iodine in a solution. The result can be used to find the reacting quantities in some redox reactions.

20.0 cm^3 of 0.100 M copper sulphate solution was reacted with an excess of potassium iodide. The iodine formed reacted with exactly 40.0 cm^3 of 0.0500 M sodium thiosulphate solution.

(a) Calculate the number of moles of thiosulphate ions, $S_2O_3^{2-}$, used in the reaction. **1**

(b) Complete the ionic equation for the reaction between iodine and thiosulphate ions.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow$$ **2**

(c) Calculate the number of moles of iodine molecules, I_2, in the reaction mixture. **1**

(d) Calculate the number of moles of copper(II) ions, Cu^{2+}(aq), in 20.0 cm^3 of 0.100 M copper sulphate solution which reacted with the potassium iodide. **1**

(e) Use oxidation numbers and your answers to *(c)* and *(d)* to complete the equation for the reaction between copper(II) ions and iodide ions. Justify your balancing of the equation.

$$Cu^{2+}(aq) + I^-(aq) \longrightarrow I_2(aq) +$$ **2**

6 *L (AS/AL)*

4

THE CHEMICAL BOND

4.1 DIAMOND AND GRAPHITE – THE DIFFERENCE LIES IN THE BONDS

One of the most famous of diamonds is the Hope diamond. This huge blazing diamond with a bluish tint was mined in India, and was once the eye of a statue of Sita, a Hindu goddess. The diamond was stolen and was said to have been cursed by the goddess Sita. Over the centuries a string of owners met with bad luck. Marie Antoinette was guillotined during the French Revolution in 1792. Henry Hope bought the diamond in 1830, but his unlucky family lost all their father's wealth and had to sell the diamond. Another owner, a European prince, gave the diamond to an actress in the Folies Bergères but afterwards shot her in a fit of jealous rage. A Greek owner drove his car over a precipice, killing himself and his family. The Sultan of Turkey acquired the diamond and shortly afterwards was overthrown in 1909 by a revolution. The history of bad luck did not deter Mrs Evalyn Walsh from buying the Hope diamond, but bad luck dogged her all the same, with her children dying in accidents and her husband becoming mentally ill. When she died a dealer bought the stone and gave it to the Smithsonian Institute in Washington, USA, so that it could be enjoyed by people in all walks of life.

Why have people always been fascinated by diamonds? The brilliance of diamonds is due to their ability to reflect light. The fire of diamonds is due to their ability to disperse white light into flashes of light of all the colours of the spectrum. There is a big difference between the refractive index of diamond for red light and that for violet light. Diamond has another outstanding characteristic. It is the hardest of natural materials. This is why diamond is used for grinding, cutting, etching, polishing, drilling and many other industrial applications. Diamond is a simple substance; it is a form of the element carbon. The reason for its amazing properties – high refractive index and hardness – is the way in which atoms of carbon are bonded together in diamond.

Graphite is a shiny dark grey solid. It is soft and, when you rub it, it leaves traces on your fingers. Although graphite appears to be so different from diamond, it is another form of the element carbon. We expect non-metallic elements to be non-conductors of electricity, but graphite is the exception. It is widely used as an electrical conductor. The striking differences between diamond and graphite are due to the different ways in which carbon atoms are bonded.

In this chapter we shall be looking at the different kinds of chemical bonds and the ways in which substances with different bonds have different characteristics.

4.2 IONS

4.2.1 SOME QUESTIONS

The background to the ionic theory

- Why are all copper(II) compounds blue, regardless of the non-metallic part of the compound?
- Why are all dichromates orange, regardless of the metallic part of the compound?
- Why do aqueous solutions of some substances conduct electricity?
- Why does a layer of copper appear on the negative electrode when a direct electric current is passed through a solution of a copper salt [see Figure 4.2A, § 4.2.3]?
- Why is chlorine evolved at the positive electrode when a direct electric current passes through a concentrated aqueous solution of a chloride?
- Why do X ray diffraction patterns of salts show a regular patter of dots [see Figure 6.2A, § 6.2]?

To answer these questions and others, the **ionic theory** was developed. According to the ionic theory, some compounds consist of tiny particles which carry an electric charge, either positive or negative, and are called **ions**. The ionic theory was developed to explain the behaviour of compounds when a direct electric current is passed through the molten compound or an aqueous solution of the compound.

4.2.2 WHICH SUBSTANCES CONDUCT ELECTRICITY?

Substances can be divided into four groups according to their ability to conduct a direct current of electricity [see Table 4.2].

Table 4.2
Electrical conductors and non-conductors

Solids: Metals and alloys and graphite conduct electricity

Liquids: Solutions of acids, alkalis and salts conduct electricity

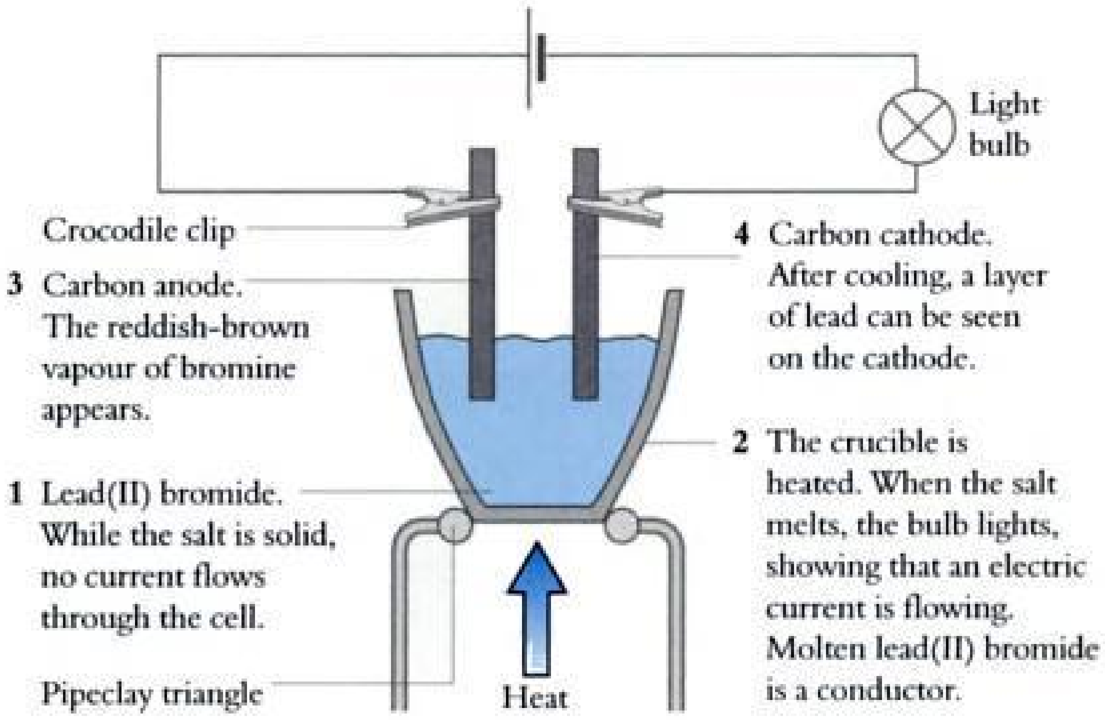
Solids	
Electrical conductors	**Non-conductors, i.e. insulators**
All metallic elements All alloys One non-metallic element, the graphite allotrope of carbon	Non-metalic elements, e.g. sulphur Many compounds, e.g. polyethene Crystalline salts, e.g. sodium chloride, copper(II) sulphate
Liquids	
Electrolytes	**Non-electrolytes**
Solutions of acids and alkalis and salts; such liquids are called **electrolytes**. Chemical changes occur at the electrodes. For example, copper(II) chloride solution changes into copper and chlorine and water.	The liquids which do not conduct electricity are water and organic compounds, such as ethanol. They are called **non-electrolytes**.

PROFILE: MICHAEL FARADAY

The scientist who did the first work on electrolysis was Michael Faraday (1791–1867). He was the son of a poor blacksmith, and at the age of 14 he became an apprentice bookbinder. He educated himself by reading the books he was asked to bind and by joining various self-improvement groups. Faraday became especially interested in chemistry and electricity. When he attended a course of lectures by Humphry Davy at the Royal Institute, Faraday made detailed notes, illustrated them with excellent diagrams, and bound them in a book. Davy was impressed with the young man's enthusiasm and offered him a job as a laboratory assistant. Faraday was soon contributing actively to the research. The variety of his achievements is amazing. He made the first electric motor, the first transformer and the first dynamo. He formulated the First and Second Laws of Electrolysis. He discovered benzene and did research on steel, optical glass and the liquefaction of gases. Faraday became a superb scientific lecturer. He gave weekly evening lectures at the Royal Institution to popularise science and started a tradition of Christmas lectures for children which is still continued.

Figure 4.2D
Michael Faraday lecturing to children

Figure 4.2E
Electrolysis of molten lead(II) bromide



4.2.4 MOLTEN SALTS

Some compounds are electrolysed when molten. These compounds are composed of ions

In a solution of a salt, the ions are free to move, and the solution can be electrolysed. Another way of enabling the ions to move is to melt the salt. You have probably seen the experiment shown in Figure 4.2E. Lead(II) bromide is a convenient salt to use because it has a fairly low melting point. The experiment shows that molten lead(II) bromide is electrolysed. In the molten salt, ions are free to move.

4.2.5 HOW DOES AN ATOM BECOME AN ION?

A metal atom may lose one or more electrons to become a cation

Atoms are uncharged. The number of protons in an atom is the same as the number of electrons [see § 1.6]. If an atom either gains or loses an electron, it will become electrically charged. Metal atoms and hydrogen atoms form positive ions. For example, a sodium atom loses one electron to form a positively charged sodium ion.

Sodium atom ⟶ Electron + Sodium ion
$\text{Na(11 protons, 11 electrons)} \longrightarrow e^- + Na^+ \text{ (11 protons, 10 electrons)}$
uncharged   charge = + 1

A magnesium atom loses 2 electrons to become a magnesium ion, Mg^{2+}.

An aluminium atom loses 3 electrons to become an aluminium ion, Al^{3+}. The charge on a cation may be +1, +2 or +3.

An atom of a non-metal may gain one or more electrons to become an anion

Non-metallic elements form negative ions (anions). They do this by gaining electrons. A chlorine atom gains one electron to become a chloride ion, Cl^-.

Chlorine atom + Electron ⟶ Chloride ion
$\text{Cl(17 proton, 17 electrons)} + e^- \longrightarrow Cl^- \text{ (17 protons, 18 electrons)}$
uncharged   charge = −1

An oxygen atom gains 2 electrons to become an oxide ion, O^{2-}. Some anions contain oxygen combined with another element. Examples are: hydroxide ion, OH^-; nitrate ion, NO_3^-; sulphate ion, $SO_4{}^{2-}$. An anion may have a charge of −1, −2 or −3. Table 4.3, § 4.3.7, lists the symbols and formulae of some common ions.

4.2.6 NON-ELECTROLYTES

Non-electrolytes consist entirely of molecules

Some liquids do not conduct electricity. It follows that these substances do not contain ions. They consist of uncharged particles called molecules [see § 4.4]. Compounds formed between metallic and non-metallic elements are usually electrolytes, and compounds formed between non-metallic elements are generally non-electrolytes, e.g. ethanol (alcohol), or weak electrolytes [see § 4.2.7].

4.2.7 WEAK ELECTROLYTES

Weak electrolytes consist mainly of molecules

Some substances conduct electricity to a very slight extent. For example, ethanoic acid is a poor conductor; it is a weak electrolyte. A solution of ethanoic acid contains a small concentration of ions, which make it conduct. The compound exists mainly in the form of molecules, which do not conduct [see § 4.4].

CHECKPOINT 4.2: ELECTRICAL CONDUCTORS

1. *(a)* Divide the following list into (i) electrical conductors and (ii) non-conductors:

   solid wax, molten wax, ethanol (alcohol), distilled water, aqueous ethanol, copper, wood, steel, sodium chloride crystals, sugar crystals, sugar solution, tetrachloromethane (CCl_4), brass, polythene, molten magnesium chloride, solid sodium hydroxide, molten sodium hydroxide, sodium hydroxide solution, PVC, petrol, silver

   (b) Say which of the conductors in the list are electrolytes.

2. Briefly explain the terms: electrolysis, electrolyte, cell, anode, cathode, ion, anion, cation.

3. Explain *(a)* why ions move toward electrodes and *(b)* why solid copper(II) sulphate is not an electrical conductor.

4. Answer the questions at the beginning of § 4.2.1.

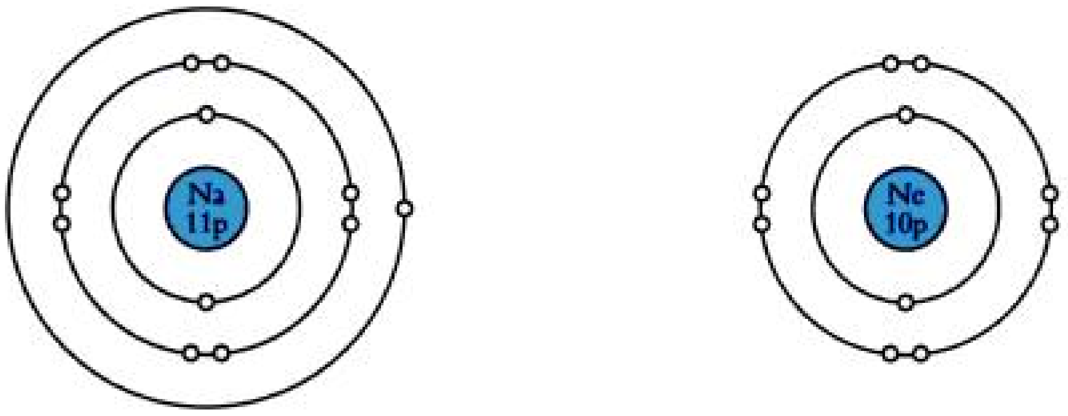
4.3 THE IONIC BOND

Let us look in more detail at how atoms are able to form ions. How can one atom be able to give up an electron to form a cation? How can another atom be able to accept an electron to form an anion?

4.3.1 SODIUM CHLORIDE

Look at the electron configuration in a sodium atom [Figure 4.3A]. There is just one electron more than there is in an atom of the noble gas, neon.

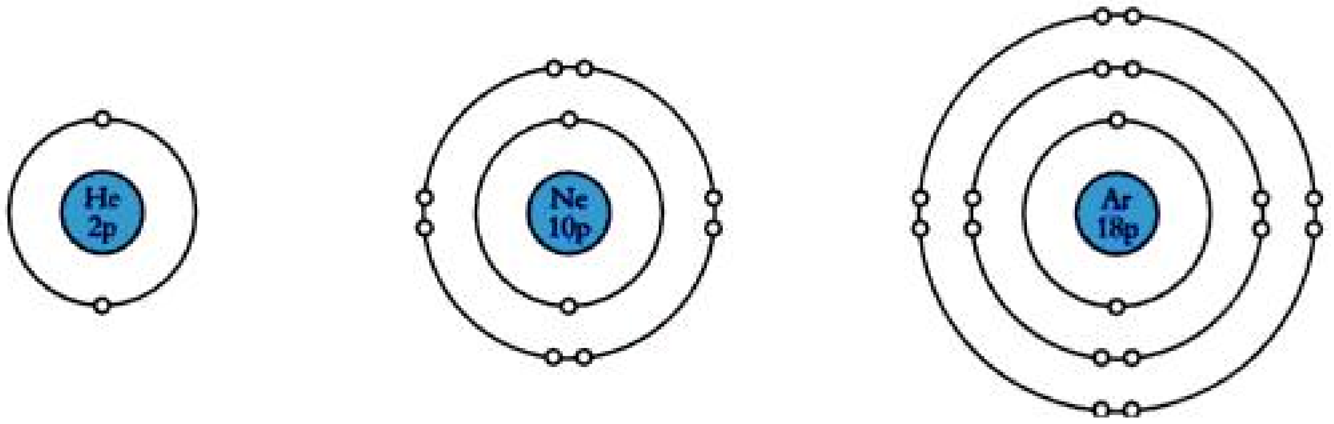
Figure 4.3A
Atoms of sodium and neon



The noble gases have a full outer shell of electrons. This electron configuration is very stable

The noble gases [see § 2.6] are helium, neon, argon, krypton, xenon and radon. They take part in hardly any chemical reactions. With the electron configuration ns^2np^6 ($1s^2$ for He) the noble gases have a full outer shell of electrons [Figure 4.3B] and it seems probable that it is this electron configuration that makes them stable, that is, chemically unreactive.

Figure 4.3B
The electron configurations in helium neon and argon



To achieve a full outer shell of electrons, a sodium atom must lose one electron ...

When a sodium atom Na(2.8.1) loses the lone electron from its outermost shell, the outer shell that remains contains 8 electrons, the same as the noble gas neon Ne(2.8). This electron configuration is associated with stability. A sodium atom cannot lose an electron unless another atom will accept it. It can, however, give an electron to a chlorine atom. In fact, sodium burns vigorously in chlorine to form sodium chloride.

... and a chlorine atom must gain one electron

How can a chlorine atom accept an electron? With the electron configuration Cl(2.8.7), one more electron gives chlorine the same electron arrangement as the noble gas argon Ar(2.8.8). A full outer shell brings with it stability [Figure 4.3C].

Figure 4.3C
The configuration of electrons in chlorine and argon

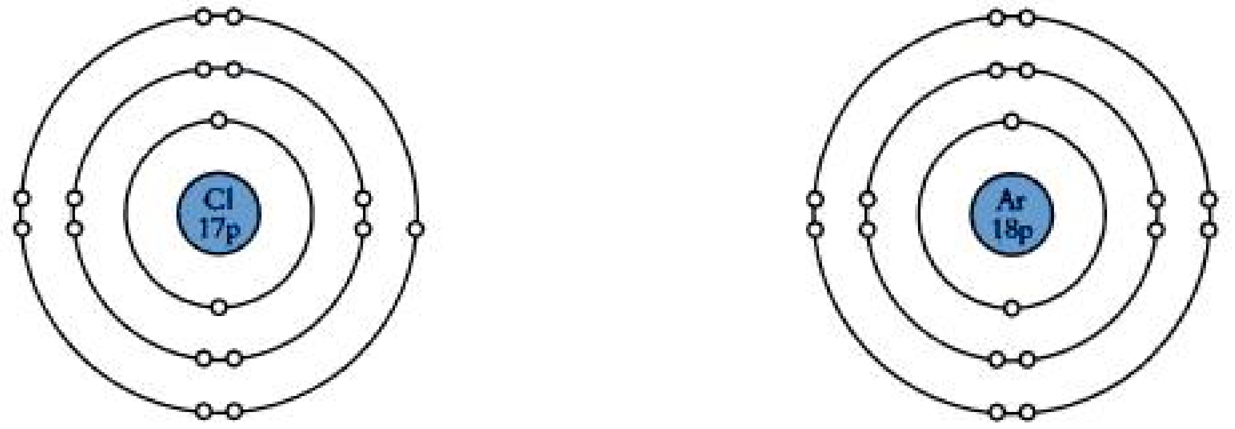
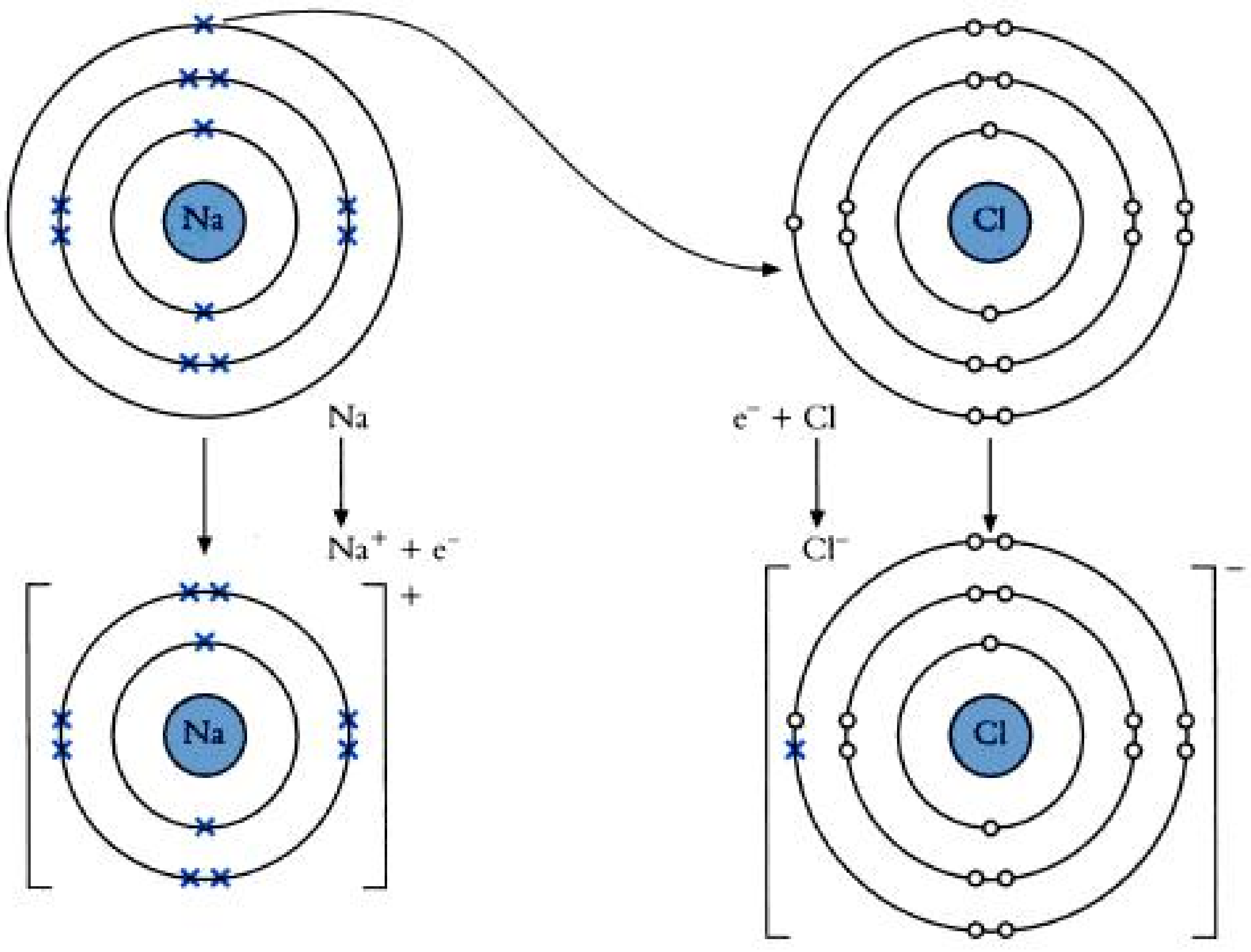


Figure 4.3D shows what happens when an atom of sodium donates an electron to an atom of chlorine. A full outer shell is left behind in sodium, and a full outer shell is created in chlorine.

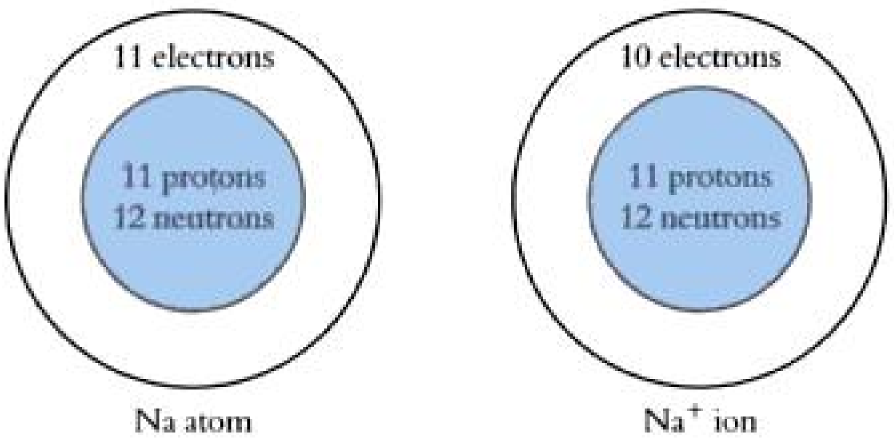
Figure 4.3D
The formation of sodium chloride. (The sodium electrons have been shown as × and the chlorine electrons as O.)



The oppositely charged ions are held together by an electrostatic attraction called an ionic bond or electrovalent bond

The electrostatic attraction between oppositely charged ions holds the ions Na^+ and Cl^- together. This electrostatic attraction is the chemical bond in the compound, sodium chloride. It is called an **ionic bond** or **electrovalent bond**. Sodium chloride is an ionic or electrovalent compound. The compounds which conduct electricity when they are melted or dissolved are electrovalent compounds.

Figure 4.3E
A sodium atom and a sodium ion



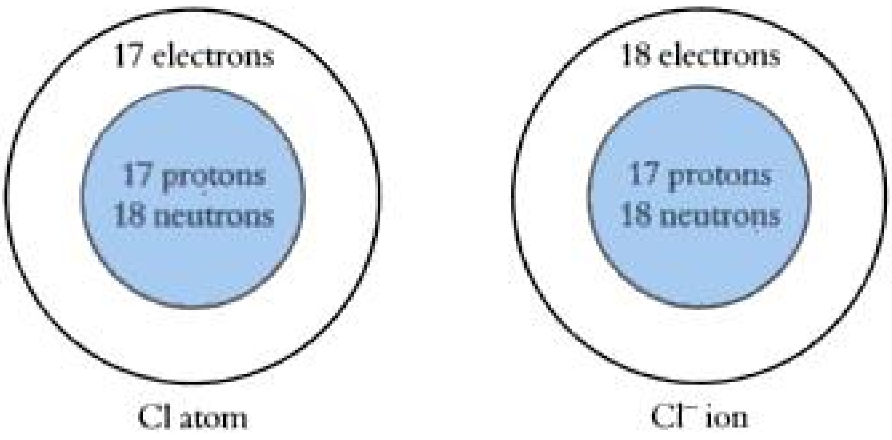
A sodium atom has 11 protons, 11 electrons and 12 neutrons. Charge = +11 – 11 = 0 charge unit.

After it loses one electron, it has 11 protons and 10 electrons. Charge = +11 – 10 = +1 charge unit. The sodium atom, Na, has become a sodium ion, Na^+.

A sodium ion is positively charged

A chloride ion is negatively charged

Figure 4.3F
A chlorine atom and a chloride ion



A chlorine atom has 17 protons, 17 electrons and 18 neutrons. Charge = +17 – 17 = 0 charge unit.

After it gains an electron, making 17 protons and 18 electrons, the charge is +17 – 18 = –1 charge unit. The chlorine atom, Cl, has become a chloride ion, Cl^-.

SUMMARY

An ionic bond is formed when an atom of a metallic element gives an electron or electrons to an atom of a non-metallic element. The ions formed are held together by an electrostatic attraction.

The theory of the chemical bond is due to the work of W Kossel and G N Lewis. In 1916, working independently, they both put forward the theory that the formation of chemical bonds can be explained by the tendency of atoms to give or receive electrons in order to attain a noble gas type of electron configuration.

4.3.2 CRYSTALS

Ionic compounds from crystals

A feature of ionic compounds is that they form **crystals**. The crystals of sodium chloride are perfect cubes. In a dilute solution of sodium chloride, sodium ions and chloride ions are moving about independently of other ions. When the solution is evaporated to the point of crystallisation, the ions are much closer together. A sodium ion attracts chloride ions, as shown in Figure 4.3G(a). Each chloride ion attracts other sodium ions, and a three-dimensional arrangement of ions called a **crystal structure** is built up [see Figure 4.3G(b)]. There is no pair of Na^+ and Cl^- ions that could be regarded as a molecule of sodium chloride. The formula NaCl represents the ratio in which ions are present in the crystal structure. A pair of ions $Na^+ Cl^-$ is called a **formula unit** of sodium chloride.

A crystal of sodium chloride is a three-dimensional structure of sodium ions and chloride ions

The crystal is uncharged because the number of sodium ions is equal to the number of chloride ions. The bonds between positive and negative ions are strong. This is why solid sodium chloride does not conduct electricity and is not electrolysed. In the solid, the ions cannot move out of their positions in the three-dimensional structure. When the salt is melted or dissolved, the ions are free to move and can travel towards the electrodes [see Figure 4.2C].

4.3.6 IONS AND THE PERIODIC TABLE

The charge depends on the number of electrons in the outermost shell ...

- Compare the charges on the ions of the following elements with the group in which you find them in the Periodic Table [p. 732].

Ions: Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, Al^{3+}, N^{3-}, O^{2-}, S^{2-}, F^-, Cl^-, Br^-, I^-

- Can you see the relationship?

... and therefore on the position of the element in the Periodic Table

Charge on ions of metallic element = Group number of element

Charge on ions of non-metallic element = 8 – Group number of element

CHECKPOINT 4.3A: BONDING IN IONIC COMPOUNDS

1. Lithium is an alkali metal with the electron configuration Li(2.1). Fluorine is a halogen with the electron configuration F(2.7). Draw the configuration of electrons *(a)* in the atoms of Li and F and *(b)* in a pair of ions in the compound lithium fluoride.

2. Sodium is a silvery-grey metal. It has to be kept under oil because it reacts rapidly with oxygen and water vapour in the air. Chlorine is a poisonous green gas. Sodium chloride is a white, crystalline solid, which we eat as 'table salt'. Explain how the sodium in sodium chloride differs from sodium metal. Explain how the chlorine in sodium chloride differs from chlorine gas.

3. Refer to Figure 4.3D for the formation of sodium chloride. Draw a similar diagram to illustrate the formation of magnesium fluoride, MgF_2.

4. Use 'dot and cross' diagrams to show how the following atoms combine:

(a) Li(2.1) and O(2.6), *(b)* Na(2.8.1) and F(2.7),
(c) Be(2.2) and F(2.7), *(d)* Al(2.8.3) and F(2.7),
(e) Ca(2.8.8.2) and O(2.6).

5. There are two differences between

(a) a sodium ion, Na^+(2.8) and a neon atom, Ne(2.8)
(b) a chloride ion, Cl^-(2.8.8) and an argon atom, Ar(2.8.8).

What are the differences?

6. Say in which group of the Periodic Table you would expect to find the elements which form the following ions:

Rb^{2+}, Ga^{3+}, Sr^{2+}, At^-, P^{3-}, Se^{2-}, Cs^+, Ra^{2+}

4.3.7 FORMULAE OF IONIC COMPOUNDS

Electrovalent compounds consist of positive and negative ions. A compound is neutral because the charge on the positive ion (or ions) is equal to the charge on the negative ion (or ions). In zinc chloride, $ZnCl_2$, one zinc ion, Zn^{2+}, is balanced in charge by two chloride ions, $2Cl^-$.

You can work out the formula of an ionic compound by balancing the charges on the ions

Let us use this principle of balancing the charges to work out the formulae of electrovalent compounds.

Compound:	*Zinc chloride*
Which ions are present?	Zn^{2+}, Cl^-
How can you balance the charges?	One Zn^{2+} ion needs two Cl^- ions.
How many ions are needed?	Zn^{2+} and $2Cl^-$ ions
What is the formula?	$ZnCl_2$

Compound:	*Sodium carbonate*
Which ions are present?	Na^+, CO_3^{2-}
How can you balance the charges?	Two Na^+ are needed to balance one CO_3^{2-}.
How many ions are needed?	$2Na^+$ and CO_3^{2-}
What is the formula?	Na_2CO_3

CHECKPOINT 4.3B: FORMULAE OF IONIC COMPOUNDS

1. Write the formulae of the following ionic compounds:

   (a) silver chloride, *(b)* potassium nitrate,
   (c) silver nitrate, *(d)* zinc bromide,
   (e) magnesium iodide, *(f)* copper(II) bromide,
   (g) ammonium chloride, *(h)* ammonium sulphate,
   (i) calcium hydroxide, *(j)* aluminium chloride,
   (k) sodium hydrogencarbonate, *(l)* sodium sulphite,
   (m) ion(II) hydroxide, *(n)* iron(III) hydroxide,
   (o) aluminium oxide.

2. Name the following compounds:

   (a) AlI_3, *(b)* $CuCO_3$, *(c)* $Zn(OH)_2$, *(d)* AgBr,
   (e) $Cu(NO_3)_2$, *(f)* $FeBr_2$, *(g)* $FeBr_3$, *(h)* Al_2O_3,
   (i) $KMnO_4$, *(j)* Na_2SiO_3, *(k)* Na_3PO_4,
   (l) KNO_2, *(m)* $K_2Cr_2O_7$, *(n)* $Ca_3(PO_4)_2$,
   (o) Na_2SO_3, *(p)* $BaSO_3$, *(q)* $Ca(HCO_3)_2$.

4.3.8 IONIC RADII

The sum of the cationic and anionic radii is equal to the interionic distance in a crystal

The distance between the centres of the ions is the sum of the **cationic radius** and the **anionic radius**. Some values of ionic radii are shown in Figure 15.2D [§ 15.2].

4.3.9 ENERGY CHANGES IN COMPOUND FORMATION

Electrovalent bonds are formed if the reaction between elements to give an ionic solid is exothermic

A detailed picture of the energy changes involved in the formation of an ionic compound was drawn by the theoreticians M Born and F Haber. They considered, for example, the formation of sodium chloride from its elements:

$$Na(s) + \tfrac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$$

They analysed the reaction as the sum of five steps. These are

1. Vaporisation of sodium $Na(s) \longrightarrow Na(g)$ *Endothermic*
2. Ionisation of sodium $Na(g) \longrightarrow Na^+(g) + e^-$ *Endothermic*
3. Dissociation of chlorine $\tfrac{1}{2}Cl_2(g) \longrightarrow Cl(g)$ *Endothermic*
4. Ionisation of chlorine $Cl(g) + e^- \longrightarrow Cl^-(g)$ *Exothermic*
5. Combination of ions to form a crystalline solid
   $Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$ *Exothermic*

The sum of the five energy changes is exothermic. [See § 10.12 for a fuller treatment.]

CHECKPOINT 4.3C: IONS

1. Write the formulae of the electrovalent compounds which contain the following pairs of ions:

   (a) Mg^{2+} and N^{3-}, *(b)* Al^{3+} and F^-, *(c)* Al^{3+} and S^{2-},
   (d) Fe^{2+} and O^{2-}, *(e)* Fe^{3+} and O^{2-}, *(f)* Co^{3+} and SO_4^{2-},
   (g) Ni^{2+} and NO_3^-

2. Write the electron configuration of each of the following ions, and give the name of the *isoelectronic* noble gas (which has the same electron configuration):

   Li^+, N^{3-}, Be^{2+}, K^+, S^{2-}

   (Atomic numbers are Li = 3, N = 7, Be = 4, K = 19, S = 16.)

3. Write the electron configurations for the following cations:

   Mn^{2+}, Cu^+, Cu^{2+}, Zn^{2+}

   (Atomic numbers are Mn = 25, Cu = 29, Zn = 30.)

The driving force behind the reaction is the fact that sodium metal and chlorine molecules can pass to a lower energy level by forming ionic bonds. The formation of sodium chloride is exothermic. This picture of electrovalency proves to be more fruitful than the simple picture of attaining a noble gas electron configuration. Elements will not form an ionic compound if it is at a higher energy level than the elements. They may combine by the formation of covalent bonds.

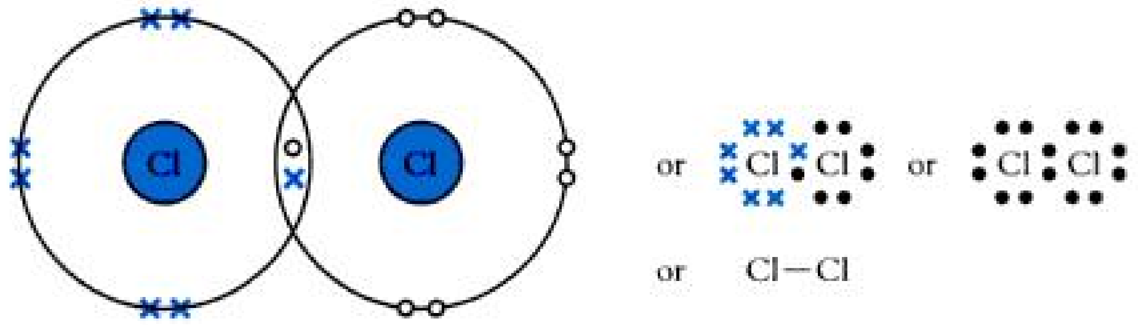
4.4 THE COVALENT BOND

Some compounds are non-electrolytes. Since these compounds do not conduct electricity, they cannot consist of ions. Non-electrolytes contain a type of chemical bond which differs from the ionic bond.

In the single covalent bond, two atoms share one pair of electrons. By sharing, the bonded atoms both gain a full outer shell of electrons

Two atoms of chlorine combine to form a molecule, Cl_2. Both chlorine atoms have the electron configuration Cl(2.8.7). G N Lewis suggested that the bond involves each of the two chlorine atoms sharing one of its outermost electrons – **valence electrons** as they are termed – with the other chlorine atom. The two atoms have to approach sufficiently closely for their atomic orbitals to overlap. The shared pair of electrons is called a **covalent bond**. They occupy the same orbital with opposing spins [§ 2.5]. The Cl_2 molecule can be represented as shown in Figure 4.4A.

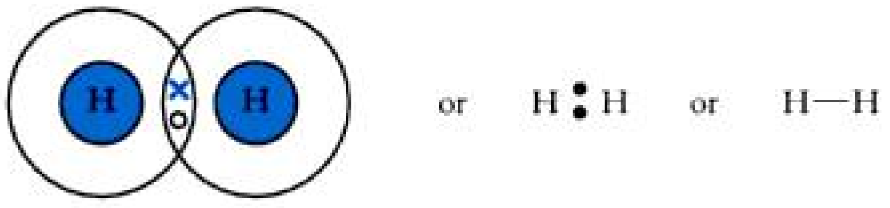
Figure 4.4A
Ways of representing the chlorine molecule



There are not really two types of electron, but it makes it easier to count the electrons if those from one atom are represented as crosses and those from the other as dots. By sharing a pair of electrons, each of the chlorine atoms has obtained eight electrons in its outer shell: it has 'completed its octet'. Electrons are shared when half-filled atomic orbitals of adjacent atoms overlap in space.

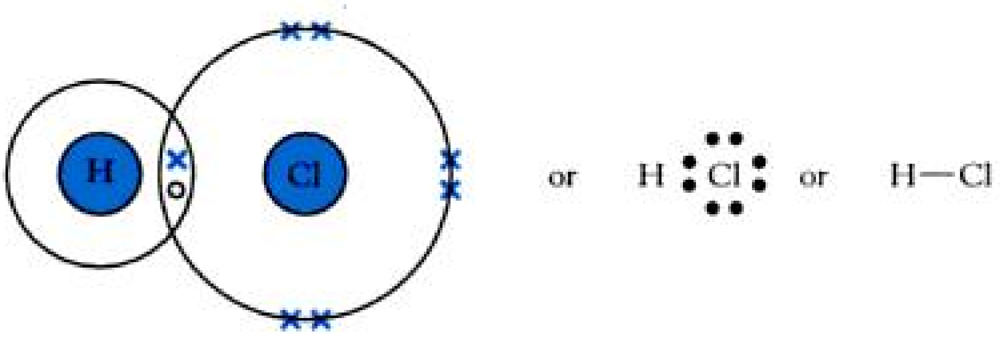
The H_2 molecule can be shown as in Figure 4.4B. Each hydrogen atom shares its electron with another hydrogen atom to gain a full outer s shell of 2 electrons.

Figure 4.4B
Ways of representing the hydrogen molecule



The HCl molecule can be shown as in Figure 4.4C.

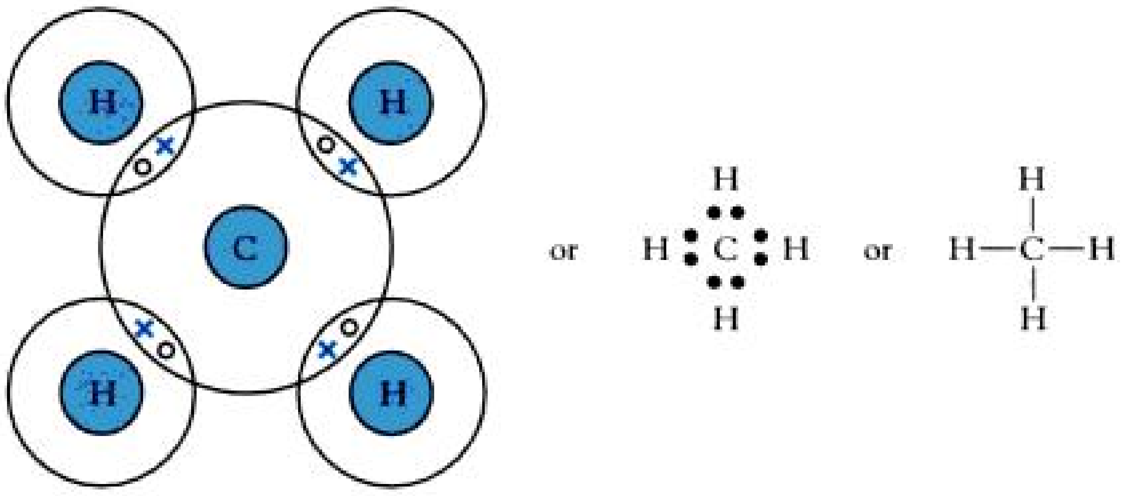
Figure 4.4C
Ways of representing the hydrogen chloride molecule



Each hydrogen atom has a full s shell with two electrons and each chlorine atom has a full octet.

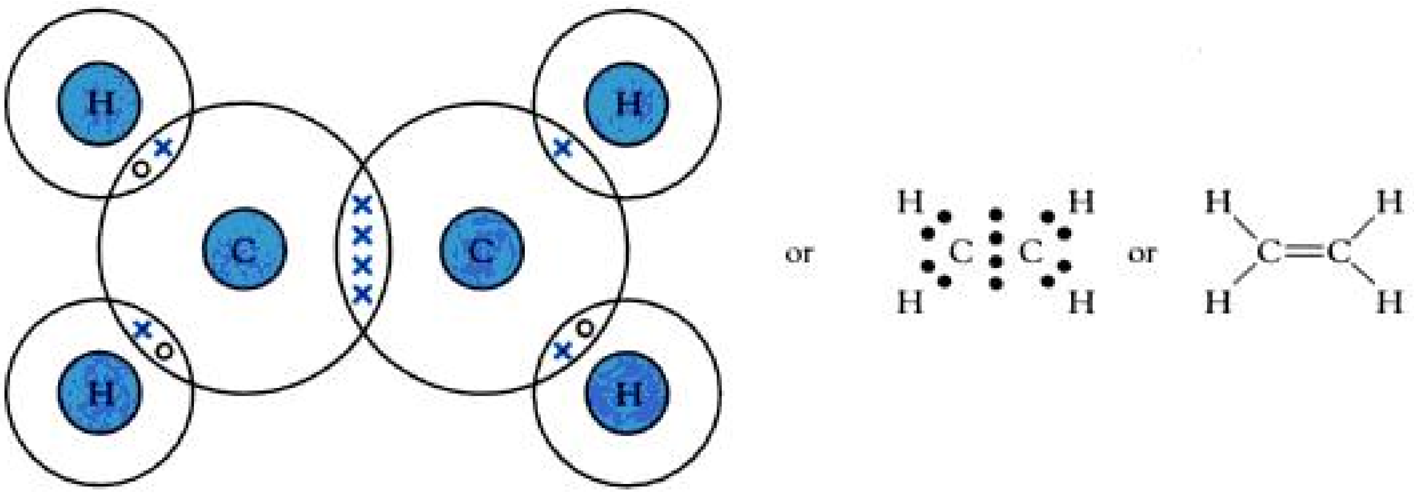
Covalent bonding is important in carbon compounds. The carbon atom, with four valence electrons, can attain a full octet by sharing one electron with each of four hydrogen atoms. The bonding in methane, CH_4, can be shown by a 'dot-and-cross' diagram [see Figure 4.4D]. The hydrogen electrons are shown as dots and the carbon electrons as crosses. Carbon has completed its octet, and hydrogen has attained the noble gas configuration of helium by completing its 1s shell.

Figure 4.4D
Ways of representing the bonding in methane



In the ethene molecule [Figure 4.4E] each carbon atom shares one pair of electrons with a hydrogen atom and two pairs of electrons with the other carbon atom. When atoms share two pairs of electrons there is a double bond between them. Each carbon atom forms single bonds to two hydrogen atoms and a double bond to the other carbon atom.

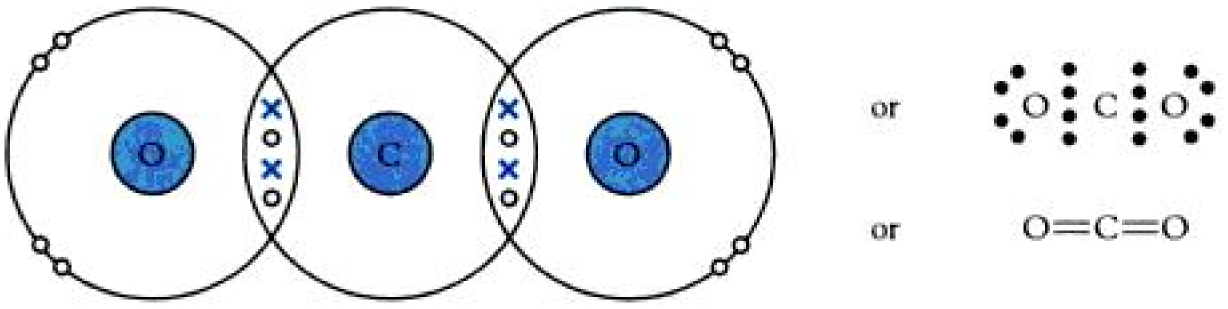
Figure 4.4E
Ways of representing the ethene molecule



A double bond is formed when two atoms share two pairs of electrons

In carbon dioxide, the carbon atom shares two electrons with each of two oxygen atoms, in order to give all three atoms a full octet of valence electrons. [See Figure 4.4F.]

Figure 4.4F
Ways of representing the carbon dioxide molecule

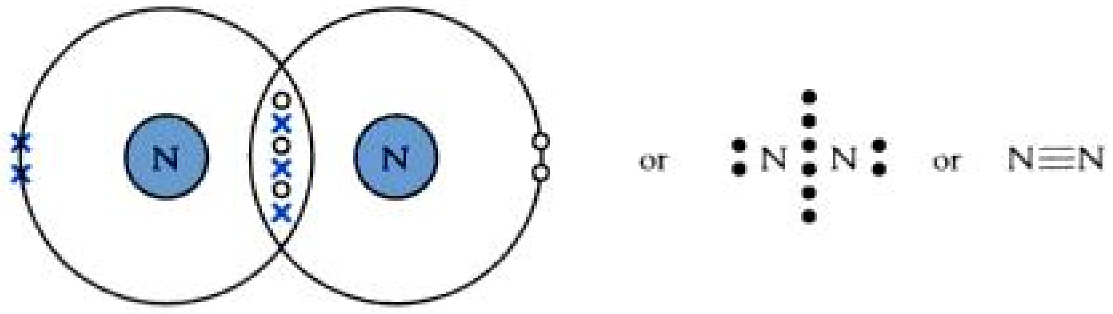


As each shared pair of electrons is a covalent bond, the two pairs of shared electrons between carbon and oxygen constitute a double bond. The pairs of electrons on the oxygen atoms which are not shared are described as **'lone pairs' of electrons**.

A triple bond is formed when two atoms share three pairs of electrons

In a molecule of nitrogen, each nitrogen atom, with five electrons, needs to share three of its electrons with the other atom of nitrogen in order to complete its octet. The bonding can be written as shown in Figure 4.4G.

Figure 4.4G
Ways of representing the N_2 molecule



The valence bond method considers the overlapping of atomic orbitals in isolation from the rest of the molecule

This method of describing molecules is called the **valence bond method**. It considers the atoms in a molecule in isolation from the rest of the molecule, except that one or more electrons in the outer shell of one atom are accommodated in the outer shell of another atom by an overlapping of atomic orbitals.

A different approach is the **molecular orbital treatment** [§ 4.6.1].

CHECKPOINT 4.4: BONDING IN COVALENT COMPOUNDS

1. The electron configurations of hydrogen and fluorine are H(1) and F(2.7). Show by means of a sketch (like those in Figures 4.4A to 4.4G) what happens when H and F combine to form a covalent bond in HF.
2. Sketch the configuration of electrons in a molecule of the covalent compound CH_3Cl. (Electron configurations are C(2.4), H(1) and Cl(2.8.7).)
3. Sketch the configuration of electrons in a molecule of the covalent compound, NH_3. (N has the electron configuration (2.5).)
4. By means of a 'dot-and-cross' diagram, such those in Figures 4.4A to 4.4G, sketch the arrangement of electrons in the molecule O_2.
5. Sketch the arrangement of electrons in a molecule of ethene, $H_2C{=}CH_2$.

4.4.1 FORMULAE OF COVALENT COMPOUNDS

The formula of a covalent compound depends on the number of pairs of electrons shared by the bonded atoms

The formulae of covalent compounds are decided by the number of pairs of electrons shared between atoms, as shown in the 'dot-and-cross' diagrams in Figures 4.4D to 4.4G.

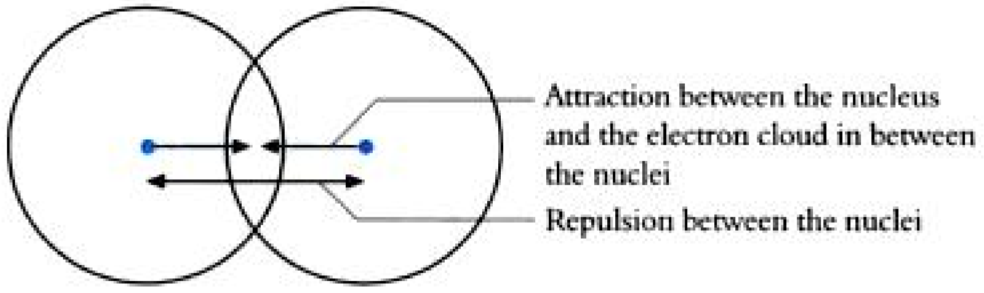
4.4.2 STRUCTURES OF COVALENT SUBSTANCES

Individual molecules

Many covalent substances are composed of individual molecules

Covalent substances can be solids, liquids or gases. Gases consist of individual molecules. The molecules move independently, with negligible forces of attraction between them. In liquids there are significant forces of attraction between the molecules. However, these are weaker forces than those in solids, and allow molecules to change their relative positions easily, so the substance can flow.

Figure 4.6B
Attraction and repulsion in the H_2 molecule



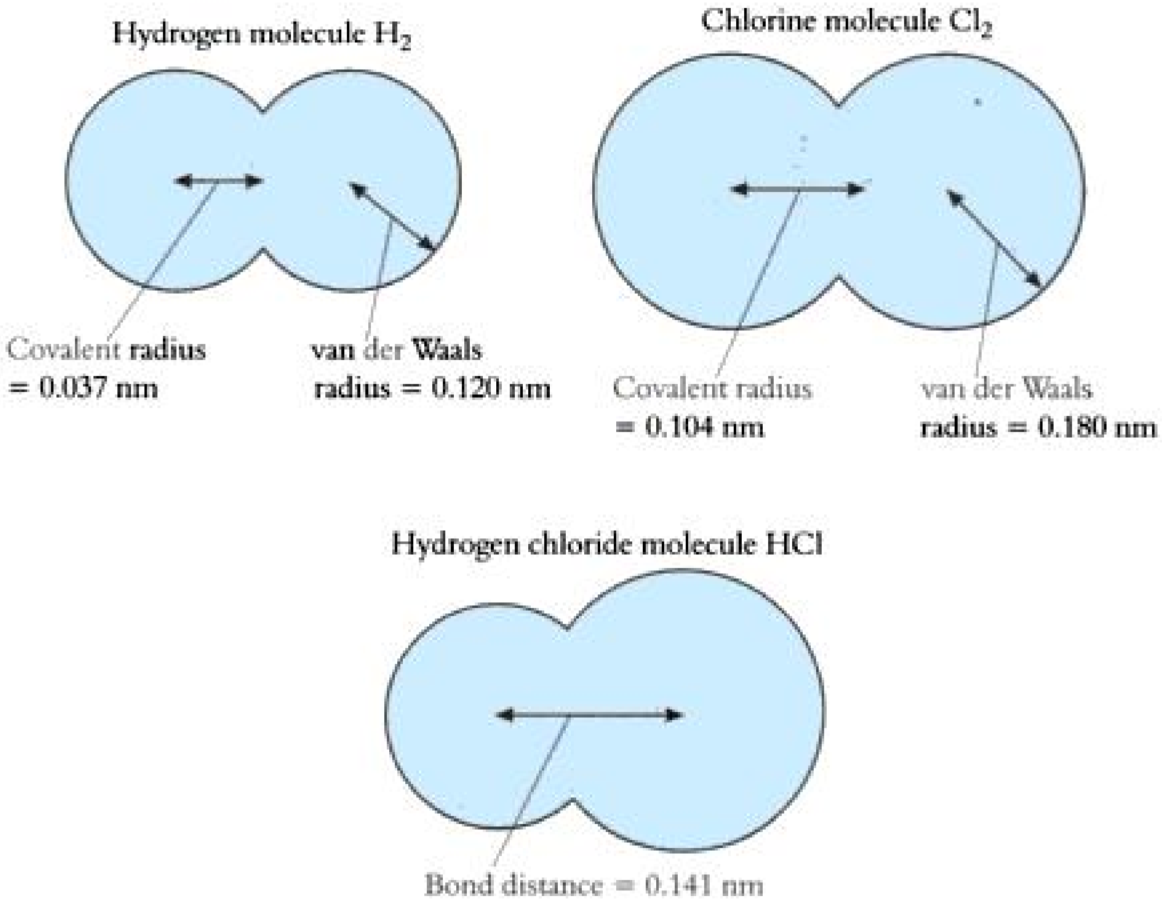
4.6.2 COVALENT RADII

Covalent radii (atomic radii)

The distance between the nuclei of covalently bonded atoms is the sum of their **covalent radii**. Covalent radii, which are also called **atomic radii**, are *additive*. The sum of the covalent radii of chlorine and hydrogen gives the length of the covalent bond in hydrogen chloride [see Figure 4.6C]. This figure also shows the **van der Waals radii**, which will be covered in § 4.8.2.

Figure 4.6C
Covalent radii and van der Waals radii for hydrogen and chlorine

In a covalent bond, distance between nuclei = sum of the covalent radii of the bonded atoms



4.6.3 ELECTRONEGATIVITY AND THE COVALENT BOND

Electronegativity is the ability of an atom in a covalent bond to attract electrons

Fluorine is the most electronegative of elements

In the bond between identical atoms, e.g. H—H, the electron density of the bonding orbital is distributed symmetrically between the bonded atoms. In a bond between different atoms, the bonding electrons may be more attracted to one of the bonded atoms than to the other. In the molecule HF, for example, the electron density of the bonding electrons lies more towards the fluorine atom than towards the hydrogen atom. The ability of an atom in a covalent bond to attract the bonding electrons is called **electronegativity**. Thus, fluorine is more **electronegative** than hydrogen. Electronegativity is not a quantity which can be measured or to which a unit can be assigned. Pauling derived a scale of relative electronegativity values. He assigned a value of 4.00 to fluorine, the most electronegative of elements. Some of his values are:

Various electronegativity values

H	Li	Be	B	C	N	O	F
2.1	1.0	1.5	2.0	2.5	3.0	3.5	4.0

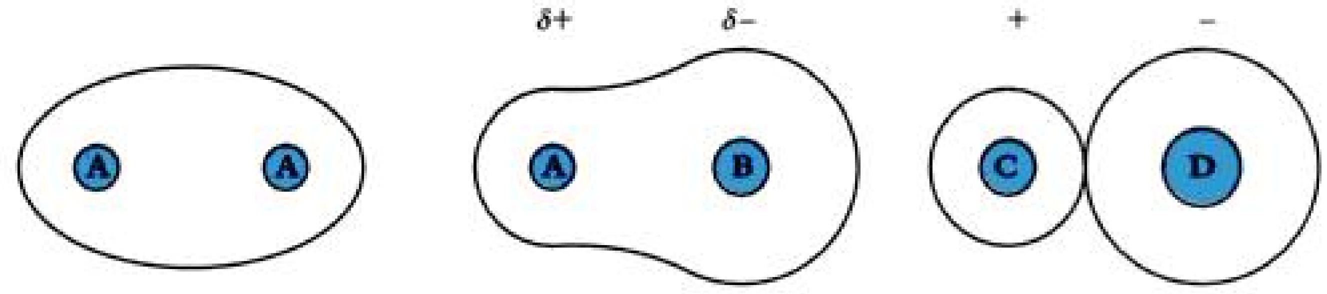
If the bonded atoms differ in electronegativity a covalent bond is polar ...

... it has a dipole

The HF molecule is described as **polar**: the centre of the negative charge (due to the electrons) does not coincide with the centre of positive charge (due to the nuclei). The molecule has a **dipole**: electric charges of equal magnitude and opposite sign separated by a small distance. There are many other covalent molecules which, like HF, are polar. There is no sharp distinction between an ionic bond and a covalent bond [see Figure 4.6D].

Figure 4.6D
Bond types

There is no sharp distinction between an ionic bond and a covalent bond



(a) Covalent bond. The electron density is symmetrically distributed.

(b) Polar covalent bond. The bonding electron density is greater in the region of **B**. **A** has a small positive (δ^+) charge, while **B** is slightly negative (δ^-).

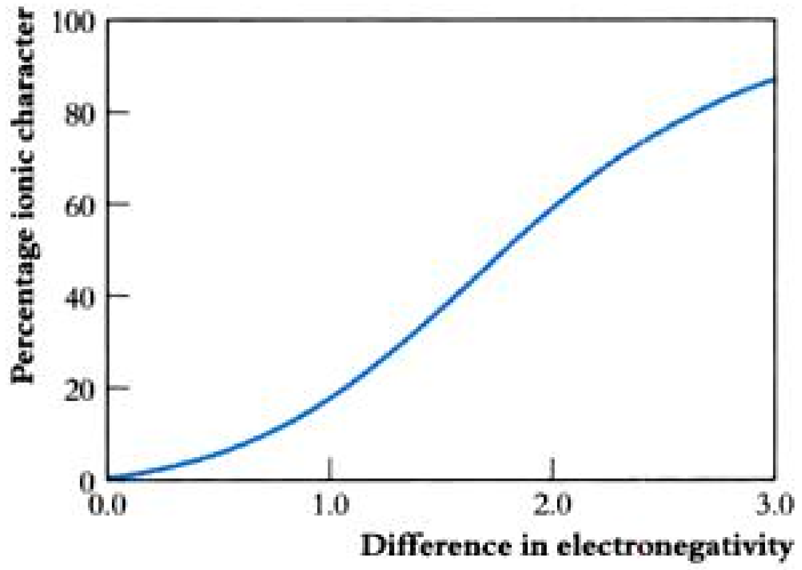
(c) Ionic bond. The electron cloud of $\mathbf{C}^+$ does not come under the influence of $\mathbf{D}^-$. The electron cloud of $\mathbf{D}^-$ is not distorted by $\mathbf{C}^+$.

Some covalent bonds have a degree of ionic character

The term **ionic bond** is used for bonds which are predominantly ionic. The term **covalent bond** is used for non-polar bonds, such as C—I, and also bonds in which there is a considerable degree of polarity. Bonds such as $C^{\delta+}$—$Cl^{\delta-}$ and $C^{\delta+}$—$O^{\delta-}$, are termed **polar covalent bonds**. The curve which Pauling drew to relate the percentage of ionic character in a bond to the difference in electronegativity between the bonded atoms is shown in Figure 4.6E. Approximate values for some covalent bonds are given:

Bond	C—I	C—H	C—Cl	C—F
Ionic character/%	0	4	6	40

Figure 4.6E
Curve relating percentage of ionic character in a bond to the difference in electronegativity between the bonded atoms



Pauling's electronegativity values can be applied to a bond between two atoms, either in a diatomic molecule or between two atoms considered in isolation from other atoms and bonds. They should *not* be applied to a formula unit in a crystal structure as they will give a wrong impression. If applied to $CaCl_2$, NaCl or LiF, electronegativity values will predict the nature of the bonding in an ion pair considered in isolation, e.g. $Na^+(g)\ Cl^-(g)$. In reality, we are interested in crystalline sodium chloride, in which each Cl^- ion is part of a crystal structure and its electron cloud is influenced symmetrically by six Na^+ ions around it. The net result is that the electron cloud of the Na^+ ion becomes rather cubical in shape, being drawn into the spaces between the ions in the structure, but sodium chloride is still overwhelmingly ionic in nature.

In some ionic compounds there is a degree of sharing of electron clouds between cations and anions

The deformation of the spherical electron clouds is more pronounced in lithium fluoride. In calcium chloride it does not occur. The reasons for these differences were explained by K Fajans.

4.6.4 FAJANS' RULES OF BOND TYPE

The distortion of an electron cloud by a neighbouring charged ion or **dipole** is called **polarisation**. Comparing ions with similar nuclear charges, large ions are more easily polarised than small ions. The electrons in small ions are more closely controlled by the positively charged nucleus.

K Fajans formulated two rules to predict the proportions of ionic and covalent character in the bond formed between two atoms.

Fajans' rules predict the ionic and covalent character of bonds

1. Bonds will tend to be ionic if the ions formed are small in charge. For example, sodium chloride is likely to be ionic because Na^+ and Cl^- bear unit charges, whereas aluminium chloride is likely to be covalently bonded because Al^{3+} ions are highly charged.
2. Bonds will tend to be ionic if the radius of the possible cation is large (e.g. the alkali metals) and the radius of the possible anion is small (e.g. the smaller halogens).

A cation with a small radius and a high charge will polarise anions ...

... with an increase in the covalent character of the bonds

The sizes of some ions are shown in Figure 15.2D, § 15.2. Compare the radii of the ions Na^+, Mg^{2+} and Al^{3+}. The high charge on the Al^{3+} ion results in a small radius because the remaining electrons are drawn in close to the nucleus. The combination of a high charge and a small radius gives Al^{3+} a high **charge density** (i.e. charge/volume ratio), and this enables the cation to attract the electron cloud of a neighbouring anion (or of a molecule). The electron cloud of the anion will be distorted in such a way as to increase the electron density near the cation: the anion has become **polarised**.

A large anion is easily polarised ...

... and its bonds will have some covalent character

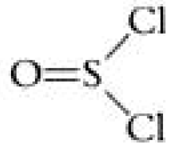
An anion is larger than the atom from which it was formed, and has one or two more electrons. The nucleus is less able to attract the electrons closely than it is in the parent atom. In a large anion, the electrons are further from the nucleus and less under its control than in a small anion, making the larger anion easier to polarise. If the cation is small and the anion is large, the cation will be able to polarise the anion, and there will be some sharing of the electron cloud of the anion: i.e. the bond will have some covalent character.

CHECKPOINT 4.6: THE COVALENT BOND

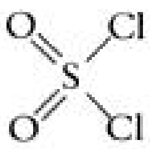
1. Draw dot-and-cross diagrams to show the bonding in

(a) $H-C\equiv N$ *(b)* CCl_4

(c)



(d)



2. Distinguish between *(a)* the intramolecular bonds, and *(b)* the intermolecular forces in chloroform, $CHCl_3$. What makes you think that the bonds in *(a)* are strong and the forces in *(b)* are weak?

3. Sodium chloride melts at 800 °C. Tetrachloromethane, CCl_4, is a liquid at room temperature. Explain how this difference arises.

4.7 THE COORDINATE BOND

A coordinate bond is a covalent bond ...

... in which both electrons in the bond come from one of the bonded atoms

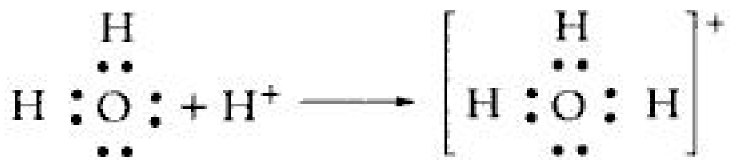
A donor atom shares a lone pair of electrons with an acceptor atom

A **coordinate bond** is a covalent bond in which the shared pair of electrons is provided by only *one* of the bonded atoms. One atom is the **donor**, the other is the **acceptor**, and the bond is sometimes called the **dative covalent bond**. Once formed, a coordinate bond has the same characteristics as a covalent bond. For an atom to act as a donor, it must have at least one pair of unshared electrons (a lone pair) in its outermost shell (the valence shell). The acceptor has at least one vacant orbital in its outer shell. It may be a metal cation or a transition metal atom or an atom in a molecule.

Once formed, a coordinate bond is like a covalent bond

In water, $H-\overline{O}-H$, the oxygen atom has two lone pairs of electrons. They can be shared with an atom which needs them to complete it valence shell. A proton H^+ has an empty 1s orbital. By accepting a pair of electrons from oxygen, it achieves a full s shell:

The oxonium ion, H_3O^+, is formed by coordination

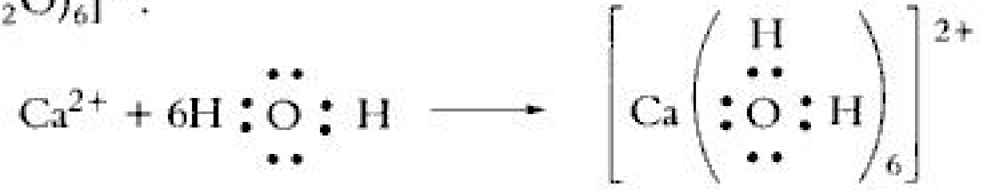


The species formed is an **oxonium** ion, H_3O^+. The positive charge contributed by the proton is spread over the whole ion. The proton has one unit of positive charge spread over a surface area which is minute compared with other ions. The high charge density makes it extremely reactive: the proton cannot exist by itself. It is stabilised by the coordination of water molecules.

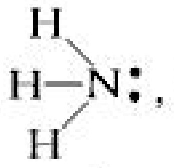
Water coordinates to metal ions ...

... an example is $[Ca(H_2O)_6]^{2+}$

Water also coordinates to metal ions. The fact that bonds are formed between metal ions and water is responsible for the solubility of many salts. Energy is required to break the bond holding ions together in a crystal structure. If energy is given out when coordinate bonds form between metal ions and water, this may swing the balance in favour of solution. Metal ions are hydrated, e.g. $[Ca(H_2O)_6]^{2+}$:



The lone pair on N in NH_3 is responsible for the formation of coordination compounds by NH_3

The nitrogen atom in ammonia, , has an unshared pair of electrons which it is able to share with an atom that needs two electrons to complete its octet. A molecule of ammonia forms a coordinate bond to a hydrogen ion in the formation of an ammonium ion. The lone pair of the nitrogen atom coordinates into the valence shell of the hydrogen ion:

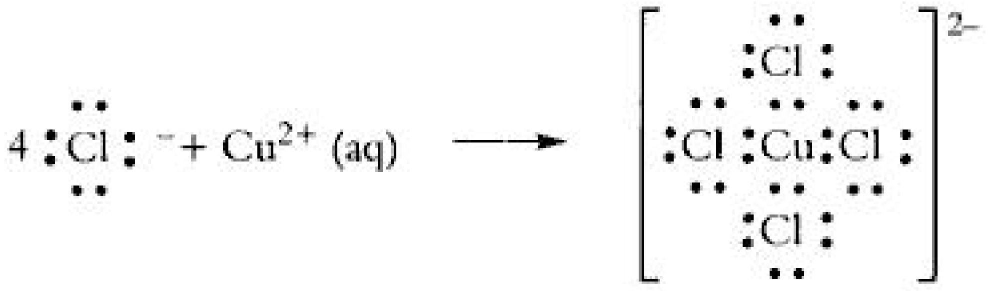
The symbol → is used for a coordinate bond, an arrow pointing from the donor towards the acceptor.

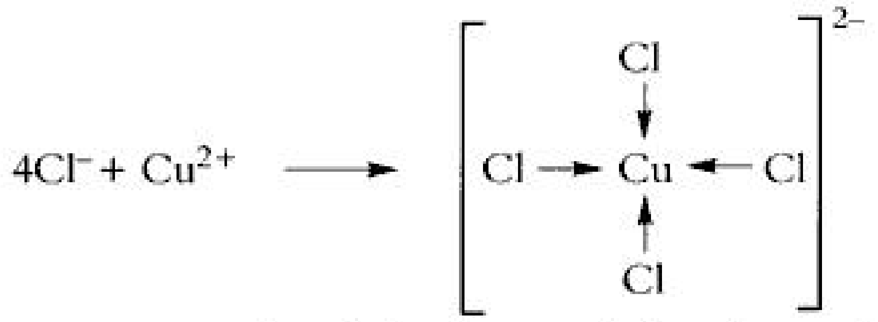
Ions such as $CuCl_4^{2-}$ are formed by coordination ...

... they are called complex ions ...

... formed by combination of an ion with an oppositely charged ion or with a molecule

Copper(II) chloride is blue in solution. In the presence of a high concentration of chloride ions, the solution turns a very deep green. The colour is due to the formation of $CuCl_4^{2-}$ ions. Coordinate bonds form between Cl^- ions and Cu^{2+} ions:





The copper atom now has eight electrons in its valence shell. Ions such as $CuCl_4^{2-}$ and $Cu(NH_3)_4^{2+}$, which are formed by the combination of an ion with an oppositely charged ion or a molecule are called **complex ions**.

CHECKPOINT 4.7: THE COORDINATE BOND

1. Draw a dot-and-cross diagram to show the arrangement of valence electrons in the complex ion $Cu(H_2O)_4^{2+}$. It is formed by coordination of H_2O molecules on to a Cu^{2+} ion.

2. Draw a dot-and-cross diagram to show the bonding in the complex ion $Fe(H_2O)_6^{3+}$. How many electrons has the iron atom in its valence shell? How can it accommodate this number?

3. Explain the bonding in the compound NH_3BF_3.

4. The formula for carbon monoxide can be written $|C \leftleftarrows O|$. Draw a dot-and-cross diagram for this molecule. The lone pair on the oxygen atom can be used to form a coordinate bond to a nickel atom. By means of a diagram, show the bonding in nickel carbonyl, $Ni(CO)_4$.

5. Explain the bonding in the tetraammine copper ion, $Cu(NH_3)_4^{2+}$.

6. The slightly soluble compound lead(II) chloride dissolves in concentrated hydrochloric acid to form a soluble complex ion. What do you think the formula of this ion might be? Explain the bonding in the ion.

4.8 INTERMOLECULAR FORCES

Dipole–dipole interactions, van der Waals forces and hydrogen bonds are all intermolecular forces

Intermolecular forces and bonds are of a number of types: dipole–dipole interactions, van der Waals forces and the hydrogen bond. Polar molecules (§ 4.6.3) have a dipole. A dipole consists of two electric charges of equal magnitude and opposite signs separated by a small distance.

4.8.1 DIPOLE–DIPOLE INTERACTIONS

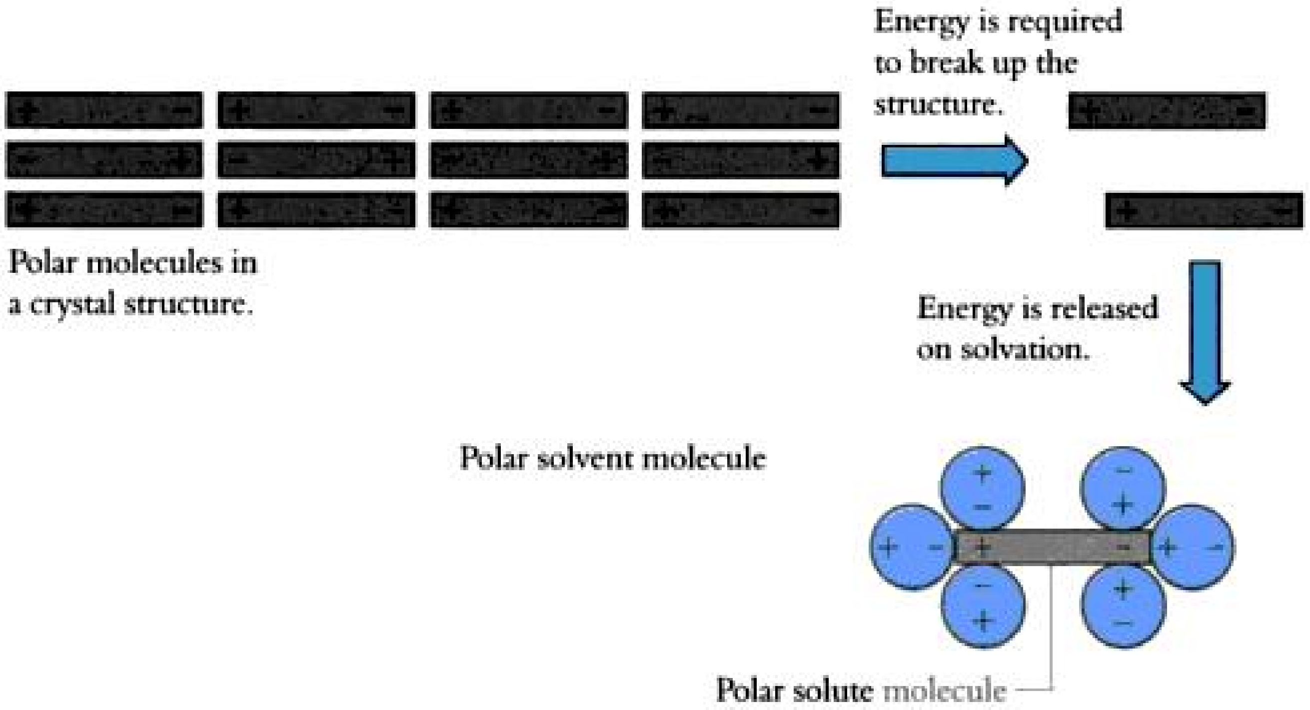
Attractions between dipoles result in an ordered arrangement of molecules

In the solid state, polar molecules interact to form an ordered arrangement. Dipole–dipole interactions between the molecules lead the molecules to pack in such a way that partial positive charges will be adjacent to partial negative charges [see Figure 4.8A].

Solvation helps solids to dissolve

Polar solids dissolve in polar solvents. The energy required to break up the crystal is recouped by the energy released when polar solute molecules interact with polar solvent molecules. [See Figure 4.8A.] This interaction is called **solvation**; if the solvent is water, it is called **hydration** [§ 17.4].

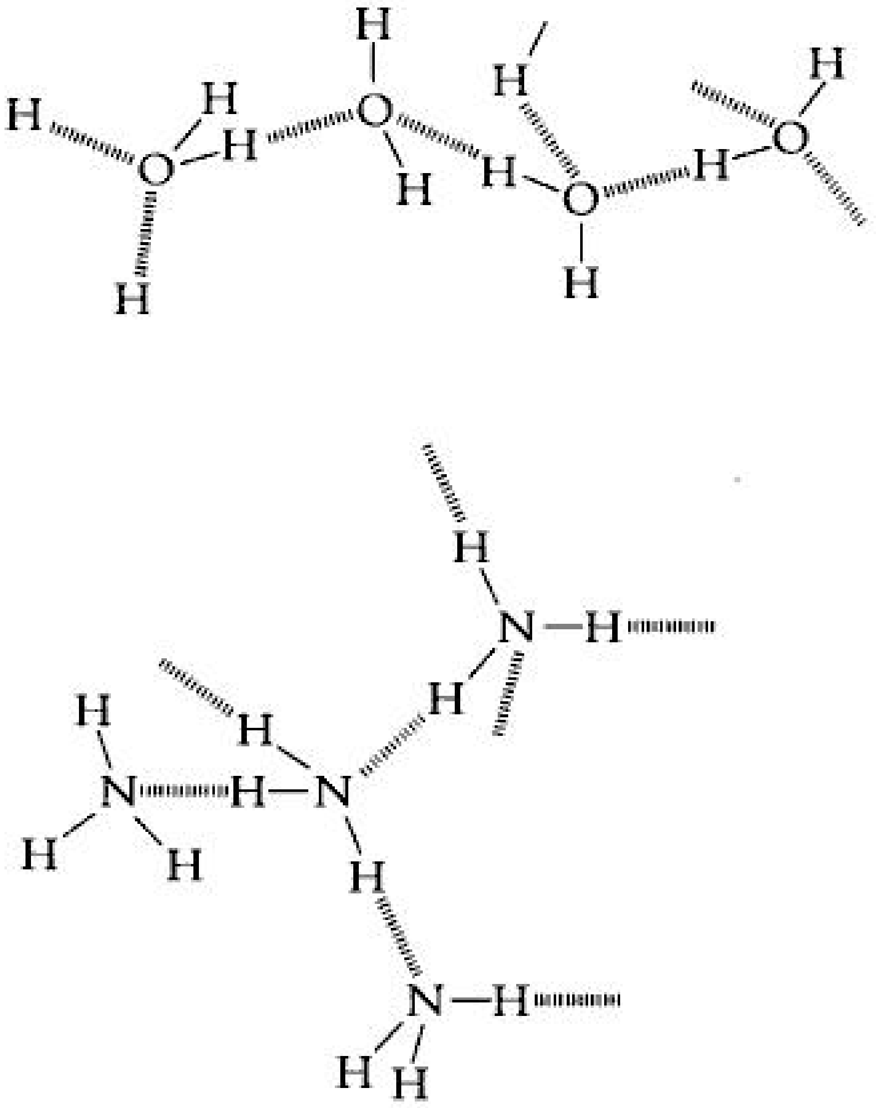
Figure 4.8A
The process of dissolution



Evidence for H bonds is given by the melting and boiling temperatures of HF, H_2O, NH_3

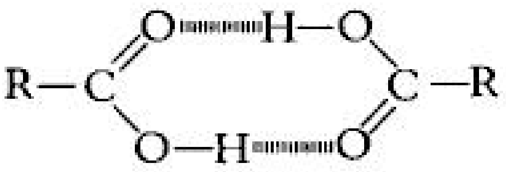
Some evidence for the existence of the hydrogen bond is shown in Figures 4.8E and 4.8F. A comparison is made of the melting temperatures and boiling temperatures of hydrogen fluoride, water and ammonia with those of other hydrides in the same groups of the Periodic Table. The melting temperatures and boiling temperatures of these compounds are much higher than those of other hydrides in the same groups. The molecules of HF, H_2O and NH_3 must be held together by intermolecular bonds stronger than those between molecules of the other hydrides. Since fluorine, oxygen and nitrogen are the most electronegative of elements, the intermolecular forces are thought to be hydrogen bonds. [See Figure 4.8G.]

Figure 4.8G
Hydrogen bonding in $H_2O(l)$ and $NH_3(l)$



When the molar masses of carboxylic acids are found from measurements in the vapour phase and from solutions in organic solvents, the values are often up to twice the values calculated from the formulae. The molecules are thought to dimerise through the formation of hydrogen bonds [see Figure 4.8H].

Figure 4.8H
H bonding in RCO_2H



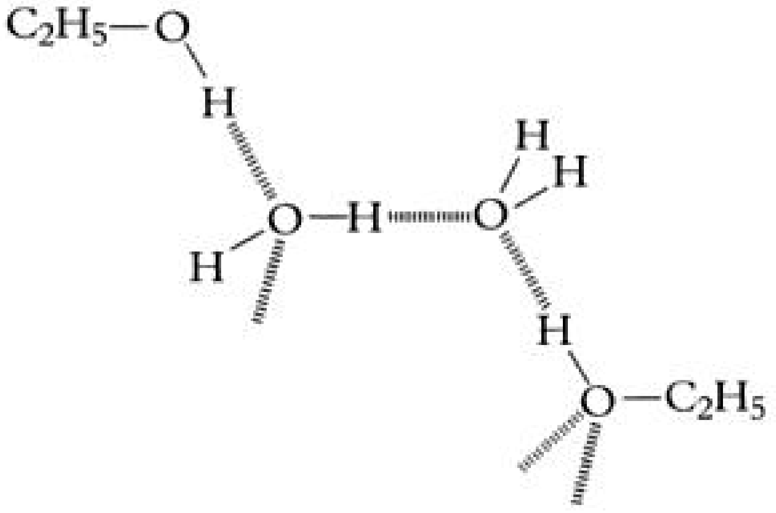
Some compounds can form **intramolecular hydrogen bonds** between two groups in the same molecule. [See Figures 4.8K to 4.8N and Question 5, Checkpoint 4.8B.]

Solubility considerations

Substances dissolve in water if they can form H bonds with it

Water is a hydrogen-bonded association of water molecules. A substance such as ethanol, C_2H_5OH, will dissolve in water as molecules of ethanol can displace water molecules in the association. New hydrogen bonds form between molecules of ethanol and water [see Figure 4.8I]. Halogenoalkanes such as chloroethane, C_2H_5Cl, do not form hydrogen bonds with water and are only slightly soluble. There are more references to solubility and hydrogen bonding in Part 4: Organic Chemistry.

Figure 4.8I
Hydrogen bonds between alcohols and water



Volatility

Hydrogen bonding occurs in alcohols and amines

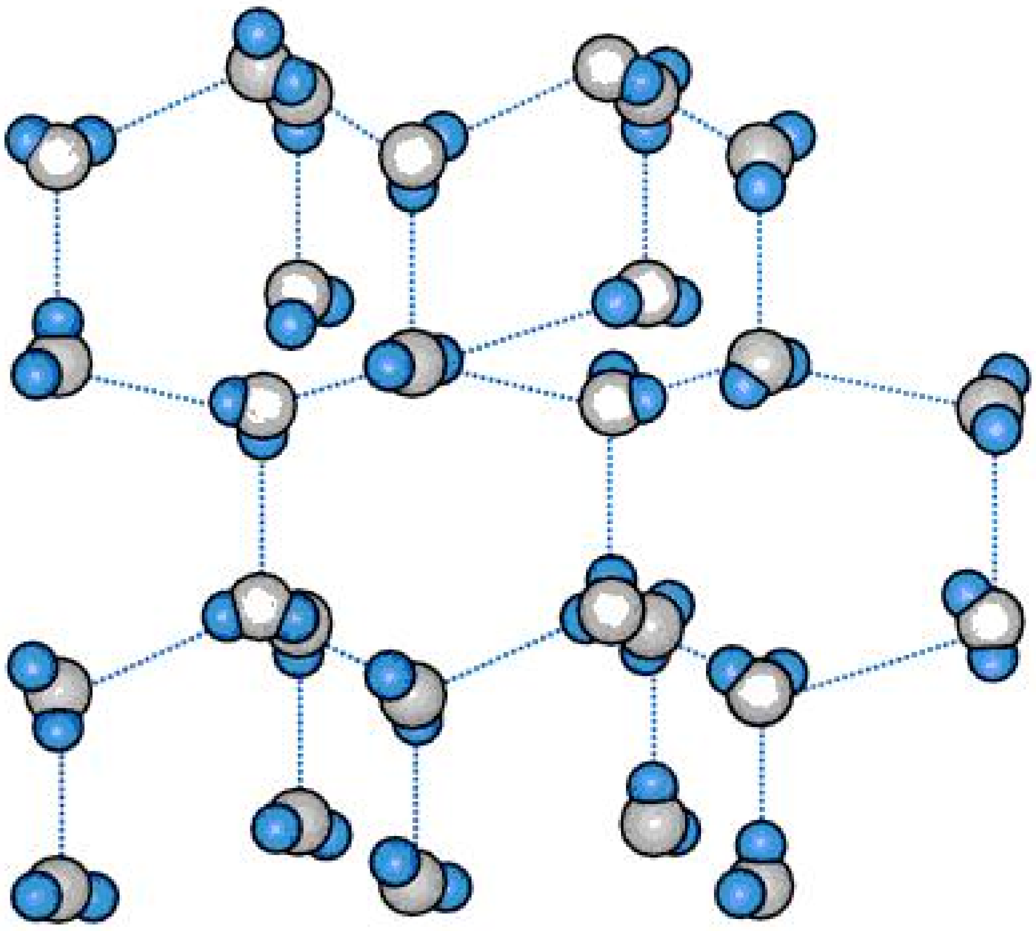
In the liquid state, the molecules of alcohols are associated by hydrogen bonding. Energy must be supplied to break these bonds when the liquid is vaporised, making the boiling temperatures of alcohols higher than those of non-associated liquids, e.g. alkanes, of comparable molar mass. Amines also are hydrogen-bonded in the liquid state [§ 32.4].

The structure of ice

Liquid water is associated by H bonding

The bonds in H_2O are inclined at approximately the tetrahedral angle of 109.5°. The lone pairs occupy the other apices of the tetrahedron [see Figure 5.2F, § 5.2.3]. Liquid water contains associations of water molecules [see Figure 4.8G]. In ice, the arrangement of molecules is similar, but the regularity extends throughout the whole structure [see Figure 4.8J].

Figure 4.8J
Hydrogen bonding in ice
Notes Each H_2O molecule uses both its H atoms to form hydrogen bonds and is also bonded to two other H_2O molecules by means of their H atoms. The arrangement of bonds about the O atoms is tetrahedral



Hydrogen bonding extends throughout the whole structure in ice ...

The structure spaces the molecules further apart than they are in liquid water. This is why, when water freezes, it expands by 9%, and why ice is less dense than water at 0 °C. The underlying structure of ice resembles that of diamond [see Figure 6.6A, § 6.6].

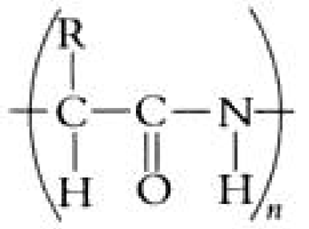
... This explains why ponds freeze from the surface downwards

The fact that ice is less dense than water at 0 °C explains why ponds and lakes freeze from the surface downwards. Water reaches its maximum density at 4 °C. As it cools further, the water at the surface becomes less dense and therefore stays on top of the slightly warmer water until it freezes. The layer of ice on the surface helps to insulate the water underneath from further heat loss. Fish and plants survive under the ice in Canadian lakes and rivers for months.

The structure of proteins

Protein molecules have H bonds ...

Hydrogen bonding is important in protein molecules. Proteins consist of long chains of formula

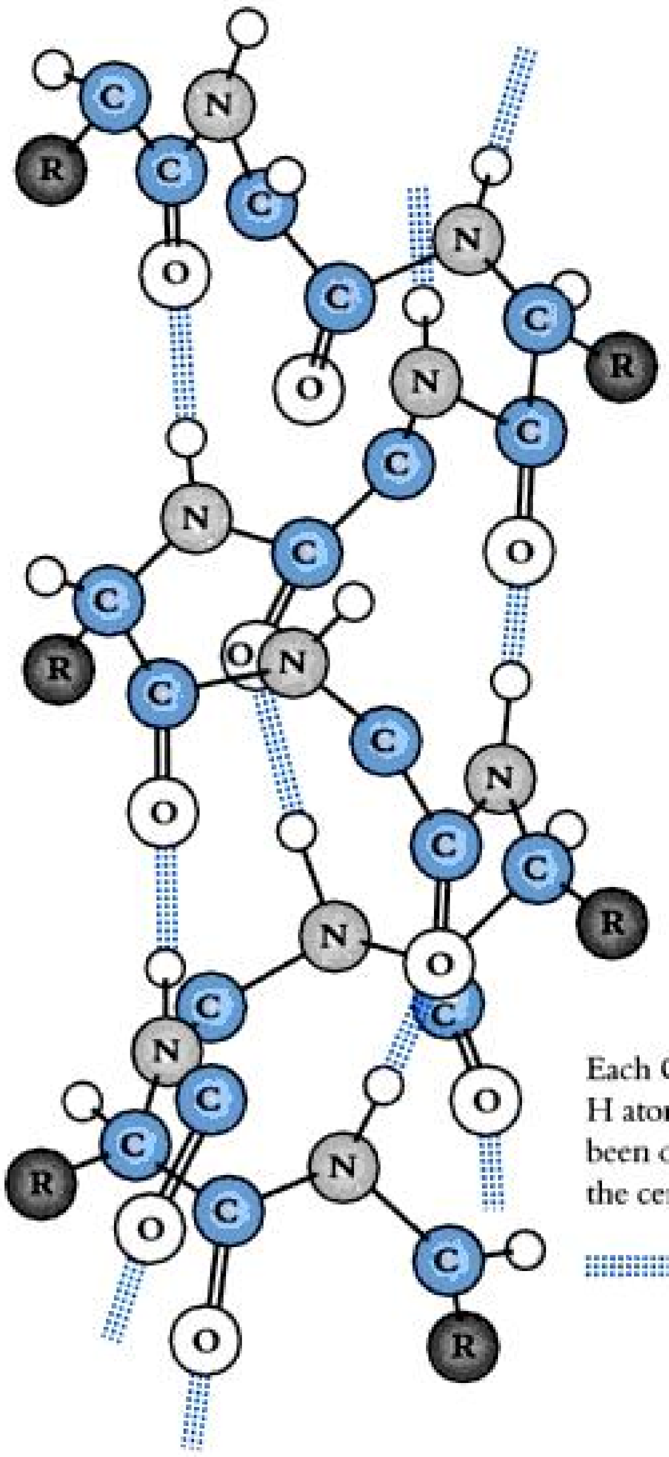


$$\left(\begin{matrix} \mathrm{R} & & \\ | & & \\ -\mathrm{C}- & \mathrm{C}- & \mathrm{N}- \\ | & \| & | \\ \mathrm{H} & \mathrm{O} & \mathrm{H} \end{matrix} \right)_n$$

... between $\rangle\overset{}{C}{=}O$ *and* $\rangle N{-}H$ *groups*

R can be a number of groups. Since both the $\rangle\overset{\delta+}{C}{=}\overset{\delta-}{O}$ group and the $\rangle\overset{\delta-}{N}{-}\overset{\delta+}{H}$

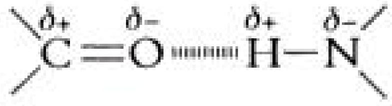
Figure 4.8K
A protein chain with the α helical structure



Each C has an R group and a H atom attached; these have been omitted from C atoms in the centre of the helix.

▦ Hydrogen bond

groups are polar, hydrogen bonding can occur between them:



$$\overset{\delta+}{\text{C}}{=}\overset{\delta-}{\text{O}}\cdots\cdots\overset{\delta+}{\text{H}}{-}\overset{\delta-}{\text{N}}$$

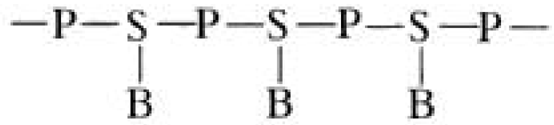
The helical structure of proteins is sustained by H bonds

A single protein molecule contains many hydrogen bonds. They are one of the forms of intramolecular attraction which hold the protein in a three-dimensional arrangement described as the *secondary structure* of the protein. Figure 4.8K shows the α helical structure proposed by Pauling and co-workers as a result of their X ray diffraction studies on protein molecules. An **α helix** is a spiral, which, looking away from you, is spiralling in a clockwise direction.

The double helix

Nucleic acids contain phosphate groups, sugar groups and bases

Hydrogen bonding is important in the famous **double helix** of DNA. **Chromosomes** are the bodies in the nuclei of the cells of living organisms which carry genetic information. They contain macromolecular substances called **nucleic acids**. These are of two types: ribonucleic acid, RNA, and deoxyribonucleic acid, DNA. The macromolecular chains in DNA are of the type



$$\begin{array}{ccccccccc} -\text{P}- & \text{S} & -\text{P}- & \text{S} & -\text{P}- & \text{S} & -\text{P}- \\ & | & & | & & | & \\ & \text{B} & & \text{B} & & \text{B} & \end{array}$$

where P is a phosphate group and S is the sugar deoxyribose.

The double helix of DNA is held in this configuration by H bonds

B is one of the four bases: adenine, thymine, cytosine and guanine. DNA consists of two macromolecular strands spiralling round each other in a double helix, as shown in Figure 4.8L. The strands are held together by hydrogen bonding between the bases, as shown in Figure 4.8M.

Figure 4.8L
The double helix

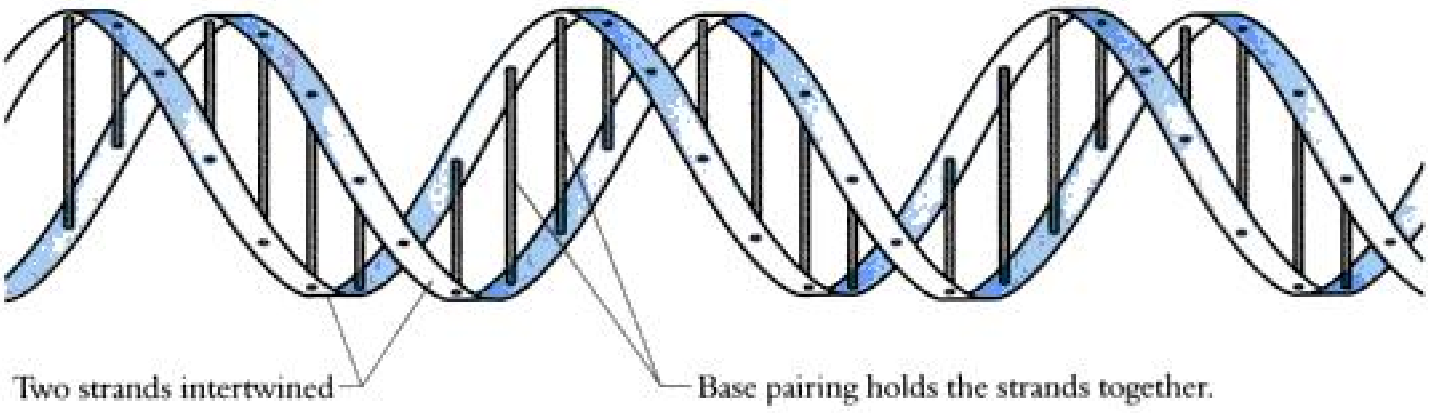
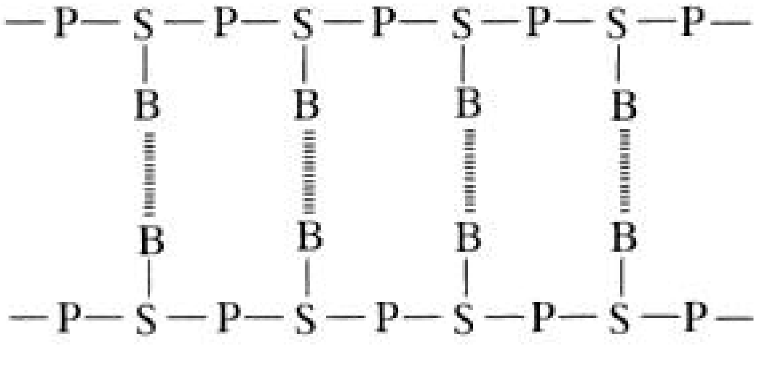


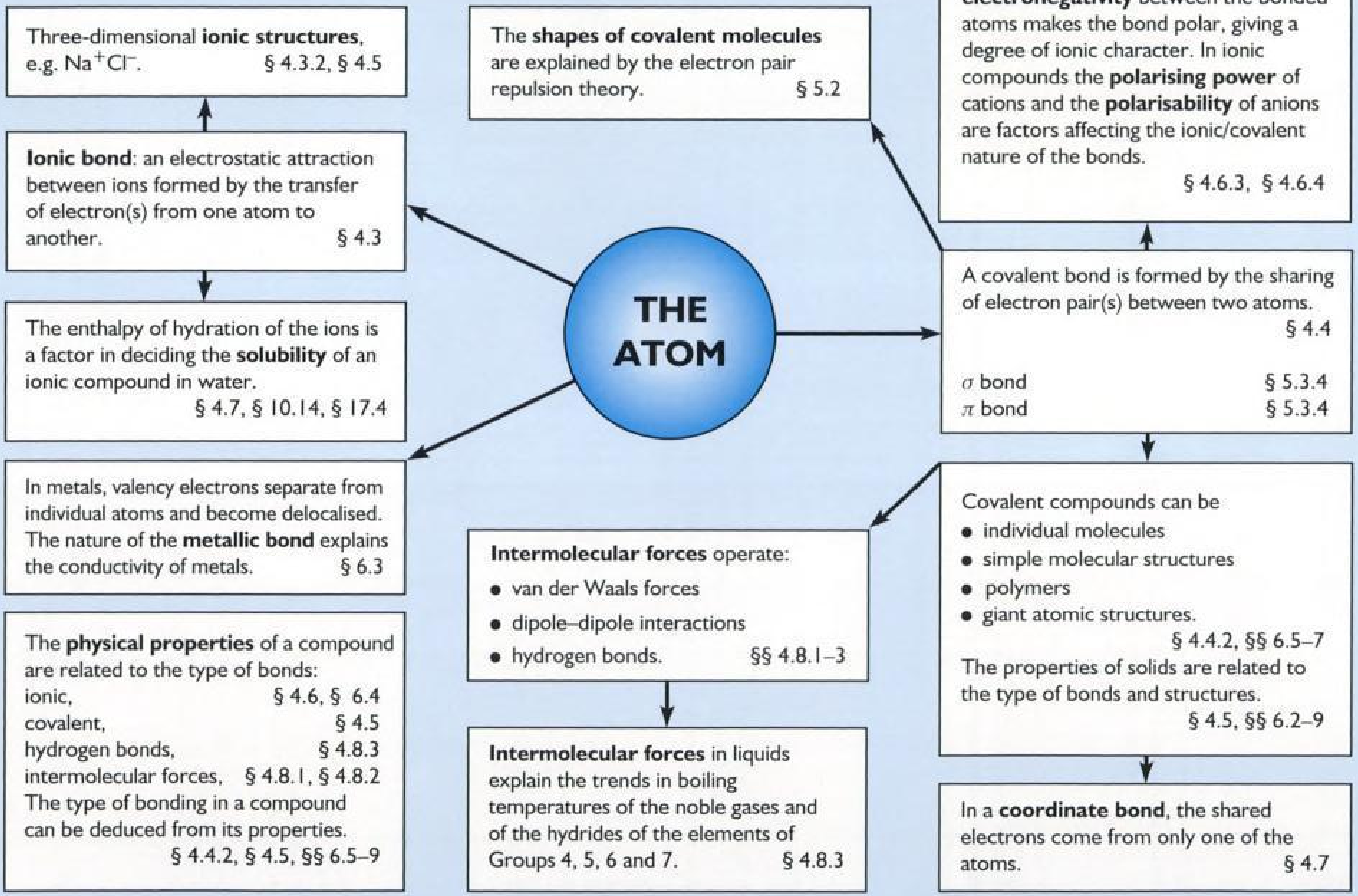
Figure 4.8M
Hydrogen bonding between strands in DNA



$$\begin{array}{ccccccccc} -\text{P}- & \text{S} & -\text{P}- & \text{S} & -\text{P}- & \text{S} & -\text{P}- & \text{S} & -\text{P}- \\ & | & & | & & | & & | & \\ & \text{B} & & \text{B} & & \text{B} & & \text{B} & \\ & \vdots & & \vdots & & \vdots & & \vdots & \\ & \text{B} & & \text{B} & & \text{B} & & \text{B} & \\ & | & & | & & | & & | & \\ -\text{P}- & \text{S} & -\text{P}- & \text{S} & -\text{P}- & \text{S} & -\text{P}- & \text{S} & -\text{P}- \end{array}$$

Of the four bases, *thymine* can pair up with *adenine* by hydrogen bonding and *cytosine* can form hydrogen bonds with *guanine*. The double helix brings these base pairs into contact so that they can form the bonds that keep the structure intact. Figure 4.8N shows the details of the hydrogen bonding.

THE CHEMICAL BOND



Three-dimensional **ionic structures**, e.g. Na^+Cl^-. § 4.3.2, § 4.5

Ionic bond: an electrostatic attraction between ions formed by the transfer of electron(s) from one atom to another. § 4.3

The enthalpy of hydration of the ions is a factor in deciding the **solubility** of an ionic compound in water. § 4.7, § 10.14, § 17.4

In metals, valency electrons separate from individual atoms and become delocalised. The nature of the **metallic bond** explains the conductivity of metals. § 6.3

The **physical properties** of a compound are related to the type of bonds:

ionic,	§ 4.6, § 6.4
covalent,	§ 4.5
hydrogen bonds,	§ 4.8.3
intermolecular forces,	§ 4.8.1, § 4.8.2

The type of bonding in a compound can be deduced from its properties. § 4.4.2, § 4.5, §§ 6.5–9

The **shapes of covalent molecules** are explained by the electron pair repulsion theory. § 5.2

THE ATOM

Intermolecular forces operate:

- van der Waals forces
- dipole–dipole interactions
- hydrogen bonds. §§ 4.8.1–3

Intermolecular forces in liquids explain the trends in boiling temperatures of the noble gases and of the hydrides of the elements of Groups 4, 5, 6 and 7. § 4.8.3

In covalent compounds, a difference in **electronegativity** between the bonded atoms makes the bond polar, giving a degree of ionic character. In ionic compounds the **polarising power** of cations and the **polarisability** of anions are factors affecting the ionic/covalent nature of the bonds. § 4.6.3, § 4.6.4

A covalent bond is formed by the sharing of electron pair(s) between two atoms. § 4.4

σ bond	§ 5.3.4
π bond	§ 5.3.4

Covalent compounds can be

- individual molecules
- simple molecular structures
- polymers
- giant atomic structures. § 4.4.2, §§ 6.5–7

The properties of solids are related to the type of bonds and structures. § 4.5, §§ 6.2–9

In a **coordinate bond**, the shared electrons come from only one of the atoms. § 4.7

8. The table below shows the melting points of the Period 3 elements except for silicon.

Element	Na	Mg	Al	Si	P	S	Cl	Ar
mp/K	371	923	933		317	392	172	84

(a) Explain in terms of bonding why the melting point of magnesium is higher than that of sodium. **3**

(b) State the type of bonding between atoms in the element silicon and name the type of structure which silicon forms. **2**

(c) Predict the approximate melting point of silicon. **1**

(d) Explain why chlorine has a lower melting point than sulphur. **2**

(e) Predict the approximate melting point of potassium and give one reason why it is different from that of sodium. **2**

10 *NEAB (AS/AL)*

9. *(a)* Naturally occurring boron contains two isotopes with mass numbers 10 and 11. The relative atomic mass of boron is 10.81.

(i) Calculate the percentage abundance of ^{10}B in naturally occurring boron. **2**

(ii) Draw the mass spectrum of naturally occurring boron. **1**

(b) Boron is used to absorb neutrons in a nuclear reactor.

Give the chemical symbol of the element **X** and state the value of a and b in the equation below.

$$^{11}\mathbf{B} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{b}_{a}\mathbf{X} + \gamma$$ **2**

(c) (i) Draw dot-and-cross diagrams to show the bonding in boron trifluoride, $\mathbf{BF_3}$, and ammonia, NH_3. **2**

(ii) By reference to your diagrams, explain how the two molecules bond together to form a compound. **2**

(d) (i) Graphite is a black slippery substance which conducts electricity. Its structure is made up of planes of hexagonal rings of carbon atoms. Explain why graphite is
I. slippery; II. conducts electricity. **2**

(ii) Boron nitride, BN, is a white slippery substance with the graphite type structure. Suggest, by means of a sketch or otherwise, the arrangement of boron and nitrogen atoms in one of the planes of atoms in boron nitride. **1**

12 *WJEC (AS/AL)*

5

THE SHAPES OF MOLECULES

5.1 HAEMOGLOBIN

The function of haemoglobin is to combine with oxygen, transport it in the blood stream to parts of the body where it is needed and then release the oxygen. The haemoglobin molecule has a complicated shape, as you can see from Figure 5.1A. The molecule consists of four protein chains, two each of different types, and four haem groups. The protein chains are held in a complicated three-dimensional arrangement by the different types of bonds that operate between them, including dipole–dipole interactions, van der Waals forces and hydrogen bonds (see Chapter 4). The four haem groups contain iron in the form of Fe^{2+}. Each haem group is able to combine with oxygen through the formation of a coordinate bond from a lone pair on an oxygen molecule to the Fe^{2+} ion. The haem groups are situated on the outside of the molecule where oxygen can easily reach them. The shape of the molecule enables it to perform its biological function.

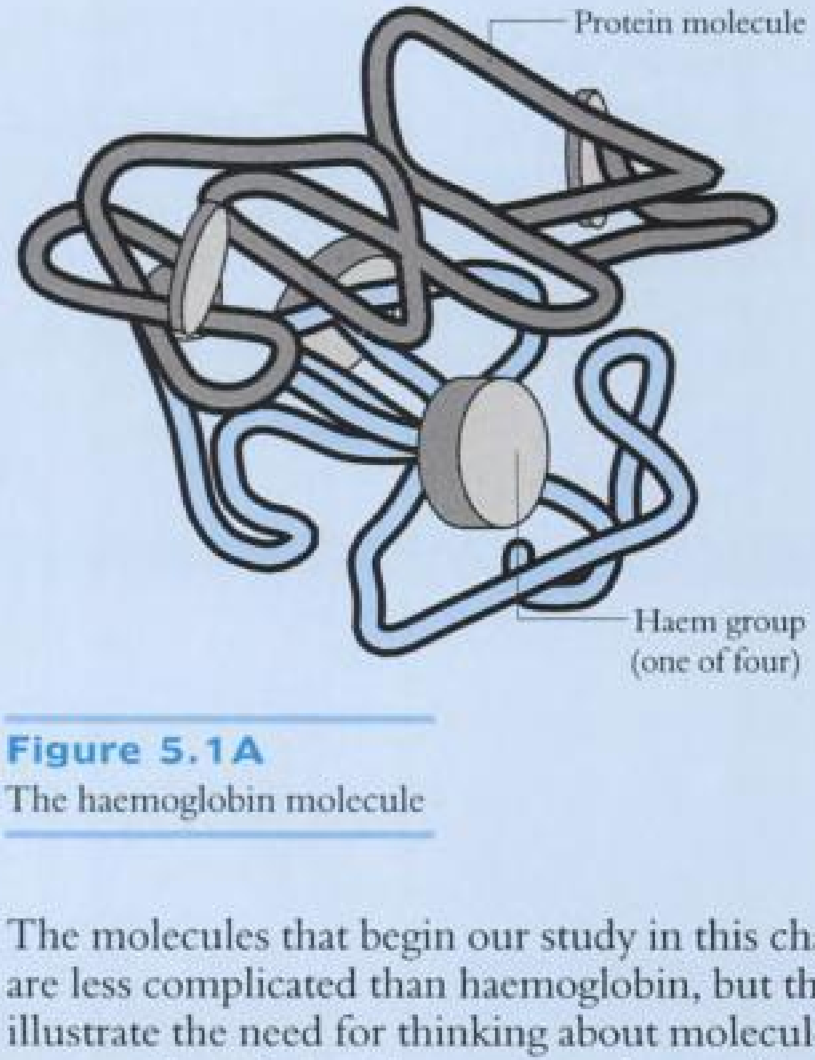


Figure 5.1A
The haemoglobin molecule

The molecules that begin our study in this chapter are less complicated than haemoglobin, but they illustrate the need for thinking about molecules in space and not just as they appear when written in two dimensions on a sheet of paper.

5.2 THE ARRANGEMENT IN SPACE OF COVALENT BONDS

Ionic bonds are not directed in space whereas ...

Electrovalent bonds are the electrostatic attractions that exist between oppositely charged ions. Since ions radiate a spherically symmetrical positive or negative field, ionic bonds are *non-directional*.

... covalent bonds have a preferred direction in space

When atoms approach one another closely, their atomic orbitals overlap and molecular orbitals are formed. Covalent bonds are formed when a bonding pair of electrons enters a molecular orbital of low energy. The bonding electrons must have opposing spins, in accordance with the Pauli Exclusion Principle [§ 2.4.1].

The more the atomic orbitals overlap, the more stable will be the molecular orbital formed. The strongest bonds will be formed if the atoms approach in such a way that there is maximum overlap between atomic orbitals. It follows that a covalent bond will have a *preferred direction*. A covalent molecule will have a shape which is determined by the angles between the bonds joining the atoms together.

$BeCl_2$ and $SnCl_2$ differ in shape ...

... BCl_3 and NH_3 differ in shape

There must be a reason why beryllium chloride, $BeCl_2$, is a linear molecule without a dipole moment, while tin(II) chloride, $SnCl_2$, is a bent molecule with a dipole moment. There must also be a reason why the four atoms in boron(III) chloride, BCl_3, are coplanar, whereas in ammonia the nitrogen atom lies above three coplanar hydrogen atoms. [See Figure 5.2A.]

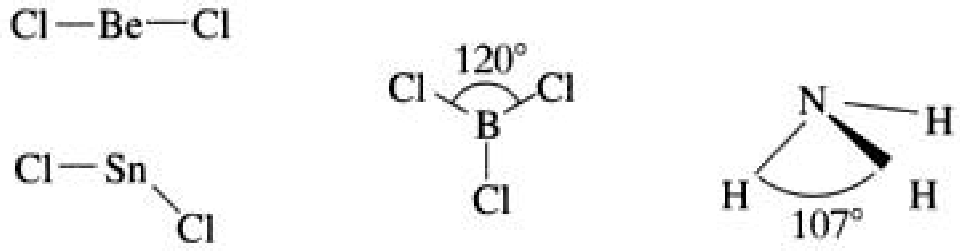


Figure 5.2A
$BeCl_2$ compared with $SnCl_2$ and BCl_3 compared with NH_3

The differences can be explained by the Sidgwick–Powell theory, which is the Valence Shell Electron Pair Repulsion Theory

A theory to account for the shapes of molecules was put forward by Sidgwick and Powell in 1940. It is known as the **Valence Shell Electron Pair Repulsion Theory**. Sidgwick and Powell considered the shapes of small molecules and molecular ions, such as $BeCl_2$, BCl_3, NH_3, NH_4^+ and CH_4. They pointed out that the arrangement of electron pairs around the central atom in a molecule depends on the number of electron pairs. Between each electron pair and any other electron pair there is a force of electrostatic repulsion, which forces the orbitals as far apart as possible. Any lone pairs of electrons on the central atom occupy atomic orbitals, and they too repel the bonding pairs of electrons and affect the geometry of the molecule.

SUMMARY

The number of electron pairs in the valence shell of an atom in a molecule decides the angle between its bonds and the shape of the molecule.

5.2.1 LINEAR MOLECULES

SUMMARY

Two bonds : bond angle 180°; linear molecule.

The molecules of gaseous beryllium chloride, $BeCl_2$, are linear. Beryllium, in Group 2 of the Periodic Table, has two electrons in its valence shell, and forms two covalent bonds. A **linear** arrangement of the atoms (a bond angle of 180 °) puts the two electron clouds as far apart as possible:

$$\mathrm{Cl{-}Be{-}Cl}$$

Other linear molecules are

Examples of linear molecules

$$\mathrm{H{-}C{\equiv}C{-}H} \qquad \mathrm{H{-}C{\equiv}N} \qquad \mathrm{O{=}C{=}O}$$

The electron pairs in a multiple bond are assumed on the Sidgwick–Powell theory to occupy the position of one electron pair in a single bond.

5.2.2 TRIGONAL PLANAR MOLECULES

The arrangement of 3 pairs of valence electrons is trigonal planar

When there are three pairs of electrons around the central atom, the bonds lie in the same plane at an angle of 120° to one another. Three atoms form a triangle about the central atom, and the arrangement is described as **trigonal planar**. An example is boron trichloride, BCl_3. Boron, in Group 3 of the Periodic Table, has

Lone pairs of electrons can determine the shape of the molecule

three valence electrons and forms three covalent bonds. Gaseous tin(II) chloride, $SnCl_2$, has a dipole moment, proving that the molecule is not linear. The reason is that tin, in Group 4, is using only two of its four electrons for bond formation. The lone pair of electrons repel the bonding pairs and a trigonal planar arrangement of orbitals results. [See Figure 5.2B.] This arrangement maximises the angle between the electron pairs and minimises the repulsion between them.

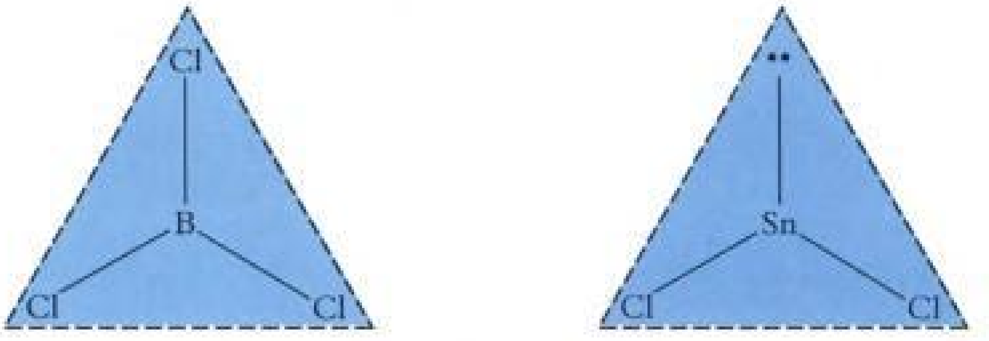


Figure 5.2B
The trigonal planar arrangement of electron pairs in BCl_3 and $SnCl_2$

Other structures based on a trigonal planar arrangement are ethene, the nitrate ion and sulphur dioxide [see Figure 5.2C].

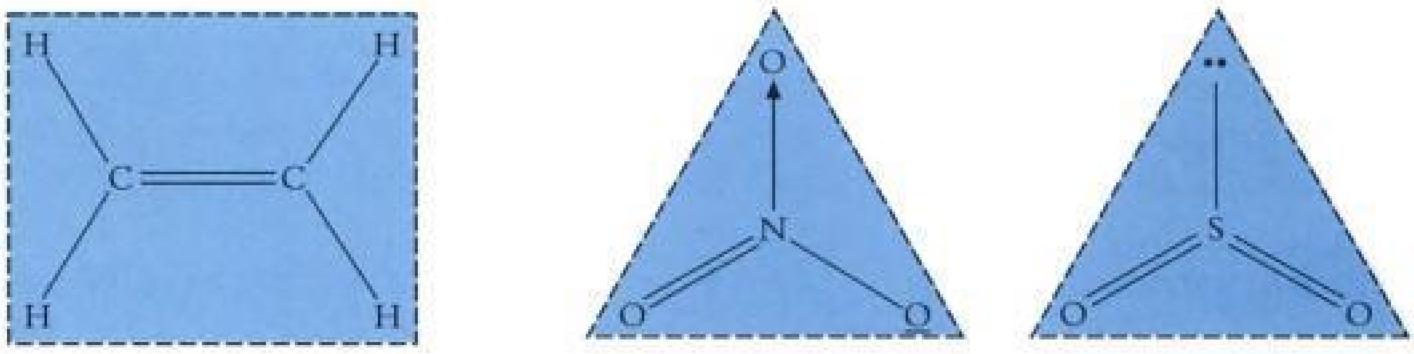
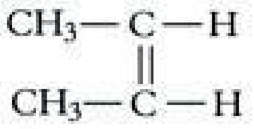


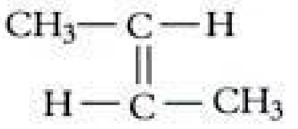
Figure 5.2C
The arrangement of electron pairs in $CH_2{=}CH_2$, NO_3^- and SO_2

SUMMARY

When an atom forms 3 bonds or 2 bonds +1 lone pair the bond angle = 120° and the arrangement of electron pairs is trigonal planar.

There is an interesting result of the coplanar arrangement. The formula of but-2-ene is $CH_3CH{=}CHCH_3$. There are two structures with this formula:

(a) 
$\begin{array}{c} CH_3-C-H \\ \| \\ CH_3-C-H \end{array}$

(b) 
$\begin{array}{c} CH_3-C-H \\ \| \\ H-C-CH_3 \end{array}$

Structure (a), in which the hydrogen atoms are on the same side of the double bond, is called *cis*-but-2-ene, and structure (b), with the hydrogen atoms on opposite sides of the double bond, is called *trans*-but-2-ene. The existence of *cis*- and *trans*- forms of compounds is covered in § 25.9.2. [See Figure 5.2D.]

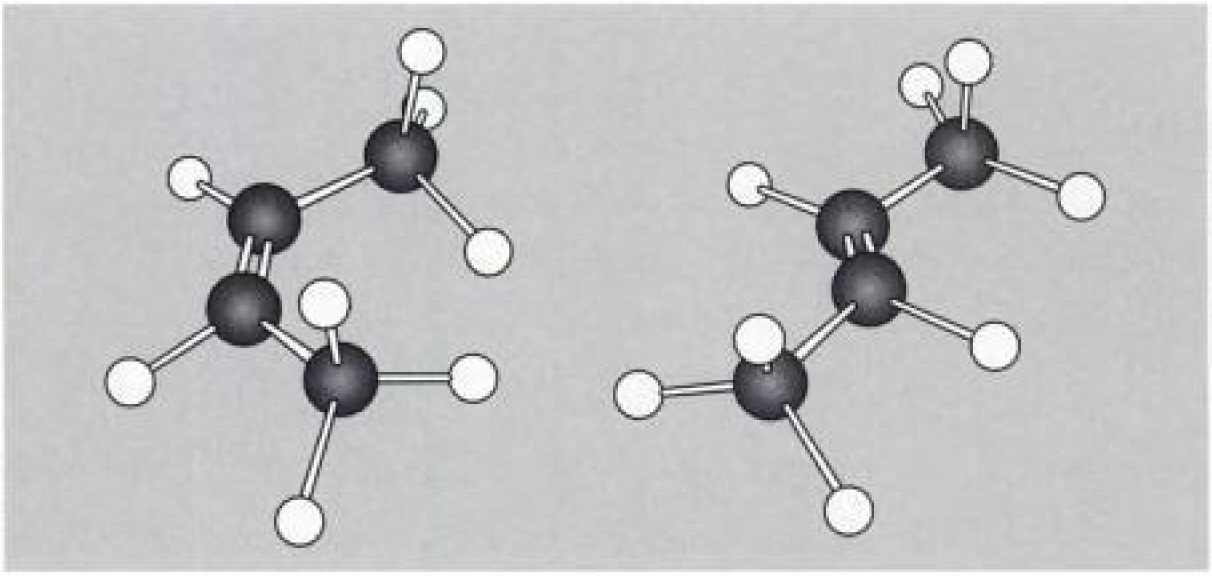


Figure 5.2D
cis- and *trans*- but-2-ene

5.2.3 TETRAHEDRAL MOLECULES

4 electron pairs adopt a tetrahedral configuration

The molecules CH_4, NH_3, NH_4^+ and H_2O all have four pairs of electrons around the central atom. Whether they are bonding pairs or lone pairs of electrons, they experience mutual repulsion. To minimise this repulsion, the four electron orbitals take up the spatial arrangement that maximises the angle between the orbitals. This is the **tetrahedral** arrangement. [See Figures 5.2E to 5.2G.]

Figure 5.2E The bonding in CH_4, NH_3, NH_4^+, H_2O

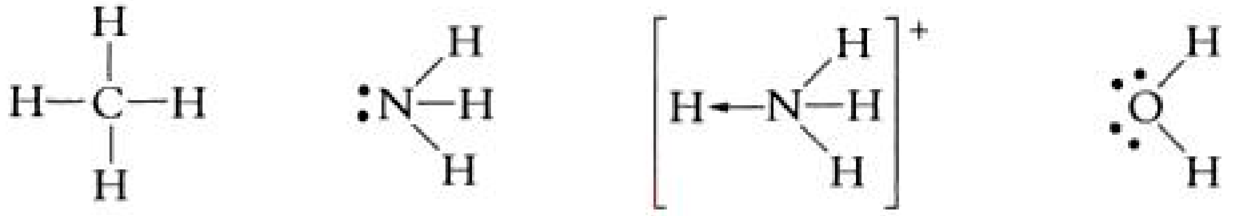
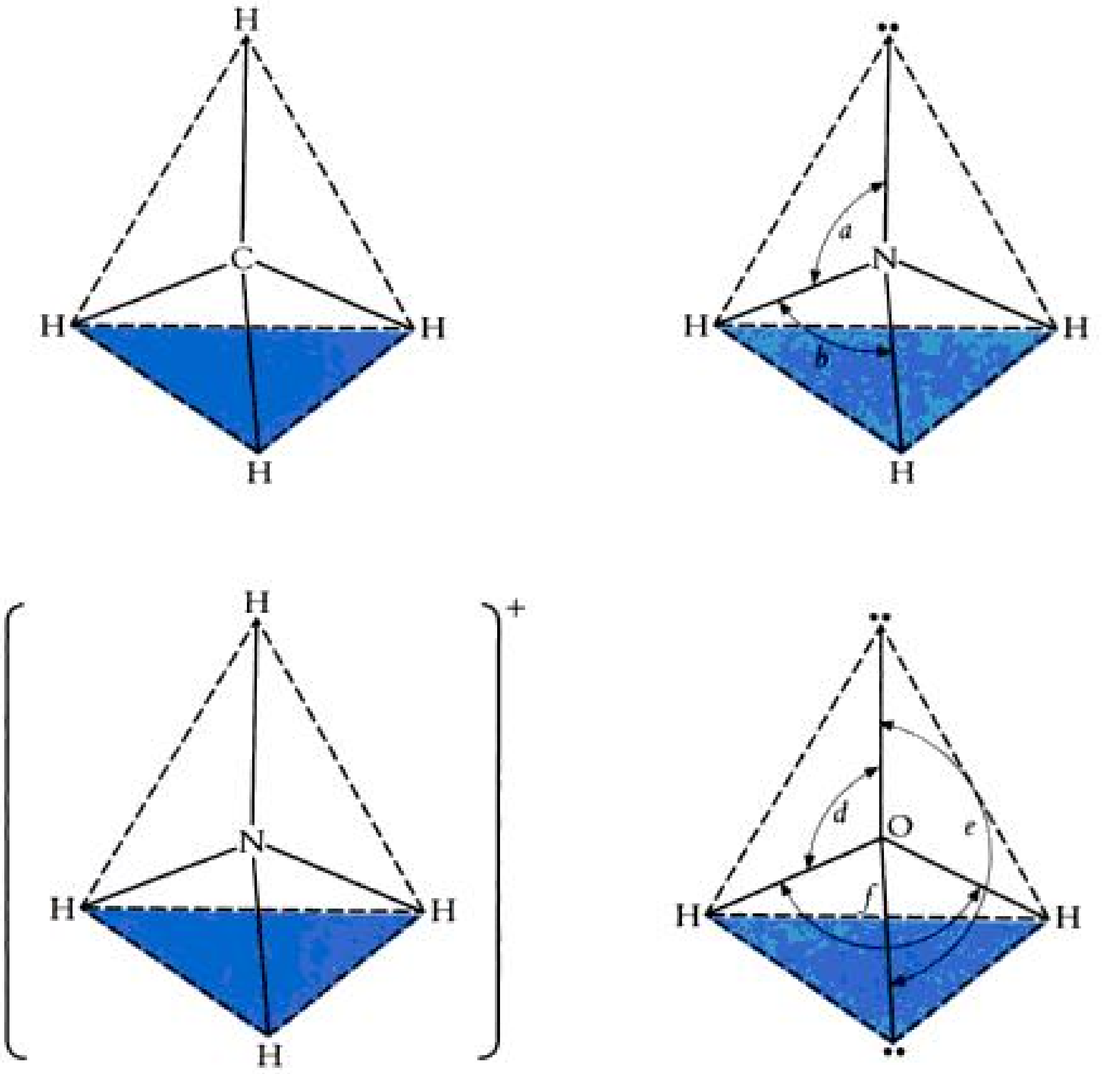


Figure 5.2F The tetrahedral arrangement of valence electron pairs in CH_4, NH_3, NH_4^+ and H_2O



The arrangements of atoms are of course *not* all the same. In CH_4 and NH_4^+, the atoms form a tetrahedron, in NH_3 they form a trigonal pyramid, and in H_2O they form a bent line.

In CH_4 and NH_4^+ all the bonds are the same. Once formed, a coordinate bond is the same as a covalent bond. The structures are perfect tetrahedra with the tetrahedral angle of 109.5° between each pair of bonds. In NH_3 the bond angle is 107°, and in H_2O it is 104.5°.

Lone pairs are closer to the nucleus than bonding pairs and exert a greater repulsive force

To account for these differences from the expected bond angle, it was suggested that, since lone pairs are closer to the nucleus than bonding pairs, they will exercise a greater force of repulsion. Repulsion between electron pairs decreases in the order

Lone pair : lone pair repulsion > Lone pair : bonding pair repulsion > Bonding pair : bonding pair repulsion

Repulsion between the lone pair and the bonding pairs in NH_3 makes the angle *a* in Figure 5.2F greater than the tetrahedral angle (109.5°) and consequently the angle *b* less than 109.5°. Similarly in H_2O, angles *d* and *e* are greater than 109.5°, and the angle *f* between the H—O—H bonds is 104.5°. Other structures based on the tetrahedron are the sulphate and sulphite ions [see Figure 5.2H].

5.2.5 STRUCTURES WITH 6 PAIRS OF VALENCE ELECTRONS

Some atoms have more than 8 electrons in the valence shell

Structures with more than four pairs of electrons about the central atom may occur if the element is in the third period or a later period. This is known as **expansion of the octet**.

SUMMARY

When an atom forms 6 bonds or 5 bonds + 1 lone pair or 4 bonds + 2 lone pairs, the arrangement of electron pairs is octahedral.

Structures with *six* pairs of electrons around the central atom are sulphur(VI) fluoride, SF_6, iodine(V) fluoride, IF_5, and the ICl_4^- ion. The **octahedral arrangement** of electron pairs is shown in Figure 5.2L.

The arrangement of *atoms* in IF_5 is **square pyramidal**, a lone pair occupying the sixth position in the octahedron. In ICl_4^- the four chlorine atoms are in a **square planar** configuration, with lone pairs occupying the axial positions of the octahedron.

5.2.6 SUMMARY

Table 5.2
A summary of the shapes of molecules

No. of valence electrons	No. of bond pairs	No. of lone pairs	Total electron pairs	Arrangement of orbitals	Arrangement of atoms	Example
4	2	0	2	Linear	Linear	$BeCl_2$
6	3	0	3	Trigonal planar	Trigonal planar	BF_3
8	4	0	4	Tetrahedral	Tetrahedral	CH_4
8	3	1	4		Trigonal pyramidal	NH_3
8	2	2	4		Bent line	H_2O
12	6	0	6	Octahedral	Octahedral	SF_6
12	5	1	6		Square pyramidal	IF_5
12	4	2	6		Square planar	ICl_4^-

CHECKPOINT 5.2: SHAPES OF MOLECULES

1. *(a)* Take three long balloons, blow them up and tie the ends. Hold the three tied ends between your finger and thumb. What positions do the three balloons adopt?
   (b) Add a fourth balloon and notice the positions which the balloons take up.

2. In BF_3, how many electron pairs are there around the B atom? Sketch the spatial distribution of bonds.

3. In BrF_3, how many electrons does Br use for bond formation? How many lone pairs does Br possess? What is the total number of electron pairs around the Br atom? Sketch the spatial distribution of bonds. How is this arrangement described?

4. Sketch the spatial distribution of bonds in HOBr. How would you describe the shape of *(a)* the electron orbitals, *(b)* the molecule?

5. Sketch the arrangement of bonds in CCl_4. If the $C^{\delta+}—Cl^{\delta-}$ bond has a dipole moment of *x* debyes, what is the dipole moment of the CCl_4 molecule?

6. In the compound XeF_4, how many electrons is the noble gas xenon using for bond formation? How many lone pairs does xenon have? What is the total number of electron pairs around the central Xe atom? Sketch the arrangement of bonds. What shape is the molecule?

7. Explain how the Sidgwick–Powell theory predicts the shape of the following molecules: *(a)* $SnCl_4$, *(b)* PH_3, *(c)* PF_5, *(d)* BH_3 and *(e)* BeH_2.

8. Sketch the spatial arrangement of bonds in the following: *(a)* F_2O, *(b)* $SeCl_4$, *(c)* SO_3, *(d)* PF_6^- and *(e)* $COCl_2$.

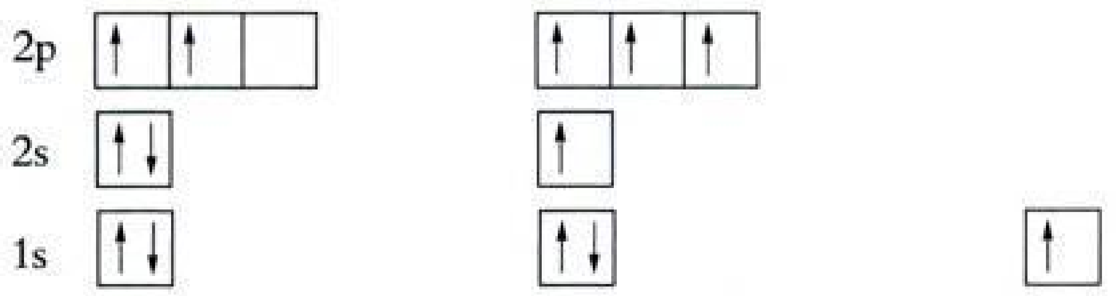
*5.3 SHAPES OF MOLECULES: A MOLECULAR ORBITAL TREATMENT

An alternative to the VSEPR treatment is the molecular orbital approach

The valence shell electron pair repulsion theory provides a simple treatment of the shapes of covalent molecules. A more precise treatment of the spatial distribution of covalent bonds about a central atom involves a consideration of the atomic orbitals used in bond formation. The shapes of atomic orbitals are described in § 2.4.2 and shown in Figures 2.4B to 2.4D. When **atomic orbitals** overlap, **molecular orbitals** are formed. The **molecular orbital approach** is illustrated in this section.

5.3.1 METHANE: sp^3 HYBRID ORBITALS

The electronic configuration of carbon in its normal, C, and excited, C*, states and hydrogen, H, are shown below:

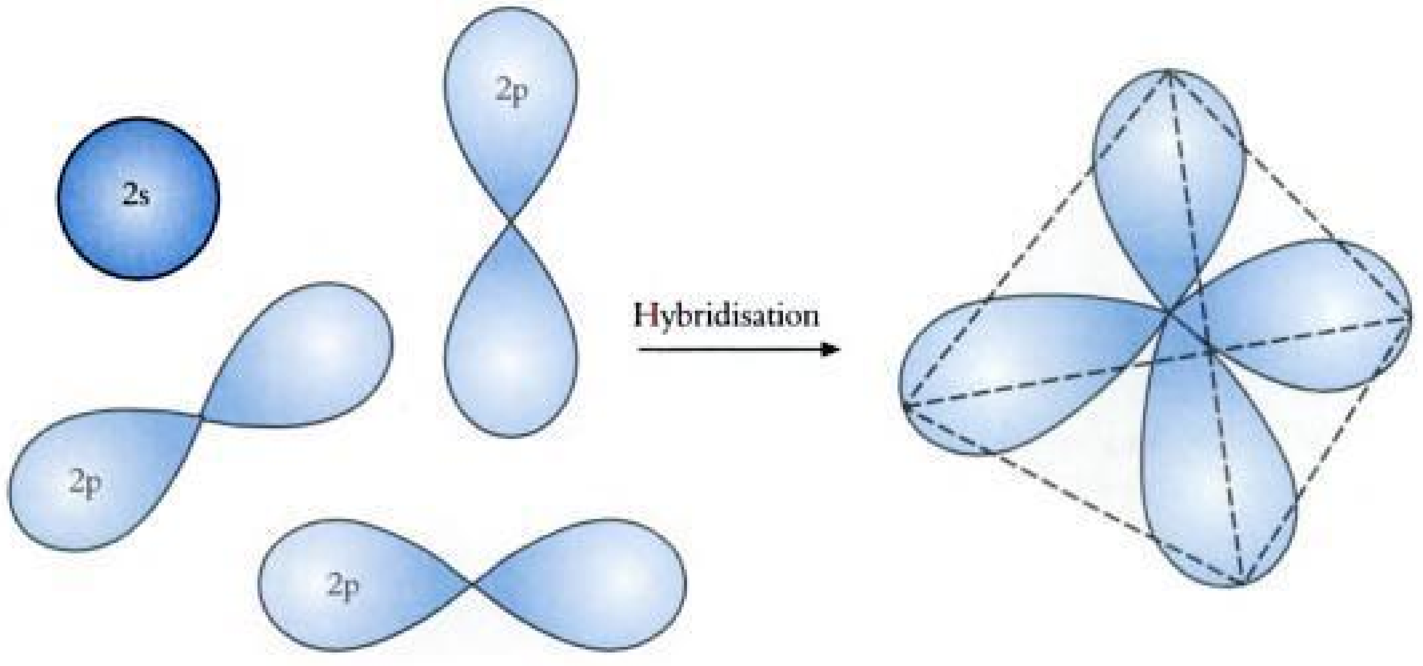


$C\ 1s^22s^22p^2$ $C^*\ 1s^22s2p^3$ $H\ 1s$

In carbon, an s electron is promoted to a p orbital

Each carbon atom, C, has two unpaired electrons, and one might expect carbon to form two bonds. It would not then attain a neon-like structure: it needs to share four electrons to do this. A sharing of four electrons can be achieved by promoting one of the 2s electrons into the 2p level. The excited carbon atom, C*, might be expected to form two different kinds of bond, using one s orbital and three p orbitals. Actually, the electron density distributes itself evenly through four bonding orbitals, which are called sp^3 hybrid orbitals (Figure 5.3A).

Figure 5.3A
The sp^3 hybrid orbitals of carbon



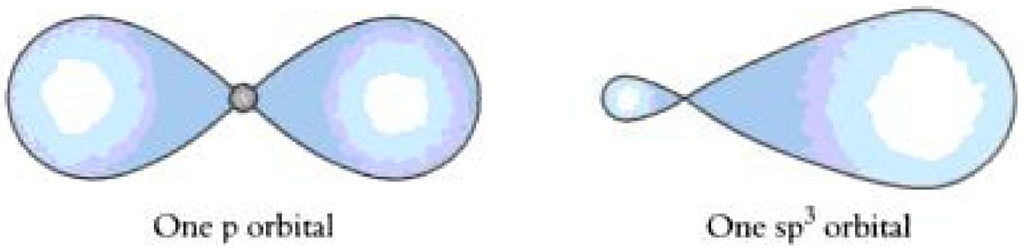
One s orbital + three p orbitals

Four sp^3 hybrid orbitals in a tetrahedral arrangement

One s orbital and three p orbitals form four sp^3 hybrid orbitals

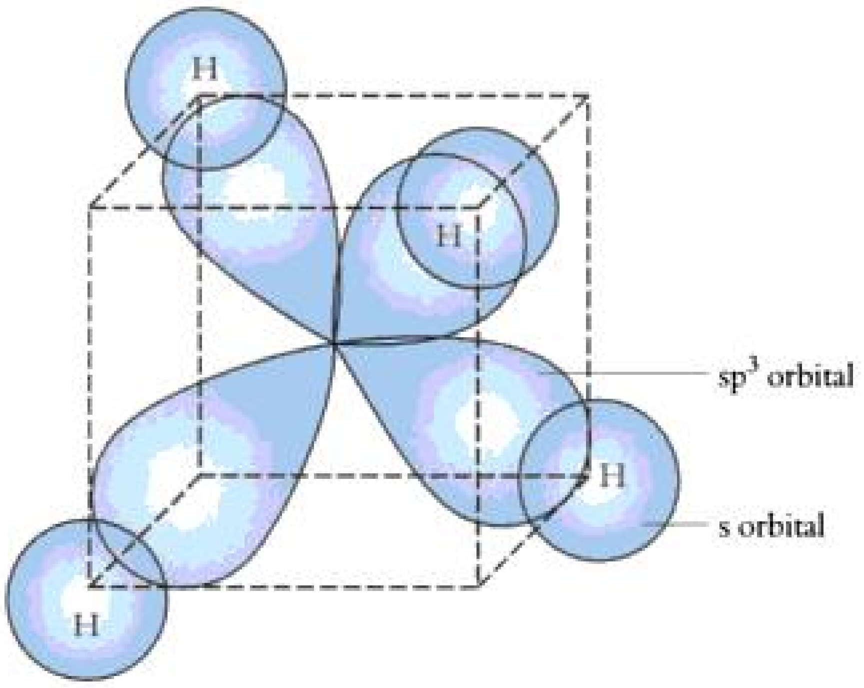
The sp^3 atomic orbital is more concentrated in direction than a p orbital [see Figure 5.3B]. An sp^3 orbital is therefore able to overlap more extensively and form stronger bonds than a p orbital.

Figure 5.3B
Comparison of atomic orbitals



The overlapping of the four sp^3 orbitals of carbon and four s orbitals of hydrogen in methane is shown in Figure 5.3C. Experimental evidence for the tetrahedral arrangement is gained from X ray diffraction studies of diamond. The angle between the bonds is shown to be 109.5° [see Figure 6.6A, § 6.6].

Figure 5.3C
Overlapping of atomic orbitals in methane



In methane, four sp^3 hybrid orbitals of C overlap with four s orbitals of four H atoms

5.3.2 DOUBLE BONDS

A double bond is less than twice as strong as a single bond …

Carbon forms double bonds in compounds such as carbon dioxide, $O{=}C{=}O$, and ethene, $H_2C{=}CH_2$. The double bond is not simply two single bonds. The amount of energy required to break a certain bond in a mole of molecules is called the **standard bond enthalpy** [§ 10.11]. Standard bond enthalpies of carbon–carbon bonds are

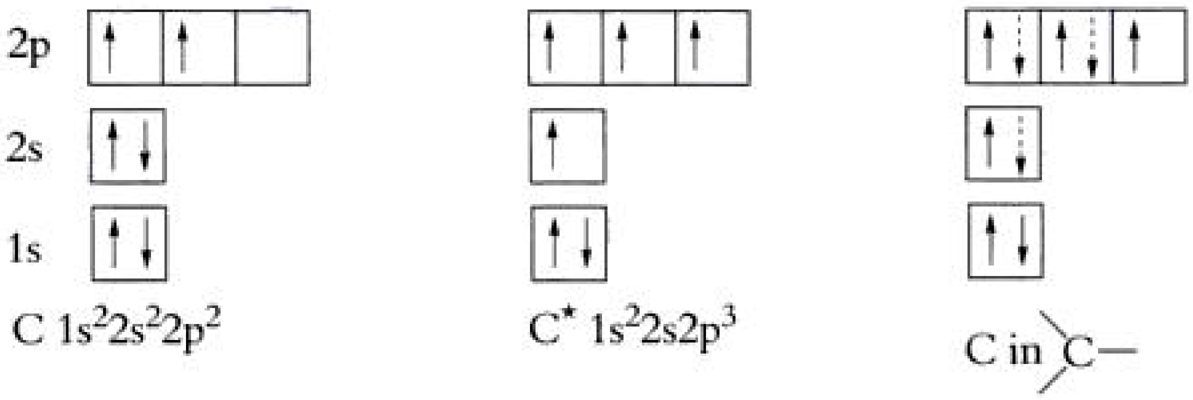
… and a triple bond has less than three times the strength of a single bond

C—C	346 kJ mol^{-1}
C=C	610 kJ mol^{-1}
C≡C	837 kJ mol^{-1}

The C=C bond is less than twice as strong as a C—C bond, and the C≡C bond is less than three times as strong as a C—C bond.

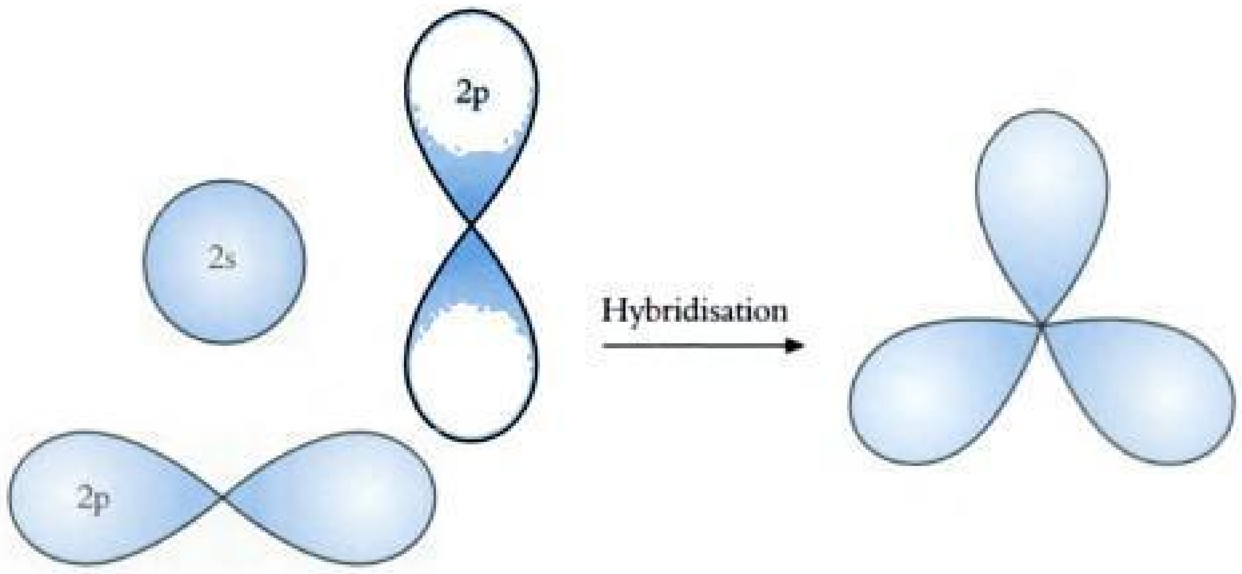
Two p orbitals and one s orbital can hybridise to form three coplanar sp^2 hybrid orbitals

In a molecule of ethene, each carbon atom uses a 2s orbital and two of the three 2p orbitals to form three sp^2 hybrid bonds [see Figure 5.3F]. The electronic configurations of carbon are shown below:



The three sp^2 hybrid orbitals are coplanar with an angle of 120° between them.

Figure 5.3D
The sp^2 hybrid orbitals of carbon



One s orbital + two p orbitals

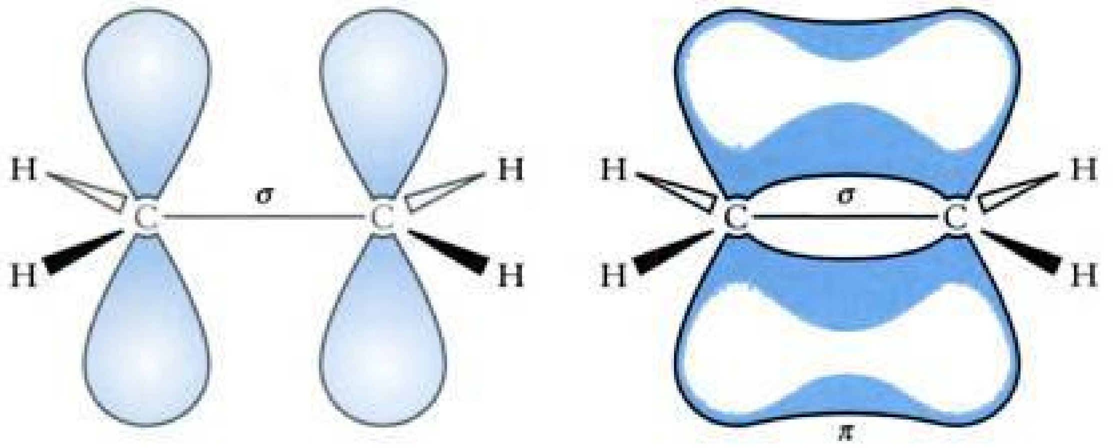
Three sp^2 orbitals forming a triangle
(a planar trigonal arrangement)

Each C has an unhybridised p orbital ...

The carbon-carbon bond formed when the sp^2 orbitals of neighbouring carbon atoms overlap is called a σ, **sigma**, bond. In σ bonds, e.g. any single bond, overlap of atomic orbitals occurs along the line joining the two bonded atoms. There is an unhybridised p orbital at right angles to the plane of the three sp^2 orbitals, and the p orbitals on adjacent carbon atoms are close enough to overlap. The overlapping occurs at the sides of the orbitals [see Figure 5.3E].

Figure 5.3E
The ethene molecule

Overlapping of atomic orbitals along the line joining the two bonded atoms is a σ (sigma) bond



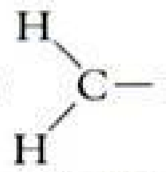
(a) The C atoms have unhybridised p orbitals.

(b) Sideways overlap between the two parallel p orbitals produces one π orbital.

... Sideways overlap between p orbitals is called a π (pi) bond ...

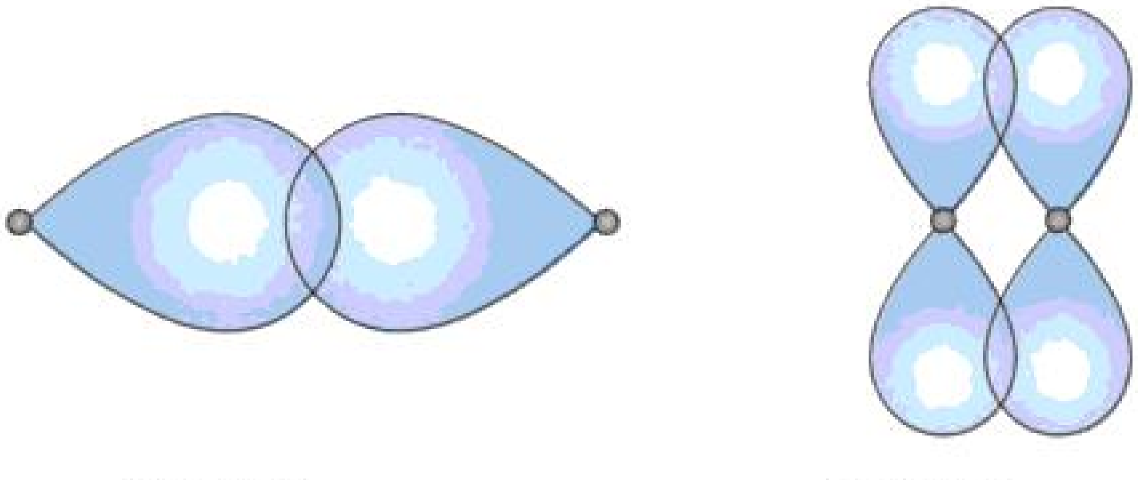
This type of bond, produced by sideways overlapping of p orbitals above and below the plane of the sp^2 bonds, is called a π, **pi**, bond. It is not as strong as a σ bond since there is less overlapping of orbitals [see Figure 5.3F]. This is why the C=C bond is less than twice as strong as a C—C bond.

... π bonds are less strong than σ bonds

Since overlapping of p orbitals on adjacent carbon atoms can occur only when the p orbitals are parallel, the two  $\mathrm{H_2C{-}}$ structures must be coplanar, i.e., lie in the same plane. If one CH_2 group twists with respect to the other, the amount of overlapping of p orbitals will decrease and the π bond will be partially broken. Since it requires energy to break a bond, the most stable arrangement of the molecules is the one in which all six atoms lie in the same plane [see Figure 27.5B(a), § 27.5.3].

For π bonds to be formed the atoms in $H_2C{=}CH_2$ must be coplanar

Figure 5.3F
The difference between σ and π bonds



(a) σ bonding.
The orbitals point towards each other.

(b) π bonding.
The orbitals are parallel and overlap sideways.

π bond formation is restricted to small atoms

The formation of strong π bonds is restricted to members of the second period: carbon, nitrogen and oxygen. In larger atoms, strong π bonds are not formed because, being removed from the line between the centres of the atoms, the π bond becomes rapidly weaker as the size of the atom increases.

CHECKPOINT 5.3: BONDING

1. Deduce the shapes of the following species:
   AsH_3, PH_4^+, H_3O^+, CS_2, $CH_2{=}C{=}CH_2$, $HC{\equiv}N$.
2. What is the arrangement of bonds around the central atom in each of the following species:
   CH_4, BF_3, NF_3, ICl_4^-, BrO_3^-, ClO_4^-, $CHCl_3$?
3. Write structures which show the arrangement of electrons in the bonding orbitals of:
   O_2, CO_2, NO_3^- and CN^-
   $\left(\text{e.g., } \mathrm{\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\!::\!\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}}\right)$
4. What can you deduce from the fact that, whereas water has a dipole moment, carbon dioxide has none?
5. Write electron structures for: PH_3, NH_3, NH_4Cl, H_2O, H_2O_2, SiH_4, HOCl
   $\left(\text{e.g., } \mathrm{H : \underset{\underset{\displaystyle H}{\cdot\cdot}}{\overset{\cdot\cdot}{P}} : H}\right)$
6. The ammonium ion and methane are said to be *isoelectronic*. What does this mean? Why do the compounds have different chemical properties?
7. *(a)* Sketch the arrangement of bonds in $CF_2{=}CF_2$.
   (b) Explain why there are two isomers with the formula $CFCl{=}CFCl$.

5.4 DELOCALISED ORBITALS

Localised electrons are to be found between the nuclei of two bonded atoms ...

In the compounds discussed so far, the electrons in the σ and π bonds have been located in the region *between* the nuclei of the bonded atoms. They are **localised** electrons. In some molecules, some of the electrons are **delocalised**: they do not remain between a pair of atoms.

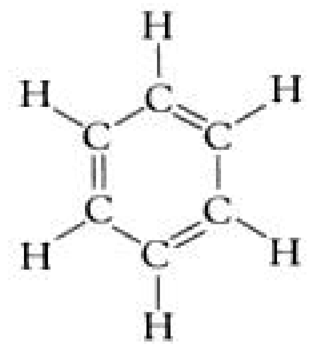
5.4.1 BENZENE

The benzene molecule has sp^2 hybrid bonds between adjacent carbon atoms ...

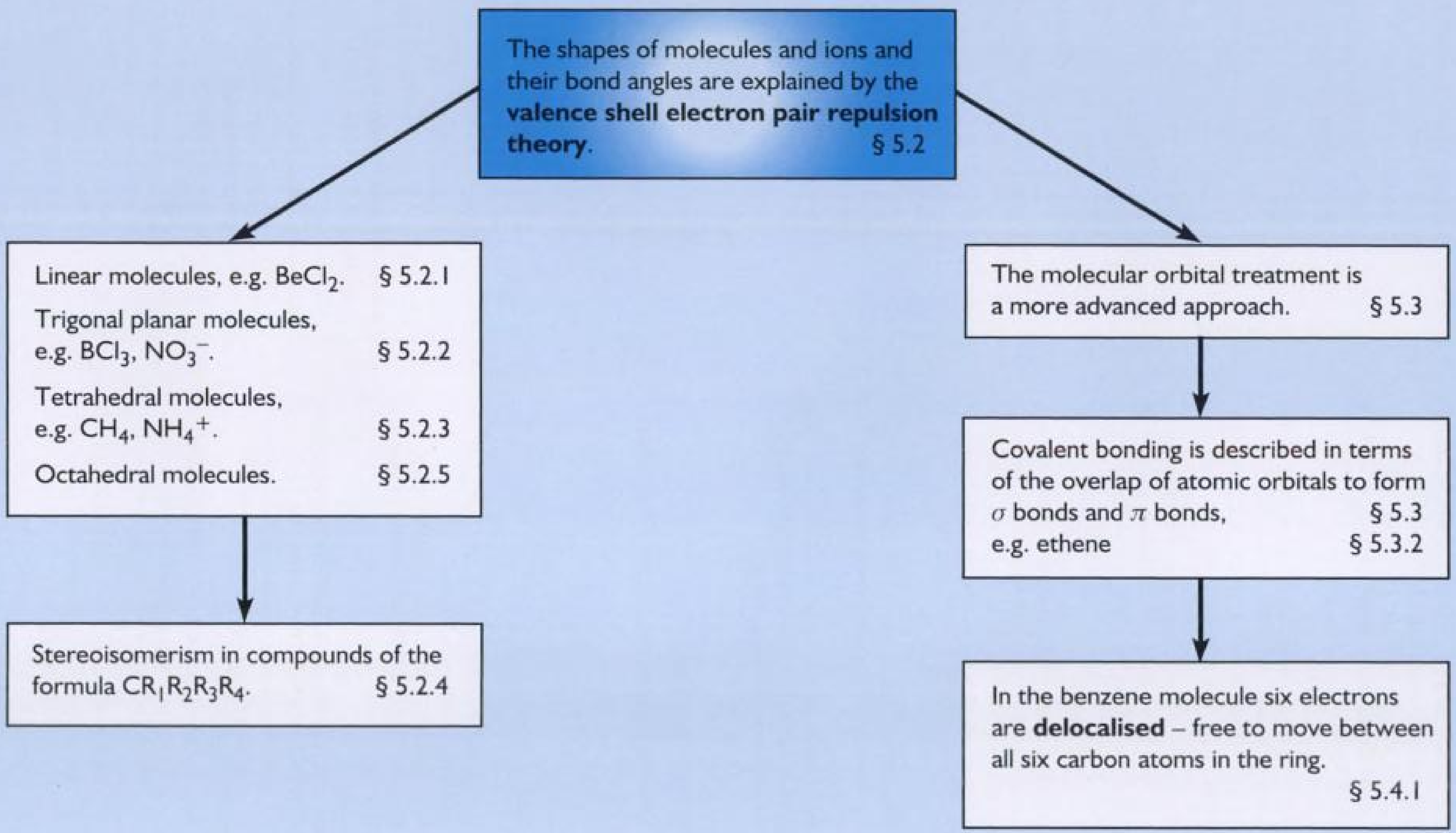
... σ bonds ...

... and each carbon atom has an unhybridised p orbital perpendicular to the plane of the ring

Benzene, C_6H_6, is an aromatic hydrocarbon [§ 25.6]. Kekulé [§ 28.2] proposed the structural formula for benzene which is shown here.



THE SHAPES OF MOLECULES



The shapes of molecules and ions and their bond angles are explained by the **valence shell electron pair repulsion theory**. § 5.2

Linear molecules, e.g. $BeCl_2$. § 5.2.1

Trigonal planar molecules, e.g. BCl_3, NO_3^-. § 5.2.2

Tetrahedral molecules, e.g. CH_4, NH_4^+. § 5.2.3

Octahedral molecules. § 5.2.5

Stereoisomerism in compounds of the formula $CR_1R_2R_3R_4$. § 5.2.4

The molecular orbital treatment is a more advanced approach. § 5.3

Covalent bonding is described in terms of the overlap of atomic orbitals to form σ bonds and π bonds, § 5.3
e.g. ethene § 5.3.2

In the benzene molecule six electrons are **delocalised** – free to move between all six carbon atoms in the ring. § 5.4.1

QUESTIONS ON CHAPTER 5

1. State the valence shell electron pair repulsion theory. Sketch the arrangement of atoms in *(a)* $BeCl_2$, *(b)* BCl_3 *(c)* CCl_4, *(d)* NH_3, *(e)* H_2O and *(f)* IF_5. Explain how the arrangement of bonds is predicted on the VSEPR theory.

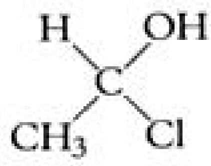
2. Give the formula of a molecule whose atoms occupy each of the following shapes: *(a)* linear, *(b)* planar trigonal, *(c)* tetrahedral and *(d)* octahedral. State the angle between the bonds in each structure.

   Some molecules which are based on a tetrahedral structure have bond angles different from the regular tetrahedral angle. Give an example, and explain the difference.

3. 'The shapes of simple molecules can be deduced from a consideration of the bonding electrons employed'. Discuss this statement. Apply the principle to the shapes of *(a)* NH_3, *(b)* H_2O, *(c)* $H_2C{=}CH_2$, *(d)* I_3^- and *(e)* SF_6.

4. *(a)* What are the main features of the electron pair repulsion model for accounting for the shapes of molecules?
   (b) By considering the numbers of lone and bonding pairs of electrons, predict the general shapes of the following molecules or ions: F_2O, H_3O^+, ClF_4^-.

5. Explain the following statements:
   (a) Two different compounds have the molecular formula

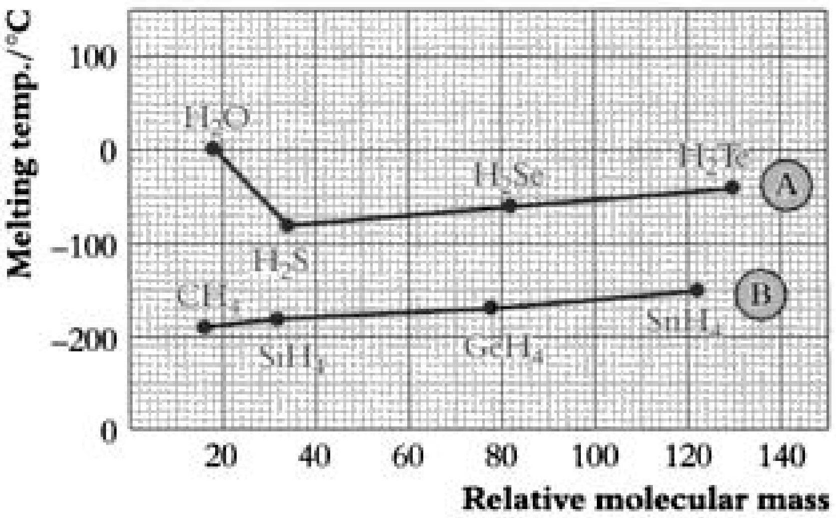


   (b) The spatial arrangement of atoms in BF_3 is different from that in NH_3.
   (c) XeF_4 is planar, whereas CCl_4 is tetrahedral.
   (d) The bond angle in NH_3 is greater than that in H_2O.

6. *(a)* (i) State the shapes of the following molecules. Using the VSEPR (Valence-Shell Electron Pair Repulsion) principle explain how the shapes of these simple molecules arise, (diagrams are not required): BF_3, CH_4, SF_6. **3**
   (ii) The bond angle $\widehat{HNH}$ in NH_4^+ is 109°.
   The bond angle in $\widehat{HNH}$ in NH_3 is 107°.
   The bond angle $\widehat{HOH}$ in H_2O is 104.5°.

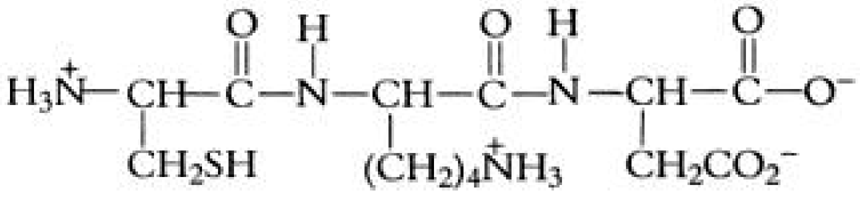
   Explain these differences in bond angles in terms of repulsion between the different types of electron pairs. **3**
   (iii) Use the VSEPR principle to predict the shapes of the following molecules: $BeCl_2$, BrF_5. **2**

   (b) The figure shows a graph of melting temperature against relative molecular mass for the hydrides shown in line **A** and line **B**.



   (i) Explain the trend in the melting temperatures of the hydrides represented by line **B**. **1**
   (ii) Explain why the first hydride in the group represented by line **A** has a higher melting temperature than the others. **1**

   (c) Bonding between peptide chains is very important biologically. The structure of a peptide chain is shown below.



$$H_3\overset{+}{N}-\underset{CH_2SH}{CH}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\underset{(CH_2)_4\overset{+}{N}H_3}{CH}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\underset{CH_2CO_2^-}{CH}-\overset{O}{\overset{\|}{C}}-O^-$$

   Give **two** features of this peptide chain which can result in bonding **between** chains. **1**

11 *WJEC (AS/AL)*

7. *(a)* In a copy of the table, give the formulae of the chlorides of the elements of Period 3, other than silicon. **2**

Element	Na	Mg	Al	Si	P	S
Formula of chloride				$SiCl_4$		

   (b) Calculate the percentage by mass of silicon in silicon tetrachloride. **2**
   (c) (i) Draw a dot and cross diagram to show the bonding in silicon tetrachloride.
   (ii) Draw the shape of this molecule. Explain your answer in terms of the Electron Pair Repulsion Theory.
   (iii) State the shape of a molecule of $AlCl_3$ and explain why it is different from that of $SiCl_4$. **6**
   (d) (i) Give an equation for the reaction of $SiCl_4$ with cold water.

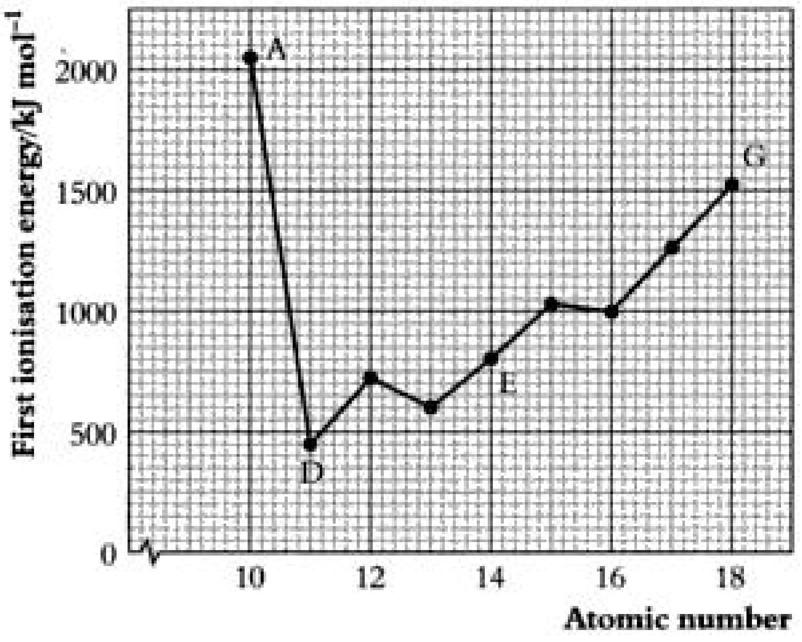
(ii) How does the behaviour of carbon tetrachloride with cold water compare with this? Explain any differences. **4**

14 *L (AS/AL)*

8. *(a)* Copy and complete the table by writing the numbers of protons, neutrons and electrons for each of the species shown. **2**

Species	**Number of protons**	**Number of neutrons**	**Number of electrons**
$^{20}_{10}\mathrm{Ne}$			
$^{23}_{11}\mathrm{Na}^{+}$			
$^{32}_{16}\mathrm{S}^{2-}$			
an α particle			

(b) The figure shows a plot of first ionisation energy against atomic number for the elements of atomic number 10 to 18. (The letters are not the chemical symbols for the elements concerned.)

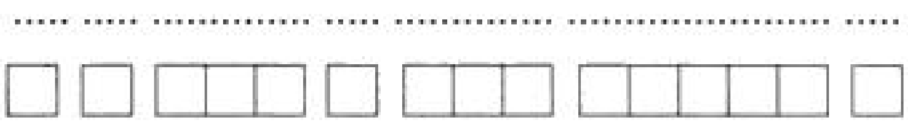


(i) I. Explain **briefly** why the ionisation energy of the element labelled **G** is less than that of the element labelled **A**.
II. Explain **briefly** why the ionisation energy of the element labelled **D** is considerably less than that of the element labelled **A**. **1**

(ii) Draw the shape of the orbital from which the electron is lost when,
I. element **A** is ionised,
II. element **D** is ionised. **1**

(iii) Give the electronic configuration of the element labelled **E** on the figure by copying and labelling **each** of the following boxes and inserting arrows, in appropriate boxes, to represent electrons.

Orbital



1½

(iv) **State** and **explain** which of the elements **D** or **E** will form a cation more readily. **1**

(c) State whether each of the following statements, concerning the covalent bond is true or false. (More than one statement may be correct.)

(i) The covalent bond has a pair of electrons with opposed spins.

(ii) Atoms which bond together covalently **usually** achieve an inert gas structure. **1**

(d) (i) Arrange in order of **increasing** repulsion (smallest first) the repulsion between: two bonding pairs of electrons, two lone pairs of electrons, and a lone pair and a bonding pair of electrons, arranged around a central atom. **½**

(ii) Explain how this sequence arises. **1**

(e) (i) State what is meant by,
I. a *dipole*, and II. a *polar* bond. **1**

(ii) I. The C — H bonds within the methane molecule are strong.
Liquid methane boils at a very low temperature.

Explain why there is no conflict between these two statements.

II. **Explain** why ammonia (NH_3) boils at −33 °C, whereas the heavier phosphine molecule (PH_3) boils at −86 °C. **2**

12 *WJEC (AS/AL)*

9. *(a)* What is a polar covalent bond? **1**

(b) In what circumstances will a covalent bond be polar? **1**

(c) In what circumstances will an anion be polarised? **1**

(d) How does a polarised anion differ from an unpolarised anion? **1**

(e) (i) Draw diagrams to show the shapes of the following molecules and in each case show the value of the bond angle on the diagram:

$BeCl_2$, NCl_3, SF_6.

(ii) State which of the above molecules is most likely to form a co-ordinate bond with a hydrogen ion. Give a reason for your answer. **8**

12 *NEAB (AS/AL)*

6

CHEMICAL BONDING AND THE STRUCTURE OF SOLIDS

6.1 PROFILE: DOROTHY CROWFOOT HODGKIN (1910–1995)

X ray crystallography has unravelled the molecular structures of three life-saving compounds: penicillin, vitamin B_{12} and insulin. This feat was accomplished by Dorothy Crowfoot Hodgkin. Dorothy Crowfoot was the daughter of archaeologists who worked in Egypt and the Sudan. Dorothy studied at the Universities of Oxford and Cambridge before becoming a fellow of Somerville College, Oxford. She decided to continue the work in X ray crystallography which she had started in Cambridge. Early in her scientific career, she married Thomas Hodgkin who gave his wife unfailing support and encouragement in all the challenges she undertook.

One of her first problems was penicillin. Although penicillin had been discovered by Sir Alexander Fleming in 1929, it was not isolated as a pure compound until 1941. At that time, Howard Florey and Ernst Chain were working to develop a method of culturing penicillin so that it could be used as a bactericide to treat casualties in the Second World War. They gave Dorothy Hodgkin 10 mg of the substance. By 1945 she had worked out its exact structure, allocating a position in space to each of the 41 atoms. The technique she used was X ray diffraction.

The next problem was even more taxing. In 1948 Glaxo laboratories gave Dorothy Hodgkin some beautiful red crystals of a substance which was effective against pernicious anaemia. The discoverers of this compound called it vitamin B_{12}. At first sight, Dorothy estimated that, with over 90 atoms, the structure of vitamin B_{12} would take many years to work out. However, she was able to use an advanced computer in the USA to perform the calculations, and the structure was completed in 1956. As a result of this work, vitamin B_{12} was synthesised.

The structure of insulin, with over 800 atoms, was a formidable task. With the new computing power at her disposal, Dorothy Hodgkin completed the work in 1969. In 1964 she received the Nobel Prize for Chemistry. Two other women have won this prize: Marie Curie in 1911 and her daughter Irene Joliot-Curie in 1935.

6.2 X RAY DIFFRACTION

A crystal is a regular three-dimensional arrangement of particles

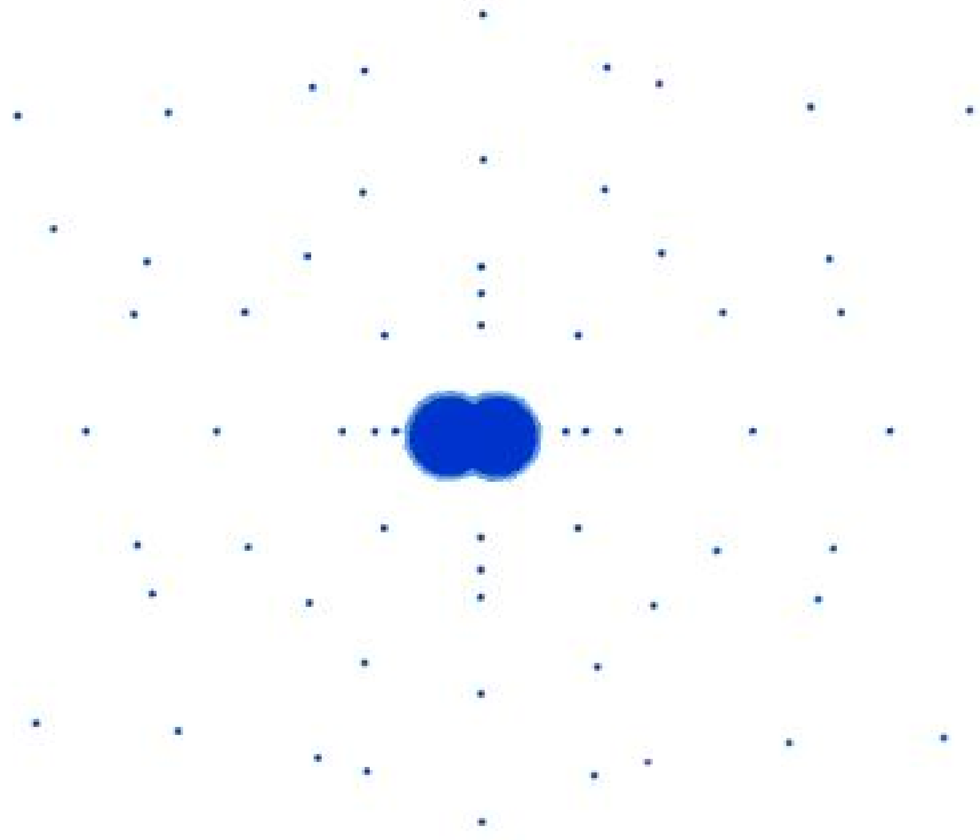
A solid in which the arrangement of atoms or ions or molecules follows a regular three-dimensional design has a crystalline form. The surfaces of the crystal are planes, called **faces**. They intersect at angles that are characteristic for the substance. The ordered arrangement of particles in the crystal is called the **crystal structure**.

A crystal acts as a three-dimensional diffraction grating for X rays

When a beam of X rays meets a crystal, X rays interact with electrons, and the beam is scattered. The scattered X rays must be made to produce a visible pattern, e.g., on a photographic film. From the pattern of scattering [see Figure 6.2A] crystallographers can work out the structure of the crystal.

Figure 6.2A shows a developed X ray film. The central spot has been produced by undeflected X rays, and the circles of spots are produced by X rays which have been diffracted through various angles by the planes of atoms or ions in the crystal.

Figure 6.2A
An X ray diffraction pattern



Hydrogen atoms do not show on X ray patterns

Since it is the *electrons* of atoms that scatter X rays, the small atoms in a compound, which have few electrons, especially hydrogen atoms, are difficult to detect. The structures of metals, ionic compounds and macromolecular substances (such as diamond and graphite) have been worked out from X ray diffraction measurements.

6.3 THE METALLIC BOND

The nature of the metallic bond must be responsible for the properties of metals

Modern technology is based on the use of metals. Most of our machines and most of our forms of transport are made of metal. There must be some feature of the bond between metal atoms that gives metals their special properties. Many metals are strong and can be deformed without breaking; many are **malleable** (can be hammered) and **ductile** (can be drawn out under tension). They are shiny when freshly cut and good conductors of heat and electricity. Any theory of the metallic bond must account for all these physical properties.

6.5 MOLECULAR SOLIDS

Van der Waals forces hold the molecules together in solid argon and in solid iodine ...

Some solids are held together by weak attractions between individual molecules. They are described as **molecular solids** and said to have a **molecular structure**. At very low temperatures, even the noble gases can be solidified. Figure 6.5A shows the structure of atoms in solid argon. The van der Waals forces between the atoms are very weak, and if the temperature rises above −170 °C the solid melts. Liquid argon consists of separate atoms. Figure 6.5B shows the structure of solid iodine.

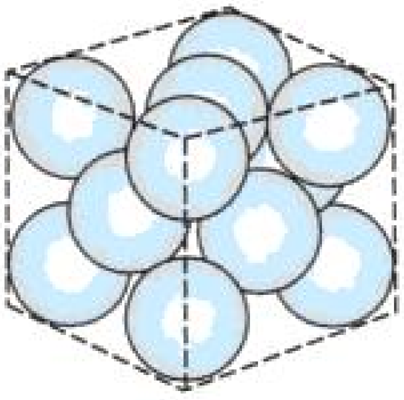


Figure 6.5A
Solid argon

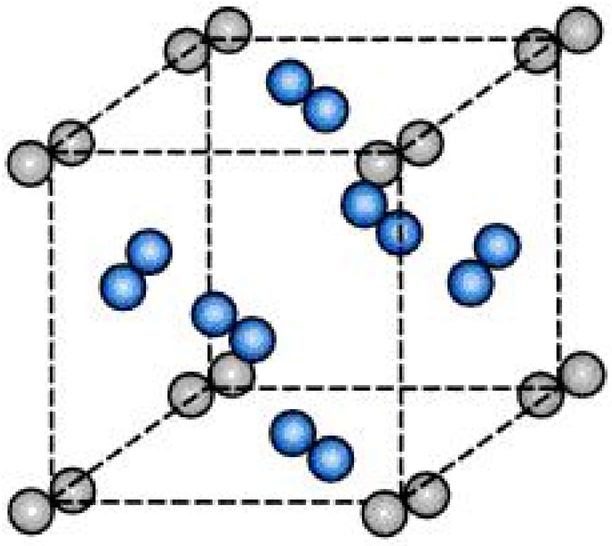


Figure 6.5B
Solid iodine

The I_2 molecules in the centre of each face are shown in blue.

solids with molecular structure are volatile ...

... e.g. iodine ...

Iodine is a molecular solid up to a temperature of 30 °C. The atoms are covalently bonded in pairs as I_2 molecules. Operating between the molecules are the much weaker van der Waals forces. As a result of the regular arrangement of molecules, iodine is a crystalline solid with regular faces, which give a shiny appearance. When solid iodine is heated, the van der Waals forces are broken and individual molecules are set free. The vapour phase, which is purple, consists of individual I_2 molecules. Bromine and chlorine adopt similar structures at lower temperatures.

... e.g. solid CO_2

Carbon dioxide is well known in its solid form as 'dry ice' or 'drikold'. Above −78 °C is sublimes, absorbing heat from its surroundings to do so. From this property arises the widespread use of solid carbon dioxide as a refrigerant, both in laboratory work and in the food industry. Pop singers sometimes like to enhance their performance by having lumps of dry ice on stage. As it sublimes, it cools the moist air, and swirling clouds of water droplets form. Solid carbon dioxide has a structure resembling that of iodine, which is shown in Figure 6.5B.

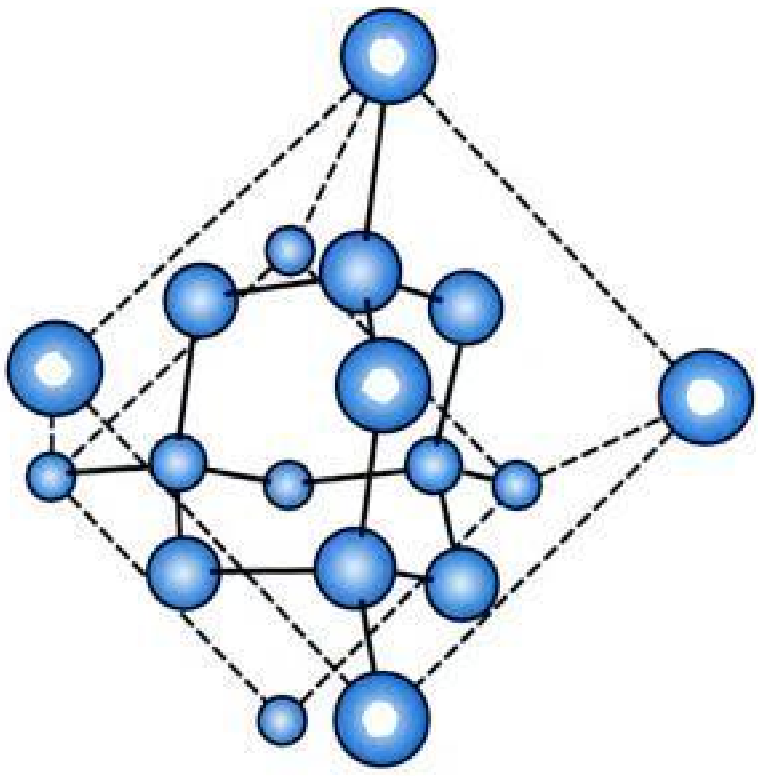
6.6 MACROMOLECULAR STRUCTURES

A macromolecular structure is held together by covalent bonds, e.g. diamond ...

A number of solids have the kind of structure described as **macromolecular** or **giant molecular**. Covalent bonds between atoms bind all the atoms into a giant molecule. Diamond, an **allotrope** [§ 21.4] of carbon, is one of the hardest substances known and has a macromolecular structure [see Figure 6.6A]. Each carbon atom forms four bonds (sp^3 hybrid bonds) to four other carbon atoms. The giant molecular structure which results is very strong. It is different from a molecular structure, in which, although the bonds between the atoms in a molecule are strong covalent bonds, the intermolecular forces of attraction are weak. Diamond remains a solid up to a temperature of 3500 °C, at which it sublimes.

Figure 6.6A
The structure of diamond

Such substances are hard and involatile, e.g. diamond and silica



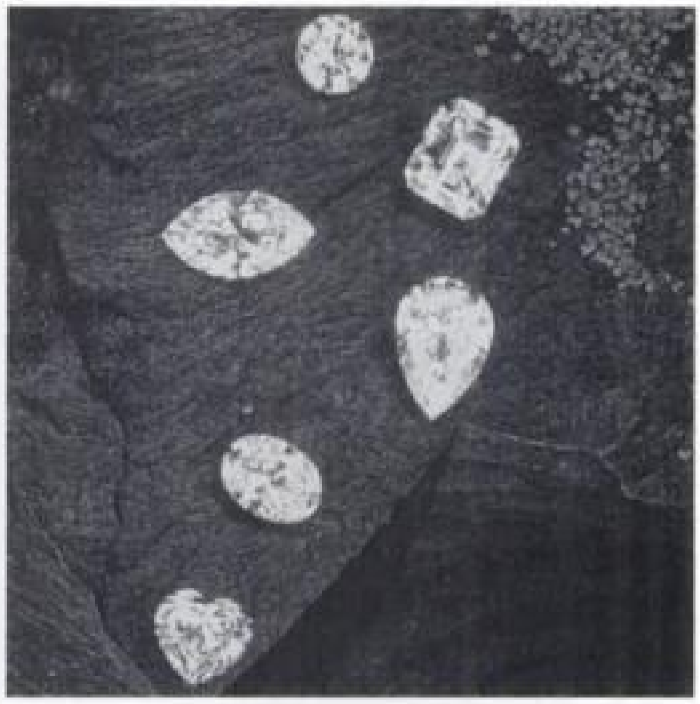
Each C atom is surrounded by 4 others: the coordination number is 4.

... in which the strong covalent bonds result in a hard, abrasive character

The hard, abrasive character of diamond finds it many uses. Diamond-tipped tools are used for cutting and engraving, and diamond-tipped tools are used by oil prospectors for boring through rock [see Figure 6.6B]. The high **refractive index*** of diamond gives it the sparkle that makes it the most prized of jewels [see Figure 6.6C].

Figure 6.6B
Diamond-studded drill bits

Figure 6.6C
A selection of diamonds



Other macromolecular structures are SiC, BN and SiO_2

Other solids with a diamond-like structure are silicon carbide $(SiC)_n$, and boron nitride $(BN)_n$. The formula unit, BN, is isoelectronic with the unit CC. Silicon(IV) oxide, SiO_2 (**silica**), also forms a three-dimensional structure. The Si—O bonds about each silicon atom are tetrahedrally distributed and each oxygen atom is bonded to two other silicon atoms [see Figure 6.6D]. The structure occurs in **quartz** and other crystalline forms of silica. Quartz remains solid up to a temperature of 1700 °C.

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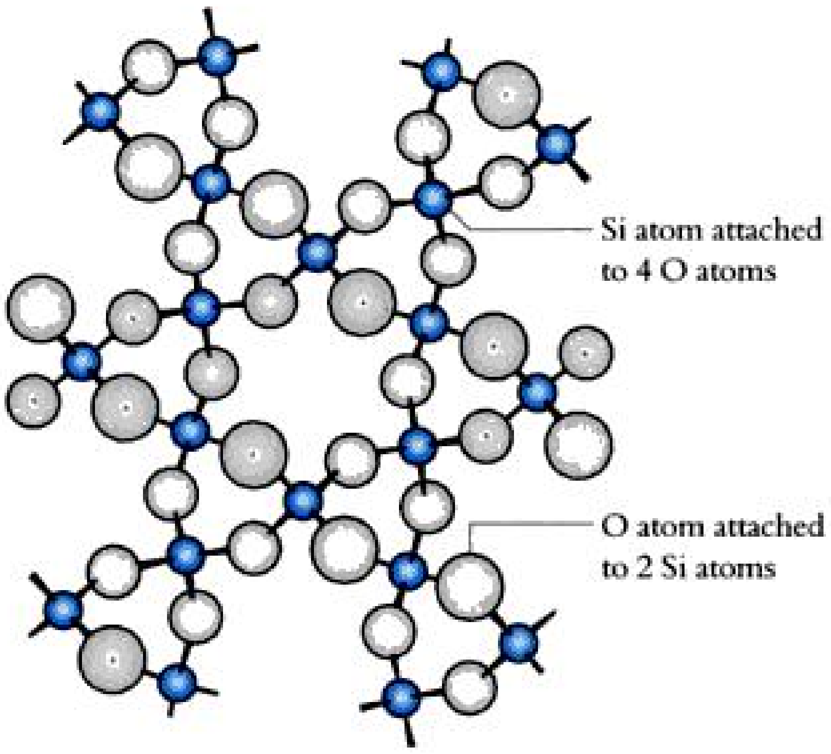
* See R Muncaster, *A-Level Physics* (Stanley Thornes).

Figure 6.6D
Silicon(IV) oxide structure

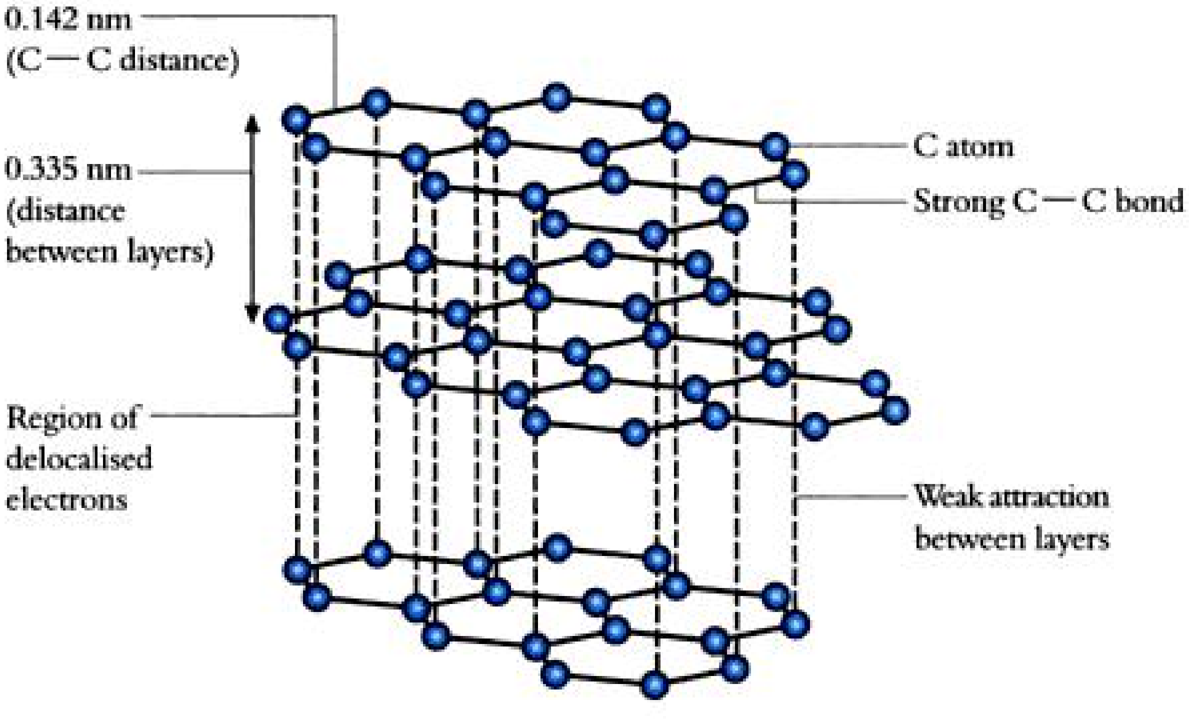


6.7 LAYER STRUCTURES

Layer structures have covalent bonds within each layer and weak van der Waals forces between layers e.g. graphite

Graphite, the other allotrope of carbon, has a **layered** structure. Within each layer, every carbon atom uses three coplanar sp^2 hybrid orbitals to bond to three other carbon atoms. A network of coplanar hexagons is formed, with a C—C bond distance of 0.142 nm. Between layers, the distance is 0.335 nm. The weak van der Waals forces of attraction between the layers allow one layer of bonded atoms to slide over another layer. The structure, which is shown in Figure 6.7A, accounts for the properties of graphite. It is a lubricant, whereas diamond is abrasive. The unhybridised p electrons form a delocalised cloud of electrons similar to the metallic bond. They enable graphite to conduct electricity and are responsible for its shiny appearance.

Figure 6.7A
The structure of graphite



CHECKPOINT 6.7: COVALENT STRUCTURES

1. *(a)* Why is it easy to rub away carbon atoms from graphite?
   (b) Why is graphite used as a lubricant?
   (c) Why is it impossible to rub away carbon atoms from a diamond?
   (d) What characteristics of (i) diamond and (ii) graphite are useful in industry?

2. Solid iodine consists of shiny black crystals. Iodine vapour is purple. What is the difference in chemical bonding between solid and gaseous iodine?

3. 'Dry ice' is a name given to solid carbon dioxide.
   (a) In what way does solid carbon dioxide resemble ice?
   (b) In what way is solid carbon dioxide (i) better than ice as a refrigerant and (ii) more convenient than ice?
   (c) Pop singers sometimes use dry ice to produce swirling clouds on stage. These clouds are clouds of condensed water vapour. Explain (i) where the water vapour comes from and (ii) why it is cool enough on stage to condense water vapour.

4. From Figures 6.6A, § 6.6, and 6.7A, § 6.7, which would you expect to have the higher density, diamond or graphite? Why is diamond used in cutting tools but not graphite?

5. What is meant by the statement that the electrons in diamond are *localised*, whereas graphite has *delocalised* electrons. Which electrons in graphite are delocalised? How do they affect the properties of graphite?

6. Sketch the structure of silicon carbide, SiC, which resembles diamond. Why do you think that carborundum (SiC) is used as an abrasive? Why does silicon carbide not exist in a graphite-type of structure?

7. Boron nitride, BN, has a structure like that of graphite. Explain the bonding in BN.

FURTHER STUDY ▼

*6.8 THE STRUCTURE OF METALS

Types of metal structures

When identical spheres pack together so as to minimise the space between them, a close-packed structure is formed ...

Metal atoms pack closely together in a regular structure. There is no way of packing spheres to fill a space completely without leaving gaps between them. Arrangements in which the gaps are kept to a minimum are called **close-packed** arrangements. X ray studies have revealed three main types of metallic structures. In the **hexagonal close-packed structure**, and the **face-centred-cubic close-packed structure**, the metal atoms pack to occupy 74% of the space. In the **body-centred-cubic structure**, the atoms occupy 68% of the total volume.

Figure 6.8A shows a face-centred-cubic close-packed structure. Since every atom is in contact with 12 others (6 in the same layer, 3 in the layer above and 3 in the layer below) it is said to have a **coordination number** of 12. The high coordination numbers in these structures arise from the non-directed nature of the metallic bond.

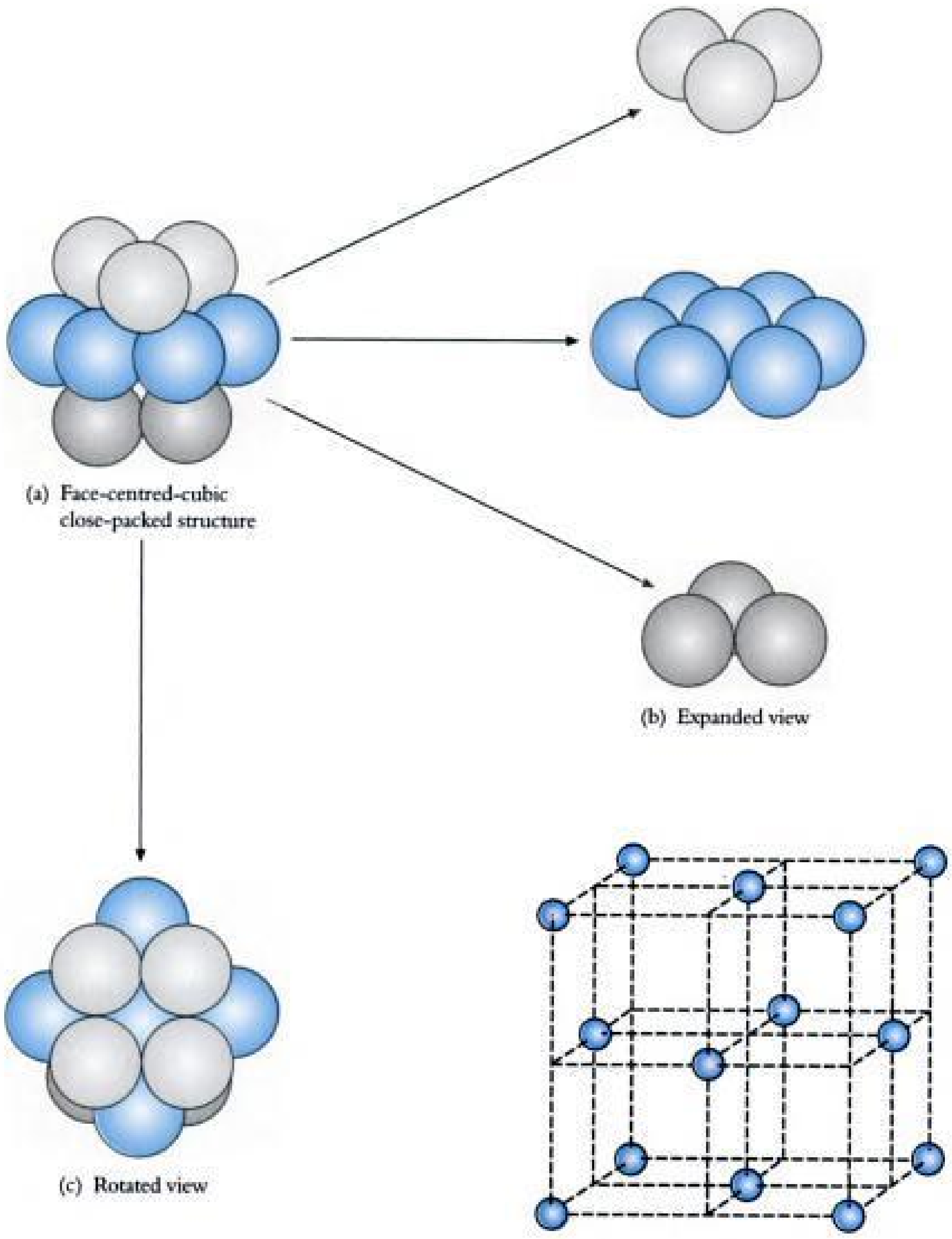
A unit cell

Also shown in Figure 6.8A is the **unit cell**. A unit cell is the smallest part of the crystal that contains all the characteristics of the structure. The whole structure can be generated by repeating the unit cell in three directions.

A body-centred-cubic structure is less close-packed

The less closely packed body-centred-cubic structure is shown in Figure 6.8B(a). With one atom at each of the eight corners of a cube and one in the centre touching these eight, the coordination number is 8. Figure 6.8B(b) shows an expanded view, and (c) shows the unit cell with tie-lines to show that the coordination number is 8.

Figure 6.8A
Face-centred-cubic close-packed structures



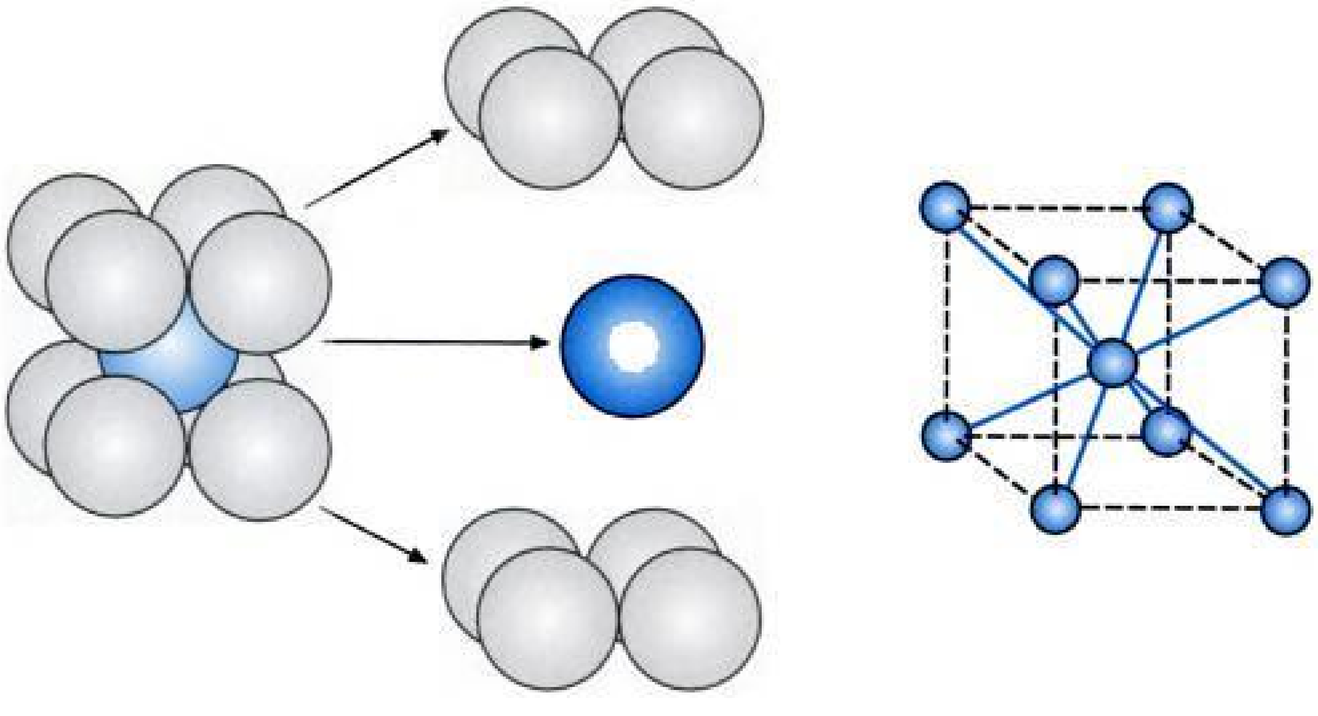
(a) Face-centred-cubic close-packed structure

(b) Expanded view

(c) Rotated view

(d) Face-centred-cubic unit cell

Figure 6.8B
Body-centred-cubic structure



(a) Body-centred-cubic structure

(b) Expanded view

(c) Unit cell with tie-lines

SUMMARY

Metals are crystalline. The atoms pack together in close-packed arrangements: the hexagonal and face-centred structures and in the body-centred cubic structure which is less close-packed. The coordination number is the number of atoms with which each atom is in contact.

6.10 LIQUID CRYSTALS

Pure solids melt sharply, the temperature remaining constant at the melting temperature until all the solid has melted. There are, however, many crystalline solids which pass at a sharp **transition temperature** to a turbid liquid phase before finally melting to form a clear liquid. The turbid liquids phases can flow as liquids do and possess some degree of order, with the result that these turbid liquids resemble crystals in certain optical properties. They are known as **liquid crystals**.

Viewed in plane-polarised light under a microscope, liquid crystals show characteristic coloured patterns. The structures and therefore the colours change with temperature so liquid crystals can be used as thermometers.

A mixture of liquid crystals which changes colour over about 3 °C in the range of body temperature is used for **skin thermography**. Skin overlying veins and arteries is slightly warmer than in other areas, and the difference in temperature can be detected by liquid crystals. Specialists can use the technique of skin thermography to detect blockages in veins and arteries. The technique has been successful in the early diagnosis of breast cancer. When a layer of cholesteric material is painted or sprayed on to the surface of the breast, a tumour shows up as a 'hot area', which is coloured blue.

Room thermometers contain liquid crystals with a suitable temperature range. Figures show up in different colours as the temperature changes.

The digital displays you see in watches and calculators contain liquid crystals. The structure of the liquid crystal can be changed by the use of a very small electric field. If the change in orientation results in a change in optical properties, the liquid crystal can be used to display information, e.g., the time, or date. The timing of a watch display is controlled by a quartz crystal. A small electric current induces quartz to resonate at 32 768 oscillations per second. A quartz watch has no mechanical moving parts, giving it a big advantage over traditional watches.

QUESTIONS ON CHAPTER 6

1. What types of intramolecular and intermolecular bonds exist in *(a)* solid argon, *(b)* solid bromine, *(c)* diamond, *(d)* graphite and *(e)* silica?

2. Crystals of salts fracture easily, but metals are deformed under stress without fracturing. Explain the difference.

***3.** What is the coordination number of an ion? What is the coordination number of the cation in *(a)* the NaCl structure and *(b)* the CsCl structure? What is the reason for the difference?

4. Say what properties you would expect of substances which are *(a)* metals, *(b)* ionic compounds, *(c)* composed of individual covalent molecules, and *(d)* macromolecular covalent compounds.

5. Explain the bonding present in the solids sodium chloride, sodium, phosphorus(V) chloride (PCl_5), graphite and ice. Point out how the type of bonding determines the physical properties of the solids.

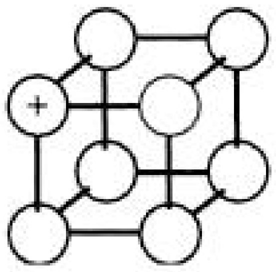
6. Give two examples of *(a)* ionic solids, *(b)* molecular solids and *(c)* covalent macromolecular solids. What are the factors that determine whether each of these types of solid will dissolve in water?

7. Describe the structure of each of the following solids. Explain how the type of chemical bonds in each solid determines the structure: sodium chloride, ice, poly(ethene), aluminium, iodine.

8. *(a)* Describe the nature of the chemical bonds present in the following solids:
(i) diamond (ii) graphite (iii) copper.
(b) Explain the following observations.
(i) Diamond is hard and an electrical insulator. Graphite is soft and a good electrical conductor.
(ii) Sodium is softer than copper.
(iii) Both sodium and copper are good electrical conductors.

***9.** *(a)* What is meant by the coordination number of a cation?
(b) What is the unit cell of a crystal structure?
(c) Explain why sodium chloride and caesium chloride have different crystalline structures.

10. *(a)* The diagram below represents part of a sodium chloride crystal with the position of one sodium ion shown by a plus (+) sign in a circle.



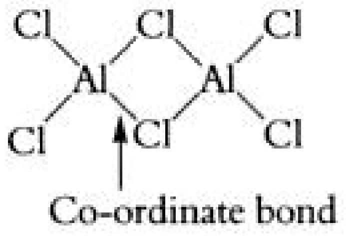
(i) Mark with minus (–) signs all the circles in a copy of the diagram which show the positions of chloride ions.

(ii) How many nearest sodium ions surround each chloride ion in a sodium chloride crystal? **2**

(b) Describe a simple test to show that sodium chloride is ionic. **2**

(c) A crystal of aluminium chloride vaporises when heated to a relatively low temperature. In the gas phase, aluminium chloride exists as a mixture of $AlCl_3$ and Al_2Cl_6 molecules. The Al_2Cl_6 molecule is formed when $AlCl_3$ molecules are linked by two co-ordinate (dative covalent bonds). The structure of Al_2Cl_6 is shown below with one of the co-ordinate bonds labelled.

(i) Explain the meaning of the term *co-ordinate bond*.



(ii) Using an arrow, indicate on a copy of the diagram the other co-ordinate bond.

(iii) Explain briefly why solid aluminium chloride vaporises at a relatively low temperature. **5**

9 *NEAB (AS/AL)*

11. *(a)* Describe the nature of the attractive forces which hold the particles together in magnesium metal and in magnesium chloride. **4**

(b) Name the type of bond between aluminium and chlorine in aluminium chloride and explain why the bonding in aluminium chloride differs from that in magnesium chloride. **3**

(c) Write an equation, including state symbols, to show what happens when magnesium chloride dissolves in water. Explain, in terms of bonding, the nature of the interaction between water and magnesium in this solution. **3**

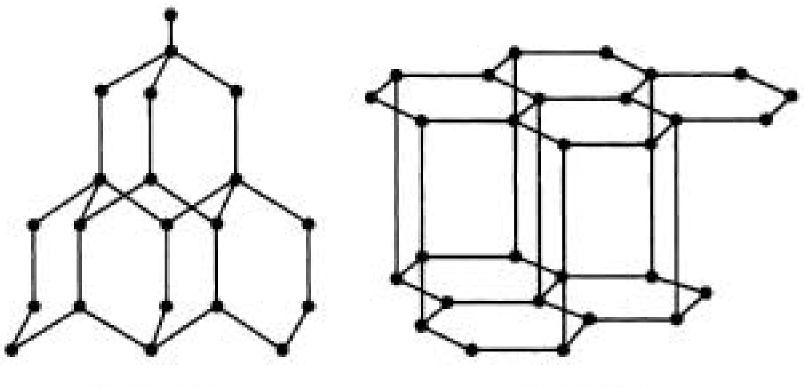
10 *NEAB (AS/AL)*

12. *(a)* Real gases do not behave ideally.

(i) State the **two** major assumptions which are made for ideal gas behaviour. **2**

(ii) I. State the *physical conditions* under which real gases approach ideal gas behaviour, and
II. explain these conditions in terms of the two assumptions in *(a)* (i). **2**

(b) The structures of diamond and graphite are shown in the diagram below.



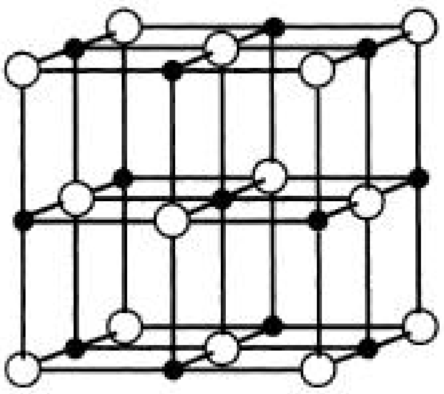
Diamond

Graphite

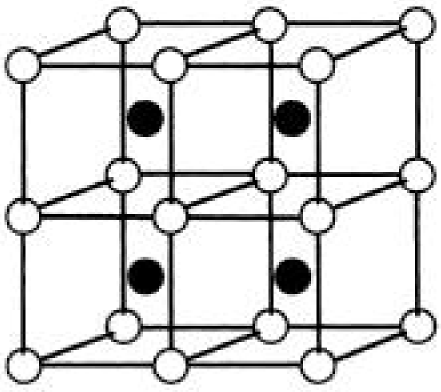
Explain the relationship between the structures of diamond and graphite and their I. hardness and II. electrical conductance. **3**

(c) (i) State the meaning of the term **coordination number** of an ion in a crystal structure. **1**

(ii) The structures of sodium chloride and caesium chloride are shown below.
What is the coordination number of the **chloride** ions in **each**? **1**



Sodium chloride



Caesium chloride

(iii) Explain why
I. Sodium chloride is soluble in water, and
II. ethanol is soluble in water while hydrocarbons are not. **3**

12 *(WJEC)*

For *(a)* see Chapter 7

Part 2

Physical Chemistry

7

GASES

7.1 AIR BAGS

If a car is in a collision, the driver often suffers injury or death by being thrown forward on to the dashboard. Many cars are now fitted with an air bag embedded in the steering wheel. If the car is in a collision and comes rapidly to a stop, the air bag inflates between the driver and the dashboard and cushions the impact. The air bag inflates within 50 microseconds. After the driver hits the bag, gas diffuses out through small holes in the bag. Air bags are becoming more widespread now that their effectiveness in saving lives has been proved. The bags are made of nylon, sometimes with a rubber coating. They do not contain air; they contain nitrogen. On impact, electronic sensors at the front of the car set off a chemical reaction in a gas generator. The generator contains sodium azide, NaN_3, potassium nitrate and silica. The electrical impulse from the sensor detonates the sodium azide:

Figure 7.1A
Air bag

$$2NaN_3(s) \longrightarrow 3N_2(g) + 2Na(s)$$

The sodium formed reacts with potassium nitrate:

$$10Na(s) + 2KNO_3(s) \longrightarrow K_2O(s) + 5Na_2(s) + N_2(g)$$

The third component of the mixture, silicon(IV) oxide, reacts with potassium oxide and sodium oxide to form a silicate glass:

$$K_2O(s) + Na_2O(s) + SiO_2(s) \longrightarrow \text{silicate glass}$$

The reason why the air bag works is that a small mass of sodium azide (126 g) can generate a large volume of nitrogen, about 70 dm^3. Why does a gas occupy such a large volume compared with a comparable mass of solid? The kinetic theory of gases, which is discussed in this chapter, will answer the question.

7.2 STATES OF MATTER

Gases differ from liquids and solids ...

Many pure substances can exist in all of the three states of matter: solid, liquid or gas, depending on conditions of temperature and pressure. There are characteristics in which gases differ from solids and liquids.

... in compressibility ...

1. Gases are highly compressible. Increasing the pressure on a gas can decrease its volume to a small fraction of the original value. Decreasing the pressure will allow the gas to expand to its original volume.

... in the degree of expansion on heating ...

2. Gases expand on heating. The increase in volume with temperature is typically about one hundred times greater than for a liquid.

... in ease of flow ...

3. Gases flow much more freely than solids or liquids. They diffuse, that is, spread from a region of higher concentration to a region of lower concentration. This allows gases to mix with other gases in any proportions to form a homogeneous mixture.

... in density

4. Gases have low densities. Compare for example iron 7.9×10^3 g dm^{-3}, water 1.0×10^3 g dm^{-3}, oxygen 1.4 g dm^{-3}. When a gas is cooled its density increases. When oxygen is cooled to −183 °C it liquefies with a density of 1.15 g cm^{-3}. This shows that the same mass of oxygen occupies as a gas 800 times the volume which it takes up in the liquid state. It follows that the molecules are much further apart in the gas than in the liquid state. It also shows that the molecules of a gas are not bonded in a structure as they are in solids and are more free to move than in a liquid.

7.3 THE GAS LAWS

7.3.1 BOYLE'S LAW

The gas laws state the results of experiments on gases

Boyle's Law relates the pressure and volume of a gas: PV = constant

A gas exerts pressure on the walls of its container. Robert Boyle measured the volume of gas at different pressures. The results of his work are known as **Boyle's Law**. The law can be expressed as: *for a fixed mass of gas at constant temperature the product of pressure and volume is constant*:

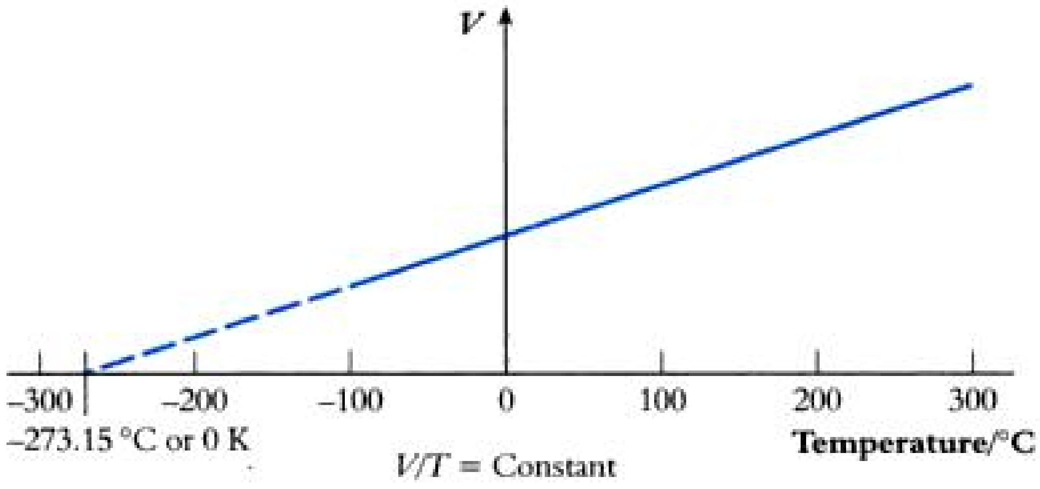
$$PV = \text{Constant}$$

7.3.2 CHARLES' LAW

Charles' Law deals with the effect of temperature on volume: V/T = constant ...

The French scientists J L Gay-Lussac and J A C Charles investigated the effect of temperature on the volume of a gas. They found that the volume increased in a linear manner with temperature [see Figure 7.3A].

Figure 7.3A
Graph illustrating Charles' Law (Plot of volume against temperature (°C) for a gas at constant pressure)



When the graph is extrapolated (the broken line beyond the experimental points) it cuts the temperature axis at −273.15 °C. The same value is obtained for all gases. It looks as though all gas volumes would become zero at −273.15 °C, but in fact gases liquefy or solidify long before they reach this temperature.

A sample calculation of the volume of a gas at stp ...

Method The experimental conditions are

$$P_1 = 1.05 \times 10^5 \text{ N m}^{-2}$$
$$T_1 = 273 + 60 = 333 \text{ K}$$
$$V_1 = 60 \text{ cm}^3$$

Standard conditions are

$$P_2 = 1.01 \times 10^5 \text{ Nm}^{-2}$$
$$T_2 = 273 \text{ K}$$

Since

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

SUMMARY

Ideal gases obey the equation of state for an ideal gas:
PV/T = constant.

The volume of gas at stp

$$V_2 = \frac{1.05 \times 10^5 \times 60 \times 273}{1.01 \times 10^5 \times 333} \text{ cm}^3$$
$$= 51 \text{ cm}^3$$

7.4 AVOGADRO'S HYPOTHESIS

Gay-Lussac's experiments ...

... showed that gas volumes combine in simple ratios

Gay-Lussac studied chemical reactions between gases. He noticed that there is always a very simple ratio between the volumes of gases that react together. For instance,

1 volume of hydrogen + an equal volume of chlorine ⟶ 2 volumes hydrogen chloride
1 volume of oxygen + 2 volumes of hydrogen ⟶ 2 volumes of water vapour

Avogadro's hypothesis offered an explanation

To explain Gay-Lussac's results, Avagadro in 1811 suggested that equal volumes of gases measured at the same conditions of temperature and pressure, contain the same number of molecules. This theory is called **Avogadro's hypothesis.** On the basis of this theory one can interpret the observation

1 volume of hydrogen + 1 volume of chlorine ⟶ 2 volumes of hydrogen chloride
as 1 molecule of hydrogen + 1 molecule of chlorine ⟶ 2 molecules of hydrogen chloride

The volume occupied by one mole of gas is the same for all gases: the gas molar volume = 22.414 dm³ at stp, 24.056 dm³ at rtp

It follows from Avogadro's hypothesis that if equal volumes of gases contain equal numbers of molecules then the volume occupied by one mole of molecules must be the same for all gases. It is called the **gas molar volume**. The value is 22.414 dm^3 at stp (0 °C and 1 atm) or 24.056 dm^3 at rtp (20 °C and 1 atm).

7.5 THE IDEAL GAS EQUATION

The ideal gas equation:

$PV = nRT$

For gases which obey the equation of state for an ideal gas,

$$\frac{P \times V}{T} = \text{Constant (for a given mass of gas)}$$

R is the universal gas constant, 8.314 J K⁻¹ mol⁻¹

Applying the equation to one mole of gas, $V = V_m$ the gas molar volume, and the constant is the **universal gas constant**, symbol R. Then

$$PV_m = RT$$

For n moles of gas,

$$PV = nRT$$

Since $R = PV_m/T$, R can be found by inserting values of P in N m^{-2}, V_m in dm^3 and T in kelvins into the equation. Then $R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$ (joules per kelvin per mole).

Using the ideal gas equation

1. The gas molar volume is used in calculations on the volumes of gases taking part in chemical reactions [see § 3.12].
2. The molar mass of a volatile liquid can be found by weighing a measured volume of its vapour [see § 8.4].

7.6 DALTON'S LAW OF PARTIAL PRESSURES

The partial pressure of a gas is the contribution which it makes to the total pressure. It is equal to the pressure which the gas would exert if it alone occupied the container

In a mixture of gases each gas behaves as if it were the only gas present, assuming there are no chemical interactions between the gases. In air, which is a mixture of approximately $\frac{4}{5}$ nitrogen and $\frac{1}{5}$ oxygen by volume, $\frac{4}{5}$ of the air pressure is due to nitrogen and $\frac{1}{5}$ is due to oxygen. The contribution which each gas makes to the total pressure is called the **partial pressure**. The partial pressure of a gas is the pressure which it would exert if it alone occupied the container. Dalton's Law of Partial Pressures states that in a mixture of gases which do not react chemically the total pressure is the sum of the partial pressures of the components.

Mole fraction of substance = moles of substance/total moles

The partial pressure of each gas depends on the total pressure and on the **mole fraction** of the gas. Mole fractions are one method of expressing the composition of a mixture. In air one fifth of the molecules are oxygen molecules so the mole fraction of oxygen $= \frac{1}{5}$. Four fifths of the molecules are nitrogen molecules so the mole fraction of nitrogen $= \frac{4}{5}$. In general, the mole fraction of **A** in a mixture of **A** and **B** is

$$\text{Mole fraction of } \mathbf{A} = \frac{\text{Moles of } \mathbf{A}}{\text{Moles of } \mathbf{A} + \text{Moles of } \mathbf{B}} = \frac{n_\mathbf{A}}{n_\mathbf{A} + n_\mathbf{B}}$$

From Avogadro's Hypothesis, it follows that

$$\frac{n_\mathbf{A}}{n_\mathbf{A} + n_\mathbf{B}} = \frac{\text{Volume of } \mathbf{A}}{\text{Total volume}}$$

A calculation of partial pressure

Example 4.00 dm^3 of oxygen at a pressure of 400 kPa and 1.00 dm^3 of nitrogen at a pressure of 200 kPa are introduced into a 2.00 dm^3 vessel. What is the total pressure in the vessel?

Method When oxygen contracts from 4.00 dm^3 to 2.00 dm^3, the pressure increases from 400 kPa to

$$400 \times \frac{4.00}{2.00} = 800\ \text{kPa}$$

The partial pressure of oxygen in the vessel is 800 kPa.

When nitrogen expands from 1.00 dm^3 to 2.00 dm^3, the pressure decreases from 200 kPa to

$$200 \times \frac{1.00}{2.00} = 100 \text{ kPa}.$$

The partial pressure of nitrogen is 100 kPa.

$$\begin{aligned}\text{The total pressure} &= p(O_2) + p(N_2)\\ &= 800 + 100 = 900 \text{ kPa}\end{aligned}$$

The total pressure in the vessel is 900 kPa.

CHECKPOINT 7.6: PARTIAL PRESSURES

1. 50.0 cm^3 of carbon dioxide at 10^5 N m^{-2} are mixed with 150 cm^3 of hydrogen at the same pressure. If the pressure of the mixture is 1.00×10^5 N m^{-2}, what is the partial pressure of carbon dioxide?

2. A mixture of gases at a pressure 1.01×10^5 N m^{-2} has the volume composition of 30% CO, 50% O_2, 20% CO_2.
   (a) What is the partial pressure of each gas?
   (b) If the carbon dioxide is removed by the addition of some pellets of sodium hydroxide, what will be the partial pressures of O_2 and CO?

3. Into a 10.0 dm^3 vessel are introduced 4.00 dm^3 of methane at a pressure of 2.02×10^5 N m^{-2}, 12.5 dm^3 of ethane at a pressure of 3.50×10^5 N m^{-2} and 1.50 dm^3 of propane at a pressure of 1.01×10^5 N m^{-2}. What is the pressure of the resulting mixture?

4. A mixture of 20% NH_3, 55% H_2 and 25% N_2 by volume has a pressure of 9.80×10^4 N m^{-2}.
   (a) What is the partial pressure of each gas?
   (b) What changes will take place in the partial pressures of hydrogen and nitrogen if the ammonia is removed by the addition of solid phosphorus(V) oxide?

7.7 THE KINETIC THEORY OF GASES

According to the kinetic theory ...

There is a need for a theory to explain the properties of gases described by the gas laws [§§ 7.1–7.6].

... most of a gas is empty space ...

... in which molecules are scattered with large distances between them

The kinetic theory of gases was put forward by R J Clausius (1857) and J C Maxwell (1859). The theory tackles these questions by making three fundamental assumptions. These are:

The gas molecules are constantly moving ...

1. The gas molecules themselves occupy only a tiny fraction of the volume in which a gas is contained. The distance between molecules is many times the diameter of a molecule. The kinetic theory model views a sample of gas as a nearly empty space. The molecules are tiny masses scattered through this space.

... in straight lines ...

... until they collide with one another or with the walls of the container ...

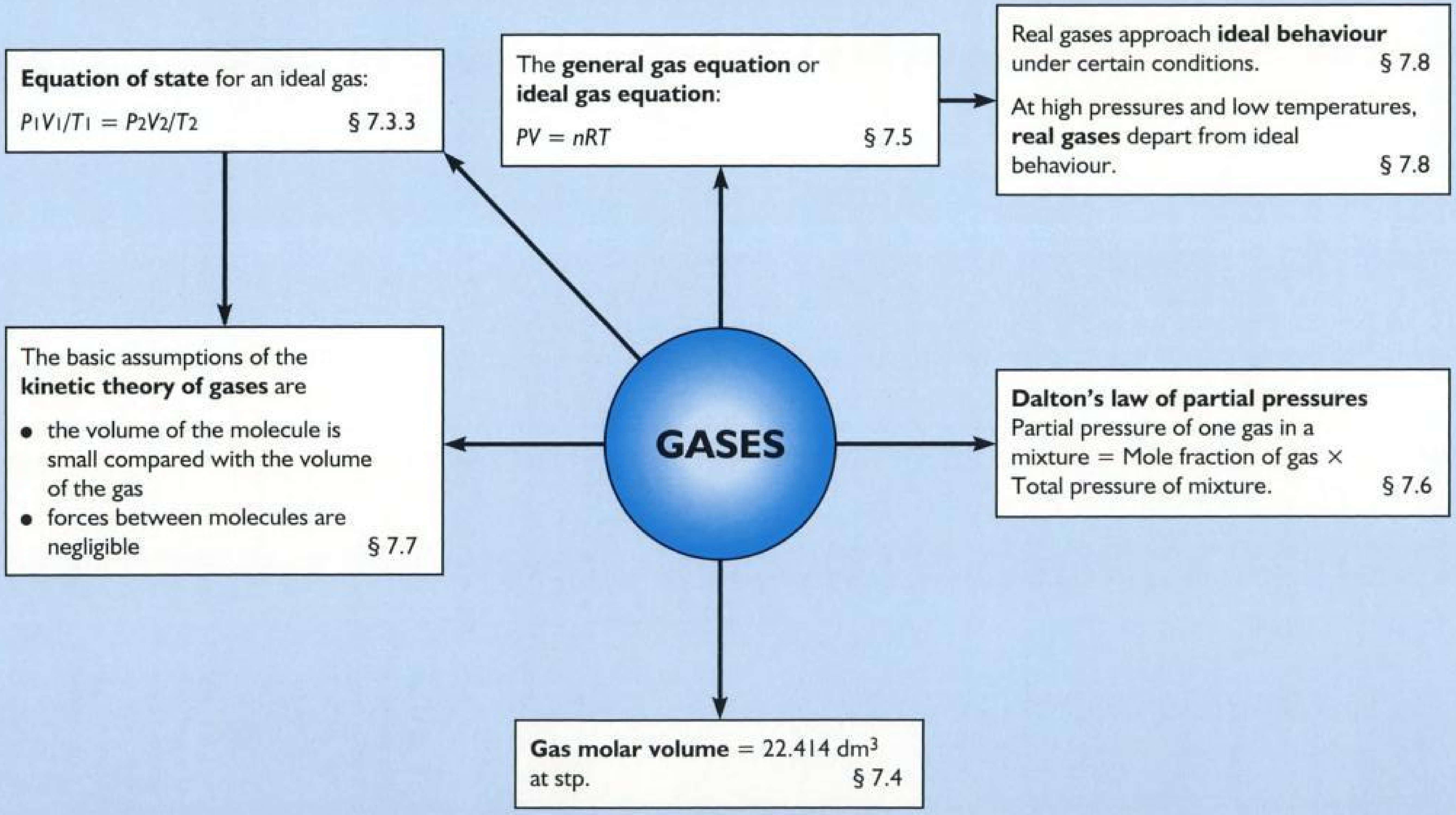
... exerting no forces between molecules ... except when they collide

2. The gas molecules are in constant motion. The name of the theory comes from the Greek word *kinein* to move. The molecules move in straight lines until they collide with each other or with the walls of the container. Except during collisions, the molecules exert no force upon one another. The collisions are **perfectly elastic**; this means that the molecules bounce apart with no loss of energy.

The average molecular speed is proportional to the absolute temperature

3. The molecules have a range of speeds. The speed of a molecule depends on its kinetic energy. As the temperature increases the kinetic energy increases and, as a result, the average speed increases. The average kinetic energy is proportional to the absolute temperature; therefore at a certain temperature all gases have the same average kinetic energy.

GASES



Equation of state for an ideal gas:

$P_1V_1/T_1 = P_2V_2/T_2$ § 7.3.3

The **general gas equation** or **ideal gas equation**:

$PV = nRT$ § 7.5

Real gases approach **ideal behaviour** under certain conditions. § 7.8

At high pressures and low temperatures, **real gases** depart from ideal behaviour. § 7.8

The basic assumptions of the **kinetic theory of gases** are

- the volume of the molecule is small compared with the volume of the gas
- forces between molecules are negligible § 7.7

Dalton's law of partial pressures
Partial pressure of one gas in a mixture = Mole fraction of gas × Total pressure of mixture. § 7.6

Gas molar volume = 22.414 dm^3 at stp. § 7.4

QUESTIONS ON CHAPTER 7

1. How does the kinetic theory of gases explain *(a)* the diffusion of gases *(b)* gas pressure and *(c)* the compressibility of gases?

2. *(a)* How does the pressure of a given mass of gas in a fixed volume change as the temperature rises? How does the kinetic theory explain this change?
(b) At stp, a certain mass of gas has a volume of 1.00 dm^3. At 30 atm pressure, the volume is 31.2 cm^3. At 60 atm, the volume is 14.9 cm^3. Does the gas show ideal behaviour? Justify your answer.

3. The ideal gas equation can be written as $PV = nRT$. Use this equation to calculate the volume of one mole of an ideal gas at 300 K and 100 kPa pressure.

4. Why does 3 mol of N_2 take up more space than 2 mol of NaN_3 [see § 7.1]?

5. What is the effect on the volume of one mole of an ideal gas when each of the following occurs?

(a) The pressure is doubled at constant temperature.
(b) The pressure is reduced by a factor of three at constant T.
(c) The absolute temperature is increased by a factor of 2.5 at constant pressure.
(d) Three moles of the gas are added at constant T and P.

6. What is the effect on the pressure of one mole of an ideal gas when each of the following happens?

(a) The temperature changes from 600 K to 300 K at constant volume.
(b) The temperature changes from 300°C to 600°C at constant volume.
(c) The volume is decreased from 8 dm^3 to 2 dm^3.
(d) Half the gas escapes through a leaky valve.

7. A weather balloon has a volume of 60.0 dm^3. It is released at sea level at 101 kPa and 23 °C. The balloon can expand to a maximum volume of 860 dm^3. It rises to an altitude at which the temperature is −5 °C and the pressure is 6.70 kPa. Does it reach its maximum volume?

8. Haemoglobin transports oxygen from the lungs to the rest of the body. One molecule of haemoglobin combines with four molecules of oxygen. If 1.00 g haemoglobin combines with 1.53 cm^3 of oxygen at 37 °C and 0.987 kPa, what is the molar mass of haemoglobin?

9. *(a)* Analysis of an organic compound **X**, which contains carbon, hydrogen and oxygen only, gave 54.5% by mass of carbon and 9.1% by mass of hydrogen.
(i) Calculate the empirical formula of **X**.
(ii) In a separate experiment, 0.539 g of a vaporised sample of **X** occupied 200 cm^3 at a temperature of 100 °C and a pressure of 95.0 kPa. Use these results to calculate the relative molecular mass of **X**.
(iii) Deduce the molecular formula for **X**. **8**
(b) A compound with molecular formula $C_3H_6O_2$ burns completely in oxygen to form carbon dioxide and water only.
(i) Write an equation for this reaction.
(ii) Calculate the volume of oxygen gas (at 298 K and 100 kPa) which is required to burn completely one mole of $C_3H_6O_2$ **3**

11 *NEAB (AS/AL)*

greater for polar molecules than for non-polar molecules and is greatest for the ions in an ionic solid. The strength of an attraction between particles decreases as the distance between them increases.

Kinetic energy of particles ...

... tends to disperse them

In a gas the strength of the attractions is smaller than the energy of movement so the particles are far apart. In a liquid the attractions are stronger because the particles are closer together, but their kinetic energy allows the particles to move about. In a solid the attractions dominate, and the particles are fixed in three-dimensional structures [see Chapter 6].

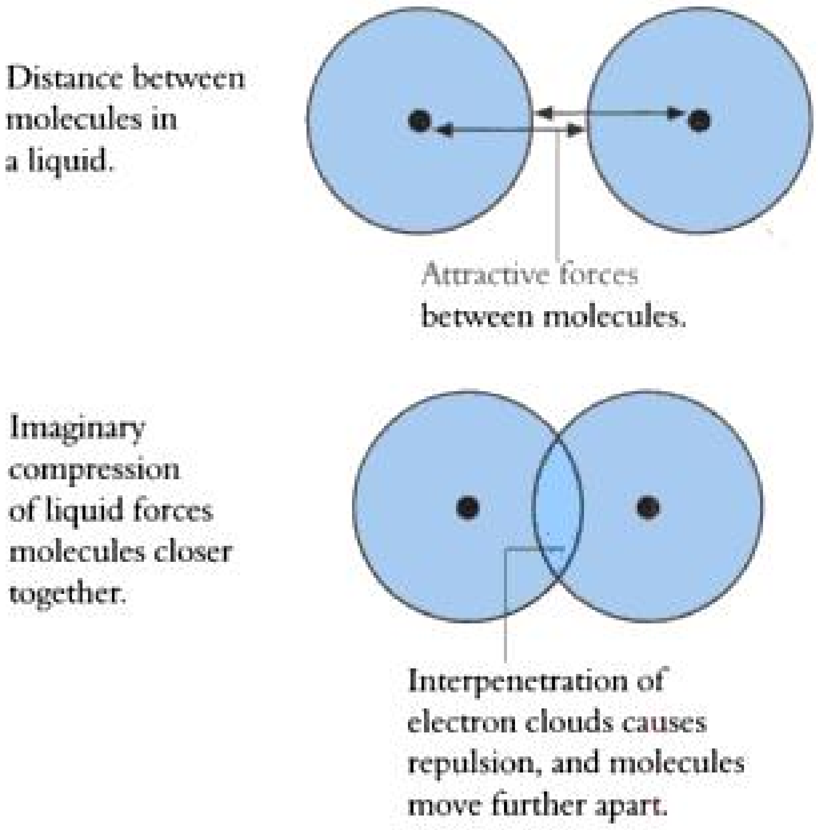
Attractive forces between particles ...

... tend to draw them together

In a gas, kinetic energy predominates

Since the particles are close together, a liquid, unlike a gas, has a definite volume. Having little space between particles, liquids are compressed only slightly by the application of pressure. The distance between the particles depends on a balance between forces of attraction between particles and forces of repulsion between neighbouring electron clouds [see Figure 8.2A]. The forces of attraction, being weaker than those in solids, are not strong enough to hold the liquid in a definite shape. A liquid flows to fit the shape of its container. The attractions between particles make liquids flow and diffuse much more slowly than gases. The particles in a solid are not much closer than those in a liquid but they are bonded together. This is why solids have a definite shape, are even less compressible than liquids and do not flow (although some solids flow extremely slowly).

Figure 8.2A
Distance between molecules of a liquid



In a solid, attractive forces predominate

In a liquid, the attractive forces between molecules are weak enough to allow the molecules to move

Changes of state

The changes of state between liquid, gas and solid are:

$$\text{Gas} \underset{\text{Vaporisation or evaporation}}{\overset{\text{Condensation}}{\rightleftharpoons}} \text{Liquid} \underset{\text{Melting}}{\overset{\text{Freezing or solidification}}{\rightleftharpoons}} \text{Solid}$$

Changes of state are governed by the balance between the kinetic energy of moving particles and intermolecular forces. As the temperature of a liquid increases, the kinetic energy increases and the most energetic particles can overcome the attractive forces, break free from the body of the liquid and move independently: they vaporise. When a gas is cooled, the kinetic energy of the particles decreases and forces of attraction draw the slower moving particles together: the gas condenses. Similarly, when a liquid is cooled sufficiently, attractive forces overcome kinetic energy, and the liquid solidifies (freezes).

SUMMARY

Solid, liquid or gas: the physical state of a substance depends on the balance between kinetic energy, which tends to disperse particles, and intermolecular forces, which tend to draw particles together. The balance changes with temperature.

When solids melt there is usually an expansion of about 10%. When liquids vaporise the expansion is much greater, for example one volume of water forms 1300 volumes of water vapour. Heat must be taken in to overcome forces of attraction between molecules of liquids and solids: melting and vaporisation are endothermic changes. When forces of attraction are set up between the molecules of a gas and they change into a liquid, and again when the molecules of liquid become ordered and solidify, heat is given out: condensation and freezing are exothermic changes.

The liquid state resembles the solid state more than the gaseous state. The quantity of heat required to melt one mole of a substance in its solid state is much smaller than the quantity of heat required to vaporise one mole of the liquid form of the same substance. This indicates that the change from solid to liquid involves less disruption of intermolecular attractions than the change from liquid to gas. For standard enthalpy of vaporisation and standard enthalpy of melting see § 10.7.2.

CHECKPOINT 8.2 LIQUIDS

1. *(a)* Why are liquids more compressible than solids and less compressible than gases?
   (b) Why do liquids flow more easily than solids and less easily than gases?
2. *(a)* Heat must be supplied to boil a liquid. What happens to this heat?
   (b) Why is less heat required to melt 1 mole of solid **X** than to vaporise 1 mole of liquid **X**?
3. What factors decide the distance between molecules in a liquid?

8.3 VAPORISATION

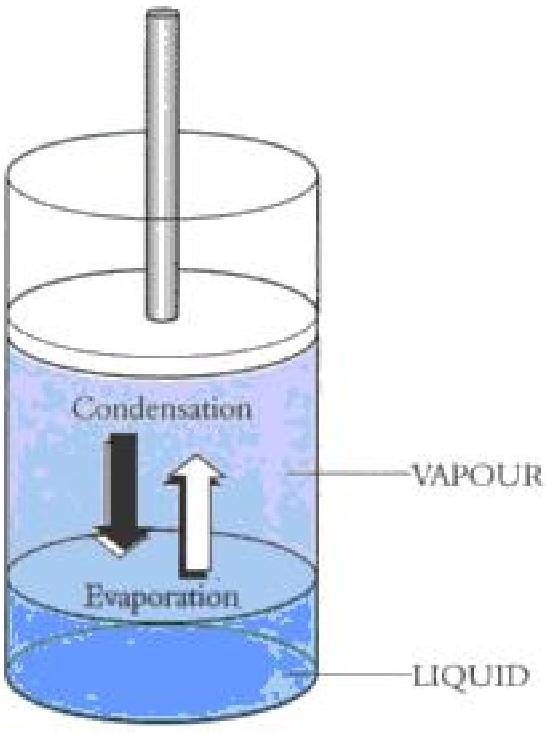
Molecules with high energy escape from the liquid to the vapour phase

Since molecules of liquid are in constant motion, some of them will have enough energy to escape from the liquid into the vapour state. (The term **vapour** is applied to a gas below its critical temperature. The critical temperature is the temperature below which a gas can be liquefied by an increase in pressure, without further cooling. Those that escape will be molecules with energy considerably above average, sufficient to remove them against the attraction of other molecules of liquid. The molecules that remain in the liquid will be of lower energy than those that escape, and the temperature of the liquid will fall. Since the fraction of molecules with high energy increases as the temperature rises, the rate of **vaporisation** or **evaporation** increases with temperature.

At equilibrium, the rate of evaporation equals the rate of condensation

Evaporation will continue until no liquid remains. If the liquid is in a closed container, however, the molecules in the vapour state will collide with the walls of the container, and some will be directed back towards the liquid. Some of these will re-enter the liquid, i.e. **condense**. [See Figure 8.3A.] **Equilibrium** will be reached when the rate at which molecules of liquid evaporate is equal to the rate at which molecules of vapour condense.

Figure 8.3A
A liquid and its vapour reach equilibrium in a closed container. The rate of evaporation is equal to the rate of condensation



FURTHER STUDY ▼

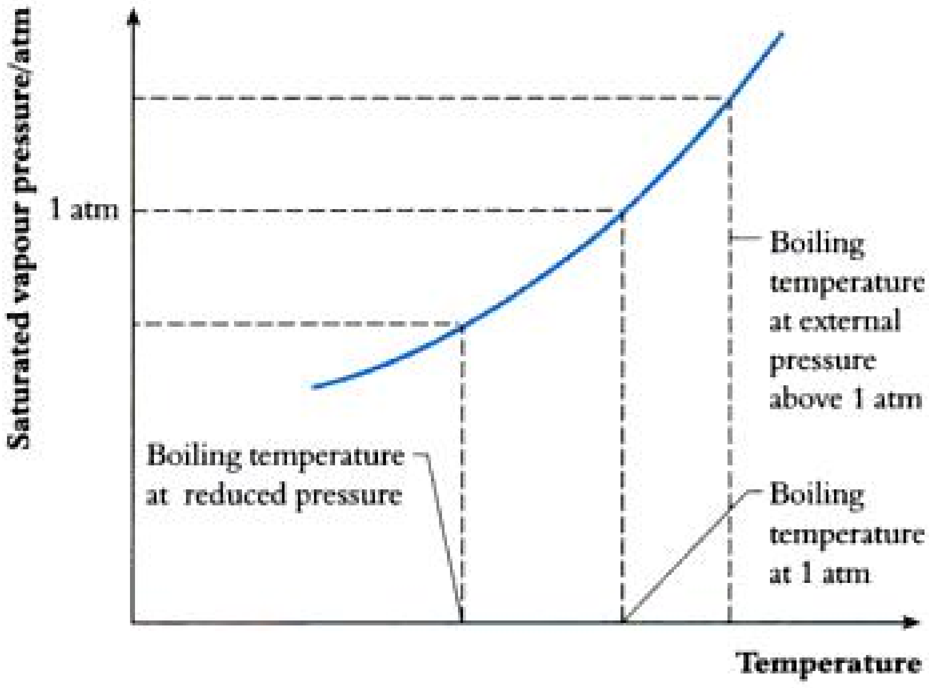
8.3.1 SATURATED VAPOUR PRESSURE

The maximum vapour pressure developed by a liquid is its saturated vapour pressure at that temperature

As the molecules of vapour collide with the walls of the container they exert a pressure. The maximum vapour pressure that can be developed by a liquid is called the **saturated vapour pressure** of that liquid. Since the fraction of molecules with high energy increases with temperature, evaporation increases as the temperature rises and the saturated vapour pressure increases with temperature. The magnitude of the saturated vapour pressure depends on the *identity* of the liquid and the *temperature*; it does not depend on the amount of liquid present. Solids have vapour pressures too, but, at room temperature, the vapour pressures of most solids are low.

A plot of saturated vapour pressure against temperature is shown in Figure 8.3B.

Figure 8.3B
Variation of saturated vapour pressure with temperature



8.3.2 DISTILLATION

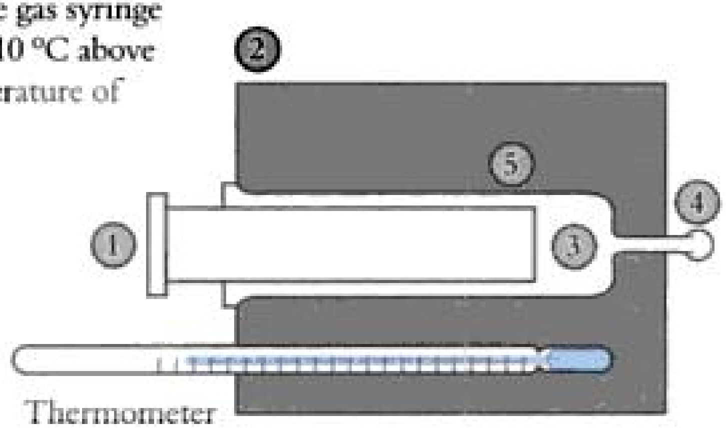
Saturated vapour pressure, svp, increases with temperature

If a liquid is heated in an open container, its saturated vapour pressure increases until it becomes equal to atmospheric pressure. When this happens, bubbles of vapour form in the interior of the liquid and escape into the atmosphere because the vapour pressure is high enough to push the air aside: the liquid boils. The **boiling temperature** of a liquid is defined as the temperature at which its saturated vapour pressure, svp, is equal to the external pressure, normally 1 atm.

*8.4 MOLAR MASS DETERMINATION

The volume of vapour formed by a known mass of liquid is measured ...

The gas syringe method of determining the molar mass of a volatile liquid is shown in Figure 8.4A. A weighed quantity of liquid is injected into a gas syringe, where it vaporises, and the volume occupied by the vapour is measured. The method does not give a very accurate result. It is used in conjunction with accurately known empirical formulae to establish the molecular formulae of compounds.



2 Furnace keeps the gas syringe at a temperature 10 °C above the boiling temperature of the liquid.

1 Gas syringe

3 The gas syringe contains air. The volume v_1 cm^3 is noted.

4 Self-sealing rubber cap. Liquid is injected through a hypodermic needle from a weighed syringe (m_1 g). The syringe is reweighed (m_2 g). The mass of liquid injected = $(m_1 - m_2)$ g.

5 When the liquid is injected, the plunger moves backwards. The volume of gas in the barrel is read (v_2 cm^3). Volume of vapour = $(v_2 - v_1)$ cm^3.

Figure 8.4A
Gas syringe method of molar mass determination

... and its molar mass is calculated ...

... A sample calculation

Method of calculation

$$PV = nRT = \frac{m}{M}RT$$

where $V = v_2 - v_1$, and $m = m_1 - m_2$
T = temperature recorded by thermometer,
P = the measured atmospheric pressure
R = the gas constant = 8.314 J K^{-1} mol^{-1}
$\therefore$ M, the molar mass of the gas, can be found.

Example $m_1 = 20.255$ g, $m_2 = 20.120$ g, $v_1 = 9.80$ cm^3, $v_2 = 65.8$ cm^3, $T = 363$ K, $P = 1.01 \times 10^5$ N m^{-2}

When these experimental results are inserted into the equation

$$PV = \frac{m}{M}RT$$

$$M = \frac{0.135 \times 8.314 \times 363}{1.01 \times 10^5 \times 56.0 \times 10^{-6}}$$

The molar mass, $M = 72$ g mol^{-1}

* Check your specification.

CHECKPOINT 8.4: MOLAR MASS OF VOLATILE LIQUIDS

($R = 8.314\ J\ K^{-1}\ mol^{-1}$, 1 atm = $1.01 \times 10^5\ N\ m^{-2}$)

1. When 0.184 g of a liquid was injected into a gas syringe at 45 °C, the volume of gas formed was 55.8 cm^3 at 1 atm. What value does this indicate for the molar mass of the liquid? By referring to the empirical formula CH_2 obtain an accurate value for the molar mass of the liquid.

2. When 0.125 g of a liquid was injected into a gas syringe at 50 °C, it formed 36.8 cm^3 of vapour at atmospheric pressure. The empirical formula of the compound is CH_2Cl. What value of molar mass do the experimental data give? What is the accurate value?

3. A sample of 0.108 g of a liquid of empirical formula CH_2 was vaporised. The volume of vapour was 50.8 cm^3, measured at 22 °C and $9.8 \times 10^4\ N\ m^{-2}$. Calculate the molar mass of the liquid.

4. By vaporising 0.100 g of a liquid at 100 °C and $1.01 \times 10^5\ N\ m^{-2}$, 20.0 cm^3 of vapour are obtained. Find the molar mass of the liquid.

8.5 SOLUTIONS OF LIQUIDS IN LIQUIDS

8.5.1 RAOULT'S LAW

A **solution** is a homogeneous (i.e., the same all through) mixture of two substances. When one liquid dissolves in another, the saturated vapour pressure of the solution depends on the saturated vapour pressures of the components and on the composition of the mixture. One way of expressing the composition of a mixture of liquids is to state the **mole fraction** of each constituent. By definition

Definition of mole fraction

$$\text{Mole fraction of } \mathbf{A} \text{ in a mixture of } \mathbf{A} \text{ and } \mathbf{B} = \frac{\text{Number of moles of } \mathbf{A}}{\text{Total number of moles}}$$

Using the symbol x for mole fraction

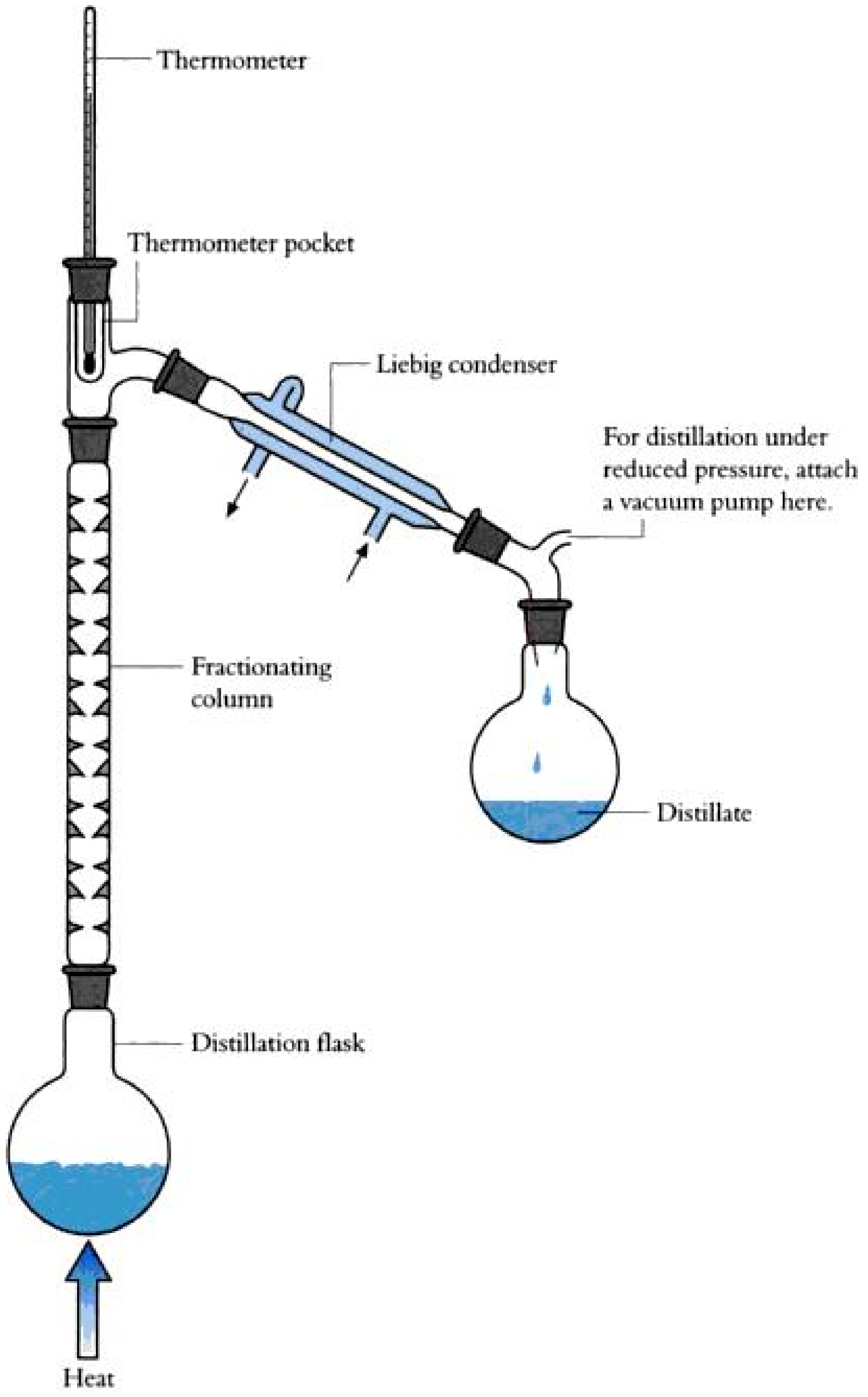
$$x_{\mathbf{A}} = \frac{n_{\mathbf{A}}}{n_{\mathbf{A}} + n_{\mathbf{B}}}$$

Figure 8.5A shows the saturated vapour pressures of mixtures of liquids **A** and **B**. **A** and **B** are completely miscible: they dissolve in each other in all proportions. The mole fraction of **A**, $x_{\mathbf{A}}$ is 1.0 at the left hand side of the graph and the saturated vapour pressure is that of pure **A**, $p^0_{\mathbf{A}}$. As the proportion of **B** increases, the mole fraction of **A** decreases and the saturated vapour pressure of **A** decreases along the line $p_{\mathbf{A}}$ until it reaches zero at $x_{\mathbf{A}} = 0$. At the left hand side of the graph, the mole fraction of **B**, $x_{\mathbf{B}} = 0$ and the vapour pressure of **B** = 0. At the right hand side, $x_{\mathbf{B}} = 1$, and $p_{\mathbf{B}} = p^0_{\mathbf{B}}$. The total vapour pressure is given by $p_{\mathbf{A}} + p_{\mathbf{B}}$.

It is possible to calculate the saturated vapour pressure of each liquid, **A** and **B**, in the mixture. **Raoult's Law** (after F Raoult) states that the saturated vapour pressure of each component is equal to the product of its saturated vapour pressure when pure and its mole fraction. Thus for **A**, the svp ($p_{\mathbf{A}}$) is given by the svp of pure **A** ($p^0_{\mathbf{A}}$) multiplied by its mole fraction $x_{\mathbf{A}}$.

$$p_{\mathbf{A}} = p^0_{\mathbf{A}} \times x_{\mathbf{A}}$$

Figure 8.5D
Fractional distillation



8.5.4 NON-IDEAL SOLUTIONS

Raoult's Law is obeyed by ideal solutions …

… non-ideal solutions have vapour pressures greater or less than those predicted

Solutions which have a vapour pressure greater than that predicted from Raoult's Law are said to show a **positive deviation** from the law. Those with a vapour pressure lower than the calculated value are said to show a **negative deviation**. [See Figure 8.5F.] Typical of a pair of liquids showing a slight positive deviation are hexane and ethanol. The molecules are very different, and molecules of ethanol can more easily escape from a mixture of ethanol and hexane than from pure ethanol, where hydrogen bonding holds molecules together. A slight negative deviation from Raoult's Law is shown by a mixture of trichloromethane, $CHCl_3$, and ethoxyethane, $C_2H_5OC_2H_5$. Forces of attraction between the two kinds of molecules tend to prevent the molecules escaping into the vapour phase. When a pair of liquids shows a very large positive deviation from Raoult's Law, the vapour pressure–composition curve has a maximum. A system with a very large negative deviation shows a minimum [see Figure 8.5F].

SUMMARY

Raoult's Law

svp of component of a mixture = svp of pure component × mole fraction of component

(svp = saturated vapour pressure)

A high svp means a low boiling temperature. Fractional distillation separates liquids on the basis of their boiling temperatures which are determined by their saturated vapour pressures.

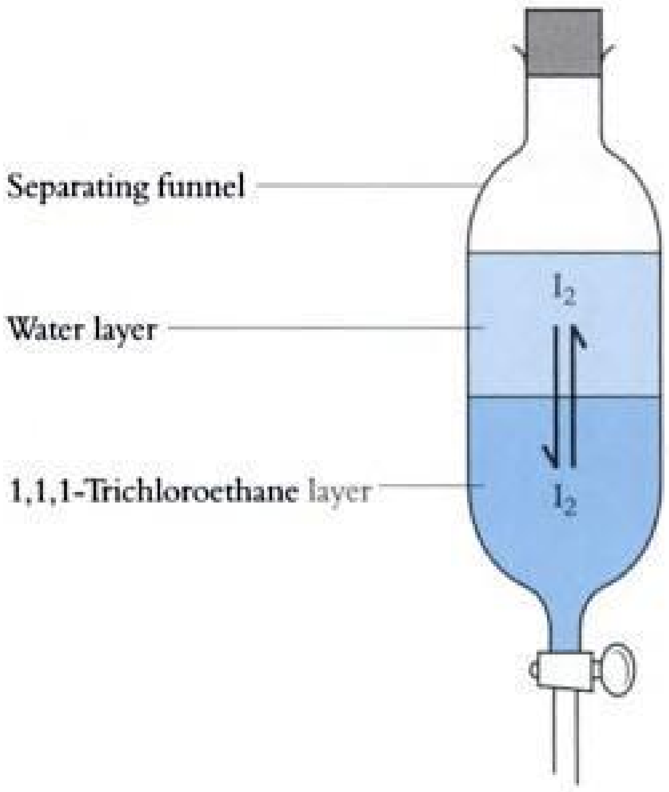
CHECKPOINT 8.5: RAOULT'S LAW

1. **X** and **Y** are two immiscible liquids which form an ideal mixture. At 20 °C, their saturated vapour pressures are $p^0_\mathbf{X} = 25$ kPa, $p^0_\mathbf{Y} = 45$ kPa. The mixture contains 1 mole of **X** and 4 moles of **Y** at 20 °C. Calculate the partial pressures of **X** and **Y** and the total pressure.
2. Liquids **A** and **B** have saturated vapour pressures of 15 kPa and 40 kPa at 25 °C. Calculate the saturated vapour pressure of an ideal solution of 2 moles of **A** in 3 moles of **B** at 25 °C.
3. Explain how fractional distillation separates crude oil into different products.
4. When a mixture of two liquids shows a positive deviation from Raoult's Law, is the total saturated vapour pressure greater or less than calculated? Is the boiling temperature higher or lower than expected?

8.6 PARTITION OF A SOLUTE BETWEEN TWO SOLVENTS

A pair of immiscible liquids form two layers. When a solute is added it may dissolve in both liquids. In this case the solute will divide itself between the two layers. It may well be more soluble in one solvent than the other. For example iodine dissolves both in water (with a low solubility) and in organic solvents such as 1,1,1-trichloroethane. The way in which iodine is distributed – or partitioned – between two solvents can be studied by shaking the mixture in a separating funnel [see Figure 8.6A].

Figure 8.6A Partition of iodine between two solvents



The mixture is shaken well and allowed to stand while the layers separate. Iodine can be seen in the water layer as a pale brown solution and in the organic layer as a pink solution. Iodine molecules pass from one layer to another until equilibrium is reached.

$$I_2(aq) \rightleftharpoons I_2(\text{organic layer})$$

Then the two layers can be run off separately and analysed. Titration against sodium thiosulphate solution gives the concentration of iodine in each layer. The results of experiments with different amounts of iodine and different volumes of solvents show that the ratio of iodine concentrations in the two solvents is always the same.

$$\frac{[I_2(aq)]}{[I_2(\text{trichloroethane})]} = \text{Constant}$$

The constant is called the **partition coefficient** or **distribution coefficient**. It is constant for a particular temperature. The general form of this equation is expressed as:

$$\frac{[\text{Solute in upper layer}]}{[\text{Solute in lower layer}]} = \text{Partition coefficient}$$

It holds provided that there is insufficient solute to saturate either solvent.

8.6.1 SOLVENT EXTRACTION

Often in the preparation of an organic compound the product is obtained as an aqueous solution. The chemist needs to separate the product from water. Solvent extraction is used. Organic compounds are more soluble in organic solvents than in water.

Ethoxyethane (ether) is a good solvent for many organic compounds, it is immiscible with water and it has a low boiling temperature (35 °C). An aqueous solution of the product is shaken with ethoxyethane in a separating funnel. The product distributes itself between the two layers in accordance with its partition coefficient between ethoxyethane and water. If the partition coefficient is high, a large fraction of the product will pass into the ethoxyethane layer. The ether layer is separated from the aqueous layer and dried by the addition of an anhydrous salt such as anhydrous calcium chloride. With its low boiling temperature, ether is easily distilled off to leave the product. The distillation is done in a fume cupboard because ether is very flammable and the vapour is denser than air and tends to accumulate at bench level where it can catch fire.

It is more efficient to use a certain volume of ether in portions for repeated extractions than to use it all in one operation. Consider an aqueous solution of 5.00 g of a product **X** in 1.00 dm^3 of water. The partition coefficient [**X** in ether]/[**X** in water] = 80.

(a) Let the mass of **X** extracted by 100 cm^3 of ether = a g

$$\frac{a/100}{(5.00 - a)/1000} = 80.0 \quad \text{and } a = 4.44 \text{ g}$$

SUMMARY

When a solute dissolves in both of a pair of immiscible liquids the distribution law states:
[solute in upper layer]/[solute in lower layer] = Constant, k
k = distribution coefficient or partition coefficient.
Solvent extraction is used to extract an organic product from an aqueous solution.

(b) Let the masses of **X** extracted by two successive 50 cm^3 portions of ether be (i) *b* g and (ii) *c* g.
then

$$\text{(i)}\quad \frac{b/50}{(5.00-b)/1000} = 80.0 \quad \text{and } b = 4.00\text{ g}$$

$$\text{(ii)}\quad \frac{c/50}{(1.00-c)/1000} = 80.0 \quad \text{and } c = 0.80\text{ g}$$

The total is 4.80 g of **X** when two portions of ether are used compared with 4.44 g of **X** when the ether is used as one portion.

CHECKPOINT 8.6: PARTITION

1. The partition coefficient of **S** between ethoxyethane and water is 5.0. A solution containing 10.0 g of **S** in 5000 cm^3 of water is extracted with 100 cm^3 of ethoxyethane. Which of the following gives the mass of **S** extracted from the water?

   A 2.5 g **B** 5.0 g **C** 7.5 g **D** 10.0 g **E** 12.5 g

2. An aqueous solution contains 5.0 g of **X** in 100 cm^3 of solution. The partition coefficient of **X** between water and an organic solvent is 0.200. Calculate the mass of **X** extracted by shaking 100 cm^3 of the aqueous solution with

   (a) 50 cm^3 of the solvent
   (b) two successive 25 cm^3 portions of the solvent.

8.7 PARTITION CHROMATOGRAPHY

8.7.1 THE THEORY

Chromatographic separations use repeated partition of solutes between two solvents

It has been shown in an example in § 8.6.1 and in Question 2, Checkpoint 8.6, that repeated extractions with organic solvents are effective in removing a considerable quantity of solute from an aqueous solution. The technique of repeated extractions can be applied to the separation of a number of solutes in a solution, provided that the solutes differ in their solubility in a second solvent.

In column chromatography ...

... the stationary phase is adsorbed on a solid which packs the column ...

In partition chromatography, many extractions are performed in succession in one operation. The solutes are partitioned between a **stationary phase** and a **mobile phase**. The stationary phase is a solvent (often water) **adsorbed** (bonded to the surface) on a solid. This may be paper or a solid such as alumina or silica gel, which has been packed into a column or spread on a glass plate. The mobile phase is a second solvent which trickles through the stationary phase.

8.7.2 COLUMN CHROMATOGRAPHY

... The moving phase is a second solvent ...

The *column* is a glass tube packed with an **adsorbent** (e.g., alumina, silica, starch, magnesium silicate). The solid adsorbent is made into a slurry with water, poured in and allowed to settle. [See Figure 8.7A.] A solution of the mixture to be analysed is poured on to the top of the column so that the components can be adsorbed on the column. The second solvent, called the **eluant**, is allowed to trickle slowly through the column.

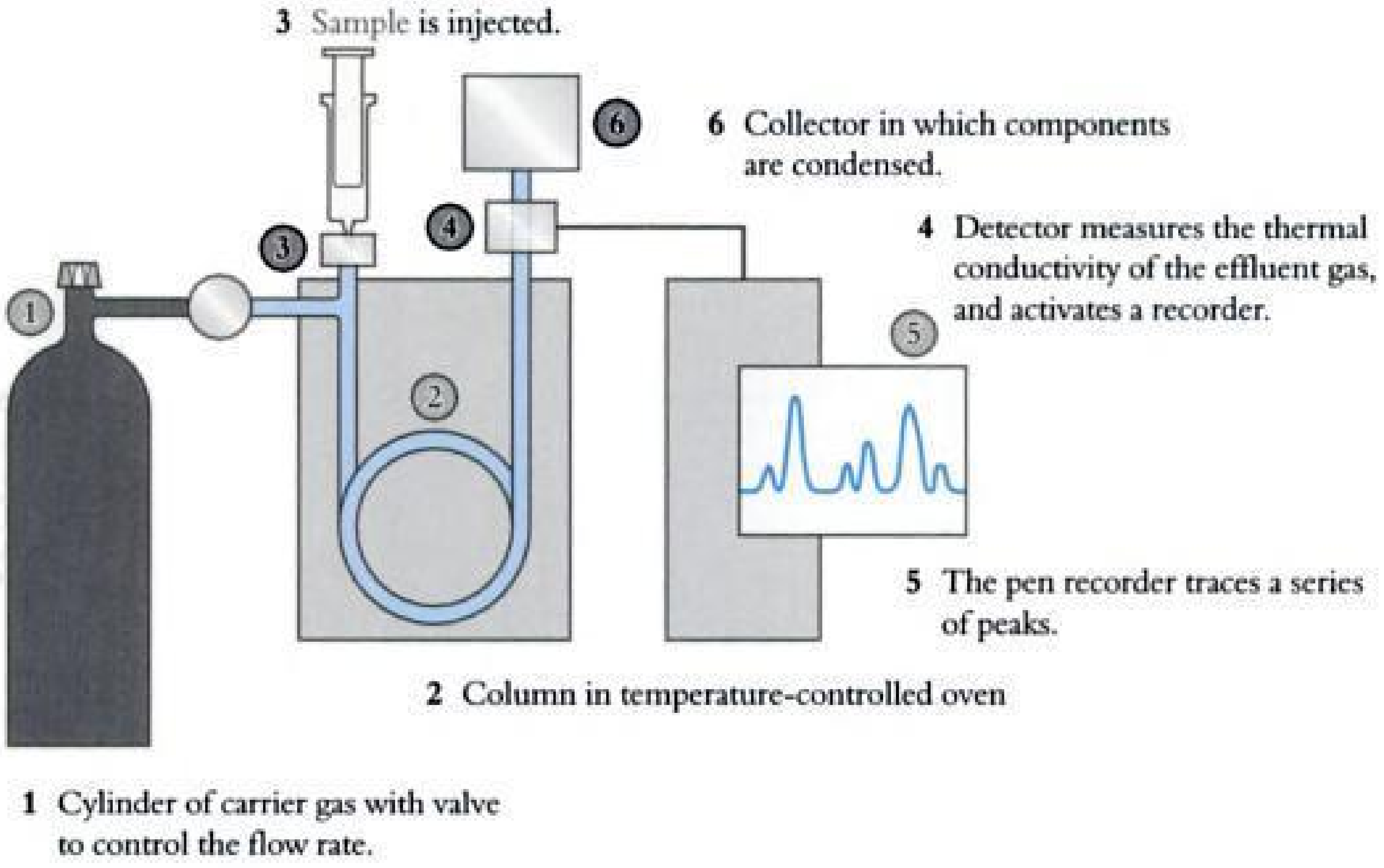


Figure 8.7D
Gas–liquid chromatography

8.7.6 ION EXCHANGE

Ion exchange resins replace cations by $H^+(aq)$ ...

... and anions by $OH^-(aq)$

Ion exchange is a type of partition of ionic compounds. The **ion exchange resin** is a polymer which contains at intervals polar groups which can remove undesirable cations (or anions) and replace them with other cations (or anions). The water softener Permutit®, is sodium aluminium silicate, which replaces calcium and magnesium ions in hard water by sodium ions. To purify water, a resin must replace all the cations and anions present by hydrogen ions and hydroxide ions. A combination of a **cation exchanger** and an **anion exchanger** is needed. Cation exchange resins often contain sulphonic acid groups, $—SO_3^-H^+$, and anion exchangers often contain quaternary ammonium groups, e.g., $—\overset{+}{N}(CH_3)_3OH^-$. If water passes slowly through a **deioniser**, equilibrium is set up at each level between hydrogen ions attached to the resin and hydrogen ions in solution:

$$—SO_3^-H^+(resin) + Na^+(aq) \rightleftharpoons —SO_3^-Na^+(resin) + H^+(aq)$$

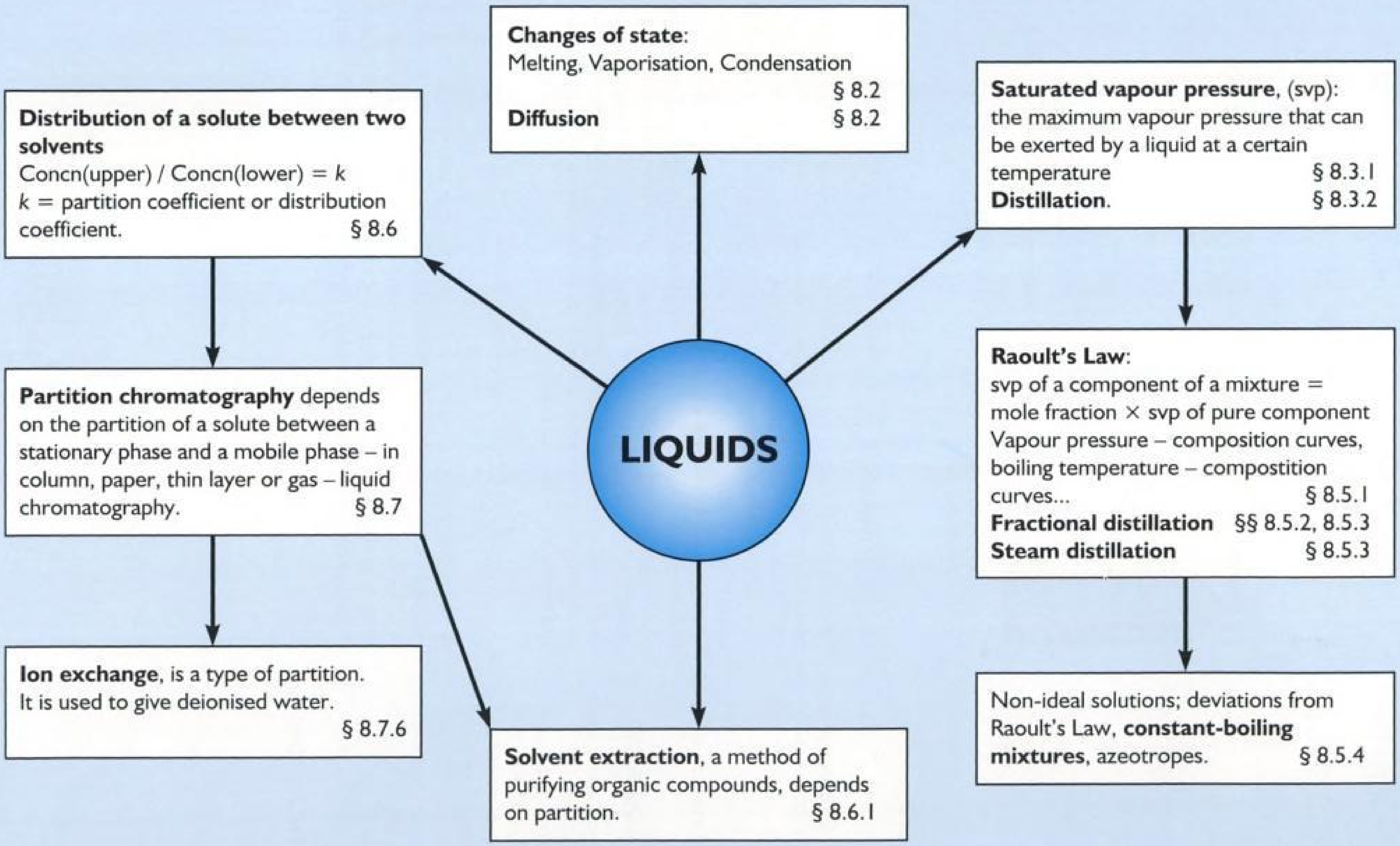
As the water moves on, two of the components in the equilibrium ($H^+(aq)$ and $Na^+(aq)$) are removed and a fresh equilibrium is established. Each successive equilibration increases the replacement of metal cations by hydrogen ions. At the same time, hydroxide ions are replacing other anions. If tap water is run slowly through an ion exchange resin, 'deionised' water of high purity can be obtained.

SUMMARY

Ion exchange is a type of partition. The method can be used to purify water. A resin removes cations and anions and replaces them with hydrogen ions and hydroxide ions to give deionised water.

FURTHER STUDY ▲

LIQUIDS



Changes of state:
Melting, Vaporisation, Condensation § 8.2
Diffusion § 8.2

Saturated vapour pressure, (svp):
the maximum vapour pressure that can be exerted by a liquid at a certain temperature § 8.3.1
Distillation. § 8.3.2

Raoult's Law:
svp of a component of a mixture = mole fraction × svp of pure component
Vapour pressure – composition curves, boiling temperature – compostition curves... § 8.5.1
Fractional distillation §§ 8.5.2, 8.5.3
Steam distillation § 8.5.3

Non-ideal solutions; deviations from Raoult's Law, **constant-boiling mixtures**, azeotropes. § 8.5.4

Distribution of a solute between two solvents
Concn(upper) / Concn(lower) = k
k = partition coefficient or distribution coefficient. § 8.6

Partition chromatography depends on the partition of a solute between a stationary phase and a mobile phase – in column, paper, thin layer or gas – liquid chromatography. § 8.7

Ion exchange, is a type of partition.
It is used to give deionised water. § 8.7.6

Solvent extraction, a method of purifying organic compounds, depends on partition. § 8.6.1

QUESTIONS ON CHAPTER 8

1. Explain
   (a) how liquids mix
   (b) why some of a liquid evaporates below its boiling temperature.

2. Describe practical methods which you have used in the laboratory for column chromatography, paper chromatography and thin-layer chromatography. Give examples of mixtures which can be separated by these methods.

3. Discuss the physical principles involved in
   (a) the ethoxyethane extraction of a product from aqueous solution
   (b) column chromatography.

4. Compare the fractional distillation of an ideal mixture, such as hexane ($T_b = 69$ °C) and heptane ($T_b = 98.5$ °C) with that of a non-ideal mixture, such as ethanol ($T_b = 78$ °C) and water. Draw boiling temperature–composition curves for the mixtures.

5. Define the term *partition coefficient*. A compound **Z** has a partition coefficient of 4.00 between ethoxyethane and water. Calculate the mass of **Z** extracted from 100 cm^3 of an aqueous solution of 4.00 g of **Z** by two successive extractions with 50 cm^3 of ethoxyethane.

***6.** *(a)* State Raoult's Law as applied to mixtures of miscible liquids.
   (b) At 50 °C the vapour pressure of hexane is 54.0 kPa and that of heptane 22.0 kPa. Draw graphs on the same axes showing how the partial vapour pressures of hexane and heptane and the total vapour pressure vary with the mole fraction for mixtures of hexane and heptane. Assume the mixture obeys Raoult's Law. Label the graphs.
   (c) Draw a temperature–composition diagram for the liquid and vapour phases of mixtures of hexane and heptane. Label the diagram.

***7.** *(a)* Draw diagrams to show how boiling temperature varies with composition for mixtures of
      (i) methanol ($T_b = 65$ °C) and ethanol ($T_b = 78$ °C), a mixture which obeys Raoult's Law almost ideally
      (ii) cyclohexane ($T_b = 81$ °C) and ethanol ($T_b = 78$ °C), a mixture which shows a positive deviation from Raoult's Law.
   Label the diagrams. Show the compositions of the liquid and the vapour.
   (b) Explain why methanol and ethanol form an ideal mixture while a mixture of cyclohexane and ethanol shows a positive deviation.

Note: * means 'check your specification'.

***8.** State Raoult's Law.
   (a) Some liquid mixtures which show a positive deviation from the law can form a constant–boiling (azeotropic) mixture. Explain how this happens with the aid of a boiling temperature–composition diagram.
   (b) (i) What is meant by a negative deviation from Raoult's law?
      (ii) A mixture of **A** and **B** shows a negative deviation from Raoult's Law. Why is it that when **A** and **B** are mixed the temperature rises?

9. *(a)* Briefly explain the term 'solvent extraction'.
   (b) Without going into calculations, explain why it is more effective to use successive small volumes of solvent rather than one large volume.

10. You are given the problem of finding the partition coefficient of ethanoic acid between water and 2-methylpropan-1-ol. Describe what measurements you would make.

11. *(a)* (i) Sketch a graph of **V** (the volume of an ideal gas) against 1/**P** (the reciprocal of its pressure) at constant temperature. 1
      (ii) State **two** factors which cause real gases to deviate from ideal behaviour. 2
   (b) (i) Sketch a graph to show the variation of the saturated vapour pressure of a liquid with temperature. 1
      (ii) Explain why the boiling temperature of a liquid varies with the external pressure. 1
      (iii) Give **one** reason why some liquids are purified by distillation under reduced pressure. 1
   (c) Calculate the molar mass of a volatile organic liquid, given that 0.597 g of the liquid when vaporised gives an ideal gas of volume 153 cm^3 at 100 °C and 1.01×10^5 Pa pressure (1 atmosphere). 3
   [1 mole of ideal gas occupies 2.24×10^4 cm^3 at 0 °C and 1.01×10^5 Pa pressure (1 atmosphere).]

9 *WJEC (AS/AL)*

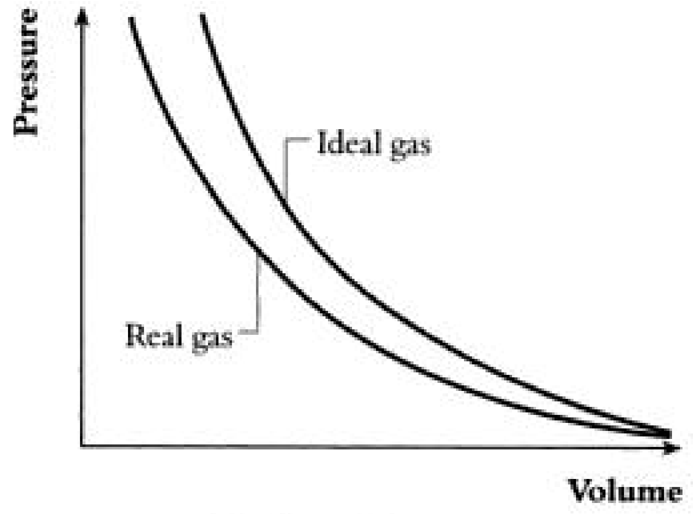
12. *(a)* (i) Iodine, (I_2), is a **molecular solid** at temperatures up to 30 °C. At temperatures in excess of 30 °C iodine sublimes (changes state from a solid to a vapour).
         I. Explain the term **molecular solid**, by reference to the bonding present within solid iodine. $1\frac{1}{2}$
         II. Explain the structural changes which occur when iodine passes directly from the solid to the vapour phase. $1\frac{1}{2}$
      (ii) Describe a simple model for bonding in metals and use this to explain the electrical conductivity of metals. 2

(b) Using a simple kinetic–molecular model describe
- (i) the nature of the liquid state, and $1\frac{1}{2}$
- (ii) vaporisation and the variation of vapour pressure with temperature. $2\frac{1}{2}$

(c) A sample of helium was compressed at **273 K** from a volume of 183 cm^3 to a volume of 0.3 cm^3.
- (i) Calculate the final pressure of the helium sample if the initial pressure was 4.78 Pa. $1\frac{1}{2}$
- (ii) Calculate the number of moles of helium present in the above sample. $1\frac{1}{2}$
  [1 mole of ideal gas occupies 2.24×10^4 cm^3 at 273 K and 1.01×10^5 Pa.]

12 *WJEC (AS/AL)*

13. *(a)* (i) The graph below shows the variation of pressure with volume at 298 K for 1 mol each of an ideal gas and a real gas.



Explain why
- (1) at low pressures, the curve for the real gas approaches that for the ideal gas
- (2) at 298 K and when contained in vessels of identical volume, 1 mol of N_2 exerts a greater pressure than 1 mol of HCl.

(ii) At 298 K, 1.0 dm^3 of N_2 at 0.20 Pa pressure was mixed with 2.0 dm^3 of O_2 at 0.40 Pa in a 4.0 dm^3 container. Assuming that both N_2 and O_2 behave ideally, calculate the pressure of the gaseous mixture at 298 K. **5**

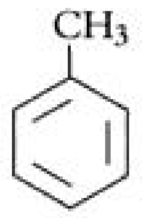
(b) Briefly describe each of the following intermolecular forces and illustrate your answer with an appropriate example in each case: dipole–dipole interactions, hydrogen bonding, van der Waals' forces **4**

(c) (i) Two miscible liquids *A* and *B* form ideal solutions when mixed. At 298 K, the vapour pressures of pure *A* and pure *B* are 32 kPa and 16 kPa respectively.

For a mixture of 1 mol of *A* and 3 mol of *B* at 298 K, calculate:
- (1) the vapour pressure of the mixture
- (2) the mole fraction of *A* in the vapour which is in equilibrium with the mixture.

(ii) Predict whether the following pairs of liquids when mixed, would give solutions showing positive deviation or negative deviation from Raoult's Law. Explain your prediction.

(1) CH_3CH_2OH and



(2) $C_2H_5OC_2H_5$ and $CHCl_3$

8 *HKALE (AL)*

14 *(a)* Explain the meaning of the terms
- (i) *empirical formula* **2**
- (ii) *molecular formula*. **2**

(b) An organic compound, **X**, has the following composition by mass:

C = 38.7%   H = 9.7%   O = 51.6%

[A_r(C) 12.0; A_r(H) 1.0; A_r(O) 16.0]

What is the *empirical* formula of the compound **X**? **2**

(c) In an experiment to determine the relative molecular mass of **X**, 0.500 g of **X** occupied 2.34×10^{-4} m^3 at a pressure of 1.00×10^5 Pa and a temperature of 350 K. [Gas constant, $R = 8.31\ J\ K^{-1}\ mol^{-1}$; $1\ J = 1\ Pa\ m^3$]
- (i) State the ideal gas equation. **1**
- (ii) Use the ideal gas equation to determine the number of moles of **X** used in this experiment. **2**
- (iii) From your answer to (ii) determine the relative molecular mass of **X**. **1**
- (iv) From your answers to parts *(b)* and *(c)*(iii) deduce the molecular formula of **X**. **1**

11 *O&C (AS/AL)*

9

SOLUTIONS

9.1 AN UNUSUAL SOLVENT

There are many people who prefer to drink decaffeinated coffee. They like the taste of coffee but they do not want the stimulation that caffeine gives, which keeps some people awake at night. Organic solvents were originally used to dissolve the caffeine out of coffee beans. Benzene, which is flammable, was the first used and was replaced by trichloroethene, which is now found to be a carcinogen. Dichloromethane is still used, but a better solvent is taking over. This is supercritical fluid carbon dioxide.

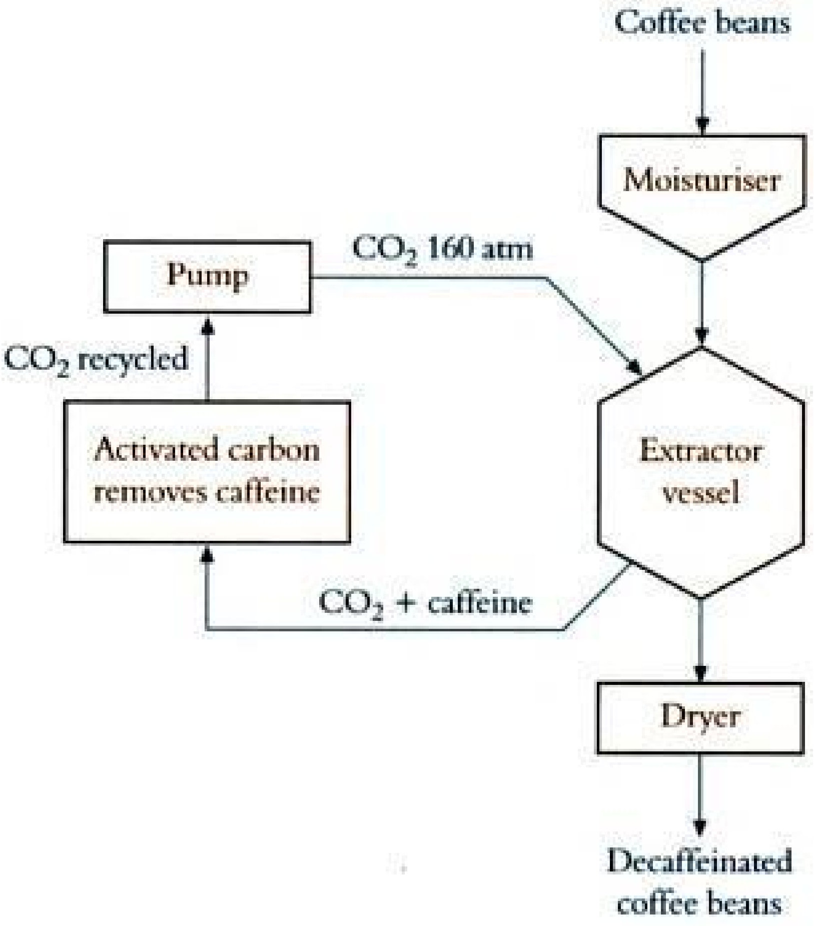


Figure 9.1A
Dissolving the caffeine out of coffee beans

Carbon dioxide has a critical temperature (above which it cannot be liquefied) of 31 °C and a critical pressure (below which it cannot be liquefied) of 74 atm. Above its critical temperature and at a pressure above its critical pressure, carbon dioxide is a **supercritical fluid**, that is, a fluid in which the distinction between liquid and gas disappears. The properties of supercritical fluids, being in between those of liquids and gases, find them many uses. Carbon dioxide as a supercritical fluid is a valuable solvent. It has the solvent properties of a liquid and flows like a gas. The first success of supercritical fluid carbon dioxide was in the decaffeination of coffee beans.

There are many advantages of supercritical fluid carbon dioxide over organic solvents. It does not damage the ozone layer. The use of carbon dioxide does not add to the greenhouse effect because the gas is extracted from the air during the production of oxygen. The carbon dioxide solvent can be recycled. Carbon dioxide is preferred over other supercritical fluids because it is readily available, completely safe to use in food processing, non-flammable and supercritical at lower pressure than some alternatives.

Hop flavours for use in beer making are also extracted by supercritical fluids on a large scale. On a smaller scale oils, flavours and essences are extracted for the pharmaceutical industry from plants and micro-organisms.

Example A chemist has prepared 10 g of compound **A**. About 0.5 g of impurity **B** are present. For both **A** and **B** the solubilities in water are 100 g kg^{-1} at 80 °C, 30 g kg^{-1} at 20 °C. Will the chemist be able to obtain pure **A** by recrystallisation?

Method Prepare a saturated solution of the mixture of **A** and **B** in 100 g of water at 90 °C. Filter the hot solution to remove insoluble impurities. Warm the filtrate to redissolve any solid that has crystallised. Cool the solution from 90 °C to 20 °C. Since at 90 °C 10 g of **A** will dissolve but at 20 °C only 3.0 g of **A** will dissolve, 7.0 g of **A** will crystallise. Since at 20 °C, the mass of **B** that can remain in solution is 3.0 g, and since only about 0.5 g is present, no **B** will crystallise. The crystals will be pure **A**. They can be filtered and dried.

SUMMARY

A saturated solution contains as much solute as can be dissolved at a stated temperature.

Solubility = mass of solid dissolved in a stated mass or volume of solvent at a stated temperature.

A solubility curve is a graph of solubility against temperature.

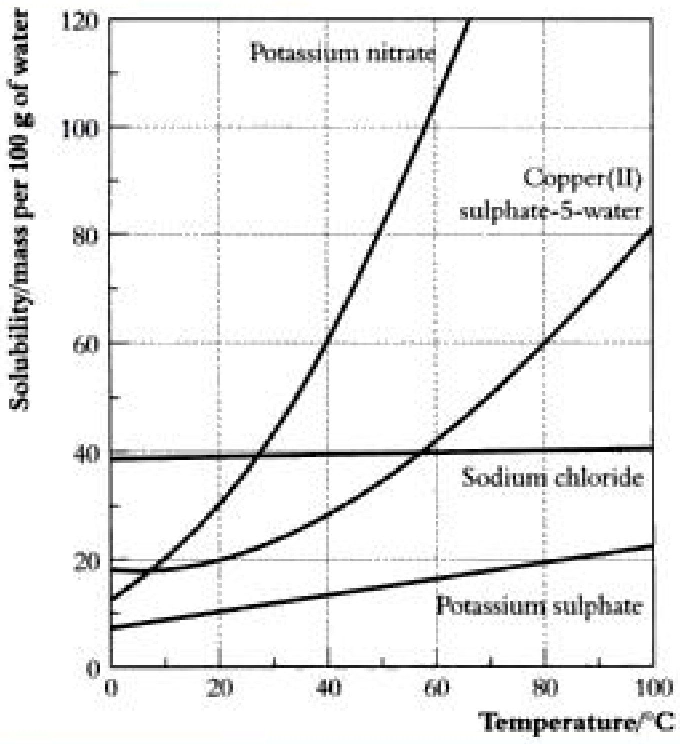
The technique of recrystallisation depends on the solubilities of a substance and the impurities present with it.

CHECKPOINT 9.3: SOLUTIONS

1. You are given a bottle of solid **A** and three aqueous solutions of **A**. One is saturated, one unsaturated and one supersaturated. How would you find out which was which?

2. Solubility curves for a number of ionic solids are given below.

Figure 9.3B
Some solubility curves



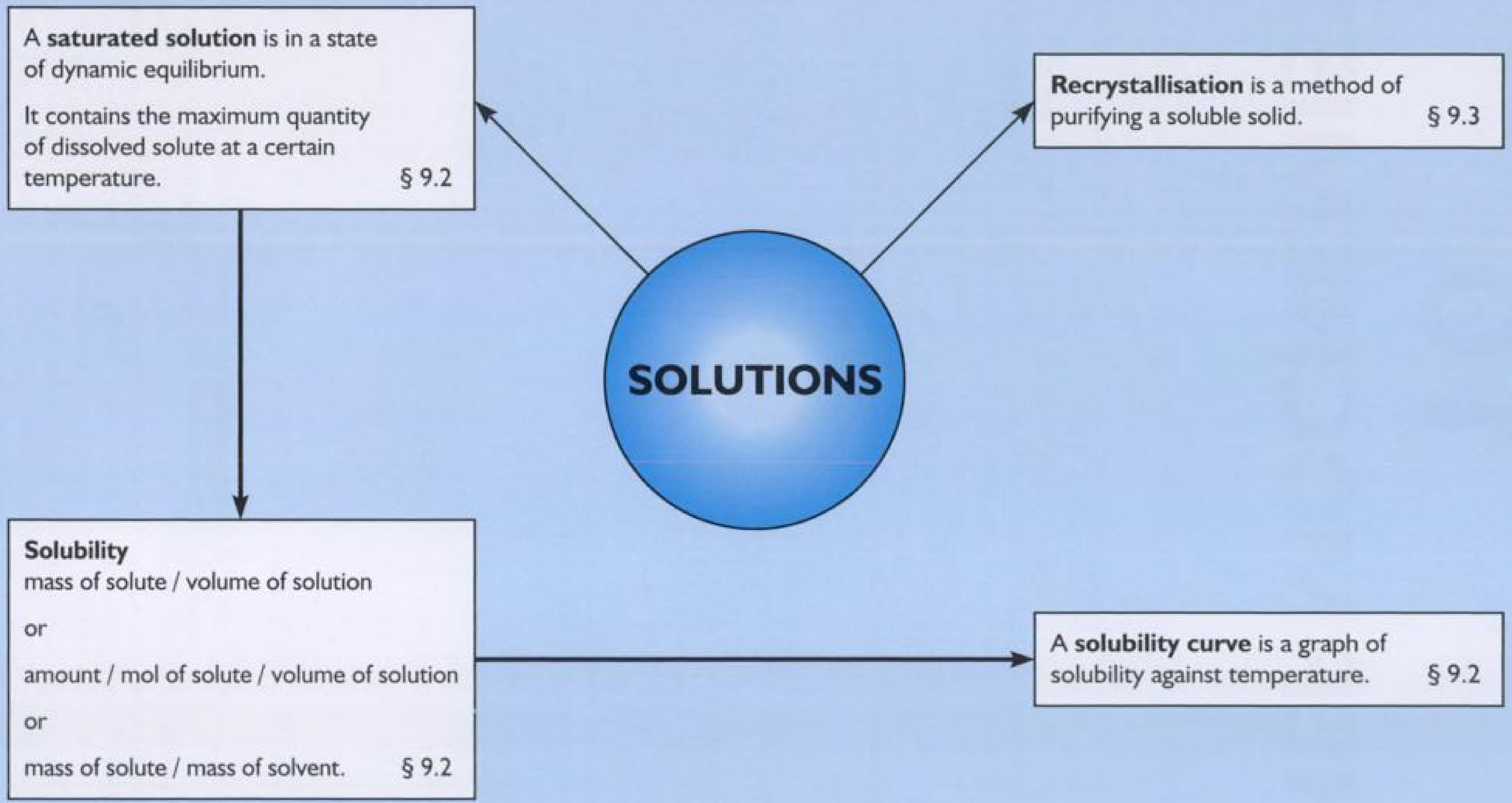
(a) (i) What mass of copper(II) sulphate-5-water will dissolve in 100 g of water at 100 °C?
(ii) What happens when the solution is cooled to 50 °C?

(b) What is the solubility at 60 °C of
(i) potassium nitrate
(ii) sodium chloride?

(c) A solution is saturated at 60 °C with potassium nitrate and with sodium chloride. A 100 g sample of solution is cooled from 60 °C to 20 °C. What mass of crystals forms?

3. A saturated solution of CaSO$_4$(aq) has some undissolved CaSO$_4$(s) lying at the bottom of the container. A little Ca^{35}SO$_4$ is mixed with the undissolved Ca^{32}SO$_4$. The isotope ^{35}S is radioactive, and, after a while, both the solution of CaSO$_4$(aq) and the undissolved CaSO$_4$(s) are found to be radioactive. Explain how the solution has been able to take up CaSO$_4$ in spite of being saturated.

SOLUTIONS



SOLUTIONS

A **saturated solution** is in a state of dynamic equilibrium.

It contains the maximum quantity of dissolved solute at a certain temperature. § 9.2

Recrystallisation is a method of purifying a soluble solid. § 9.3

Solubility
mass of solute / volume of solution

or

amount / mol of solute / volume of solution

or

mass of solute / mass of solvent. § 9.2

A **solubility curve** is a graph of solubility against temperature. § 9.2

10

THERMOCHEMISTRY

10.1 SOURCES OF ENERGY

As the twenty first century begins, the human race needs urgently to consider its use of energy. The world's supply of fuel is diminishing. For some nations this threatens a drop in the standard of living. For less developed countries, it may be a question of survival. There are many chemical aspects of energy production and utilisation. There is no greater scientific challenge offered to chemists and engineers today than the problem of energy.

Reliance on wood and coal as sources of energy at the start of the twentieth century has been overtaken by the use of petroleum. The fossil fuels [§ 10.2] are still our major source of energy, but the pollution they cause and the limited reserves mean that fossil fuels cannot provide for our energy needs for ever. It is estimated that 90% of our known oil reserves could be used up by 2020, and oil companies are actively exploring to find new reserves. Deposits of coal are much greater than known reserves of oil.

Coal, biomass and hydrogen are the most important fuels for the future. Coal is a polluting fuel [see § 10.2], but there are ways of making clean fuels from it. In the process of coal gasification, coal is heated to form methane and carbon.

Biomass (animal and plant matter) can be used as a source of energy. Sugar, cellulose and other plant materials are converted into fuels. Ethanol is one such fuel, which is mixed with petrol and sold as gasohol [see § 30.5.3]. Methane is produced in biogas generators through the microbial breakdown of plant and animal waste [see § 26.1].

Hydrogen produces about one-third as much energy per mole as methane on combustion. The product of combustion, water vapour, is non-polluting. Hydrogen is a renewable fuel because the water produced returns as rain. However, energy must be spent in making hydrogen from water by electrolysis.

To conserve our resources and to develop new fuels we need to understand how energy is released in chemical reactions, such as combustion. This is one of the areas we study in thermochemistry.

10.2 FOSSIL FUELS

Fossil fuels were formed from decayed plant and animal matter

They derive their energy indirectly from the Sun

Most of the energy used in the world comes from the combustion of organic compounds These include the complex organic compounds in wood and the hydrocarbons of natural gas, coal, petroleum oil and other **fossil fuels.** These are so-called because they were formed from the decayed animal and vegetable matter of living things that inhabited the Earth millions of years ago. The ultimate source of the energy in fossil fuels is the Sun. Solar radiation enables green plants to carry out photosynthesis, the process during which they synthesise carbohydrates. Fossil fuels are **finite resources**: when we have used up Earth's reserves no more will be formed.

Fossil fuels are of enormous value to society

Wood and fossil fuels have many advantages. The appliances needed to burn them and harness their energy are easy to construct and simple to use. The products of combustion, provided that there is an ample supply of oxygen, are the harmless substances carbon dioxide and water. There are some drawbacks, however. Some fossil fuels contain sulphur compounds, and measures must be taken to remove the combustion product sulphur dioxide [see Acid rain, § 21.10]. There is also the problem of the enhanced greenhouse effect [see § 23.6]. As the demand for energy and the combustion of fossil fuels have increased over the last century, the level of carbon dioxide in the atmosphere has increased and with it the threat of global warming.

The combustion of fossil fuels to release energy is an important area of study

Obtaining energy from fossil fuels

We obtain energy from fuels by combustion, e.g. the combustion of the hydrocarbon methane in natural gas:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

and octane in petrol:

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

The products are carbon dioxide and water, provided that sufficient oxygen is present. If the supply of oxygen is insufficient carbon monoxide and carbon are produced also. In the combustion of octane in a plentiful supply of air, 40 MJ of energy are obtained for every litre of octane used, enough to drive an average car 7–9 miles.

Combustion is **oxidation** with the release of energy. When combustion is accompanied by a **flame** we call it **burning**. Substances which release a lot of energy on combustion are used as **fuels**.

10.3 WHY DO REACTIONS HAPPEN?

This chapter will tackle the question of why chemical reactions and physical changes happen

It is important for us to understand combustion. We can ask the question, 'Why do fuels burn?' 'Why does methane react rapidly with oxygen to form carbon dioxide and water vapour?' 'Why do carbon dioxide and water vapour *not* react to form methane, however long you leave them together? There are other puzzling questions apart from combustion. 'Why does a garden fork rust if it is left outside?' 'Why does a rusty fork never become shiny again?' 'Why does a sugar lump dissolve in a cup of coffee?' 'Why does it never reappear out of the solution?' Such questions lead to the more fundamental questions, 'Why do chemical reactions happen?' and 'Why do physical changes happen?'

Some changes are spontaneous ...

... happening without external help

Our experience of such changes tells us that there are **spontaneous changes**, which occur by themselves and there are changes that do not occur unless we make them happen. Spontaneous changes seem to have a driving force that sends them in a certain direction. To send such a process in the reverse direction, we have to expend energy. For example, with a little heating, magnesium burns rapidly to form magnesium oxide. To reverse the process is difficult: to split magnesium oxide into magnesium and oxygen, energy must be supplied in the electrolysis of molten magnesium oxide. Some spontaneous processes release energy, for example when water vapour condenses to form liquid water, heat is given out. Other spontaneous processes take in energy, for example when ammonium nitrate dissolves in water the temperature of the solution falls.

This chapter investigates the importance of heat changes in chemical and physical changes ...

In this chapter we work towards an understanding of why chemical reactions and physical changes happen. We study methods of measuring the heat changes that take place in chemical and physical changes. Since laboratory reactions usually take place at constant pressure, we explore the convenience of studying heat change at constant pressure, a quantity called the **change in enthalpy.** We refine this to **standard enthalpy change** because we must compare enthalpy changes under identical conditions.

... and also changes in the degree of disorder in a system ...

... and reaches the conclusion that the change in free energy is the factor that decides whether a change will happen

It turns out that the standard enthalpy change is not always successful in predicting whether a reaction will happen. We have to consider another quantity, called **entropy**. This is the degree of disorder in a system. For example, in ice the molecules are ordered in a crystal structure, while in liquid water they are free to move so a certain mass of liquid water contains more entropy than the same mass of ice. A positive change in entropy means that the degree of disorder in the system increases.

The two factors, enthalpy change and entropy change are included in the **free energy change**. Finally we have an answer to the question, 'Will a change happen?' A change happens if the free energy decreases, that is if the free energy of the products is less than the free energy of the reactants.

So, a change happens if it is accompanied by a decrease in free energy. This is not the end of the story, however. We still want to know how fast a change will happen. The answer to that question will be tackled in Chapter 14: Reaction kinetics.

10.4 FORMS OF ENERGY

There are many forms of energy ...

... All are either kinetic or potential energy ...

Heat is kinetic energy

The energy of chemical bonds is potential energy

There are many forms of energy: heat, light, chemical energy, nuclear energy, etc., but basically there are only two kinds of energy, **kinetic energy** and **potential energy**. The energy which an object possesses because it is moving is called kinetic energy. The amount of kinetic energy that an object possesses is the amount of work that it can do before it comes to rest, having used up all its kinetic energy. The energy which an object possesses because of its position or because of the arrangement of its component parts is called potential energy. **Heat** is a form of kinetic energy: it is the kinetic energy associated with the motion of atoms and molecules. The energy of chemical bonds is a form of potential energy, arising from the positions of atoms and molecules with respect to one another. Any piece of matter therefore possesses energy, potential energy, due to the arrangement of its particles. When the matter changes into a different type of matter, in a change of state or a chemical reaction, the positions of the particles relative to one another change: the potential energy of the matter has changed. Energy is taken in or given out by the piece of matter to bring about the change.

The study of the energy changes that accompany chemical reactions is called **thermochemistry** or **chemical thermodynamics**.

The First Law of Thermodynamics states that energy is conserved

Energy can be converted from one form into another. Electrical energy can be converted into heat energy. Our bodies can convert the energy of the chemical bonds in food into other kinds of energy. Calculations on energy conversions show that energy is never created and never destroyed. Observations on physical changes and chemical reactions are summarised in the **First Law of Thermodynamics**. This law states that *energy can be changed from one form into another, but it can neither be created nor destroyed.*

$$\begin{pmatrix}\text{Heat absorbed at}\\ \text{constant pressure}\end{pmatrix} = \begin{pmatrix}\text{Change in}\\ \text{internal energy}\end{pmatrix} + \begin{pmatrix}\text{Work done on}\\ \text{surroundings}\end{pmatrix}$$

The quantity of heat absorbed at constant pressure is called the change in enthalpy, ΔH

Since most laboratory work is carried out at constant pressure, it is usual to deal with the heat absorbed at constant pressure. This quantity is called the change in enthalpy, ΔH. <u>The change in enthalpy is equal to the heat absorbed at constant pressure</u>. Reactions of solids and liquids do not involve large changes in volume, the work done on the surroundings is small, and the change in enthalpy ΔH is close to the change in internal energy.

10.6.1 STANDARD CONDITIONS

Standard conditions: gases at 1 atm, solutions 1 M, solids in their standard states

The value of an enthalpy change depends on the temperature, on the physical states of the reactants (s, l, g), the pressures of gaseous reactants and products and the concentrations of solutions. Enthalpy changes are therefore stated under standard conditions and are denoted by the symbol $\Delta H^\ominus$. **Standard conditions** are: gases at a pressure of 1 atm, solutions at unit concentration and substances in their standard states. The **standard state** of a substance is the pure substance in a specified state (solid, liquid or gas) at 1 atmosphere pressure. A standard enthalpy change may be written $\Delta H^\ominus_T$, meaning the standard enthalpy change at temperature T or $\Delta H^\ominus$, in which case the temperature is 298 K (25 °C). Thus ΔH refers to heat absorbed at constant pressure and $\Delta H^\ominus$ refers to heat absorbed at constant pressure under standard conditions.

10.7 STANDARD ENTHALPY CHANGES

The standard enthalpy changes for some physical and chemical changes are defined below.

10.7.1 CHEMICAL REACTIONS

Standard molar enthalpy change ΔH⊖ ...

... of formation ...

Standard enthalpy of formation, $\Delta H^\ominus_F$, is the heat absorbed per mole when a substance is formed from its elements in their standard states. For example, the standard enthalpy of formation of sodium chloride is calculated for the reaction between solid sodium and gaseous chlorine molecules, Na(s) and Cl_2(g). It follows from this definition that all elements in their standard states have a value of zero for their standard enthalpies of formation. Figure 10.7A illustrates how the value of $\Delta H^\ominus$ may be negative (as for sodium chloride) or positive (as for ethyne). If the enthalpy absorbed is negative, enthalpy is released and the reaction is exothermic.

... of combustion ...

Standard enthalpy of combustion, nation $\Delta H^\ominus_C$, is the heat absorbed per mole when a substance is completely burned in oxygen at 1 atm. Since heat is usually evolved in such a reaction, $\Delta H^\ominus_C$ will be negative.

... of neutralisation ...

Standard enthalpy of neutralisation is the heat absorbed per mole when an acid and a base react to form water under standard conditions.

... of reaction ...

Standard enthalpy of reaction, $\Delta H^\ominus_R$, is the heat absorbed in a reaction at 1 atm between the number of moles of reactants shown in the equation for the reaction.

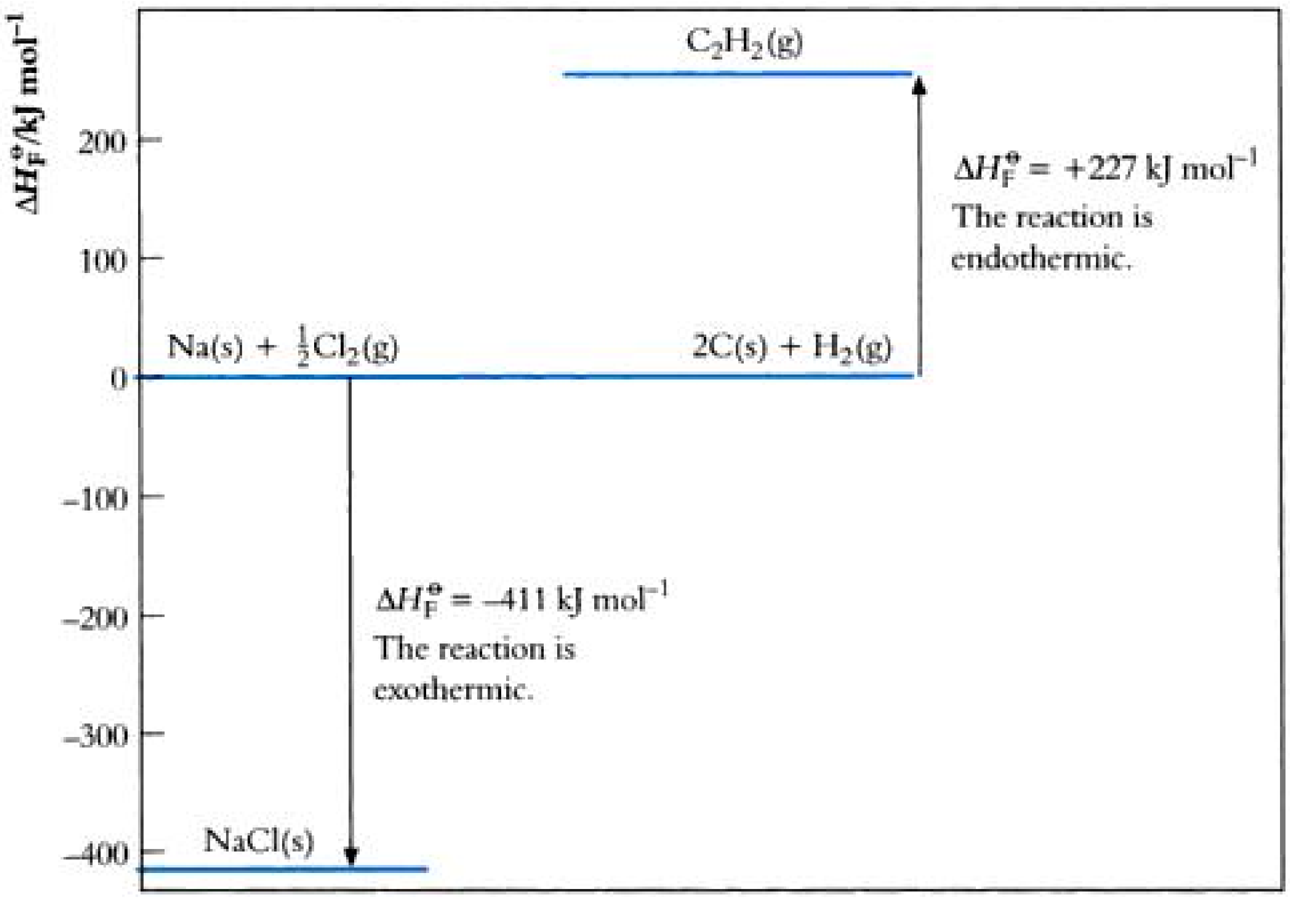


Figure 10.7A
Standard enthalpy of formation

In the reaction

$$4H_2O(l) + 3Fe(s) \longrightarrow Fe_3O_4(s) + 4H_2(g)$$

there is no reason why the standard enthalpy of reaction should be related to 1 mole of iron or 1 mole of steam or 1 mole of iron oxide. Instead, it is related to the whole reaction, as written, between 4 moles of water and 3 moles of iron.

... of dissolution ...

Standard enthalpy of dissolution is the heat absorbed per mole when a substance is dissolved at 1 atm in a stated amount of solvent. This may be 100 g or 1000 g of solvent or it may be an 'infinite' amount of solvent, i.e., a volume so large that on further dilution there is no further heat exchange.

of atomisation

Standard enthalpy of atomisation is the enthalpy absorbed per mole when a substance decomposes to form gaseous atoms.

10.7.2 CHANGES OF STATE

Melting

A change of state ...

... melting, freezing, vaporisation, condensation ...

... involves a change in enthalpy

The particles of a solid are arranged in a regular three-dimensional structure. When a solid is heated the particles gain energy and vibrate more vigorously. Eventually they are able to leave their positions in the structure and move past one another; they flow as a liquid. Melting is endothermic.

- The **enthalpy of melting** or **enthalpy of fusion** of a substance is the enthalpy change per mole when a substance melts.
- The **enthalpy of freezing** of a substance is the enthalpy change per mole when a substance freezes.

Definitions of ...

... ΔH melting ...

... ΔH freezing ...

These changes do not take place under standard conditions. Enthalpy changes of melting and freezing are quoted at 1 atm and at the temperature at which the change of state takes place, that is, the melting temperature. The enthalpy of freezing is the negative of the enthalpy of melting:

$$\Delta H_{\text{freezing}} = -\Delta H_{\text{melting}}$$

Vaporisation

... ΔH *vaporisation* ...

The particles of a liquid are in motion. Forces of attraction keep them in the liquid phase. When a liquid is heated the average energy of the molecules increases. Some molecules, with energy above average, are able to break away from the attraction of other molecules and enter the vapour phase. Vaporisation is endothermic. The **enthalpy of vaporisation** is the difference in enthalpy between the vapour and the liquid state of a substance per mole of substance:

$$\Delta H_{\text{vaporisation}} = \text{Enthalpy of vapour} - \text{Enthalpy of liquid}$$

Enthalpy changes of vaporisation are quoted at 1 atm and at the temperature at which the change of state takes place.

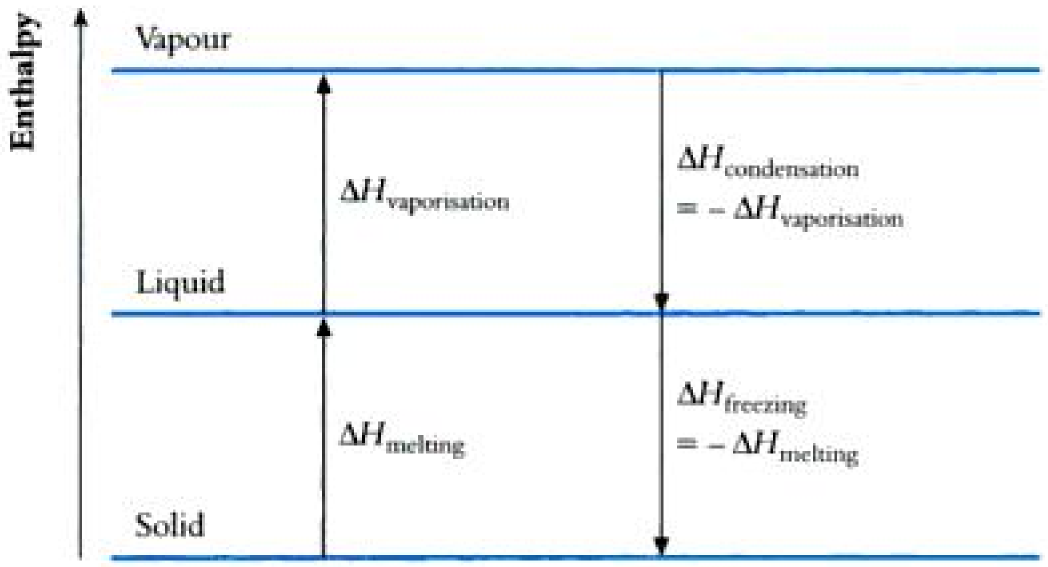
Condensation

... ΔH *condensation* ...

Condensation is the reverse of vaporisation, and is exothermic.

$$\Delta H_{\text{condensation}} = -\Delta H_{\text{vaporisation}}$$

Figure 10.7B
Enthalpy changes of changes of state



SUMMARY

The internal energy of matter is the sum of the kinetic energy and potential energy which it possesses.

Change in enthalpy = Change in internal energy + Work done on surroundings
= Heat absorbed at constant pressure

Standard enthalpy change, $\Delta H^{\ominus}$, = molar enthalpy change under standard conditions. These are: substances in their normal physical states, gases at 1 atm, solutions at 1 mol dm^{-3}. The temperature must be stated.

Definitions of $\Delta H^{\ominus}$ for some chemical reactions and ΔH for some changes of state are given.

10.8 METHODS FOR FINDING THE STANDARD ENTHALPY OF REACTION

10.8.1 THE EXPERIMENTAL METHODS

The methods of finding the standard enthalpy changes of chemical reactions depend on measuring the change in temperature that results as heat is given out

Example 25.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid at 21.5 °C were placed in a polystyrene cup. 25.0 cm^3 of 1.00 mol dm^{-3} sodium hydroxide at 21.5 °C were added. The mixture was stirred, and the temperature rose to 28.2 °C. The density of each solution = 1.00 g cm^{-3}, and the specific heat capacity of each solution = 4.18 J K^{-1} g^{-1}. Calculate the standard molar enthalpy of neutralisation.

Method Mass of solution = 50.0 g

$$\Delta T = 28.2\,°\text{C} - 21.5\,°\text{C} = 6.7\,°\text{C} = 6.7\text{ K}$$

$$\begin{aligned}\text{Heat} &= m \times c \times \Delta T\\ &= 50.0\text{ g} \times 4.18\text{ J K}^{-1}\text{ g}^{-1} \times 6.7\text{ K} = 1400\text{ J}\end{aligned}$$

$$\begin{aligned}\text{Amount of water formed} &= 25.0 \times 10^{-3}\text{ dm}^3 \times 1.00\text{ mol dm}^{-3}\\ &= 2.50 \times 10^{-2}\text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Standard molar enthalpy of neutralisation} &= 1400\text{ J}/2.50 \times 10^{-2}\text{ mol}\\ &= -56.0\text{ kJ mol}^{-1}\end{aligned}$$

The value you will find in tables is -57.9 kJ mol^{-1}. The low experimental value shows that some heat has been lost to the surroundings.

In this example, the heat capacity of the calorimeter is taken to be that of the aqueous solutions in it. The heat capacity of the polystyrene cup is ignored. In more accurate measurements, the heat capacity of the calorimeter is measured and this quantity is used in the calculation.

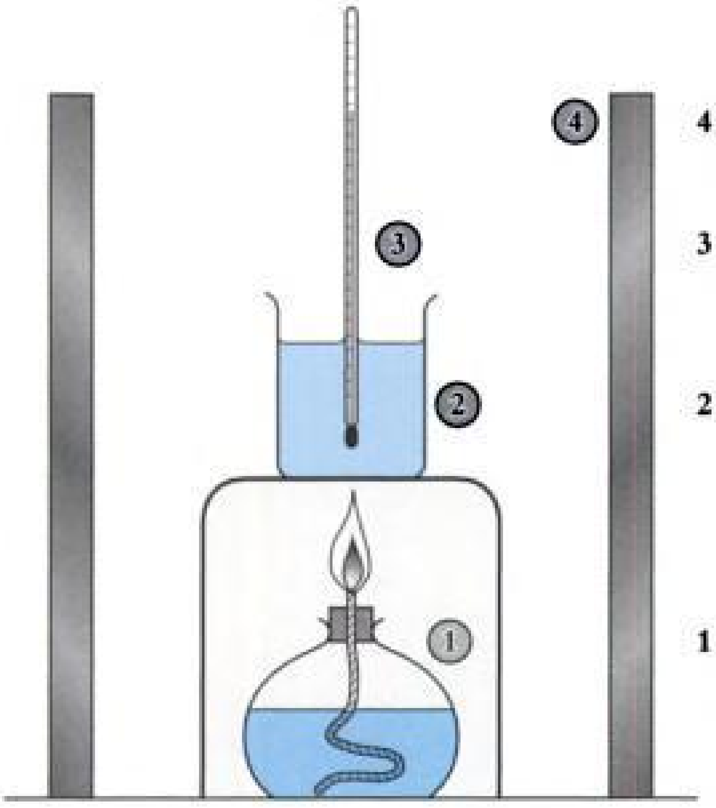
10.8.4 EXPERIMENTAL METHOD FOR FINDING ENTHALPY OF COMBUSTION

Figure 10.8A shows a simple method for obtaining an approximate value for the enthalpy of combustion of a fuel.

$$\text{Fuel(l)} + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$$

Note that the enthalpy of combustion is not $\Delta H^{\ominus}_{\text{combustion}}$ because conditions are not standard. The water formed is not produced in the standard state – liquid; it is water vapour.

Figure 10.8A
Apparatus for finding enthalpy of combustion



4 Shield reduces heat loss to surroundings.

3 Thermometer records rise in temperature, *t* °C.

2 Metal calorimeter contains a known mass of water, m_2 g.

1 Spirit burner contains fuel. Weighing before and after burning gives mass of fuel burnt, m_1 g.

Figure 10.9A
Climbing a mountain

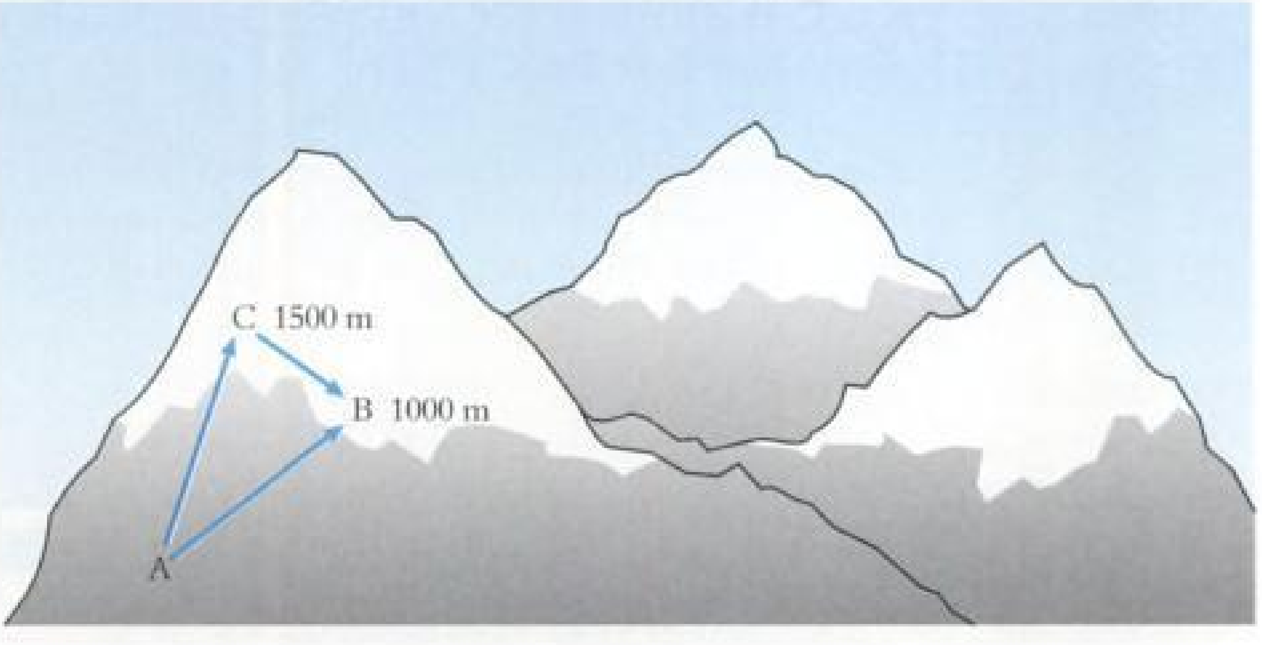
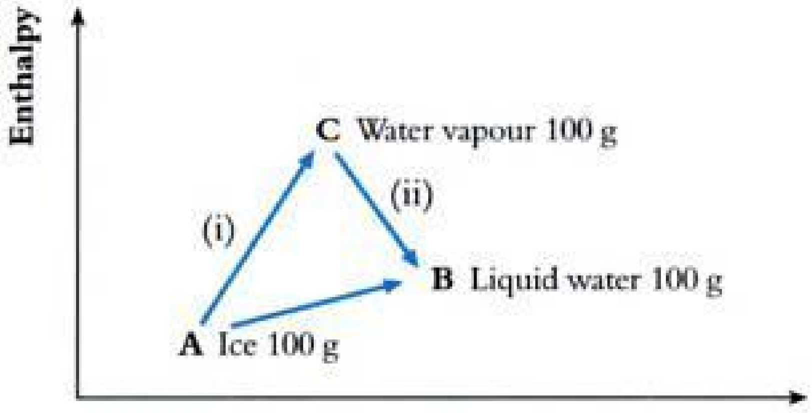


Figure 10.9B
Vaporisation



You may find it helps to compare enthalpy with altitude. The difference in altitude between two places on a mountainside does not depend on the route you take from one to the other. The change in enthalpy when system **A** *changes to system* **B** *does not depend on the reaction route from* **A** *to* **B**

The system **B** consists of 100 g of liquid water at temperature T. To arrive at **B** from **A** by route **A** ⟶ **B**, 100 g of ice is melted.

$$\Delta H = H_{\text{liquid}} - H_{\text{ice}}$$

To arrive at **B** from **A** by route **A** ⟶ **C** ⟶ **B**, 100 g of ice is converted into vapour (by sublimation) and the water vapour is condensed to liquid. The enthalpy changes in (i) **A** ⟶ **C** and (ii) **C** ⟶ **B** are given by

$$\Delta H(\text{i}) = H_{\text{vapour}} - H_{\text{ice}}$$

$$\Delta H(\text{ii}) = H_{\text{liquid}} - H_{\text{vapour}}$$

For route **A** ⟶ **C** ⟶ **B**

$$\begin{aligned}\Delta H &= \Delta H(\text{i}) + \Delta H(\text{ii})\\ &= H_{\text{vapour}} - H_{\text{ice}} + H_{\text{liquid}} - H_{\text{vapour}}\\ &= H_{\text{liquid}} - H_{\text{ice}}\end{aligned}$$

SUMMARY

Hess's Law: If a change can take place by more than one route, the overall change in enthalpy is the same, whichever route is followed.

This ΔH is the same as for route **A** ⟶ **B** so to calculate the change in enthalpy from **A** to **B** you need to know the enthalpies of the initial state **A** and the final state **B**, but you do not need to know what happened on the route from **A** to **B**. J Hess summarised this in **Hess's Law**, which states

> If a change can take place by more than one route, the overall change in enthalpy is the same, whichever route is followed.

Now look at a chemical reaction.

will result in the formation of a mixture of hydrocarbons. However, standard enthalpies of combustion can be measured accurately for all the substances in the equation. They are

[a] $C(s) + O_2(g) \longrightarrow CO_2(g); \Delta H^{\ominus}_{C} = -394\ \text{kJ mol}^{-1}$

[b] $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \Delta H^{\ominus}_{C} = -286\ \text{kJ mol}^{-1}$

[c] $C_2H_2(g) + 2\frac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l); \Delta H^{\ominus}_{C} = -1300\ \text{kJ mol}^{-1}$

The method of calculating $H^{\ominus}_{F}$ (C_2H_2) from these values of $\Delta H^{\ominus}_{C}$ involves three steps:

1. Write the equation for the combustion of ethyne, since this is the reaction for which $\Delta H^{\ominus}$ can be measured.
2. Under each species, write $\Delta H^{\ominus}_{F}$. You can see from equations [a] and [b] that the standard enthalpies of formation of carbon dioxide and water are −394 and −286 kJ mol⁻¹ respectively.

   $C_2H_2(g) + 2\frac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l); \Delta H^{\ominus}_{3} = -1300\ \text{kJ mol}^{-1}$

   $\Delta H^{\ominus}_{F}(C_2H_2)\ 0 \qquad 2(-394) \quad (-286)$

3. Since

   $\Delta H^{\ominus} = \text{Total } H^{\ominus} \text{ of products} - \text{Total } H^{\ominus} \text{ of reactants}$

   $\Delta H^{\ominus}_{3} = -1300 = 2(-394) + (-286) - \Delta H^{\ominus}_{F}(C_2H_2)$

   $\Delta H^{\ominus}_{F}(C_2H_2) = +226\ \text{kJ mol}^{-1}$

   The standard enthalpy of formation of ethyne is 226 kJ mol⁻¹.

Ethyne is described as an **endothermic compound** since $\Delta H^{\ominus}_{F}$ is positive.

$$\boxed{\Delta H^{\ominus}_{\text{Formation}} = \Delta H^{\ominus}_{\text{Combustion}} \text{ of elements} - \Delta H^{\ominus}_{\text{Combustion}} \text{ of compounds}}$$

10.10.2 FINDING THE STANDARD ENTHALPY OF A REACTION

When a physical change or a chemical reaction takes place,

- Standard enthalpy change = Standard enthalpy of products − Standard enthalpy of reactants.
- The standard enthalpy of a substance = its standard enthalpy of formation.

The equation for the hydration of ethene to form ethanol is

Calculating the standard enthalpy of reaction ...

$$CH_2{=}CH_2(g) + H_2O(l) \longrightarrow C_2H_5OH(l)$$
$$(+52) \qquad (-286) \qquad (-278)$$

Written beneath each species is the value of ΔH^{θ}_{F} in kJ mol⁻¹. The **standard enthalpy of reaction** is given by

$$\Delta H^{\ominus}_{R} = -278 - (52 - 286)$$
$$= -44\ \text{kJ mol}^{-1}$$

The reaction is exothermic by 44 kJ mol⁻¹. In short

... The method

$$\boxed{\Delta H^{\ominus}_{\text{Reaction}} = \Sigma\Delta H^{\ominus}_{\text{Formation}} \text{ of products} - \Sigma\Delta H^{\ominus}_{\text{Formation}} \text{ of reactants}}$$

Method In the C_2H_6 molecule are

one C — C bond of standard enthalpy = 348 kJ mol^{-1}

six C — H bonds of standard enthalpy = 2478 kJ mol^{-1}

The total standard enthalpy of the bonds = 2826 kJ mol^{-1}

This is the energy given out when the atoms combine:

$$2C(g) + 6H(g) \longrightarrow C_2H_6(g);\ \Delta H^\ominus = -2826\ \text{kJ mol}^{-1}$$

The standard enthalpy of formation of C(g) from C(s) is 718 kJ mol^{-1}. The standard enthalpy of formation of H(g) from $\frac{1}{2}H_2(g)$ is 218 kJ mol^{-1}. These values of the standard enthalpy content of each species can be put into the equation:

$$\begin{aligned}
&\underset{2(718)}{2C(g)} + \underset{6(218)}{6H(g)} \longrightarrow \underset{\Delta H_F^\ominus}{C_2H_6(g)};\ \Delta H^\ominus = -2826\ \text{kJ mol}^{-1}\\
&\Delta H^\ominus = \Delta H_F^\ominus(\text{product}) - \Delta H_F^\ominus(\text{reactants})\\
&-2826 = \Delta H_F^\ominus - 2(718) - 6(218)\\
&\Delta H_F^\ominus = -82\ \text{kJ mol}^{-1}
\end{aligned}$$

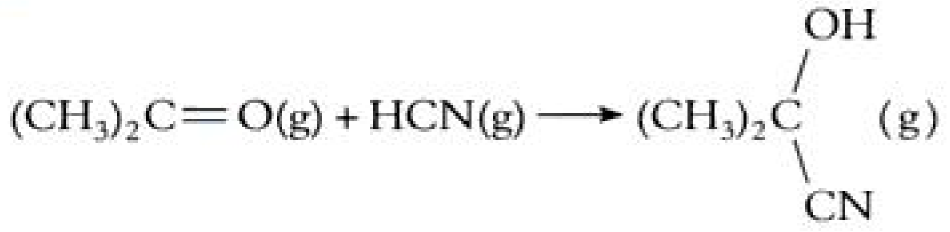
The standard enthalpy of formation of ethane is −82 kJ mol^{-1}.

10.11.1 STANDARD ENTHALPY OF REACTION FROM AVERAGE STANDARD BOND ENTHALPIES

When the standard enthalpy change for a reaction cannot be measured, an approximate value can be obtained by using average standard bond enthalpies. During a reaction, energy must be supplied to break bonds in the reactants, and energy is given out when the bonds in the products form. The standard enthalpy of reaction is the difference between the sum of the average standard bond enthalpies of the products and the sum of the average standard bond enthalpies of the reactants.

Method for calculation of ΔH_R from bond energy terms

Example Calculate the standard enthalpy change of the reaction



$$(CH_3)_2C{=}O(g) + HCN(g) \longrightarrow (CH_3)_2C(OH)(CN)\ (g)$$

Mean standard bond enthalpies/kJ mol^{-1} are C = O, 743; C — H, 412; C — O 360; C — C, 348; H — O, 463.

Method Bonds broken are one C = O of $\Delta H^\ominus$ = 743 kJ mol^{-1}
one C — H of $\Delta H^\ominus$ = 413 kJ mol^{-1}

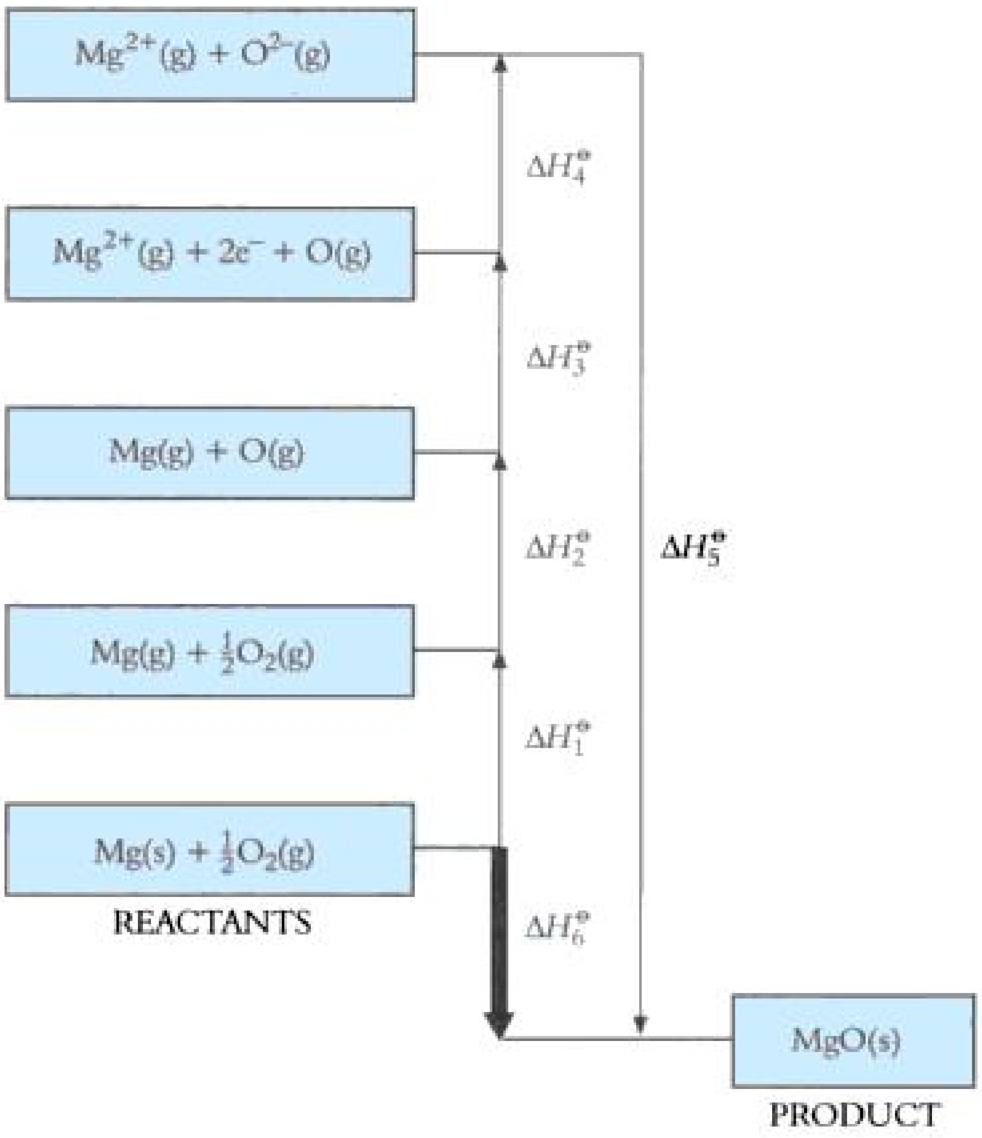
Total standard enthalpy absorbed = 1156 kJ mol^{-1}

Bonds created are one C — O of $\Delta H^\ominus$ = 360 kJ mol^{-1}
one O — H of $\Delta H^\ominus$ = 463 kJ mol^{-1}
one C — C of $\Delta H^\ominus$ = 348 kJ mol^{-1}

Total standard enthalpy absorbed = −1171 kJ mol^{-1}

Standard enthalpy change of reaction = −1171 + 1156
= −15 kJ mol^{-1}

Figure 10.12B
Born–Haber cycle for magnesium oxide



SUMMARY

The **Born–Haber cycle** shows the standard enthalpy terms which are involved when an ionic solid is formed. The cycle is usually employed to calculate electron affinity.

10.13 LATTICE ENTHALPIES

Small ions can approach closely

Some values of lattice enthalpies/kJ mol^{-1} are NaCl −771, KCl −707, NaF −918, CsF −747, NaI −699, MgO −3791, BaO −3054. Where do the differences in lattice enthalpies arise? The question can be answered with the help of ionic radii. Ionic radii/nm are Na^+ 0.102, K^+ 0.138, Cs^+ 0.170, Mg^{2+} 0.072, Ba^{2+} 0.136, F^- 0.133, Cl^- 0.180, I^- 0.219, O^{2-} 0.140.

Multiple charged ions have strong forces of attraction between them

- Comparing NaCl and KCl, the ion Na^+ has a smaller radius than K^+ and can approach more closely to the Cl^- ion. When the ions are closer together the forces of attraction between them are stronger.
- Comparing NaCl and NaF, F^- has a smaller radius than Cl^- and can approach more closely to Na^+.
- Comparing MgO and BaO, Mg^{2+} is much smaller than Ba^{2+}. In MgO the ions are much closer together than in BaO and the forces of attraction between them are stronger.
- Comparing NaCl and MgO, in MgO the ions Mg^{2+} and O^{2-} have two charges each and the forces of attraction are greater than between singly charged ions.

Lattice enthalpy is proportional to product of charges on ions/sum of ionic radii

In general,

$$\text{Lattice enthalpy} \propto \frac{(\text{Charge on cation}) \times (\text{Charge on anion})}{\text{Sum of ionic radii}}$$

CHECKPOINT 10.14: STANDARD ENTHALPY OF REACTION

1. Refer to Figure 10.12B. To what do the symbols $\Delta H_1^\ominus$ to $\Delta H_5^\ominus$ refer? What is the significance of an arrow pointing upwards? Given that the values, in kJ mol^{-1} are: $\Delta H_1^\ominus = +153$, $\Delta H_2^\ominus = +248$, $\Delta H_3^\ominus = +2180$, $\Delta H_4^\ominus = +745$, and $\Delta H_5^\ominus = -3930$, calculate $\Delta H_6^\ominus$, the standard enthalpy of formation of magnesium oxide.

2. The following values are $\Delta H_F^\ominus$/kJ mol^{-1} at 298K:

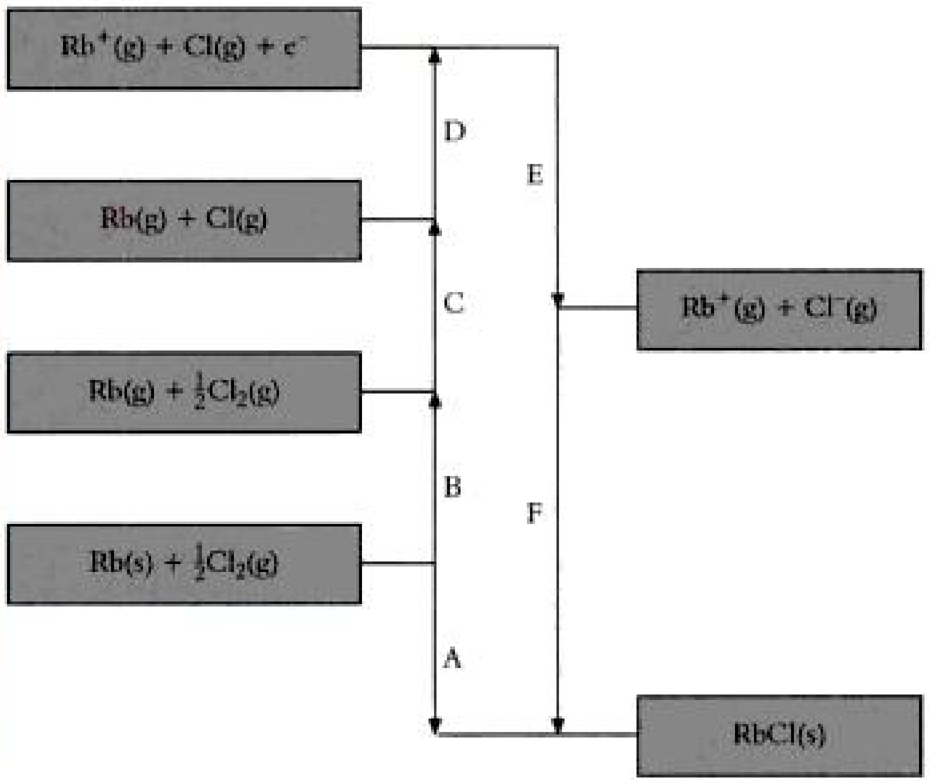
   CH_4(g) – 76; CO_2(g) – 394; H_2O(l) – 286;
   H_2O(g) – 242; NH_3(g) – 46.2;
   C_2H_5OH(l) – 278; C_8H_{18}(l) – 210;
   C_2H_6(g) – 85

   Calculate the standard enthalpy changes at 298 K for the reactions:

   (a) $C_2H_6(g) + 3\tfrac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$
   (b) $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$
   (c) $H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l)$
   (d) $C_8H_{18}(l) + 12\tfrac{1}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(l)$

3. The Born–Haber cycle for rubidium chloride is shown in Figure 10.14C: The letters **A** to **F** represent standard enthalpy changes. Give the names of these quantities. Their values in kJ mol^{-1} are: **A** = –431, **B** = +86, **C** = +122, **D** = +408, **F** = –675. Calculate the value of **E**.

Figure 10.14C
Born–Haber cycle for rubidium chloride (not to scale)



10.15 ENTROPY

A spontaneous change happens without external help

A **spontaneous change** is a change that happens naturally; it tends to occur without the need to be driven by an external influence. One can accept that exothermic reactions can happen spontaneously because they involve a decrease in the enthalpy of the system. It is rather analagous to a ball spontaneously rolling downhill. It is more difficult to explain why an endothermic reaction can happen spontaneously with an increase in the enthalpy of the system. One does not expect a ball to roll uphill spontaneously: some force must be applied to it. There must be a factor in addition to the enthalpy change that enables some endothermic changes to occur spontaneously. What are the conditions that decide whether a change can occur spontaneously?

Consider some spontaneous changes.

Spontaneous changes involve an increase in disorder ...

- When gases come into contact they diffuse to form a homogeneous mixture. Instead of a tidy arrangement of different molecules in different containers, the molecules become mixed up in a random arrangement. The pattern is that mass tends to become more disordered.

... e.g. diffusion ...

... dissolution ...

... melting ...

- Potassium chloride dissolves endothermically. The solid is a highly ordered arrangement of potassium ions and chloride ions. When it dissolves, this regular arrangement is replaced by a random distribution of ions in solution.

  $$KCl(aq) + aq \longrightarrow KCl(aq);\ \Delta H^\ominus = +19 \text{ kJ mol}^{-1}$$

10.17 LINK WITH KINETICS

Which decides whether reactions happen, thermodynamics or kinetics?

Thermodynamic studies tell us $\Delta G^\ominus$ and therefore whether a change is feasible ...

If $\Delta G^\ominus$ for a change is negative, we can state that the reactants are thermodynamically unstable relative to that change. Methane is thermodynamically stable with respect to dissociation into its elements:

$$CH_4(g) \longrightarrow C(g) + 2H_2(g); \Delta G^\ominus = +51 \text{ kJ mol}^{-1}$$

Methane is thermodynamically unstable relative to oxidation:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l); \Delta G^\ominus = -580 \text{ kJ mol}^{-1}$$

... Kinetic studies tell us the energy of activation and therefore how fast a change will happen

Thermodynamic instability ($\Delta G^\ominus$ is negative) relative to a certain change is a necessary condition for that change to occur, but it is not the only necessary condition. Methane does not react with air at a measurable rate at room temperature (in the absence of UV light). The reason is that a large amount of energy, called the **activation energy**, must be supplied to enable the molecules to react. The concept of activation energy is covered in Chapter 14. Briefly, the idea is that, although the product molecules have a lower free energy content than the reactant molecules, there is an energy barrier in between the reactant and the product molecules. The reactant molecules must be given enough energy to surmount this barrier in order to react. Very, very few molecules of reactant acquire this activation energy at room temperature. In consequence, the overall rate of reaction is so slow as to be unobservable. The reaction is described as being **under kinetic control**. If the temperature is raised sufficiently, the proportion of energetic molecules increases, and the reaction takes place at a measurable rate. Substances which react slowly because the activation energy of the reaction is high and the temperature is too low are described as **unreactive** or **non-labile** or **inert**.

SUMMARY

Will a change happen? Thermodynamics does not tell the whole story. Even when a reaction is favoured by thermodynamics, it may take place so slowly as to be unobservable. The reason is the kinetic factor. The activation energy must be supplied before reaction can happen; see Chapter 14.

FURTHER STUDY ▲

(ii) Why is the term *mean bond enthalpy* used in the table instead of just *bond enthalpy*?

(iii) Use the data above to predict what happens first when a sample of propane, C_3H_8, is cracked in the absence of air and explain your prediction. **5**

(c) Use the following data to calculate the standard enthalpy of formation of propane. **4**

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) \quad \Delta H^{\ominus} = -2220 \text{ kJ mol}^{-1}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \ \Delta H^{\ominus} = -286 \text{ kJ mol}^{-1}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g) \ \Delta H^{\ominus} = -394 \text{ kJ mol}^{-1}$$

10 *NEAB (AS/AL)*

16. When methane is burned in air, the following reactions, **I**, **II**, and **III**, are all feasible.

$$\textbf{I}\ CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$$
$$\Delta H^{\ominus}_{298} = -802 \text{ kJ mol}^{-1}$$
$$\Delta S^{\ominus}_{298} = -5.10 \text{ J K}^{-1}\text{ mol}^{-1}$$

$$\textbf{II}\ CH_4(g) + \tfrac{3}{2}O_2(g) \rightleftharpoons CO(g) + 2H_2O(g)$$
$$\Delta H^{\ominus}_{298} = -519 \text{ kJ mol}^{-1}$$
$$\Delta S^{\ominus}_{298} = +81.7 \text{ J K}^{-1}\text{ mol}^{-1}$$

$$\textbf{III}\ CH_4(g) + O_2(g) \rightleftharpoons C(s) + 2H_2O(g)$$
$$\Delta H^{\ominus}_{298} = -409 \text{ kJ mol}^{-1}$$
$$\Delta S^{\ominus}_{298} = -8.00 \text{ J K}^{-1}\text{ mol}^{-1}$$

Some further thermodynamic data for reaction **II** are shown in the table below. Similar data for reactions **I** and **III** are shown in graphical form below.

Temperature/K	**$\Delta G^{\ominus}$/kJ mol^{-1}**
1500	−642
3000	−764
4000	−846

(a) State the meaning of the term *mean bond enthalpy*. Show how mean bond enthalpy data could be used to estimate the enthalpy change in reaction **I**. **5**

(b) (i) Calculate the value of $\Delta G^{\ominus}_{298}$ for reaction **II** and, on a copy of the graph below, plot the value you calculate, together with values from the table above.

(ii) Explain how the gradient of the graph for reaction **I** is related to the entropy change, ΔS, for that reaction.

(iii) Explain why $\Delta S^{\ominus}_{298}$ for reaction **I** is similar to that for reaction **III**, whereas $\Delta S^{\ominus}_{298}$ for reaction **II** is very different from the other two. **10**

(c) (i) Explain the term *feasible reaction* and explain how feasibility is related to the change in free energy, $\Delta G^{\ominus}$, and to the value of the equilibrium constant, K_c.

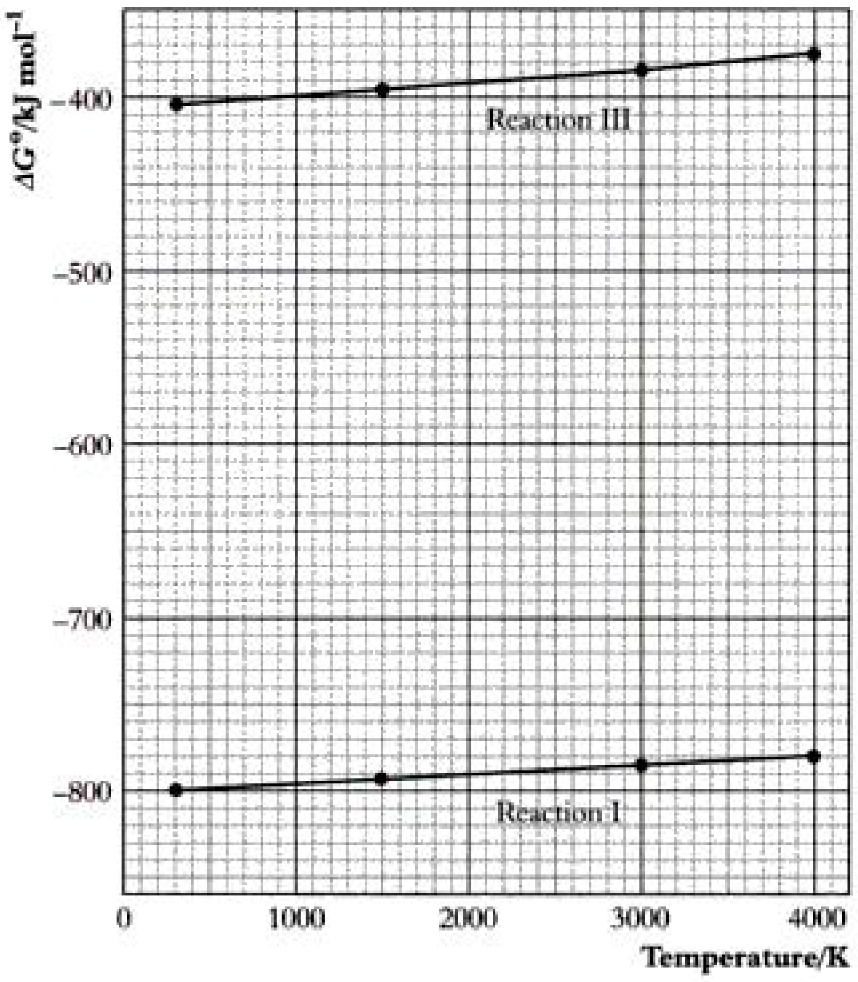
(ii) All three reactions **I**, **II** and **III**, are said to be feasible at temperatures between 0 K and 4000 K. Justify this assertion and explain why, despite this, methane is not oxidised appreciably by air at room temperature. Deduce which of the three reactions is the most feasible at 3000 K. Hence explain why a smoky Bunsen flame (which results from reaction **III**) must be the consequence of a reaction which does not reach equilibrium. **5**

(d) (i) Write expressions for the equilibrium constants K_c(I) (which refers to reaction **I**) and K_c(II) (which refers to reaction **II**), and also for K_c(IV) (the equilibrium constant for reaction **IV** below).

$$\textbf{IV}\ CO(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$$

Show that $K_c(\text{IV}) = \dfrac{K_c(\text{I})}{K_c(\text{II})}$

(ii) There exists a temperature T_x, at which reactions **I** and **II** are equally feasible. Deduce the value of T_x from your graph and using the expression in part *(d)* (i), deduce also the value of K_c(IV) at this temperature. Derive the units of K_c(IV). **10**



For part *(d)* see Chapter 11.

30 *NEAB (AL)*

Square brackets represent concentrations in mol dm^{-3}. The ratio, K_c, has a constant value at a particular temperature, no matter what amounts of HI, I_2 and H_2 are taken initially. K_c is the **equilibrium constant** for the reaction in terms of concentration.

The esterification reaction reaches equilibrium ...

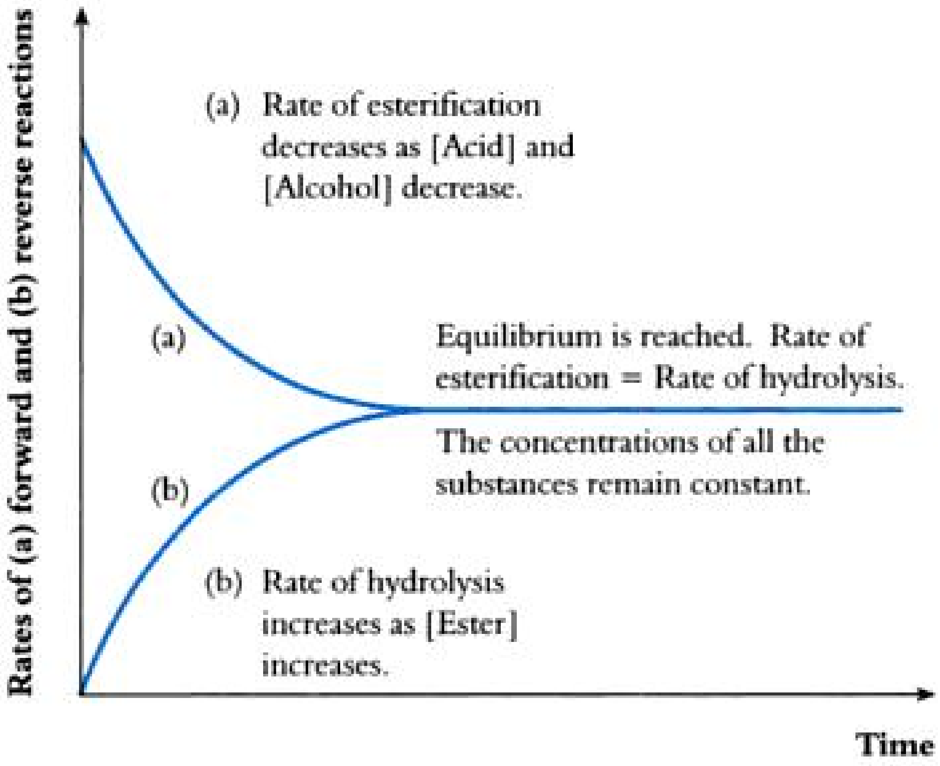
An example of a reversible reaction in solution is the esterification of ethanoic acid by ethanol to make ethyl ethanoate. This ester is hydrolysed by water to ethanoic acid and ethanol:

$$CH_3CO_2H(l) + C_2H_5OH(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$$

Figure 11.2B shows what happens when ethanoic acid and ethanol are mixed and allowed to come to equilibrium.

Figure 11.2B
An esterification reaches equilibrium

... because the ester is partially hydrolysed to form acid + alcohol



The concentrations of the reactants and products at equilibrium fit the equilibrium law

The equilibrium concentrations of acid, alcohol, ester and water obey the law

$$\frac{[CH_3CO_2C_2H_5][H_2O]}{[CH_3CO_2H][C_2H_5OH]} = K_c$$

K_c is the equilibrium constant for the esterification.

Esterification is catalysed by inorganic acids. The presence of a catalyst does not alter the equilibrium constant. Its effect is to decrease the time needed for the system to reach a state of equilibrium.

The reaction between iron and steam reaches equilibrium provided that it takes place in a closed container

These two reactions are examples of **homogeneous** equilibria, the first in the gas phase and the second in the liquid phase. If the reactants are in different phases, the equilibrium is described as **heterogeneous**. An example of a heterogeneous equilibrium is the reaction between steam and heated iron to form iron(II) iron(III) oxide Fe_3O_4, and hydrogen:

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

If the reaction takes place in a closed container, the system reaches equilibrium. In an open container, hydrogen escapes. In an effort to restore equilibrium, more iron reacts with steam to make more hydrogen. When this reaction was used industrially to make hydrogen, the yield was increased by passing a stream of steam over heated iron, and not allowing the system to come to equilibrium [see also § 11.6.3].

3. In the equilibrium

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g);\ \Delta H^{\ominus} = 90\ \text{kJ mol}^{-1}$$

what is the effect on (*a*) the position of equilibrium and (*b*) the equilibrium constant of (i) increasing the temperature, (ii) decreasing the volume of the container (iii) adding a catalyst, (iv) adding $Cl_2(g)$ and (v) adding a noble gas? Explain your answers.

4. The freezing of water at 0 °C is represented

$$H_2O(l, \rho = 1.00\ \text{kg dm}^{-3}) \rightleftharpoons H_2O(s, \rho = 0.92\ \text{kg dm}^{-3})$$

Explain why the application of pressure to ice at 0°C makes it melt. Why do most other solids not show the same behaviour?

11.6 EXAMPLES OF REVERSIBLE REACTIONS

11.6.1 REACTION 1: ESTERIFICATION

Ethanoic acid and ethanol react to form ethyl ethanoate and water

$$CH_3CO_2H(l) + C_2H_5OH(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$$

The mixture reaches equilibrium:

$$\frac{[CH_3CO_2C_2H_5][H_2O]}{[CH_3CO_2H][C_2H_5OH]} = K_c$$

The reaction is catalysed by acid. The value of K_c can be found by the following method.

A method of finding K_c for the esterification reaction between ethanol and ethanoic acid

1. A number of mixtures are made up, containing ethanol, ethanoic acid, ethyl ethanoate and water. Each mixture is different. Every mixture contains a small amount of hydrochloric acid to catalyse the reaction.
2. The mixtures are put into stoppered bottles and left for a week in a thermostat bath.
3. At the end of the week, the contents of each flask are titrated against standard sodium hydroxide solution, using phenolphthalein as indicator. The titration gives the amount of CH_3CO_2H + the amount of HCl. The amount of HCl is still the same as that present initially. The amount of CH_3CO_2H is found by subtraction.
4. The amounts of the other substances present are calculated.

A sample calculation A 10.0 cm^3 mixture contains the initial amounts/mol ethanol 0.0515; ethanoic acid 0.0525; water 0.0167; ester 0.0314; $H^+(aq)$ 1.00×10^{-3}.

The equilibrium amount of ethanoic acid = 0.0255 mol.
Since the amount of ethanoic acid has decreased by 0.0270 mol, ethanol has decreased by the same amount, and ester and water have both increased by this amount.

Species	$CH_3CO_2H +$	$C_2H_5OH \rightleftharpoons$	$CH_3CO_2C_2H_5 +$	H_2O
Initial amount/mol	0.0525	0.0515	0.0314	0.0167
Equilibrium amount/mol	0.0255	0.0245	0.0584	0.0437

Since

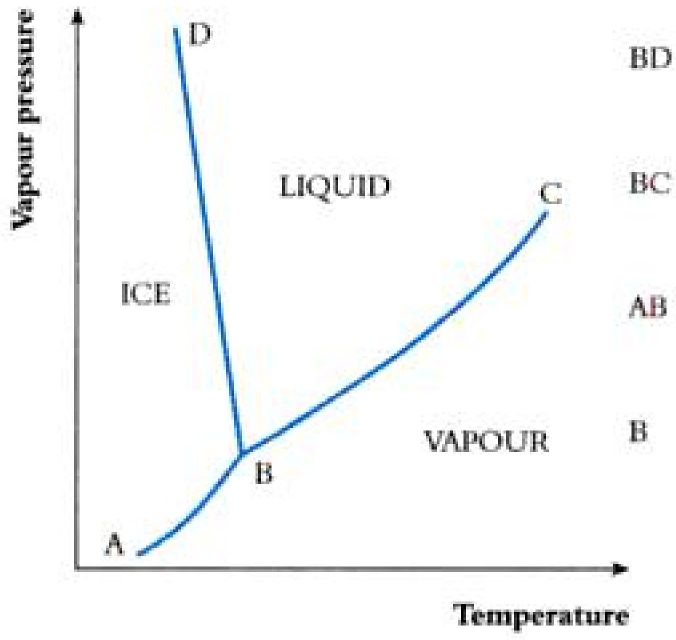
$$K_c = \frac{[CH_3CO_2C_2H_5][H_2O]}{[CH_3CO_2H][C_2H_5OH]}$$

Figure 11.8A
Phase equilibrium diagram for water (not to scale)

... an area = one phase ...

... a line = two phases ...

... a point = three phases, and is named a triple point

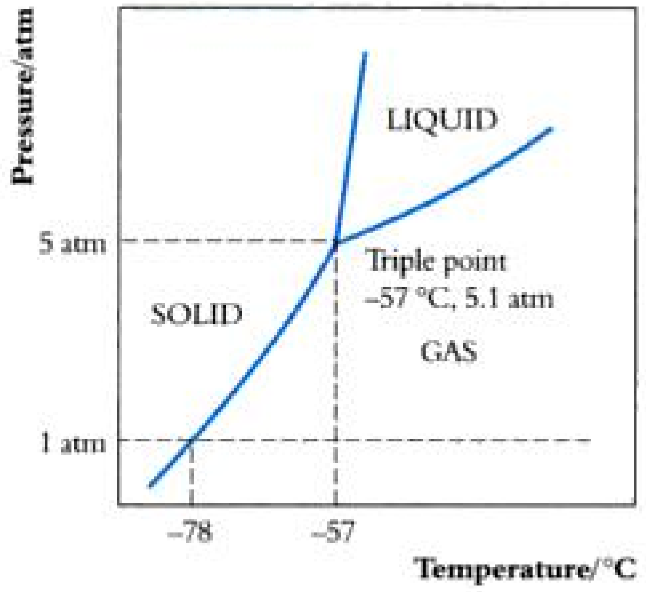


BD = Effect of pressure on freezing temperature of water.
BC = Effect of temperature on saturated vapour pressure of water.
AB = Effect of temperature on saturated vapour pressure of ice.
B = Conditions under which solid, liquid and gaseous forms can coexist – a triple point.

11.8.2 CARBON DIOXIDE

Figure 11.8B shows the phase diagram for carbon dioxide.

Figure 11.8B
Phase equilibrium diagram for carbon dioxide (not to scale)



Many other chapters deal with systems which come to equilibrium; they include chromatography § 8.7, acids and bases Chapter 12 and electrochemical cells Chapter 13.

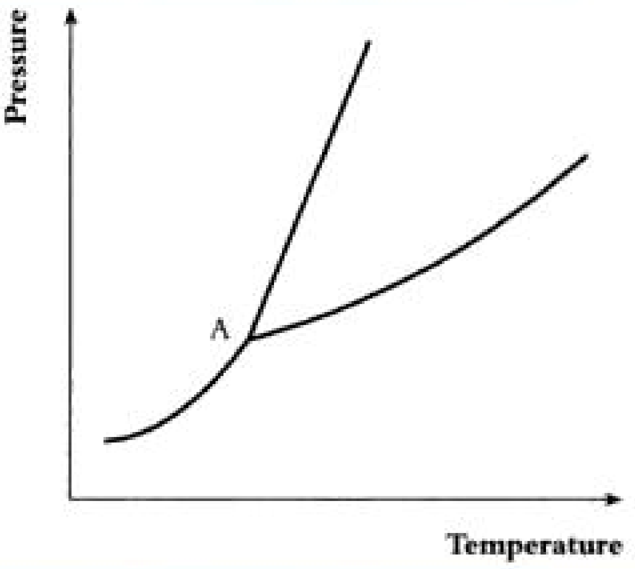
CHECKPOINT 11.8: PHASE EQUILIBRIA

1. Figure 11.8C shows the pressure–temperature phase diagram for substance **X**.

(a) Trace the figure. On your copy, mark the areas S (solid) L (liquid) and G (gas).
(b) Name the point A, and explain its significance.
(c) Say, with an explanation, how the freezing temperature of pure X varies with an increase in pressure.

2 *(a)* What is sublimation?
(b) Which line in Figure 11.8B represents sublimation?
(c) State one respect in which the phase diagram of carbon dioxide differs from that of water.

Figure 11.8C
Pressure-temperature phase diagram



12

ELECTROCHEMISTRY

12.1 SIR HUMPHRY DAVY (1778–1829) AND MICHAEL FARADAY (1791–1867)

The science of electrochemistry was developed by Davy and Faraday.

Sir Humphry Davy is famous for his invention of the miner's safety lamp. He refused to patent his invention, saying, 'My sole object was to serve the cause of humanity'. A group of mine owners who appreciated the benefit to their workers presented Davy with a silver dinner service. The silver dinner service was sold and the funds used to endow the Royal Society Davy medal, which is awarded annually for the most important chemical discovery in Europe and North America. The first person to receive it, in 1877, was Robert Bunsen.

Davy was born in Penzance, Cornwall, in 1778, the eldest son of a woodcarver. On leaving school at 16, he was employed by a surgeon, who encouraged Davy to educate himself. At the age of 19, Davy went to work in an institute for medical research in Bristol. Within a few months, he had discovered the anaesthetic properties of laughing gas, N_2O. Davy was quick to take advantage of Volta's invention of the galvanic pile, which gave a reliable source of electricity that could be used to investigate electrolysis. It enabled Davy to isolate by electrolysis six new elements: sodium, potassium, magnesium, calcium, strontium and barium. He demonstrated that chlorine is an element and identified iodine. Davy was appointed to a lectureship in the Royal Institution. He gave spectacular lectures which were so popular that traffic jams formed in the street outside whenever he lectured. At the age of 34, Davy was knighted.

Another of Davy's discoveries was Michael Faraday (see § 4.2). Faraday put the new science of electrochemistry on a quantitative basis. (see § 12.2). While Davy had a social life and a number of hobbies, including travel, hunting and fishing, Faraday's time was fully occupied with his work and his religion. He had no students and did all his experiments himself. He turned down offers of a knighthood and the presidency of the Royal Society. He made time to be active in church work. Like Davy, Faraday was an inspiring lecturer. He followed Davy as professor of chemistry in the Royal Institution and continued the popular science lectures for the public that Davy had started.

12.2 ELECTROLYSIS

Some compounds conduct electricity when in the molten state or in solution [§§ 4.2.3, 4.2.4]. When compounds conduct electricity, chemical changes occur and new substances are formed. The compounds which conduct electricity and are decomposed by it are called **electrolytes**, and the chemical changes **electrolysis**. The container in which electrolysis takes place is called a **cell**, and the conductors which carry electricity into and out of the cell are called **electrodes**. In an electrolysis cell, an electric current brings about a chemical change. There is another type of cell, a chemical cell in which a chemical change gives rise to an electric current, which you will meet in Chapter 13. The reactions in both types of cell are called **electrochemical reactions**.

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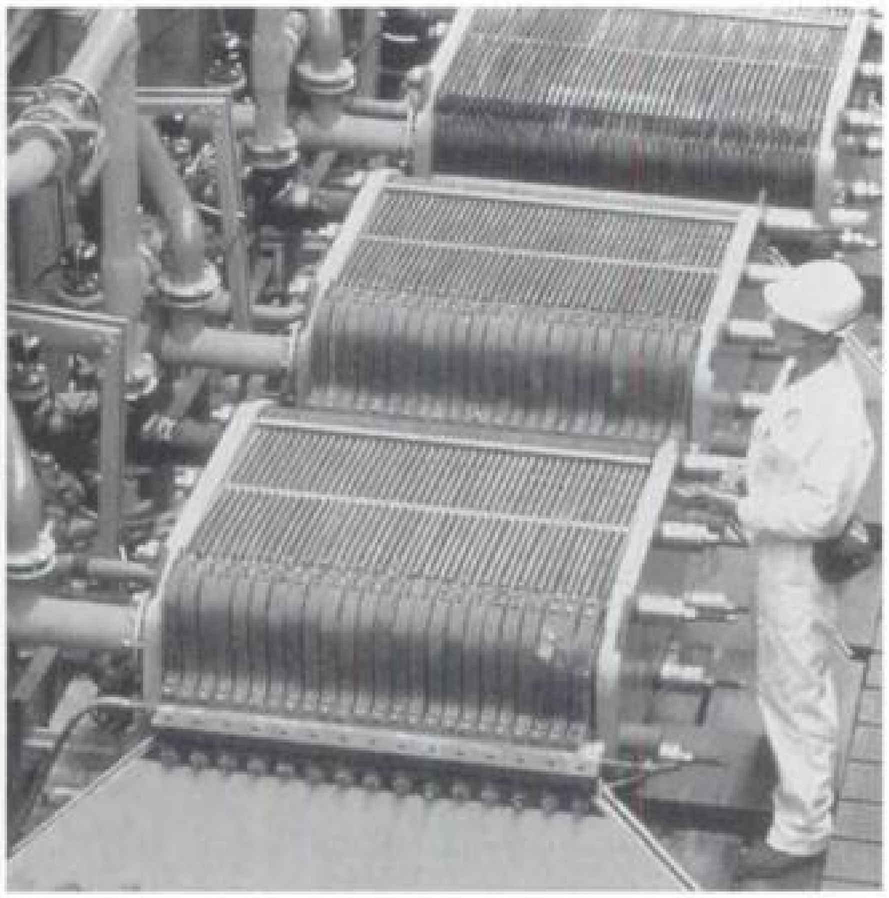
Figure 12.3A
Manufacture of sodium hydroxide and chlorine by electrolysis of brine in diaphragm cells at ICI, Lostock



12.4 EXPLANATION OF ELECTROLYSIS

12.4.1 ELECTROLYSIS OF AN AQUEOUS SALT

Figure 12.4A
Electrolysis of aqueous lead(II) chloride

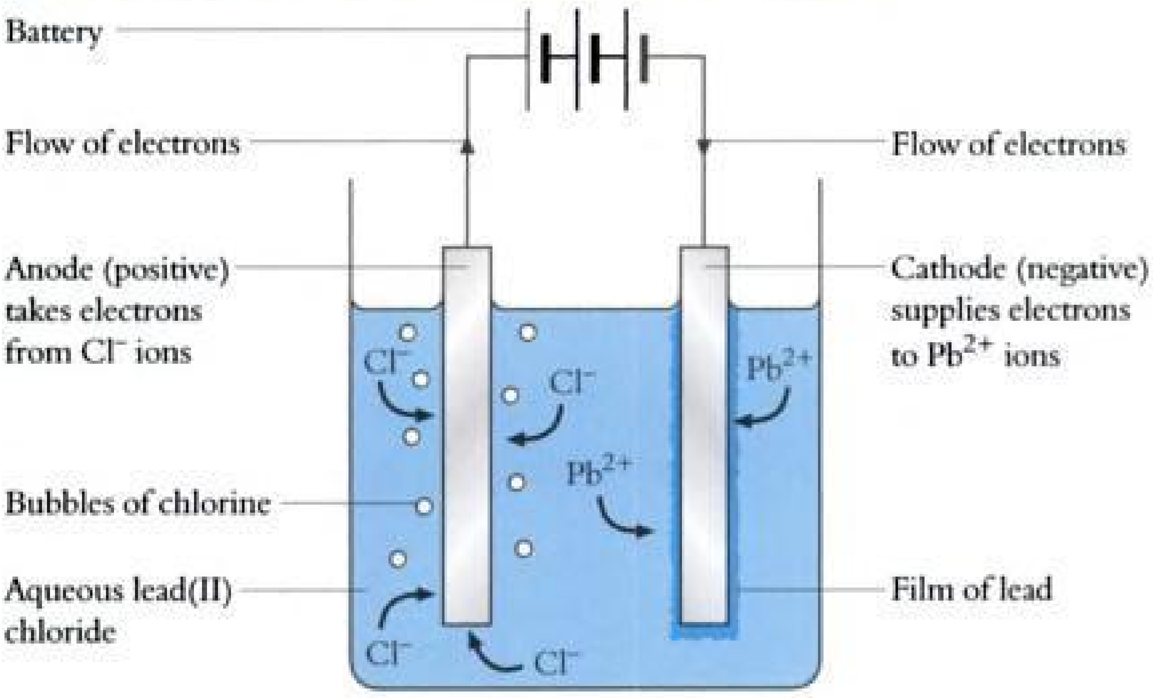


Figure 12.4A shows what happens when aqueous lead(II) chloride is electrolysed. Lead cations are attracted to the cathode. This negative electrode supplies electrons which discharge the cations to form atoms of lead.

Equations for electrode processes

$$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$$

The chloride anions are attracted to the anode. Being positively charged, the anode takes electrons from the anions, thus discharging them:

$$Cl^-(aq) \longrightarrow Cl(g) + e^-$$

The electrode process is followed by the formation of chlorine molecules:

$$2Cl(g) \longrightarrow Cl_2(g)$$

The flow of current through the external circuit

As the anode takes electrons from Cl^- ions and the cathode supplies electrons to Pb^{2+} ions, electrons flow through the external circuit from anode to cathode. The electric current is conducted through the cell by ions and through the external circuit by electrons.

CHECKPOINT 12.5: ELECTROLYSIS

1. The same current was passed through molten sodium chloride and through molten cryolite containing aluminium oxide. If 4.60 g of sodium were liberated in one cell, what mass of aluminium was liberated in the other?

2. What mass of each of the following substances will be liberated by the passage of 0.200 mol of electrons?

   (a) Mg(s) from $MgCl_2(l)$, *(b)* $Cl_2(g)$ from NaCl(aq), *(c)* Cu(s) from $CuSO_4(aq)$, *(d)* Pb(s) from $Pb(NO_3)_2(aq)$, *(e)* $H_2(g)$ from NaCl(aq).

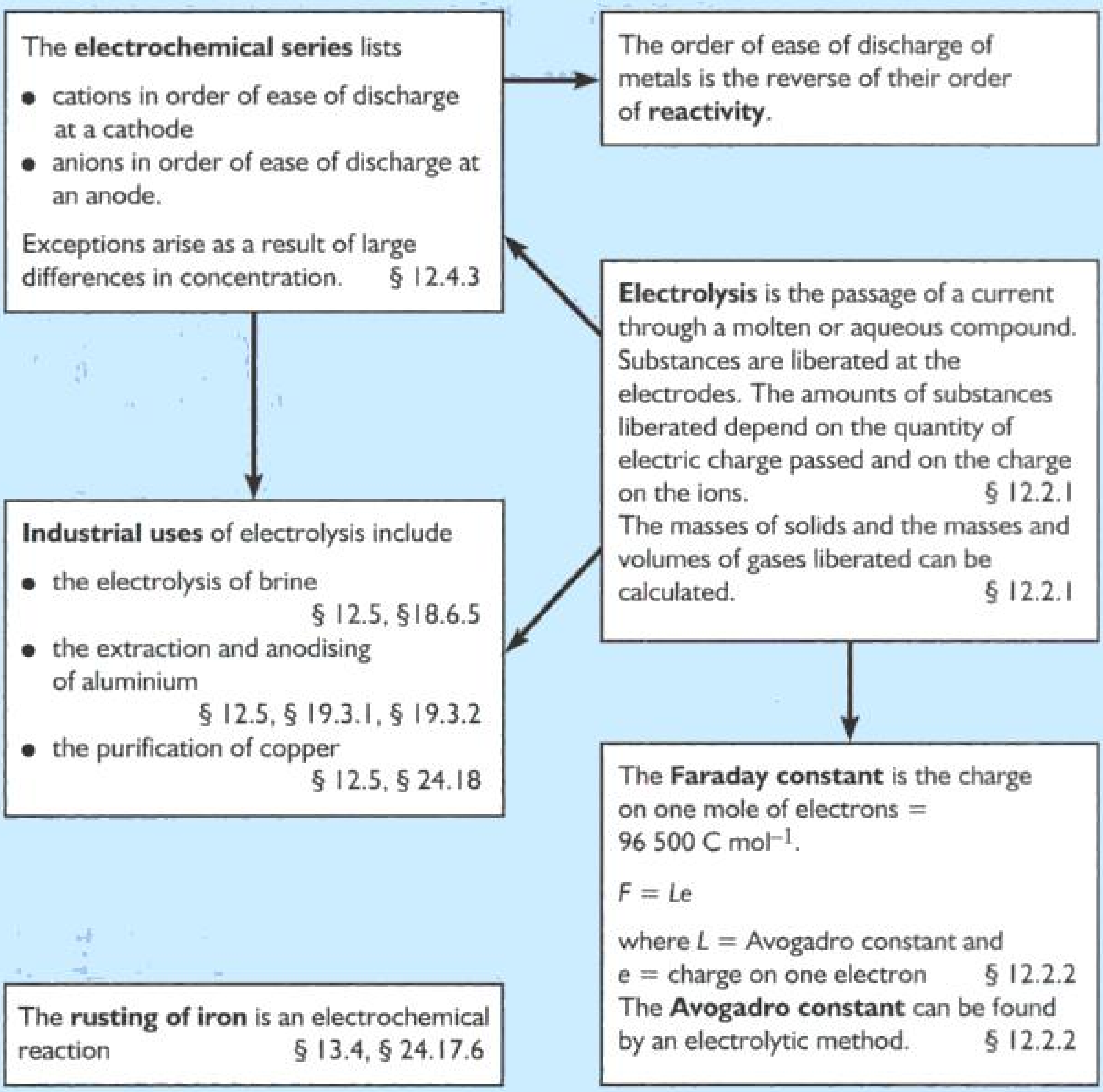
3. During the electrolysis of a 1.00 mol dm^{-3} solution of copper(II) sulphate at 20 °C, a current of 0.100 A was passed for 1.00 h. The mass of the copper cathode increased by 0.118 g. State how the change in mass would be affected if the experiment were repeated

   (a) at a current of 0.200 A, *(b)* at 30 °C, *(c)* with a 2.00 mol dm^{-3} solution of copper(II) sulphate, *(d)* for a time of 2.00 h.

4. When a metal of relative atomic mass 207 is deposited by electrolysis, a current of 0.0600 A flowing for 66 min increases the mass of the cathode by 0.254 g.

   Find the number of moles of metal deposited and the number of moles of electrons that have passed. Deduce the number of units of charge on the cations of this metal.

ELECTROLYSIS



The **electrochemical series** lists
- cations in order of ease of discharge at a cathode
- anions in order of ease of discharge at an anode.

Exceptions arise as a result of large differences in concentration. § 12.4.3

The order of ease of discharge of metals is the reverse of their order of **reactivity**.

Electrolysis is the passage of a current through a molten or aqueous compound. Substances are liberated at the electrodes. The amounts of substances liberated depend on the quantity of electric charge passed and on the charge on the ions. § 12.2.1
The masses of solids and the masses and volumes of gases liberated can be calculated. § 12.2.1

Industrial uses of electrolysis include
- the electrolysis of brine § 12.5, §18.6.5
- the extraction and anodising of aluminium § 12.5, § 19.3.1, § 19.3.2
- the purification of copper § 12.5, § 24.18

The **Faraday constant** is the charge on one mole of electrons = 96 500 C mol^{-1}.

$F = Le$

where L = Avogadro constant and
e = charge on one electron § 12.2.2
The **Avogadro constant** can be found by an electrolytic method. § 12.2.2

The **rusting of iron** is an electrochemical reaction § 13.4, § 24.17.6

Method

Since

... Calculation of pOH

$$[OH^-] = 0.01 = 10^{-2}\ \text{mol dm}^{-3}$$

$$pOH = 2$$

$$pH = 14 - pOH = 12 \text{ at } 25\ °C$$

At 25 °C, solutions with a pH of 7 are neutral, solutions with a pH less than 7 are acidic, and solutions with a pH greater than 7 are alkaline. The relationship between pH and $[H_3O^+]$ and $[OH^-]$ is illustrated in Table 12.6.

Table 12.6
pH values of acidic and alkaline solutions

$[H_3O^+]$/ mol dm^{-3}	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
$[OH^-]$/ mol dm^{-3}	10^{-14}	10^{-13}	10^{-12}	10^{-11}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1
pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	◄ Strongly acidic	►	◄ Weakly acidic				Neutral	► ◄		Weakly alkaline			► ◄ Strongly alkaline		►

CHECKPOINT 12.6A: ACIDS AND BASES

1. Define the terms *Brönsted acid* and *Brönsted base*. Give two examples of each, explaining how they fit the definitions. Define the terms *Lewis acid* and *Lewis base*, and give one example of each.

†2. Explain the following statements:

(*a*) $[Al(H_2O)_6]^{3+}$ is classified as an acid [§ 19.4.1].
(*b*) $ClCH_2CO_2H$ is a stronger acid than CH_3CO_2H [§ 12.6.6].
(*c*) The Friedel–Crafts catalyst, $AlCl_3$, is classified as a Lewis acid [§ 28.8.7].

3. How are Lewis acids and bases different from Brönsted–Lowry acids and bases and from Arrhenius acids and bases?
In the equilibrium

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

which species is the acid and which the base, according to the definitions of (*a*) Arrhenius and (*b*) Lowry and Brönsted?

4. According to the Brönsted–Lowry theory, water can function as an acid and as a base. Quote one reaction in which water acts as an acid and one in which it acts as a base.

5. At 0 °C, $K_w = 1.14 \times 10^{-15}\ \text{mol}^2\ \text{dm}^{-6}$. Find:

(*a*) pK_w, at 0 °C
(*b*) the pH at 0 °C of a 0.01 mol dm^{-3} solution of sodium hydroxide

6. Name the Lewis acid and the Lewis base in the following reactions:

(*a*) $RCOBr + FeBr_3 \rightleftharpoons RCO^+FeBr_4^-$
(*b*) $Ag^+ + 2NH_3 \longrightarrow Ag(NH_3)_2^+$
(*c*) $CH_3CO_2^- + 2HF \longrightarrow CH_3CO_2H + HF_2^-$

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CHECKPOINT 12.6B: pH AND DISSOCIATION CONSTANTS

1. The value of K_w, the ionic product for water, increases with temperature. Will the pH of pure water be greater or less than 7 at 100 °C?

2. The pH values of 0.100 mol dm^{-3} solutions of hydrochloric acid and ethanoic acid are 1 and approximately 3 respectively. How does this difference arise?

3. Give an expression for the dissociation constant, K_a, of a weak acid. How is pK_a related to K_a? If two acids, H**A** and H**B**, have pK_a values of 3.4 and 4.4, what can you say about the relative strengths of the two acids?

4. Explain what is meant by a conjugate acid–base pair. Give two examples.

5. Find the pH of the following solutions at 25 °C:

(a) 0.001 00 mol dm^{-3} HCl(aq)
(b) 2.50×10^{-2} mol dm^{-3} $HClO_4$(aq) (a strong acid)
(c) 3.60×10^{-5} mol dm^{-3} HNO_3(aq)
(d) 2.50×10^{-2} mol dm^{-3} NaOH(aq)
(e) 3.00×10^{-3} mol dm^{-3} $Ca(OH)_2$(aq)

6. Find the pH of the following solutions:

(a) 1.00×10^{-2} mol dm^{-3} ethanoic acid (pK_a = 4.76)
(b) 0.100 mol dm^{-3} methanoic acid (pK_a = 3.75)

7. Find the dissociation constants of the following acids from the data:

(a) A solution of 2.00 mol dm^{-3} hydrogen cyanide has a pH of 4.55.
(b) A solution of 1.00 mol dm^{-3} iodic(I) acid has a pH of 5.26.

12.7 INDICATORS

Indicators are weak acids or weak bases ...

The indicators used in acid–base titrations are weak acids or weak bases. The ions are of a different colour from the undissociated molecules. Litmus is a weak acid, which can be represented by the formula HL. In solution

$$HL + H_2O \rightleftharpoons H_3O^+ + L^-$$

... Litmus

The molecules HL are red, and the anions L^- are blue. The dissociation constant of the indicator is

$$K_a = \frac{[H_3O^+][L^-]}{[HL]}$$

In acid solution, $[H_3O^+]$ is high, and H_3O^+ ions combine with L^- ions to form HL molecules, which are red. In alkaline solution, H_3O^+ ions are removed to form molecules of water, and HL molecules react with OH^- ions to form L^- ions, which are blue:

$$HL + OH^- \rightleftharpoons L^- + H_2O$$

Their molecules and ions differ in colour ...

If [HL] = [L^-], the indicator appears purple. Since

$$[H_3O^+] = K_a \frac{[HL]}{[L^-]}$$

this happens when

$$[H_3O^+] = K_a$$

and $$pH = pK_a$$

... They change colour over 2 units of pH ...

If the ratio $[HL]/[L^-] \geqslant 10/1$, the solution appears red. If the ratio $[HL]/[L^-] \leqslant 1/10$, the solution appears blue. Thus litmus changes from red to blue over a range of 2 pH units.

ACID–BASE EQUILIBRIA

According to the Brönsted–Lowry theory

- **acids** are proton-donors
- **bases** are proton-acceptors

Acid –base conjugate pairs are:

$\mathbf{A}H + \mathbf{B} \rightleftharpoons \mathbf{A} + \mathbf{B}H$

acid + base $\rightleftharpoons$ conjugate base of **A** + conjugate acid of **B**

§12.6.1

Neutralisation is the reaction

acid + base → salt + water

In all cases the fundamental reaction is

$H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$

The reaction is exothermic. For a strong acid + a strong base, $\Delta H^\ominus = -57\ \text{kJ mol}^{-1}$. For a weak acid or a weak base, the value of $\Delta H^\ominus$ is lower because the salt formed is hydrolysed so the reaction does not go to completion.

§ 12.9.1

Strong acids and strong bases are completely dissociated. § 12.6.1

Weak acids and weak bases are only partially dissociated. § 12.6.4, §12.7.2

Hydrogen ion concentration is expressed as **pH**:

$pH = -lg[H^+(aq)/mol\ dm^{-3}]$

§ 12.6.2, § 12.6.3

When a solution of an acid is titrated against a solution of a base, a plot of pH against volume of titrant can be plotted – a **titration curve**. The pH changes rapidly at equivalence point.

§ 12.7.1

An **indicator** should be chosen to change colour over this range of pH.

§ 12.7, § 12.7.1

For a weak acid,

$H\mathbf{A} + H_2O \rightleftharpoons H_3O^+ + \mathbf{A}^-$

The **dissociation constant** is given by

$K_a = [H_3O^+]\,[\mathbf{A}^-]/[H\mathbf{A}]$

§ 12.6.4

The pH of a solution of a weak acid can be calculated from the concentration of the weak acid and the value of K_a:

$K_a = [H_3O^+]^2/[H\mathbf{A}]$ § 12.6.5

Water is slightly dissociated:

$2H_2O \rightleftharpoons H_3O^+ + OH^-$

The ionic product for water

$K_w = [H_3O^+][OH^-]$

$= 1.0 \times 10^{-14}\ mol^2\ dm^{-6}$ at 298 K.

§ 12.6.2

Buffer solutions

A solution of weak acid or a weak base + a salt of a weak acid or a salt of a weak base acts as a buffer. It absorbs small amounts of hydrogen ion and hydroxide ion with only a small change in pH. The pH of a solution of a weak acid H**A** and its salt Na**A** is given by

$pH = pK_a + lg\ \{[\mathbf{A}^-]/[H\mathbf{A}]\}$

where K_a = dissociation constant of H**A**

§ 12.8

Amino acids have a buffering action:

$H_2NCHRCO_2H(aq) + H^+(aq) \rightleftharpoons H_3N^+CHRCO_2H(aq)$

$H_2NCHRCO_2H(aq) + OH^-(aq) \rightleftharpoons H_2NCHRCO_2^-(aq) + H_2O(l)$

§ 12.8.2, § 33.17

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Figure 14.1C
Ageing is a slow process

The study of the factors which affect the speeds of chemical reactions is called **reaction kinetics**. In this topic we shall begin by examining the factors that affect reaction rates and go on from this to study how the rate of a reaction can be expressed quantitatively in the form of a **rate law**. We shall examine the stages which a reaction may pass through and model the species that exists for a fraction of a second at the instant when the chemical bonds in the reactants are breaking and the new bonds in the products are forming.

CHECKPOINT 14.1: SOME REVISION QUESTIONS

- Why do flour mills consider there is a danger that finely divided flour can explode, yet you probably do not think of flour as a dangerous substance?
- The fireworks called 'sparklers' contain iron dust glued to an iron rod. Why do they burn rapidly in air whereas a solid iron rod can be heated in a flame without catching fire?
- Why does a soluble aspirin work faster than a tablet that has to be swallowed whole?
- Why do medical doctors use a higher concentration of penicillin to treat meningitis than to treat tonsillitis?
- Why do surgeons lower a patient's body temperature during heart surgery? The answer can mean the difference between life and death to a patient having open-heart surgery.
- Why do we raise the temperature of foods to cook them – accelerating reactions which lead to the breakdown of cell walls and decomposition of proteins?
- Fritz Haber wanted to make the very unreactive gas nitrogen combine with hydrogen to form ammonia – which could then be used to make fertilisers. How did he do it?

Before you reach the end of this chapter, you will be able to answer these questions.

14.2 FACTORS WHICH AFFECT THE SPEEDS OF CHEMICAL REACTIONS

A number of factors can be changed to alter the speed of a chemical reaction. These are:

1. the size of the particles of a solid reactant
2. the concentrations of reactants in solution
3. the pressures of gaseous reactants
4. the temperature

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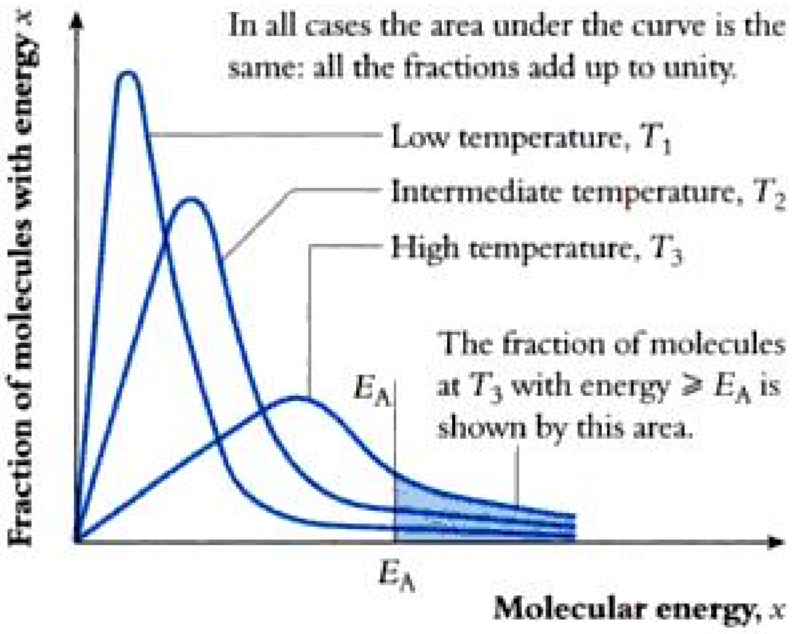


In all cases the area under the curve is the same: all the fractions add up to unity.

The fraction of molecules at T_3 with energy $\geqslant E_A$ is shown by this area.

Figure 14.3C
The Maxwell–Boltzmann distribution of molecular energies (not to scale: E_A is typically 30–40 times the value of x at the top of the curve.)

Now look at the value of the activation energy, E_A. The fraction of molecules with energy $\geqslant E_A$ at each temperature is represented by the shaded area below the curve. Maxwell and Boltzmann calculated that

$$\text{Fraction of molecules with energy} \geqslant E = e^{-E/RT}$$

You can see that the shaded area under the curve, the fraction of the total number of molecules with energy $\geqslant E_A$, is greatest at the highest temperature, T_3. So, with a rise in temperature,

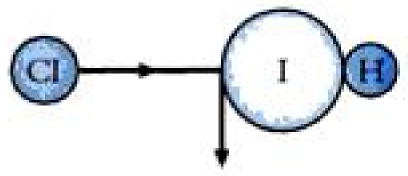
- the average kinetic energy of the molecules increases
- the fraction of molecules with higher than average kinetic energy increases.

Molecules must collide, they must have enough kinetic energy – and what else? They must also collide in an orientation which favours reaction; see Figure 14.3D which shows the reaction,

$$Cl(g) + HI(g) \longrightarrow HCl(g) + I(g)$$

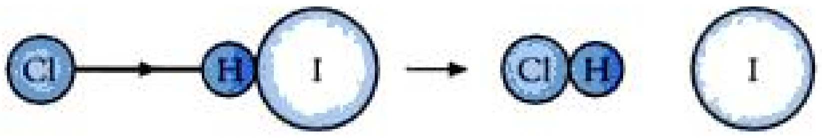
Figure 14.3D
Approach of Cl to HI
(a) without reaction
(b) followed by reaction

(a) Cl atom approaches HI molecule from the iodine side.



Repulsion between the chlorine atom and the iodine atom in the hydrogen iodide molecule prevents reaction from occurring.

(b) Cl atom approaches HI molecule from the hydrogen side.



Reaction occurs as the chlorine atom bonds to the hydrogen atom and displaces the iodine atom.

The collision theory was developed for gaseous reactions, but it has been found to apply to reactions in solution also. Although solvent molecules prevent molecules of reactant coming together as frequently as they would in the gas phase, once molecules have come together they are less able to escape and will collide repeatedly. The repeated collisions may well lead to reaction.

14.9 LINK WITH THERMODYNAMICS

For a reaction to happen spontaneously ...

... there must be a decrease in free energy ...

... and the activation energy must not be too high

In Chapter 10 you saw that there is a condition for changes to proceed spontaneously – to happen without external help. The condition is that the change involves a decrease in free energy, ΔG. The value of the standard free energy, $\Delta G^{\ominus}$ is given by

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

where $\Delta G^{\ominus}$ = Change in standard free energy
$\Delta H^{\ominus}$ = Change in standard enthalpy
$\Delta S^{\ominus}$ = Change in standard entropy

If $\Delta G^{\ominus}$ for a reaction is negative, we say that the reactants are thermodynamically unstable with respect to the reaction: the reaction can occur. If $\Delta G^{\ominus}$ for a reaction is positive, we say that the reactants are thermodynamically stable with respect to the reaction: the reaction cannot occur. We say the reaction is **under thermodynamic control**. Thermodynamic instability ($\Delta G^{\ominus}$ negative) is not the only condition necessary for a change to occur. The molecules must possess enough energy to climb the energy barrier between reactants and products (Figure 14.3A). For example methane is a fuel; the oxidation of methane is thermodynamically unstable with respect to the products of oxidation:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);\ \Delta G^{\ominus} = -580\ \text{kJ mol}^{-1}$$

Yet oxidation does not proceed at room temperature because at room temperature very, very few molecules of methane and oxygen collide with energy equal to the activation energy. As a result, the reaction takes place so slowly as to be unobservable, and we say the reaction is **under kinetic control**. At higher temperatures the fraction of molecules which collide with enough energy to react increases and the reaction takes place more rapidly.

SUMMARY

Reaction under thermodynamic control: $\Delta G^{\ominus}$ for the reaction is positive,
Reaction under kinetic control: $\Delta G^{\ominus}$ for the reaction is negative, but the activation energy is high.

CHECKPOINT 14.9: THERMODYNAMICS

1. What is a spontaneous reaction? Do spontaneous reactions always take place rapidly? Give examples. In what way does a catalyst affect the spontaneous reaction?
2. According to thermodynamics, an exothermic reaction is *feasible*. Why do some exothermic reactions proceed very slowly?

FURTHER STUDY ▼

14.10 THE STUDY OF REACTION KINETICS

We shall now take the study of reaction kinetics further. We need to go into more detail of measurements of the rates of reactions and interpreting the results of those measurements.

reaction depends on the concentrations of the reactants, the temperature and other factors. The results of such studies can be interpreted to give a detailed picture of what happens during a chemical reaction.

14.13.1 THE EFFECT OF PARTICLE SIZE ON REACTION RATE

Solids react faster in finely divided form

Reactions of solids take place faster when the solids are in a finely divided state. This is because the ratio of surface area to mass is greater in small particles than in large particles, and the area over which the solid can come into contact with liquid or gaseous reactants is greater. Examples are the reaction of powdered zinc and granulated zinc with acids and the reaction of powdered calcium carbonate and marble chips with acid.

14.13.2 THE EFFECT OF CONCENTRATION ON REACTION RATE

Consider a reaction between **A** and **B**:

$$\mathbf{A} + \mathbf{B} \longrightarrow \text{Products}$$

The way in which rate is related to concentration is governed by the order of the reaction

The rate of reaction depends on the concentrations of **A** and **B**, but one cannot simply say that the rate of reaction is proportional to the concentration of **A** and proportional to the concentration of **B**. The relationship is

$$\text{Reaction rate} \propto [\mathbf{A}]^m[\mathbf{B}]^n = k[\mathbf{A}]^m[\mathbf{B}]^n$$

An expression of this kind is called a **rate equation**. The powers m and n are usually integers, often 0, 1 or 2, and are characteristic of the reaction. The reaction is of **order** m with respect to **A** and of order n with respect to **B**. The overall order of reaction is $(m + n)$. The proportionality constant k is called the **rate constant** or **velocity constant** for the reaction.

The rate constant for a reaction relates the rate to the concentrations of the reactants

Example (a) A solution of **Q**, of concentration 0.20 mol dm^{-3} undergoes a **first-order** reaction at an initial rate of 3.0×10^{-4} mol dm^{-3} s^{-1}. Calculate the rate constant.

Method Since, for a first-order reaction

$$\text{Initial rate} = k[\mathbf{Q}]_0$$

$$3.0 \times 10^{-4}\ \text{mol dm}^{-3}\,\text{s}^{-1} = k \times 0.20\ \text{mol dm}^{-3}$$

$$\text{The rate constant } k = 1.5 \times 10^{-3}\,\text{s}^{-1}$$

The unit of a first-order rate constant is time^{-1}.

First-order and second-order rate constants have different dimensions

Example (b) A **second-order** reaction takes place between the reactants **P** and **Q**, which are both initially present at concentration 0.20 mol dm^{-3}. If the initial rate of reaction is 1.6×10^{-4} mol dm^{-3} s^{-1}, what is the rate constant?

Method

$$\text{Initial rate} = k[\mathbf{P}]_0[\mathbf{Q}]_0$$

$$\therefore 1.6 \times 10^{-4}\ \text{mol dm}^{-3}\,\text{s}^{-1} = k \times (0.20\ \text{mol dm}^{-3})^2$$

$$\text{The rate constant, } k = 4.0 \times 10^{-3}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$$

A second-order rate constant has the unit concentration^{-1} time^{-1}.

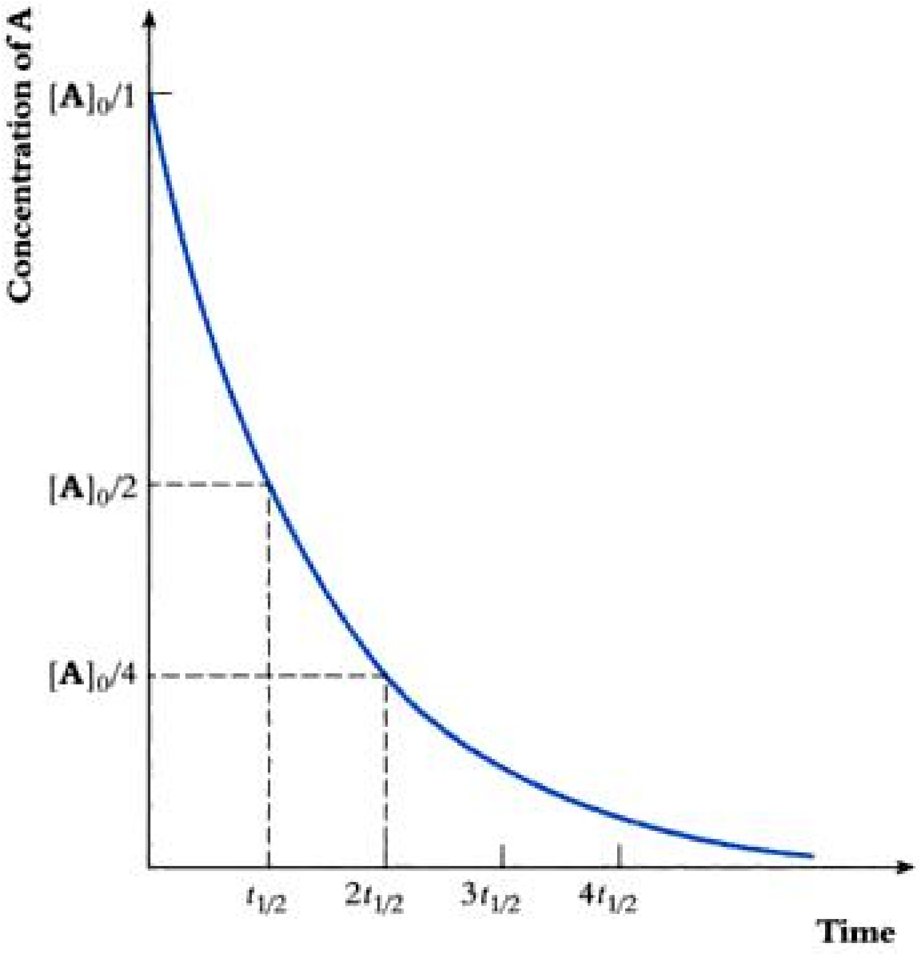


Figure 14.14B A plot of [Reactant] against time for a first-order reaction; $t_{1/2}$ = half-life

Example (a) The half-life of radium is 1590 years. How long will it take for a sample of radium to decay to 25% of its original radioactivity?

Method To decay to 50% of its original activity takes one half-life = 1590 years. To decay from 50% to 25% of its original activity takes another half-life of 1590 years.
Total = 3180 years

Example (b) A radioactive sample of caesium-136 decays from 480 cpm to 60 cpm in 42 days. What is its half-life?

Method Decrease in amount of caesium-136 = (60 cpm/480 cpm) × 100% = 12.5%

The isotope has decayed from $100\% \longrightarrow 50\% \longrightarrow 25\% \longrightarrow 12.5\%$ that is 3 half-lives.
Therefore 42 days = 3 half-lives and $t_{1/2} = 14$ days.

14.14.4 PSEUDO-FIRST-ORDER REACTIONS

The acid-catalysed hydrolysis of an ester, e.g., ethyl ethanoate

$$CH_3CO_2C_2H_5(l) + H_2O(l) \xrightarrow{\text{acid}} CH_3CO_2H(aq) + C_2H_5OH(aq)$$

is first order with respect to ester and first order with respect to water. If water is present in large excess, only a small fraction of the water will be used up in the reaction. The concentration of water is practically constant, and the rate depends on the concentration of ester alone:

If the concentration of one reactant is very large, the reaction appears to be zero order with respect to that reactant

$$-d[CH_3CO_2C_2H_5]/dt = k'[CH_3CO_2C_2H_5]$$

k' = a first-order rate constant. The reaction appears to be zero order with respect to water.

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CHECKPOINT 14.17: REACTION KINETICS

1. Explain the following statements:
   - *(a)* The rate of a bimolecular reaction cannot be calculated from the collision frequency alone.
   - *(b)* The increase in the rate of a chemical reaction with an increase in temperature is much greater than the corresponding increase in the collision frequency.
   - *(c)* The presence of a catalyst can make a big change in the rate of a chemical reaction.

2. The Collision Theory postulates that collisions between molecules are necessary before reaction can occur. The theory was developed for bimolecular reactions in the gas phase. How does the Collision Theory apply to reactions in solution?

3. Describe what is meant by a *chain reaction*. By referring to a chosen example, explain what are chain-initiating steps, chain-propagating steps and chain-terminating steps.

4. Why does the probability that a collision will result in reaction depend on the orientation of the colliding molecules? Illustrate your answer with reference to the reactions

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

$$CH_3Br + I^- \xrightarrow{\text{in propanone}} CH_3I + Br^-$$

$$(CH_3)_3N + C_2H_5I \xrightarrow[\text{solvent}]{\text{in an organic}} (CH_3)_3\overset{+}{N}C_2H_5 + I^-$$

14.18 RATE-DETERMINING STEP

When a reaction takes place in a number of steps, the rate of the reaction is determined by the rate of the slowest step: the **rate-determining step**. It is like an assembly line in a factory. Imagine Mr Murphy, Mr Shah, Mr Evans and Mr O'Connor all working at different stages on the line. Mr Murphy can do his adjustments on 40 units an hour, Mr Shah and Mr Evans can both process 30 units an hour, while Mr O'Connor, with a more demanding task, can only manage 20 units an hour. The rate at which units leave the assembly line is 20 units an hour – the rate of the slowest step.

Two reactions which take place in a number of steps will be described.

14.18.1 THE IODINATION OF PROPANONE

In a kinetic study of the iodination of propanone ...

The iodination of propanone

$$CH_3COCH_3(aq) + I_2(aq) \longrightarrow CH_3COCH_2I(aq) + HI(aq)$$

is a reaction with interesting kinetics. The reaction is acid-catalysed. From the equation, one might postulate that the rate equation would be

$$-\frac{d[I_2]}{dt} = k[CH_3COCH_3]^a[I_2]^b$$

A study of the reaction will involve finding a and b.

First: find the order with respect to iodine

... the concentration of propanone is kept approximately constant

It is arranged that the propanone concentration is much greater than the iodine concentration, e.g., $[CH_3COCH_3] = 1.00\ \text{mol dm}^{-3}$ and $[I_2] = 0.00500\ \text{mol dm}^{-3}$ so that, at the end of a run, $[CH_3COCH_3] = 0.995\ \text{mol dm}^{-3}$, a decrease of 0.5%. One can say that $[CH_3COCH_3]$ is effectively constant, and

$$-\frac{d[I_2]}{dt} = k_1[I_2]^b \text{ so that } b \text{ can be found.}$$

Solutions of known concentration of (a) propanone, (b) iodine in potassium iodide, and (c) an acid buffer of known pH are prepared and brought to the required temperature in a thermostat bath. The reaction is started by pipetting volumes of the three solutions into a flask, and a stop watch is started. After a few

QUESTIONS ON CHAPTER 14

1. Explain what is meant by the terms *rate constant* and *order of reaction*.

2. For the hydrolysis of ethyl ethanoate

$$CH_3CO_2C_2H_5(l) + H_2O(l) \longrightarrow CH_3CO_2H(aq) + C_2H_5OH(aq)$$

the rate equation is

$$\text{Rate} = k[CH_3CO_2C_2H_5]$$

(a) What is the order of reaction?
(b) Why does $[H_2O]$ not come into the rate equation?

3. In the reaction

$$\mathbf{A} \longrightarrow \mathbf{B} \longrightarrow \mathbf{C}$$

what are the units of the rate constant for

(a) a zero-order reaction, *(b)* a first-order reaction and *(c)* a second-order reaction?

4. The radioactive isotope $^{24}Na^+(aq)$ is injected into an animal. If the half-life is 15 hours, how long will it take before the radioactivity has fallen to 25% of the original value?

5. A radioactive isotope decays from an initial count of 160 cpm to 20 cpm in 27 days. What is its half-life?

6. The following results were obtained in a study of the reaction

$$S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

between peroxodisulphate and iodide ions:

Experiment	**$[S_2O_8^{2-}]$/ mol dm^{-3}**	**$[I^-]$/ mol dm^{-3}**	**Initial rate $\frac{d[S_2O_8^{2-}]}{dt}$ /mol dm^{-3} s^{-1}**
1	0.040	0.040	9.6×10^{-6}
2	0.080	0.040	1.92×10^{-5}
3	0.080	0.020	9.6×10^{-6}

Find the order of reaction with respect to *(a)* $S_2O_8^{2-}$, *(b)* I^- and *(c)* find the rate constant. What is the initial rate of the reaction when $[S_2O_8^{2-}]_0 = 0.12$ mol dm^{-3}, and $[I^-]_0 = 0.015$ mol dm^{-3}?

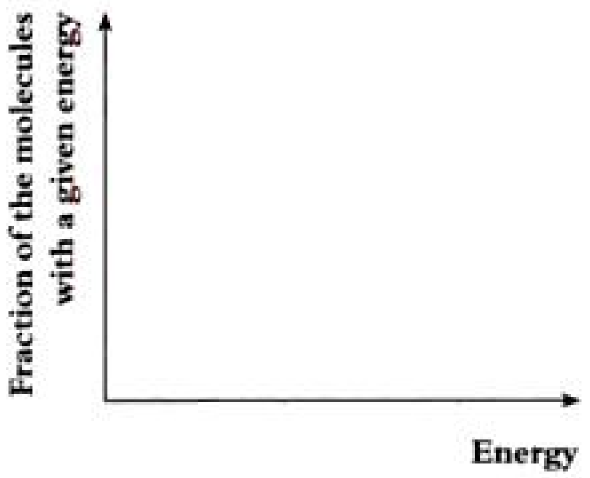
7. What is meant by the *mechanism* of a chemical reaction? Explain why, when chemical reactions take place in more than one step, the overall rate of the reaction is determined by the rate of the slowest step. Give an example of a reaction of this kind.

8. *(a)* Write an equation for the decomposition of hydrogen peroxide.
(b) Explain how you could find the rate of decomposition of hydrogen peroxide in aqueous solution, in the presence of a catalyst, using (i) a gas syringe, (ii) a standard solution of potassium manganate(VII).
(c) Tabulated below are values of the initial rate of decomposition at different concentrations of hydrogen peroxide. Plot a graph of initial rate against concentration.

$[H_2O_2]$/mol dm^{-3}	0.100	0.175	0.250	0.300
Rate/10^{-4} mol dm^{-3} s^{-1}	0.593	1.04	1.48	1.82

(d) From the graph, find the order of reaction and the rate constant.

9. *(a)* (i) Sketch on a copy of the given axes the distributions of molecular energies for a given mass of a gas at two temperatures, $\mathbf{T}_1$, and $\mathbf{T}_2$, where $\mathbf{T}_1$ is higher than $\mathbf{T}_2$. **2**
(ii) State how the areas under your curves are related to each other. **1**
(iii) Using the curves explain why the rates of reaction increase with temperature. **1**



(b) The decomposition of gaseous dinitrogen pentoxide is represented by

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

and is first order with respect to dinitrogen pentoxide.
(i) Write down the rate equation for the decomposition.
(ii) A proposed mechanism for the reaction is made up of the following steps:

$$N_2O_5 \longrightarrow N_2O_3 + O_2 \qquad \text{I}$$

$$N_2O_3 \longrightarrow NO + NO_2 \qquad \text{II}$$

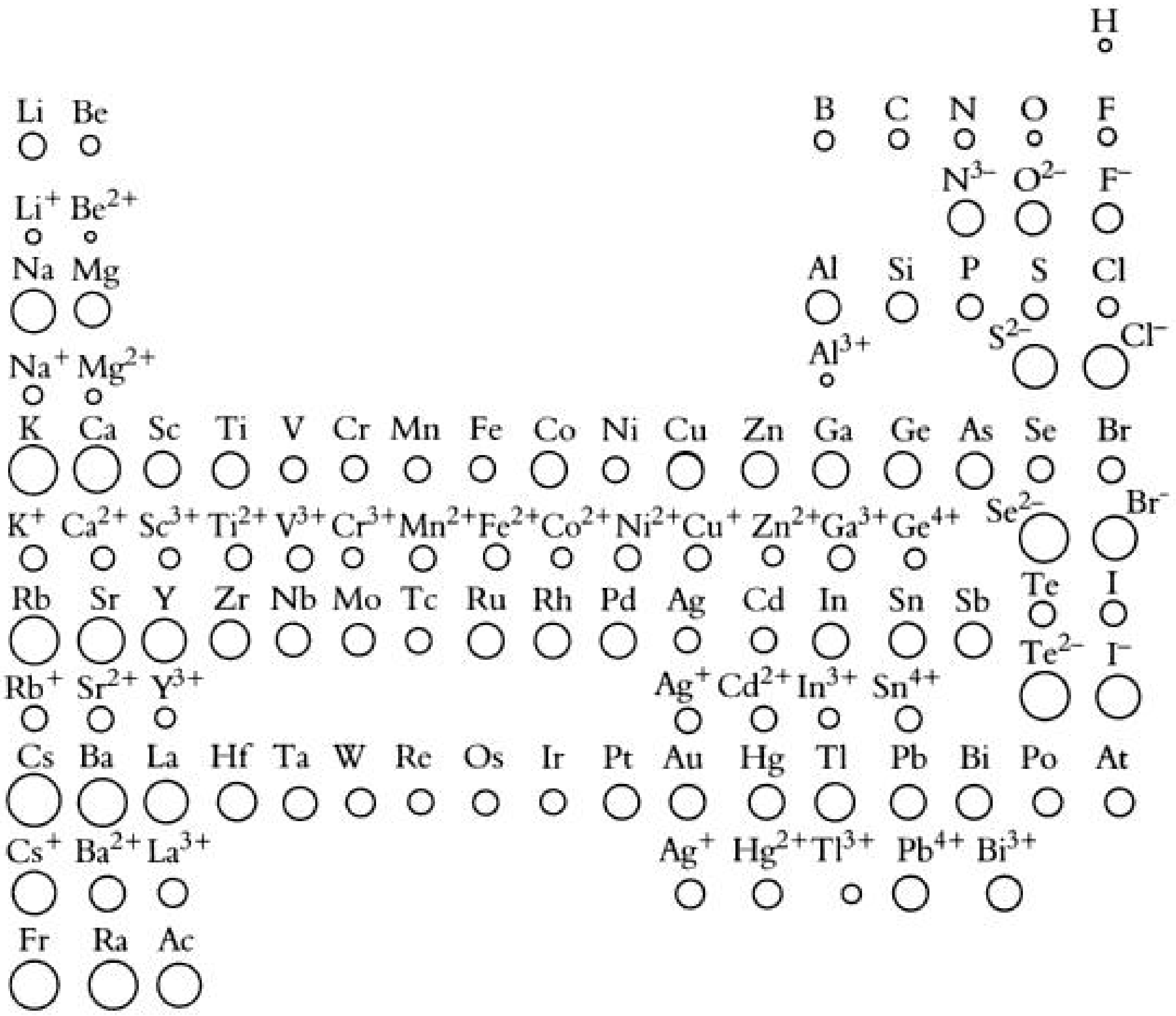
$$NO + 2N_2O_5 \longrightarrow 3NO_2 + N_2O_5 \qquad \text{III}$$

From your rate equation in *(b)*(i), write down which of the steps would be expected to be the rate-determining step. **1**

Part 3

Inorganic Chemistry

Figure 15.2D
Atomic and ionic radii
(○ = 0.10 nm = 100 pm)



... as shells are added ...

... and decrease from left to right across a period as the effective nuclear charge increases

Covalent and ionic radii both decrease from left to right across any period of the Periodic Table. In the second period, (Li–F), the nuclear charge increases from 3 to 9. As the nuclear charge increases, it pulls the $n = 1$ electrons closer to the nucleus, and the radius of the $n = 1$ shell decreases. The effect on the $n = 2$ electrons is complicated by the fact that they are *screened* or shielded from the nucleus by the $n = 1$ shell, so that the effective nuclear charge is less than the actual nuclear charge. For example, in lithium the outermost electron is attracted by a nucleus with a charge of +3 screened by two electrons. The net nuclear charge is closer to +1 than +3. In beryllium, the $n = 2$ electrons are attracted by a nucleus which has a charge of +4, and is screened by 2 electrons, which make its effective charge close to +2. Nevertheless, reading from left to right across a period, the effective nuclear charge increases and causes a steady decrease in atomic radius across a period [see Figure 15.2D]. A comparison of ions with the same numerical charge, e.g., $\mathbf{M}^{2+}$, shows that ionic radii follow the same pattern.

A series of transition metals differ little in atomic radius

Transition metals show a very small change in atomic radius across a series. In the first transition series, beginning with scandium, the size of the atoms is governed by the $n = 4$ shell while the additional electrons are entering the $n = 3$ shell.

Ionisation energy varies in a periodic manner ...

... reaching a peak at each noble gas

The first ionisation energy [see Figure 15.2E] shows periodic variation. It reaches a peak at each noble gas. From helium to lithium and from neon to sodium, the ionisation energy decreases sharply. The additional electrons (a 2s electron in Li and a 3s electron in Na) are much more easily removed than the electrons in the noble gases. Across the periods from lithium to neon and from sodium to argon, the increasing nuclear charge makes it more difficult to remove an electron, and the ionisation energy increases. The increasing ionisation energies for the removal of successive electrons are shown in Figure 2.5C, § 2.5.

The solutions of chlorides and other salts of highly polarising cations are acidic on account of salt hydrolysis [§§ 12.9, 19.4.1].

$$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$$

Chlorides

No chloride of argon exists. The chlorides of Period 3 are shown in Table 15.5B.

15.5.3 HYDRIDES

Ionic hydrides

Ionic hydrides are formed by Group 1 and 2 metals

The hydrides react with water and burn in air

Ionic hydrides are formed by the metals of Groups 1 and 2. They are made by passing hydrogen over the heated metal. These hydrides are crystalline solids with structures similar to the corresponding halides. They react vigorously with water to give hydrogen, and burn vigorously in air:

$$H^-(s) + H_2O(l) \longrightarrow H_2(g) + OH^-(aq)$$

$$2H^-(s) + O_2(g) \longrightarrow O^{2-}(s) + H_2O(g)$$

Figure 15.6F shows where in the Periodic Table ionic hydrides are formed.

Covalent hydrides

Covalent hydrides are molecular and often gaseous

Covalent hydrides are molecular. Except for water and hydrogen fluoride, which are associated by hydrogen bonding, covalent hydrides are gaseous.

Interstitial hydrides

In a metallic structure (e.g. Figures 6.8A and B) there are holes between the metal atoms. Some of these holes are small enough to retain hydrogen atoms with the formation of an **interstitial hydride**. The composition of an interstitial hydride depends on the hydrogen pressure. The formula may be between $\mathbf{MH_2}$ and $\mathbf{MH_0}$. (where **M** is the symbol of the metal).

Trends across period 3 hydrides

	Na Mg	Al	Si P	S Cl	Ar
Bonding	Ionic	Unstable >150 °C	Unstable	Covalent	None formed
Reaction with water	Basic	Reacts ⟶ H_2	Insoluble	Acidic	

The hydrides show gradation ...

... from ionic and basic to covalent and acidic

The hydrides of Groups 1 and 2 are ionic and basic, e.g.

$$Na^+(s)H^-(s) + H_2O(l) \longrightarrow Na^+(aq)OH^-(aq) + H_2(g)$$

The hydrides of Groups 6 and 7 are covalent and acidic, e.g.

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

15.5.4 SALTS

Thermal stability is related to bond character

Nitrates, sulphates and carbonates in which the electrovalent character of the bonds is high are stable to heat. Salts with more polarising cations are more easily decomposed by heat: calcium carbonate is decomposed, whereas sodium carbonate is stable. Hydrogencarbonates do not exist after Group 2, and solid hydrogencarbonates are obtained only in Group 1.

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