FOR THE
IB DIPLOMA

Chemistry

Study and Revision Guide

OPTIONS

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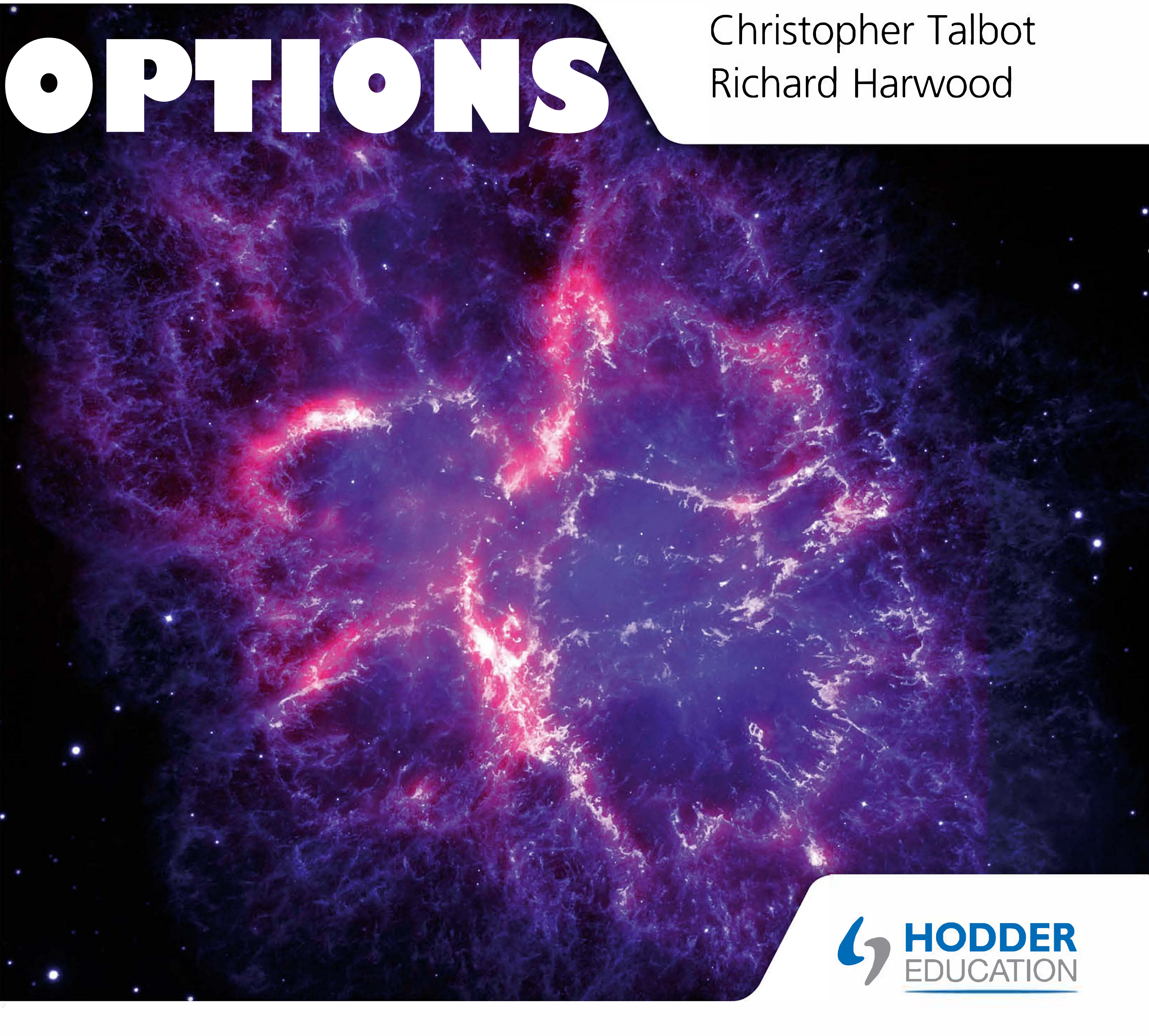


HODDER
EDUCATION

22 Option A Materials

22.1 Materials science introduction

Revised ☐

Essential idea: Materials science involves understanding the properties of a material, and then applying those properties to desired structures.

Introduction

Revised ☐

- Materials are classified based on their uses, properties, or bonding and structure.
- The properties of a material based on the degree of covalent, ionic or metallic character in a compound can be deduced from its position on a bonding triangle.
- Composites are mixtures in which materials are composed of two distinct phases, a reinforcing phase that is embedded in a matrix phase.

Classifying materials

Revised ☐

Materials science is the scientific study of the structure and properties of materials (substances). Materials can be classified based on their properties, uses, bonding or structure. Typically materials are classified as metals, ceramics, polymers or composites.

Metals (including alloys formed only of metals) are excellent electrical and thermal conductors, are lustrous (shiny), sonorous (emit a bell sound when struck), ductile (able to be drawn into wires) and malleable (able to be beaten into thin sheets). They have a high tensile strength.

The elements present in ceramics may be metallic or non-metallic. Many ceramics are silicate-based containing silicon, oxygen and metals. The structural units are ionically or covalently bonded and arranged in a three-dimensional structure. The tetrahedral SiO_4^{4-} unit is a 'building block' for silicates (Figure 22.1). The structure can be modified, for example, silica (SiO_2) changed into amorphous glass.

Expert tip

Glasses are amorphous or non-crystalline. Metals are polycrystalline and made of many small crystals (known as grains (Figure 22.2).

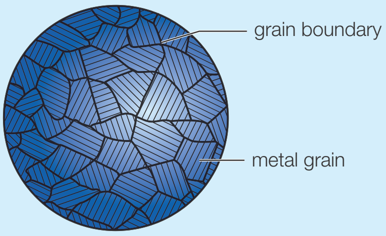


Figure 22.2 Arrangement of metal grains

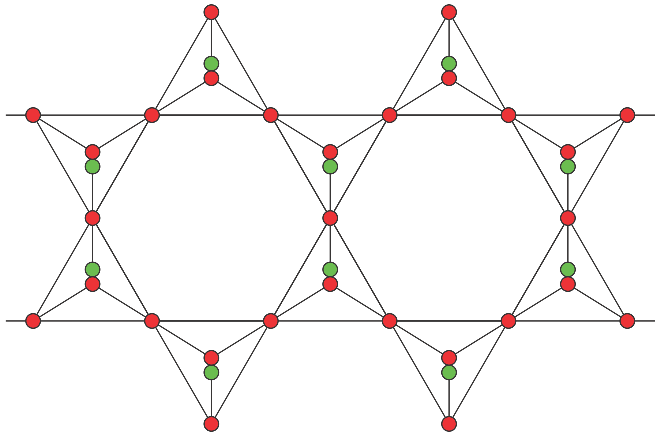


Figure 22.1 Double strands of silicate tetrahedra

Ceramics are hard, with high melting points, are electrical and thermal insulators, and are opaque, rather brittle and resistant to corrosion. They are very stable to decomposition at high temperatures. Ceramics are made by compressing powders into shape and firing them (heating in an oven or furnace).

■ QUICK CHECK QUESTION

1 Deduce the charges on silicate anions in $CaAl_2Si_2O_8$, $[Ca_3Al_2(SiO_4)_3]$ and (Al_2SiO_5).

Expert tip

Because the toughness of ceramics is low, small defects, e.g. surface scratches or lumps, can reduce the strength drastically.

Polymers are usually long chain carbon-based molecules. Their structure is determined by covalent bonds and the intermolecular forces between chains. The polymer molecules may be linear, branched or cross-linked. Most polymers are electrical and thermal insulators. Highly cross-linked polymers are often hard and brittle (with the exception of rubber).

Composites are mixtures in which materials are composed of two distinct phases; a reinforcing phase embedded in a matrix phase. Figure 22.3 shows a composite from a bullet-proof vest. Other common composites include ceramic composites, fibre-glass, concrete (stones and cement) and bone (minerals and protein fibres).

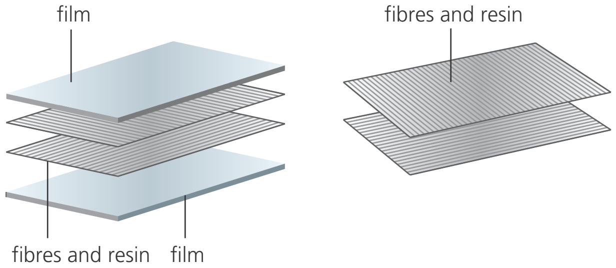


Figure 22.3 The arrangement of fibres of poly(ethene) in a resin matrix

QUICK CHECK QUESTIONS

2 Describe how the structure of ceramics differs from that of metals.

3 Aluminium oxide, Al_2O_3, and silicon nitride, Si_3N_4, are examples of ceramic materials. State the name of the predominant type of bonding in each material.

Relationship between physical properties and bonding and structure

Revised

Melting point

Metals are bonded by sharing of electrons over the lattice of metal cations. The effect of this delocalization is to overcome the repulsive forces between the positively charged cations, leading to a stable lattice. Because the lattice energy is high, metals often have high melting points.

Ceramics usually have a combination of ionic bonding (between a metal and non-metal) and covalent (between non-metals) bonds within a giant covalent structure (usually three-dimensional). Most ceramics have higher melting points than metals due to the strong directional bonding in these materials.

In polymers (plastics) without covalent cross-linking, only the weak intermolecular forces between the polymer chains need to be overcome and so they tend to have relatively low melting points. Cross-linked polymers will have higher melting points and often undergo decomposition before melting.

Expert tip

The strength of ionic bonding depends on the size of the charge on each ion and on the radius of each ion. In covalent bonding, the greater the number of electron pairs being shared between the atoms, the greater the force of attraction, and the stronger the covalent bond.

Permeability

Permeability is the ability of a porous material to allow liquids, such as water, and gases to pass through it. This depends on the type of particles and bonding within the substance, which can attract or repel water molecules, and the size of the spaces between the particles in the lattice of the substance.

Metals and most ceramics have tightly packed structures and are impermeable to water and gases. However, some ceramics, such as the zeolites and concrete, contain pores, and water is able to penetrate them. The majority of polymers are generally impermeable to water due to the non-polar nature of the carbon backbone. However, they are often quite permeable to small molecules of gases, such as oxygen or nitrogen. Increasing the crystallinity of the polymer increases its density and decreases permeability to both water and gases.

Conductivity

Metals are excellent thermal and electrical conductors due to the presence of delocalized valence electrons that form an electric current when a voltage is applied. The majority of ceramics and polymers are non-conducting due to the absence of delocalized electrons in the solid state.

QUICK CHECK QUESTION

4 List properties that describe ceramics and properties that describe metals.

Elasticity

Initial deformation – elasticity

Elasticity is the defining property of solids. A material is described as elastic when it is stretched due to the application of a force, but returns to its original shape when the force is removed.

All solids are elastic but they vary enormously in their elastic limit – the amount of extension which can take place reversibly. Metals and ceramics show elastic properties over small ranges (a few percent at most and often less than 1%), whereas rubbers can be elastic to extensions of 500% (and are often described as highly elastic).

Failure: brittleness versus toughness

When a material is stressed beyond its elastic limit it undergoes irreversible deformation – failure. The bonds between atoms in ceramics and glasses are very strong and the lattice is strongly bonded in all directions. Ceramics have very small elastic limits and fail by brittle fracture. In contrast, metals are malleable and ductile because the close packed layers of cations can slide over each other but still maintain metallic bonding.

Most plastics are flexible and undergo reversible deformation at room temperature. The polymer is rubbery and the chains can be extended and will readopt their shape once the force is removed. However, at low temperatures they become glassy solids with the properties of glass, i.e. they become very hard and brittle.

Bond triangle diagrams

Revised ☐

The properties of a substance depend, partly, on the degree of covalent, ionic or metallic character in the compound. The type of bonding in a compound – ionic, metallic, covalent and polar covalent bonding – can be deduced from the van Arkel–Ketelaar triangle of bonding diagram.

The position of a binary compound in the triangle is worked out by using the electronegativity values of its elements. The difference in electronegativity is plotted against the average electronegativity. The different types of bonding are rationalized in terms of these two parameters (Figure 22.4). The triangle can also be used predictively with unknown binary compounds to predict their bonding type. Compounds bordering the metallic region of the triangle typically have semiconducting properties.

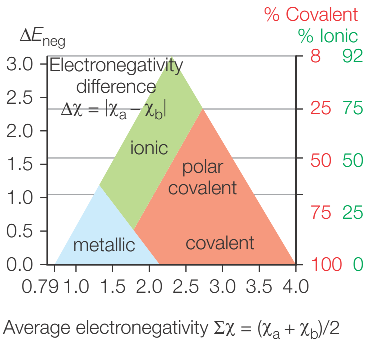


Figure 22.4 van Arkel–Ketelaar triangle of bonding diagram

QUICK CHECK QUESTIONS

5 Deduce the nature of bonding in the following compounds: $ICl(s)$, $MgO(s)$, $GaAs(s)$, $Si(s)$, $Cd_3Mg(s)$, $P_4O_{10}(s)$, $NCl_3(l)$

6 Determine the percentages of ionic and covalent character in P_2H_4, Al_2Cl_6 and OsO_2.

7 Determine the percentage ionic character in magnesium boride (MgB_2). State the likely type of bonding present.

NATURE OF SCIENCE

The terms Stone Age, Bronze Age (an alloy of copper and tin) and Iron Age provide a classification for studying ancient societies. Different countries and different cultures entered and left the different ages at different times. The modern age is based on metals, alloys, plastics and a wide range of ceramics, many of which have been developed following a scientific understanding of their properties at the atomic and molecular level.

22.2 Metals and inductively coupled plasma (ICP) spectroscopy

Revised ☐

Essential idea: Metals can be extracted from their ores and alloyed for desired characteristics. ICP-MS/OES spectroscopy ionizes metals and uses mass and emission spectra for analysis.

Metals and inductively coupled plasma (ICP) spectroscopy

Revised ☐

- Reduction by coke (carbon), a more reactive metal or electrolysis is a way to obtain some metals from their ores.
- The relationship between charge and the number of moles of electrons is given by Faraday's constant, *F*.
- Alloys are homogeneous mixtures of metals with other metals or non-metals.
- Diamagnetic and paramagnetic compounds differ in electron spin pairing and their behaviour in magnetic fields.
- Trace amounts of metals can be identified and quantified by ionizing them with argon gas plasma in inductively coupled plasma (ICP) spectroscopy using mass spectrometry (ICP-MS) and optical emission spectroscopy (ICP-OES).

Extraction of metals from their ores

Revised ☐

An ore is a naturally occurring substance from which an element may be extracted. The extraction of a metal from its ore involves reduction. The ease of reduction depends upon the position of the metal in the activity series.

Expert tip

The extraction of a metal from its ore by a process involving melting and a chemical reducing agent is called smelting.

Metals very low in the activity series are very unreactive and form stable compounds. They may be found chemically uncombined (native).

Metals slightly higher up the activity series (Figure 22.5) can be extracted by heating the ore strongly or by heating with a chemical reducing agent, such as hydrogen, carbon (in the form of coke), carbon monoxide gas or a more reactive metal.

potassium calcium sodium magnesium	extracted by electrolysis of molten or fused ore
aluminium titanium chromium zinc iron lead	extracted by chemical reduction in a furnace
copper silver gold	extracted by thermal decomposition

Figure 22.5 Activity series

Extraction of metals from their sulfide ores involves a combination of roasting to convert them to their oxides, followed by reduction with carbon (coke), for example:

$$2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$$

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

The extraction of the most active metals from their compounds requires electrolysis. It is an expensive process, but produces very pure metals.

For example, sodium is extracted by the electrolysis of a molten mixture of sodium chloride with a small amount of calcium chloride (to lower the melting point of sodium chloride).

Cathode: $Na^+(l) + e^- \rightarrow Na(l)$

Anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

Expert tip

Metals below carbon in the activity series can be reduced by heating with coke (carbon).

Extraction of iron

Industry produces iron from its oxide ores in large blast furnaces (Figure 22.6).

Coke (impure carbon) burning in air heats the furnace:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

Coke also produces the active reducing agent by reacting with carbon dioxide further up the furnace to form carbon monoxide:

$$C(s) + CO_2(g) \rightarrow 2CO(g)$$

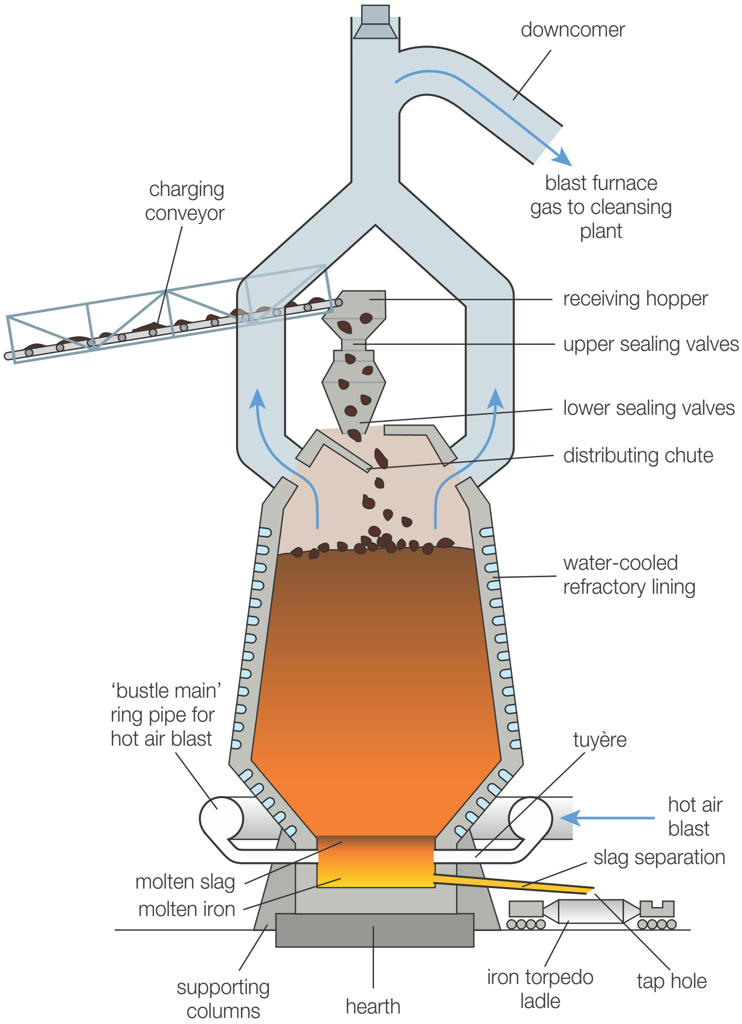


Figure 22.6 A diagram of the blast furnace for extracting iron from iron ore

The carbon monoxide reduces the ore to iron, for example,

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

When the furnace is hot enough, carbon can also act as the reducing agent:

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

Limestone (calcium carbonate) undergoes thermal decomposition to form calcium oxide, which combines with silicon dioxide and other non-metallic impurities to form a liquid slag, for example:

$$CaO(s) + SiO_2(s) \rightarrow CaSiO_3(l)$$

The molten metal and slag sink to the bottom of the furnace. The slag floats on the metal so it can be tapped off separately.

Extraction of aluminium

The main ore of aluminium is bauxite, which is impure aluminium oxide. Impurities are removed by heating powdered bauxite with concentrated sodium hydroxide solution. Aluminium oxide (alumina), which is amphoteric, reacts and forms a soluble product. After filtering, small crystals of pure aluminium oxide (alumina) are added and hydrated aluminium oxide crystallizes as the solution cools. The hydrated crystals are heated to form the anhydrous aluminium oxide. Aluminium is obtained by electrolysis (Figure 22.7) of aluminium oxide melted with a small amount of sodium aluminium fluoride, Na_3AlF_6.

Aluminium ions undergo reduction at the cathode:

$$Al^{3+}(l) + 3e^- \rightarrow Al(l)$$

QUICK CHECK QUESTIONS

8 Iron can be obtained from its oxide, Fe_2O_3, by reaction with carbon, aluminium or hydrogen. Write an equation for the reaction in each case.

9 State the raw materials needed to produce iron from iron ore in the blast furnace.

Explain why iron produced by the blast furnace is not as useful as steel.

10 Antimony is a solid element that is used in industry. The method used for the extraction of antimony depends on the grade of the ore. Antimony can be extracted by reacting scrap iron with low-grade ores that contain antimony sulfide (Sb_2S_3).

- **a** Write an equation for the reaction of iron with antimony sulfide to form antimony and iron(II) sulfide.
- **b** Write a half-equation to show what happens to the iron atoms in this reaction.
- **c** In the first stage of the extraction of antimony from a high-grade ore, antimony sulfide is roasted in air to convert it into antimony(III) oxide (Sb_2O_3) and sulfur dioxide. Write an equation for this reaction.
- **d** Identify **one** substance that is manufactured directly from the sulfur dioxide formed in this reaction.

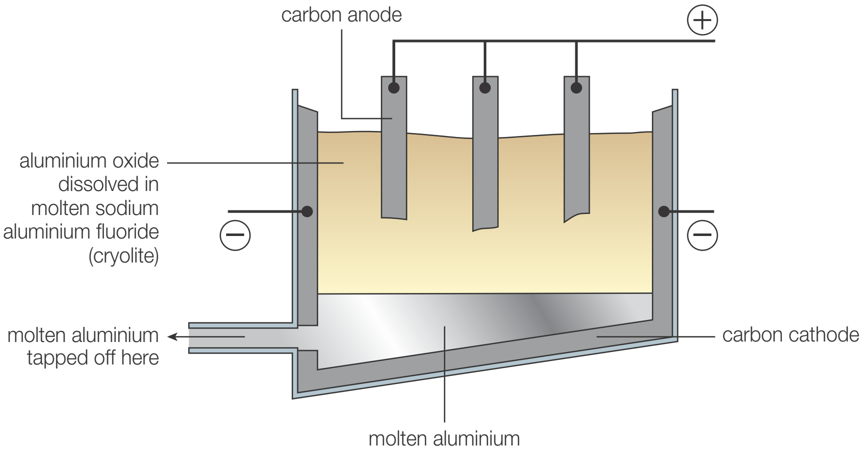


Figure 22.7 Cross-sectional diagram of an electrolytic cell for extracting aluminium

Expert tip

The presence of sodium aluminium fluoride (cryolite) lowers the melting point of the aluminium oxide from about 2000 °C to about 1000 °C. This is a physical effect and reduces the cost of extraction and energy use.

The aluminium collects at the bottom of the electrolytic cell and is tapped off.

Oxide ions undergo oxidation at the anode:

$$2O^{2-}(l) \rightarrow O_2(g) + 4e^-$$

Some of the oxygen gas released reacts with the carbon of the anodes forming carbon dioxide. The anodes combust away and have to be replaced regularly.

Electrolysis calculations

Revised ☐

One mole of any substance contains the Avogadro constant of particles per mole. One mole of ions, electrons or atoms contains the Avogadro constant ($6.02 \times 10^{23}\,mol^{-1}$) of particles.

The charge on a unipositive cation, such as the silver(I) ion, is the same as the charge on an electron.

$$Ag^+(aq) + e^- \rightarrow Ag(s)$$

One unipositive cation requires one electron to discharge it as an atom. One mole of unipositive cations, for example, Ag^+, therefore requires one mole of electrons for discharge.

The quantity of electricity required to discharge one mole of unipositive cations can be determined by experiment. This quantity of electricity is therefore the quantity of electric charge per mole of electrons. It is called the Faraday constant (F) and its value is $96\,500\,C\,mol^{-1}$.

Electrolysis calculations can be performed with the appropriate equations and the following expressions:

Charge passed (C) = current (amps) × time(s)

amount of electrons (mol) = charge passed (C)/Faraday constant ($C\,mol^{-1}$)

amount (mol) = mass (g)/molar mass ($g\,mol^{-1}$)

Expert tip

Any times expressed in minutes or minutes and seconds must be expressed in seconds (SI base units).

■ QUICK CHECK QUESTIONS

11 Calculate the mass of aluminum produced in 1.00 hour by the electrolysis of molten $AlCl_3$ if the electrical current is 10.0 A.

12 Calculate the mass of manganese metal plated out at the cathode of an electrolytic cell when a current of 235 mA is passed through an aqueous solution of manganese(II) sulfate, $MnSO_4$, for 250.0 minutes.

13 The following series of questions relate to the electrolytic extraction of aluminium from bauxite.
  - **a** Explain the function of cryolite in the electrolytic process.
  - **b** State the ionic equation for the reactions at the anode and cathode during the electrolysis.
  - **c** Explain with the help of an equation why the anode decreases in mass.
  - **d** Explain how the production of pure aluminium from bauxite takes advantage of the amphoteric nature of aluminium oxide.
  - **e** State **two** properties which make aluminium a useful metal.
  - **f** State why aluminium is not obtained from its oxide by carbon reduction (smelting).

Alloys

Revised ☐

Alloys (Topic 4 Chemical bonding and structure) are homogeneous mixtures of metals with other metals or non-metals. Many alloys involve transition metals and/or carbon. Alloys containing iron, carbon and other metals are known as steels.

Owing to the comparable sizes of transition metal atoms, one metal atom can displace another metal atom in the lattice and this results in alloy formation. The alloys formed are usually hard and corrosion resistant, and have an increased tensile strength with high melting and boiling points. Some properties such as density and electrical conductivity do not usually change significantly upon alloy formation.

Alloys are usually harder and stronger than the component metals because the presence of different sized metal cations makes the arrangement of the lattice less regular. This stops the layers of cations from sliding over each other so readily when a force is applied (Figure 22.8).

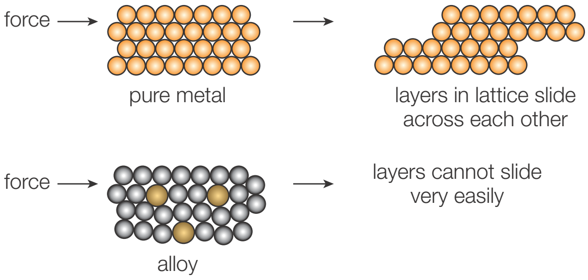


Figure 22.8 The effect of a force on a pure metal and an alloy

■ QUICK CHECK QUESTIONS

14 Describe an alloy.

15 Explain why an alloy of copper and silver melts at a lower temperature than either pure silver or pure copper.

NATURE OF SCIENCE

The Bronze Age began when it was discovered that mixtures of two metals, or alloys, were stronger than either of the metals taken individually. The discovery that tin alloy additions strengthen copper was the basis of the Bronze Age. From a technological viewpoint, accidental improvement in properties of metals is very different from the intentional mixing of two or more ores or refined (purified) metals to obtain an alloy with specific desired properties. However, by 3000BCE, ancient metallurgists were mixing ores of copper and tin to produce bronze that is very similar in composition to modern alloys.

Magnetism

Revised ☐

There are two types of magnetic behaviour shown by a given substance. Diamagnetic substances are repelled by a magnetic field, due to the absence of unpaired electrons. Paramagnetic substances are attracted by a magnetic field, due to the presence of unpaired electrons. The magnetic moment increases with the number of unpaired electrons.

Expert tip

To determine if the compound of a metal is paramagnetic or diamagnetic then draw orbital diagrams ('electrons in boxes') for the metal atom or ion and look at the valence electrons. Note: all zinc(II) compounds are diamagnetic due to the $3d^{10}$ configuration.

Paramagnetism occurs because an electron spins on its axis and generates a magnetic field similar to that of a bar magnet (Figure 22.9).

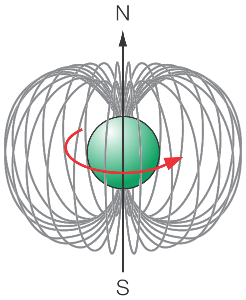


Figure 22.9 A spinning electron and its magnetic field; its magnetic dipole is pointing in the S to N direction

■ QUICK CHECK QUESTION

16 Predict the magnetic properties of iron(II) oxide, FeO, and zinc oxide, ZnO, in terms of the electron structure of the metal ion.

Detection of trace amounts of metals

Revised ☐

Very small amounts of metals can be simultaneously detected and determined quantitatively by ICP spectrometry, via ICP-OES (Figure 22.10) or ICP-MS. Typical uses of ICP spectrometry include analysis of biological samples, geological samples, polluted water, food and drinks, and medicinal drugs.

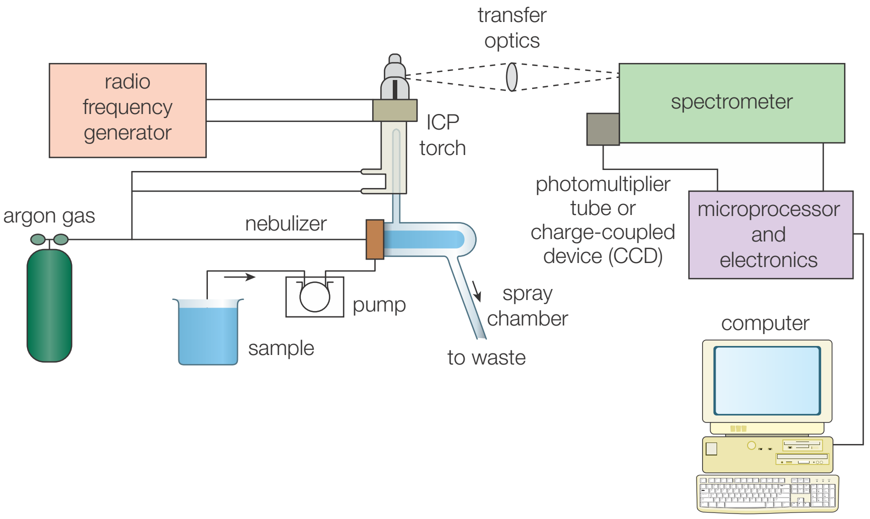


Figure 22.10 Schematic of an ICP-OES instrumentation

ICP-OES is based upon the emission of photons from atoms and ions (Figure 22.11) that have been excited in a plasma at a very high temperature (6000–10 000 K). (Excitation takes place by collisions, not because of the radio frequency radiation. The radio frequency radiation helps to maintain the plasma. The heat of the plasma excites the analytes.) Liquid and gas samples may be injected directly into the instrument, while solid samples usually require extraction or reaction with acid so that the analytes are present in a solution.

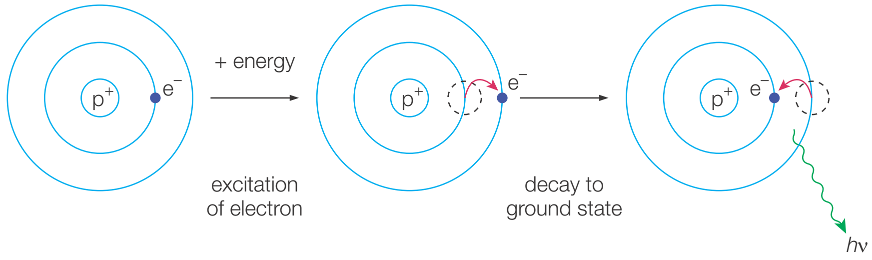


Figure 22.11 Emission of radiation from excited electrons in a metal atom or cation as they return to the ground state

The sample solution is converted to an aerosol and directed into the central channel of the plasma. At its core, the inductively coupled plasma (ICP) maintains a temperature of close to 10 000 °C, so the aerosol is quickly vaporized.

Analyte metals are released as free atoms in the gaseous state. Further collisional excitation within the plasma transfers additional energy to the atoms, promoting them to excited states. Sufficient energy is often available to convert the atoms to ions and then promote the ions to excited states (Figure 22.12).

Determining how much of each metal is present in the sample is done using plots of emission intensity versus concentration, termed calibration curves. Solutions with known ion concentrations of the metals to be tested are introduced into the ICP-OES instrument and the intensity of the characteristic emission for each metal element (analyte) is measured.

These intensities can then be plotted against the concentrations of the standards to form a calibration curve (Figure 22.13) for each metal. When the emission intensity from an analyte is measured, the intensity is compared with that metal's calibration line to determine the concentration corresponding to that intensity.

Expert tip

The analytes refer to the elements (usually metals) that will be detected and their concentrations determined by ICP-OES. Virtually all elements in the periodic table can be determined by ICP-OES or ICP-MS, except for the noble gases, hydrogen, oxygen, nitrogen and fluorine.

Expert tip

A plasma can be regarded as the 'fourth state of matter'. It is a full or partially ionized gas consisting of cations (with different charges) and electrons. The plasma is usually neutral overall.

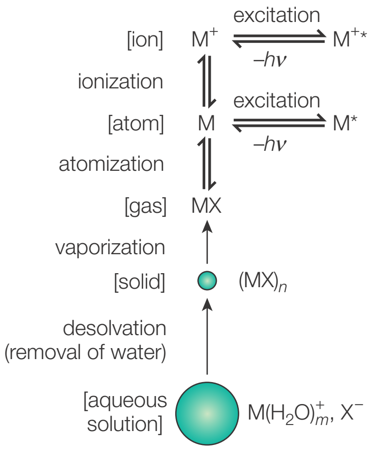


Figure 22.12 The vaporization and ionization of metals and metallic compounds in an ICP discharge (assuming the compound is in aqueous solution)

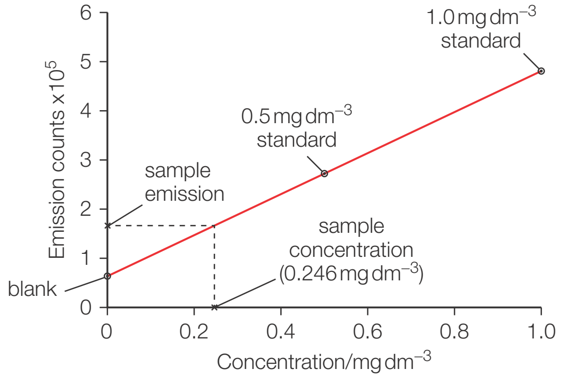


Figure 22.13 Calibration curve used for ICP-OES

Expert tip

In ICP-MS, the positive ions (cations) produced in the ICP plasma at high temperatures are detected by a mass spectrometer according to their mass to charge ratio (*m/z*). In this case, it is not the light produced by the analyte that is recorded, but the analyte itself. Most ions have a +1 charge, so each analyte is identified by their unique mass.

The output (Figure 22.14) of an ICP-OES instrument consists of a series of emission lines with each wavelength corresponding to a specific metal. The height of each emission line is proportional to its amount or concentration.

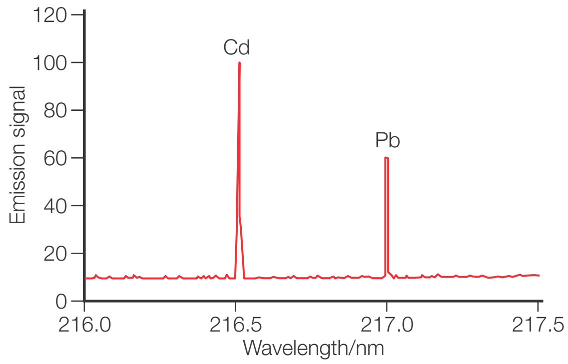


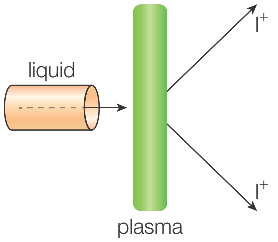
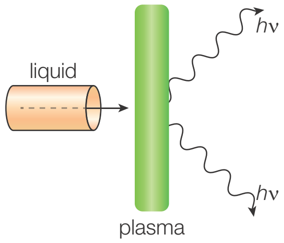
Figure 22.14 ICP-OES spectrum of a solution containing 60 ng cm^{-3} Pb and 100 ng cm^{-3} Cd

Comparison of ICP-OES and ICP-MS techniques

Revised ☐

Table 22.1 shows a comparison of the ICP-MS and ICP-OES techniques for the detection and quantification of trace metals.

Table 22.1 A comparison of ICP-MS and ICP-OES for trace metal analysis

ICP-MS	ICP-OES
Uses mass spectrometry (MS) for detection  	Uses optical emission spectroscopy (OES) for detection 
Ions created in the plasma are sent through a mass spectrometer where positive ions are deflected according to their mass : charge ratio (*m*/*z*)	Electrons in the atoms are excited in the plasma; they then fall back to their ground states, emitting a photon (light). A spectrometer is used to determine the wavelength and intensity of light emitted
Masses detected are isotope specific: analysing ions with a single positive charge	The wavelength of the light emitted is specific to a given element (as in a flame test or a flame photometer)
The peak height at each mass is related to amount of isotope present	The intensity of light emitted is related to the amount (concentration) of element present
Extremely high sensitivity (to 0.001 ppb)	Good sensitivity (to 0.1 ppb)
Difficult to analyse species having charge > +1	Able to analyse species with different ionic charges
Useful for analysing samples containing unknown elements	Useful for quantifying samples where elements are known

Expert tip

The techniques of ICP-OES and ICP-MS are very sensitive, particularly the latter (see Table 22.1). They are capable of measuring the presence of metal ions to concentrations of 'parts-per-billion' (ppb). You will be familiar with ppm (parts per million) used when discussing the concentration of dilute solutions or air pollution, for instance. In terms of solution concentrations, **1 ppm = 1 mg dm^{-3}**.

'Parts per billion' is a much more sensitive measure of concentration:

1 ppb = 1 µg dm^{-3} (1 microgram per decimetre cubed)

Accuracy at such levels is important in measuring the pollution of water supplies with dangerous trace metals such as lead or cadmium, for instance. The maximum contamination level (MCL) for arsenic in drinking water in the USA is set at 0.010 ppm (so 0.010 mg dm^{-3}). That is a level of 10 ppb (µg dm^{-3}).

QUICK CHECK QUESTIONS

17 State the purpose of the plasma in ICP-OES.

18 Outline the role of a nebulizer in ICP-OES.

19 Samples of water from a highly corroded galvanized water storage tank were analysed for trace metal contamination using ICP-OES. Of particular concern were the levels of cadmium present. A series of standard solutions of known concentration of cadmium were analysed to construct a calibration curve for the instrument.

The values obtained for these standards are shown in the table below.

Cadmium concentration/ µg dm^{-3}	Intensity at λ = 216.5 nm
0.0	0.0
10.0	5.5
20.0	11.5
30.0	18.0
40.0	22.0
50.0	28.5

a Using the values in the table, plot a calibration curve.

b The water sample from the contaminated tank gave an intensity reading of 9.5 at 216.5 nm. Use your graph to estimate the cadmium concentration of the sample in ppb.

22.3 Catalysts

Revised ☐

Essential idea: Catalysts work by providing an alternate reaction pathway for the reaction. Catalysts always increase the rate of the reaction and are left unchanged at the end of the reaction.

Catalysts

Revised ☐

- Reactants adsorb onto heterogeneous catalysts at active sites and the products desorb.
- Homogeneous catalysts chemically combine with the reactants to form a temporary activated complex or a reaction intermediate.
- Transition metal catalytic properties depend on the adsorption properties of the metal and the variable oxidation states.
- Zeolites act as selective catalysts because of their cage structure.
- Catalytic particles are nearly always nanoparticles that have large surface areas per unit mass.

Introduction

Revised ☐

Catalysis is very important and 90% of all chemical products use a catalyst during their manufacture. Changes in catalysts have a large influence on reaction rates and the selectivity of reactions. If there are two competing reactions then there will be selective production of the product from the one with the faster rate. A catalyst is often specific to one reaction, but can promote more than one product if there are competing reactions.

Catalyst

Revised ☐

A catalyst is a substance which increases the rate of a reaction without itself being consumed during the process. The catalyst is recovered chemically unchanged at the end of the reaction. However, a heterogeneous catalyst taken out of reaction does have to have some post-treatment/regeneration in order to return it to its fresh state.

Catalysts are used in small amounts and increase the rates of reaction by decreasing the activation energy barrier (Figure 22.15). They provide an alternative pathway (mechanism) which requires less kinetic energy in molecular collisions. Catalysts increase the rates of the forward and backward reaction by the same factor. Hence, although it increases the rate constant, a catalyst does not affect the equilibrium constant.

Expert tip

The phenomenon of increase in the rate of a reaction in the presence of a catalyst is known as catalysis.

Reaction occurs via a catalytic cycle:

reactants + catalyst → complex

complex → products + catalyst

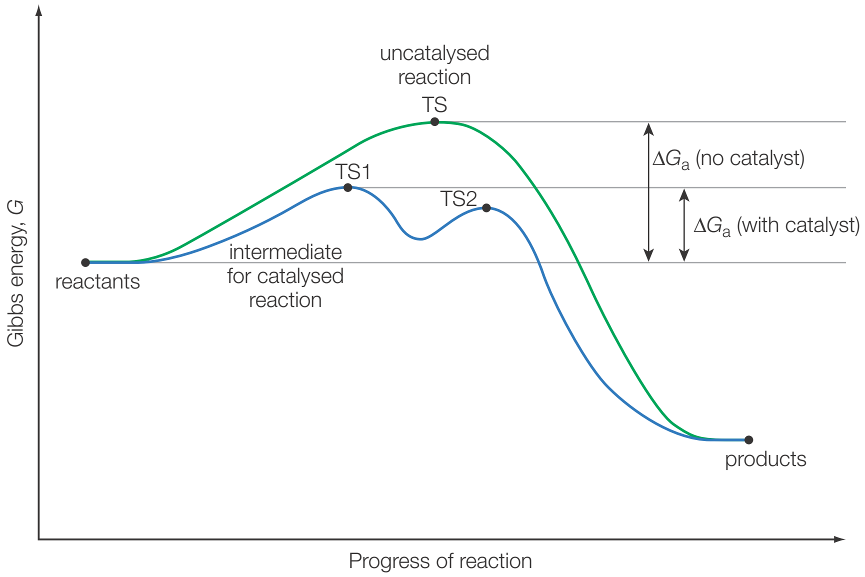


Figure 22.15 The effect of a catalyst on the Gibbs free energy of activation for a reaction (TS, transition state or activated complex)

Expert tip

A catalyst is neither a reactant or product.

Types of catalyst

Revised ☐

Catalysts may be in the same phase as the reactants, in which case they are known as a homogeneous catalyst. In homogeneous catalysis the catalyst, reactants and products are often all dissolved in aqueous solution. Homogeneous catalysts are often acids or bases, metal salts or radical initiators (for polymerization reactions).

A homogeneous catalyst will react with one or more reactants, forming an intermediate compound, which then combines with one of the reactants to form the products and regenerates the catalyst.

Expert tip

A phase is similar to a state of matter except there is a boundary between two phases. An aqueous solution is a phase but not a state of a matter.

Heterogeneous catalysis

Heterogeneous catalysis (Figure 22.16) occurs when the reactants and catalyst are in different phases. For many industrial processes, this means that the catalyst is a solid and the reactants are gases (though some are liquids). It is also known as surface catalysis because the reaction occurs on the surface of the solid catalyst.

The reactants interact with the surface of the catalyst, either via the formation of chemical bonds (chemisorption) or weaker intermolecular forces (physisorption). The reactants are brought close together in a favourable orientation. The reactants form the products that are adsorbed on the surface and later desorbed.

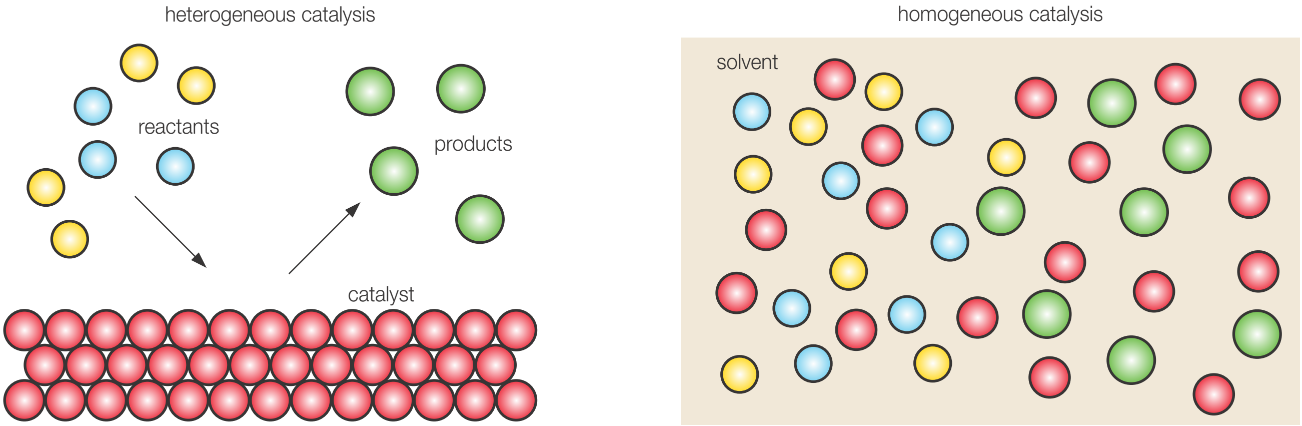


Figure 22.16 The difference between **a** heterogeneous and **b** homogeneous catalysis

Homogeneous catalysis

Because transition metal ions can exist in more than one stable oxidation state they tend to make good homogeneous catalysts. In the reaction between peroxodisulfate(VI) ions and iodide ions experimental evidence suggests that the iron(II) ions are oxidized to iron(III) ions and then back to iron(II) ions.

$$S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$$

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

Common mistake

A common misconception is that a catalyst remains unchanged during reaction.

Heterogeneous catalysts in industry

Revised ☐

Important examples of heterogeneous catalysts include vanadium(V) oxide, V_2O_5, in the Contact process, iron in the Haber process and platinum, palladium and rhodium in the catalytic convertors of cars.

One of the best studied reactions involving heterogeneous catalysis is the catalytic hydrogenation (reduction) of alkenes by molecular hydrogen using platinum or palladium (Figure 22.17).

An important feature of heterogeneous catalysis is activity, the extent to which the catalyst increases the rate of the reaction (per unit area). It depends, partly, on the strength of the adsorption of the molecules onto the active sites of the catalyst. A larger surface area of the catalyst is preferred.

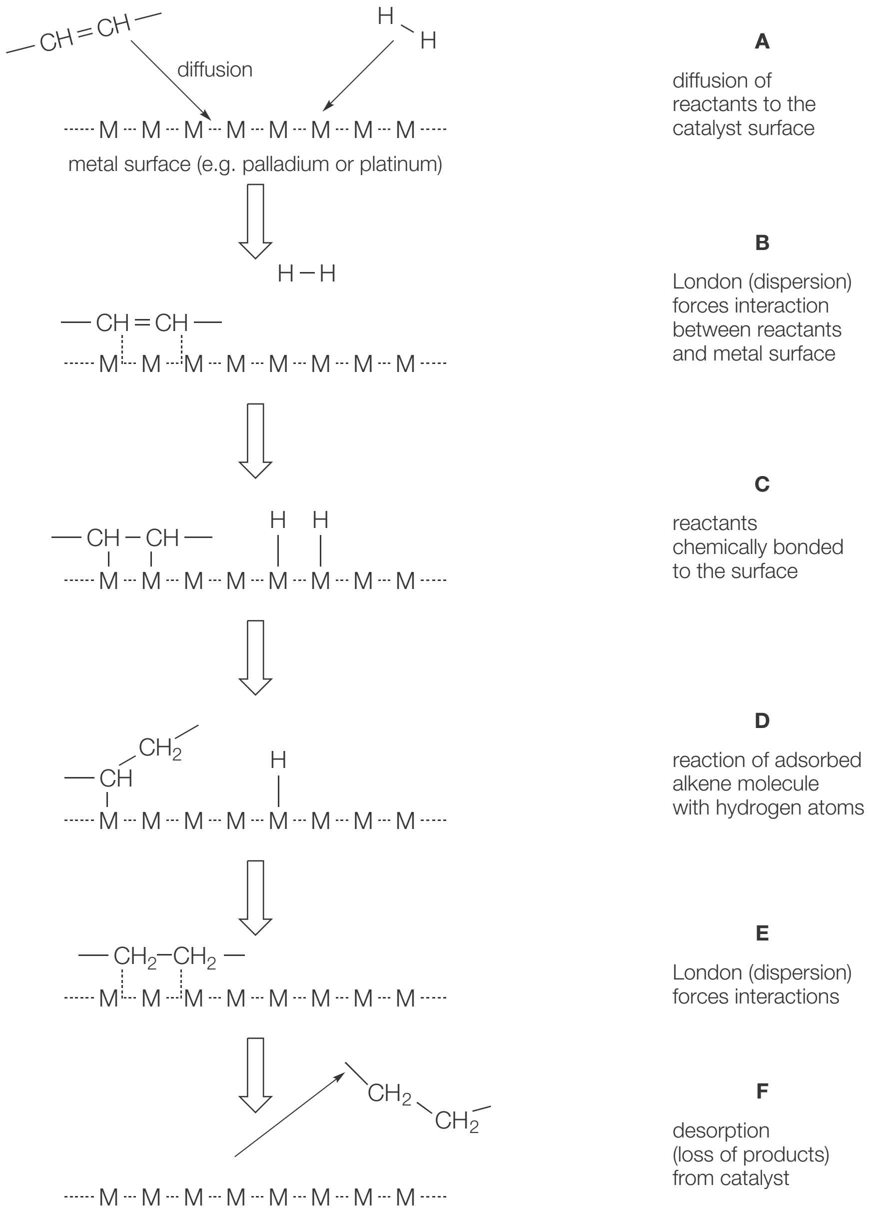


Figure 22.17 Mechanism of heterogeneous catalysed hydrogenation

■ QUICK CHECK QUESTION

20 A catalytic convertor can convert carbon monoxide in a car's exhaust to carbon dioxide.

- **a** State and explain what type of catalyst is present.
- **b** Outline four steps that occur during this type of catalysis.
- **c** Explain why 'lead-free' petrol must be used.

Expert tip

An active site is a part of the catalytic surface which is particularly good at adsorbing molecules and helping them to react. Active sites can be blocked by molecules and the catalyst will lose its activity. This is known as 'poisoning' (Figure 22.18).

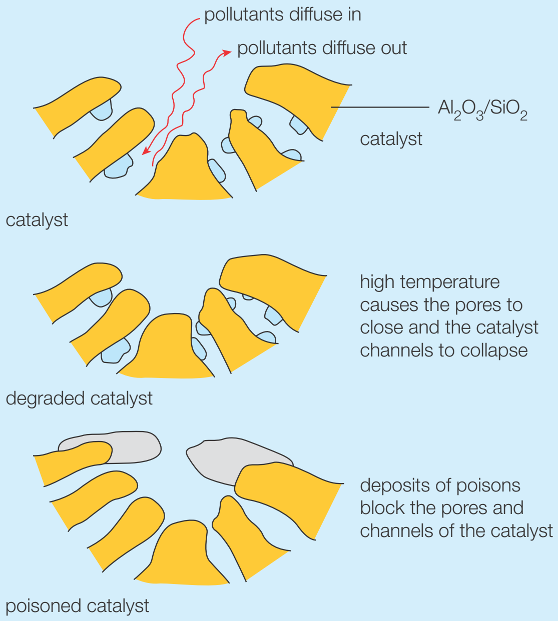


Figure 22.18 Structure and operation of a heterogeneous catalyst

Another important feature of heterogeneous catalysis is the ability of a catalyst to direct a reaction to yield a particular product, for example:

$$CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO \text{ and } Cr_2O_3} CH_3OH(g)$$

$$CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$$

$$CO(g) + H_2(g) \xrightarrow{Cu} H_2CO(g)$$

Zeolites

Revised ☐

Zeolites (Figure 22.19) are shape-selective catalysts and this property depends upon the size and shape of the holes present inside the zeolite and the sizes of the reactant and product molecules. Zeolites are a family of cage-like alumino-silicates each with specific holes. They are formed from silicate, SiO_4, and aluminate, AlO_4, tetrahedra. A zeolite will only catalyse reactions involving reactant molecules having a shape and size comparable to the holes. Zeolites are mainly used in the petrochemical industries (for example, catalysing cracking) and ion exchange, (for example, water softening).

QUICK CHECK QUESTION

21 Explain how zeolites act as selective heterogeneous catalysts.

Choice of catalyst

Revised ☐

When choosing a catalyst for catalysing a chemical reaction the following factors should be considered.

- **Selectivity**: Will the catalyst produce only the desired product? Or are there competing products?
- **Efficiency**: Will the catalyst cause a considerable increase in the rate of reaction compared to the uncatalysed reaction? Will it continue to work well under severe conditions, such as high temperature or high pressure?
- **Environmental impact:** Will it be easy to recycle or dispose of the catalyst without causing damage to the environment? Some transition metals and lead are classed as heavy metals and can cause problems if they enter soil or ground water.
- **Potential for poisoning**: Catalysts rely on reactants occupying the active site reversibly. A catalyst poison will occupy the active site irreversibly so blocking access to reactants.
- **Cost**: Industry is focused on generating profits. Many transition metals such as rhodium, platinum and palladium and rare earth metals are expensive and the cost to benefit ratio needs to be determined.
- **Activity**: The increase in the rate of a specified chemical reaction caused by an enzyme or other catalyst under specified conditions.

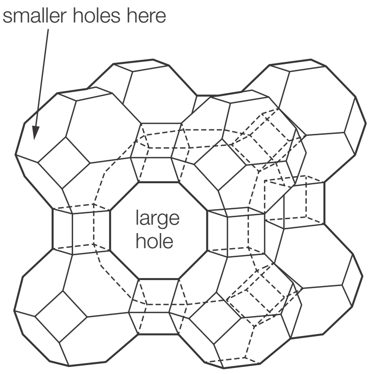


Figure 22.19 Outline of the cage structure of a zeolite, with formula $Na_{12}(Al_{12}Si_{12}O_{48}).27H_2O$

NATURE OF SCIENCE

Although the effects of catalysis have been known from very ancient times, the understanding of the phenomena started only in the 18th century. Only after chemical thermodynamics had been defined did a rational approach to discover new catalytic processes become possible. It took nearly a century before the molecular basis of catalytic processes, now widely applied on very larges scales, became understood.

Expert tip

The supported-metal catalysts for hydrogenation are also ‘nano’ since they comprise active metal nanoparticles supported on an ‘inert’ high surface area support.

Nanocatalysts

Revised ☐

A nanocatalyst (Figure 22.20) is a substance or material with catalytic properties that has nanoscale dimensions. A nanocatalyst has a very high surface area to volume ratio. This increases the efficiency of the catalyst. Nanocatalysts can be either heterogeneous or homogeneous, depending on whether a catalyst exists in the same phase as the substrate. Nanocatalysts include graphite, carbon nanotubes, fullerenes, metal oxides, certain metals and clays.

The benefits of nanocatalysts in industry are summarized in Figure 22.21 and include the increased selectivity and activity of catalysis by controlling pore size and particle characteristics and replacement of expensive metal catalysts.

QUICK CHECK QUESTION

22 Identify two concerns of using nanoscale catalysts.

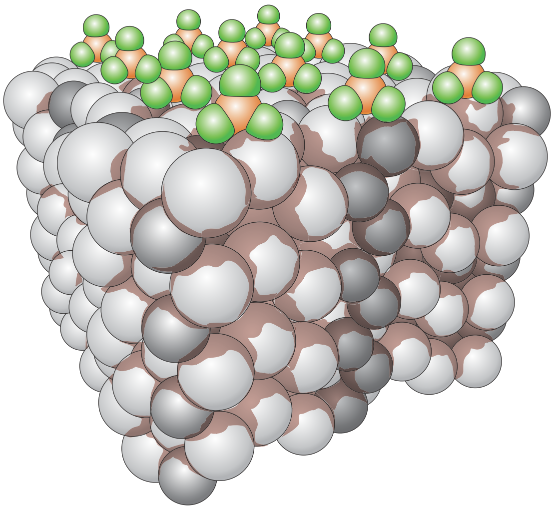


Figure 22.20 Reacting molecules on the surface of a nanocatalyst

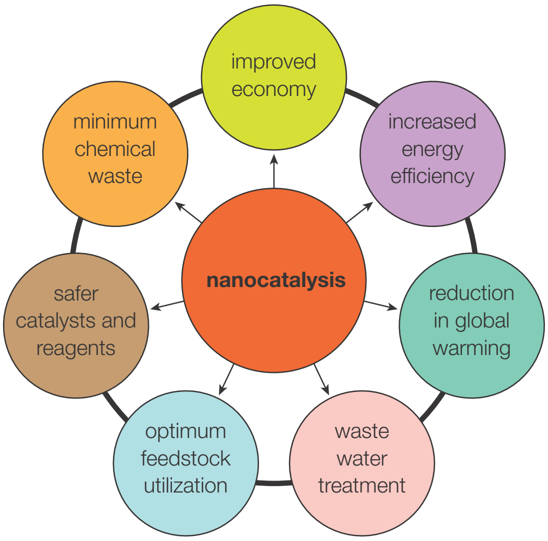


Figure 22.21 Benefits of nanocatalysts in industry

22.4 Liquid crystals

Revised ☐

Essential idea: Liquid crystals are fluids that have physical properties which are dependent on molecular orientation relative to some fixed axis in the material.

Liquid crystals

Revised ☐

- Liquid crystals are fluids that have physical properties (electrical, optical and elasticity) that are dependent on molecular orientation to some fixed axis in the material.
- Thermotropic liquid-crystal materials are pure substances that show liquid-crystal behaviour over a temperature range.
- Lyotropic liquid crystals are solutions that show the liquid-crystal state over a (certain) range of concentrations.
- Nematic liquid crystal phase is characterized by rod-shaped molecules which are randomly distributed but on average align in the same direction.

Expert tip

Liquid crystals are not crystals, but liquids with some remaining crystalline order. They are often regarded as an intermediate state of matter, but in fact are a separate state of matter.

Liquid crystals

Revised ☐

Liquid crystals are fluids with physical properties (optical, electrical, elastic, magnetic, etc.) that are dependent on the molecular orientation relative to a fixed axis in a material. This is known as anisotropy. They show physical characteristics which could be considered those of both a liquid and a solid. For example, a liquid crystal might flow like a liquid but exhibit an ordered molecular arrangement a little like a solid.

Common mistake

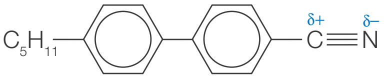
It should also be noted that a molecule is not a liquid crystal in the same way that a molecule is not a solid or a liquid. Liquid crystallinity is a bulk property which cannot be attributed to a single molecule.

Structural features of molecules that behave as liquid crystals

Certain structural features are often found in molecules forming liquid crystal phases, and they may be summarized as follows:

- Normally, one or both of the terminal groups will be a flexible alkyl chain.
- The molecules are usually elongated. Liquid crystallinity is more likely to occur if the molecules have flat segments, e.g. benzene rings.
- A rigid backbone containing double bonds defines the long axis of the molecule.
- The existence of strong dipoles and easily polarizable groups in the molecule.

Many substances can exist in the liquid crystal state (under certain conditions) including DNA, soap, spider silk, graphite, cellulose, viruses, Kevlar, cholesterol molecules in cell membranes and many synthetic molecules with liquid crystal properties, such as the biphenyl nitriles (Figure 22.22).



the molecule is polar because nitrogen has a higher electronegativity than carbon

Figure 22.22 The structure of 4´-pentylbiphenyl-4-carbonitrile (known as 5CB)

NATURE OF SCIENCE

In 1888, the Austrian chemist Friedrich Reinitzer was performing experiments on a cholesterol-based substance to determine the formula and molecular mass of cholesterol. When he tried to determine the melting point, an important indicator of the purity of a substance, he observed that the substance seemed to have two melting points. At 145.5 °C the solid crystal melted into a cloudy liquid which existed until 178.5 °C where the cloudiness suddenly disappeared, giving way to a clear transparent liquid. At first Reinitzer thought that this might be a sign of impurities in the material, but further purification did not bring any changes to this behaviour.

Thermotropic and lyotropic liquid crystals

Thermotropic liquid crystals

Thermotropic liquid crystals, for example, the biphenyl nitriles, are pure substances that occur as liquid crystals over a certain temperature range between the solid and liquid states of a material. Below this temperature range, the substance turns into a solid without fluidity, while above this range, the substance turns into a liquid without long-range order (Figure 22.23).

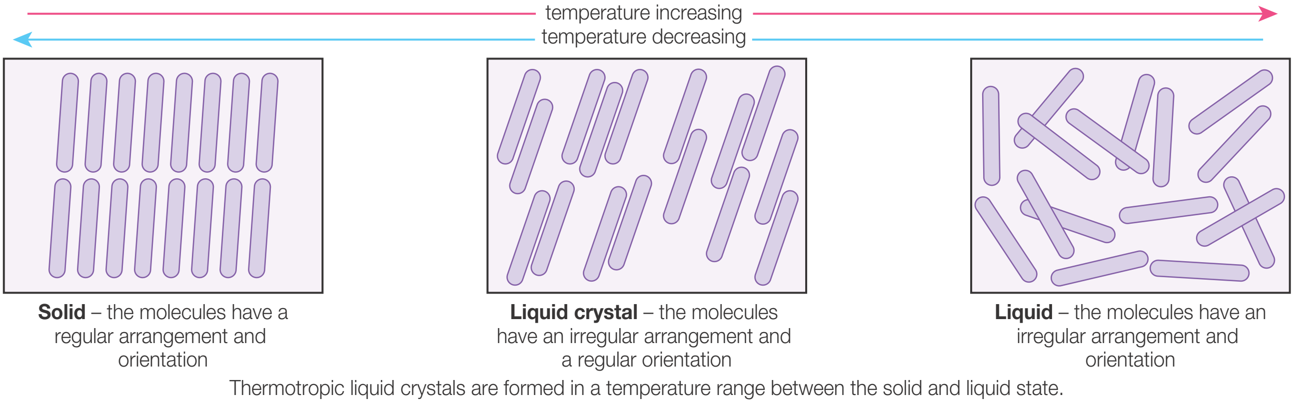


Figure 22.23 A representation of the transition of a substance from the solid state to the thermotropic liquid crystal state and then to the isotropic liquid

Thermotropic liquid crystals often show liquid crystal mesophase behaviour just above the melting point: the compound will flow but it is cloudy rather than forming a clear liquid. Various types of mesophases can form. In a nematic mesophase, the molecules preferentially point in one direction but there is no positional correlation at all, while in smectic mesophases, the molecules are loosely correlated into layers, again with orientational correlation.

In the nematic phase all molecules are aligned approximately parallel to each other. At each point a unit vector can be defined, parallel to the average direction of the long axis of the molecules in the immediate neighbourhood. This vector, known as the director, is not constant throughout the whole medium, but is a function of space.

Some mesophases have chiral analogues that form when materials that are enantiomerically pure (or at least in enantiomeric excess) are used. For example, there is a chiral nematic phase which has a helical structure, caused by the fact that neighbouring molecules can no longer arrange themselves parallel, rather being mutually twisted (Figure 22.24).

Lyotropic liquid crystals

Lyotropic liquid crystals are solutions which show a liquid crystal phase at specific concentrations of solvent in the solute (Figure 22.25). For example, a soap solution above a certain concentration results in a more ordered orientation of the molecules in the soap, creating a liquid crystal phase.

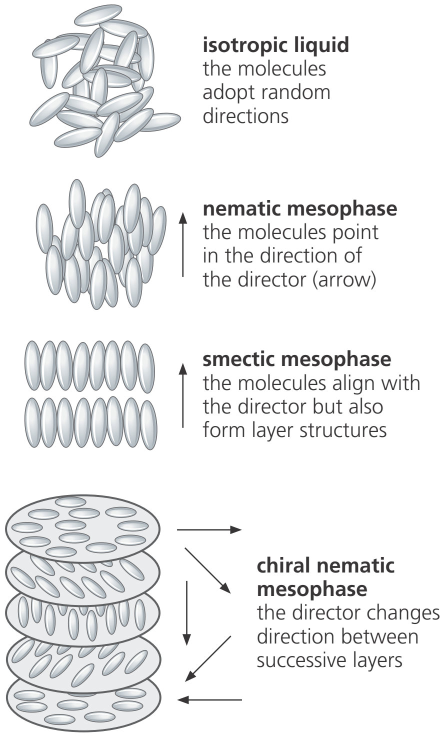
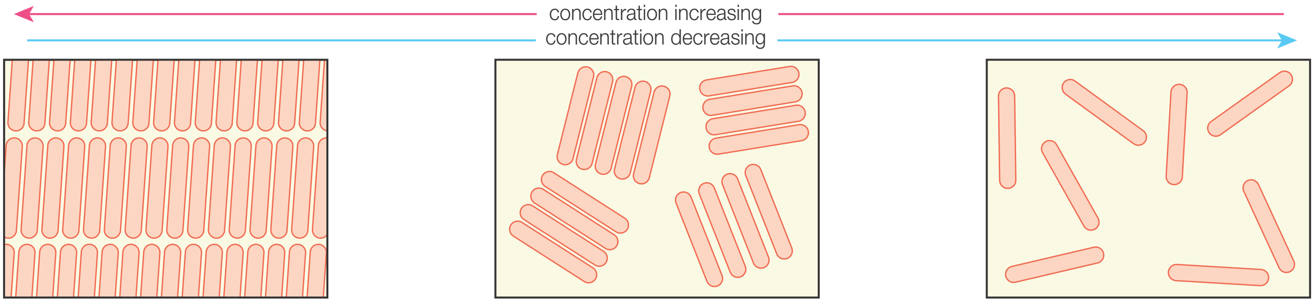


Figure 22.24 The different types of mesophases formed by liquid crystal molecules



Solid – the molecules have a regular arrangement and orientation

Liquid crystal – the molecules have an irregular arrangement and a regular orientation

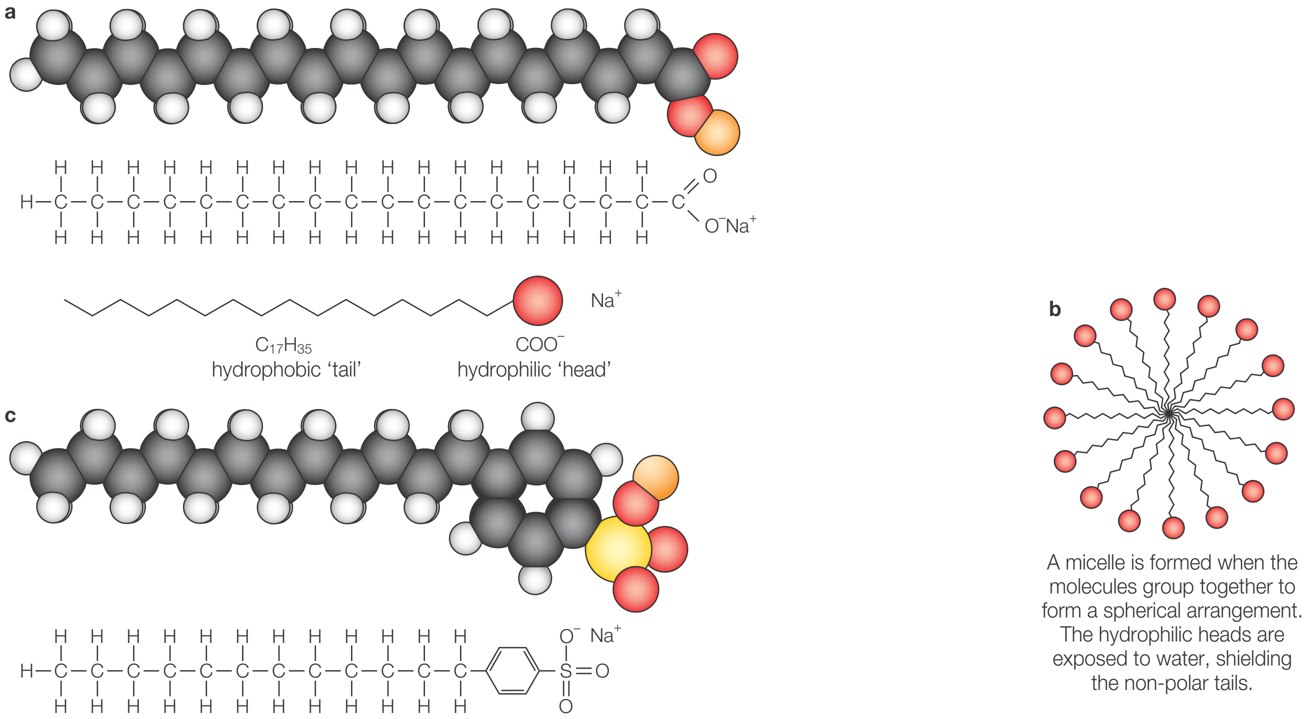
Liquid – the molecules have an irregular arrangement and orientation

The phase transitions of lyotropic liquid crystals depend on both temperature and concentration.

Figure 22.25 The formation of a lyotropic liquid crystal state by certain substances in solution

Thermotropic and lyotropic behaviour

In lyotropic liquid crystals, composed of soap or detergent molecules (Figure 22.26), the liquid crystal phase tends to be made up of micelles (spheres or rods) or bilayers (stacks of sheets) – bilayers can self-organize to form a lamellar (layered) phase liquid crystal. Bilayers occur at higher concentrations than micelles (Figure 22.27).



A micelle is formed when the molecules group together to form a spherical arrangement. The hydrophilic heads are exposed to water, shielding the non-polar tails.

Figure 22.26 a Soap molecules, such as sodium stearate (octadecanoate) shown here, have the structure of the type required to form a lyotropic liquid-crystal state in aqueous solution. **b** Soap and detergent molecules can form micelles in aqueous solution. **c** A molecule of a synthetic detergent shows similar structural features to a soap molecule: long hydrophobic tail and polar, hydrophilic head group

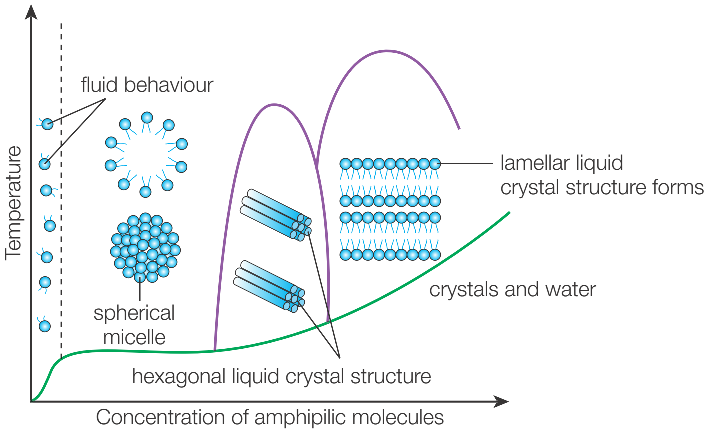


Figure 22.27 Typical phase diagram for a typical lyotropic liquid crystal: various liquid crystal phases are observed

Thermotropic behaviour in the nematic liquid crystal phase is nearer that of a liquid than the smectic phase (higher temperature). The generally rod-shaped molecules are distributed randomly in the nematic phase, but, on average, point toward one direction (directional order), grouped in a bunch. Seeing as they have no defined positional order, these molecules can flow past one another.

If temperature in a nematic phase liquid crystal is increased further, the substance will change into an isotropic liquid phase, with freely flowing molecules. If it is cooled further, the smectic phase of the liquid crystal will be reached, where the molecules have some positional order, and if even further, the substance will turn into a solid, with a rigid structure.

Applications of liquid crystals

Revised ☐

A liquid crystal thermometer relies on the fact that the pitch (the distance over which the helical twist in a chiral nematic liquid crystal repeats) is about the same as the wavelength of visible light, leading to diffraction (strictly it is the pitch multiplied by the average refractive index). However, the pitch changes with temperature and so the colour also changes. By varying the chemical structure of the molecules of the liquid crystal or the composition of a mixture of liquid crystals, the temperature range over which colour changes can be seen is controlled.

Liquid crystal displays (LCDs) rely on the polar nature of chiral liquid crystal molecules, which means that the direction of alignment is influenced by an electric field (voltage). The passage of plane polarized light through a thin liquid crystal layer (held between two thin glass plates) can be controlled by switching the orientation of the molecules in the layer (Figure 22.28).

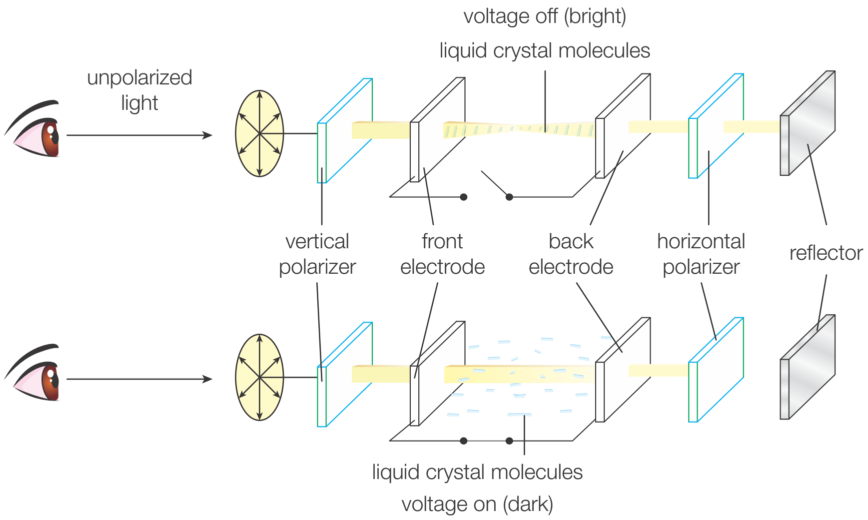


Figure 22.28 Schematic illustration of the operation of a twisted nematic liquid crystal display (LCD)

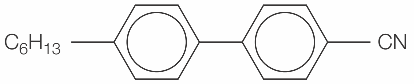
Properties needed for the liquid crystal molecules in LCDs include: chemical stability, a nematic phase which is stable over a suitable temperature range, polarity so they can change orientation when an electric field is applied, and a rapid switching speed which requires low viscosity. It is very important to note that the applied field is low and it is this that makes the displays small, flat and portable – i.e. small power source.

■ QUICK CHECK QUESTIONS

23 Complete the following table by adding yes or no.

	Crystalline solid	Nematic phase liquid crystal	Pure liquid
Positional order of particles			
Directional order of particles			

24 Biphenyl nitriles, such as the molecule shown below, were the first thermotropic liquid crystal molecules to be synthesized.



Explain why the nitrile functional group enables these molecules to be used in liquid crystal displays (LCDs). State what is meant by a thermotropic liquid crystal.

25 Outline **two** principles of a liquid-crystal display (LCD) device.

22.5 Polymers

Revised ☐

Essential idea: Polymers are made up of repeating monomer units which can be manipulated in various ways to give structures with desired properties.

Polymers

Revised ☐

- Thermoplastics soften when heated and harden when cooled.
- A thermosetting polymer is a prepolymer in a soft solid or viscous state that changes irreversibly into a hardened thermoset by curing.
- Elastomers are flexible and can be deformed under force but will return to nearly their original shape once the stress is released.
- High-density poly(ethene) (HDPE) has no branching, allowing chains to be packed together.
- Low-density poly(ethene) (LDPE) has some branching and is more flexible.
- Plasticizers added to a polymer increase the flexibility by weakening the intermolecular forces between the polymer chains.
- Atom economy is a measure of efficiency applied in green chemistry.
- Isotactic addition polymers have substituents on the same side.
- Atactic addition polymers have the substituents randomly placed.

Types of polymer

Revised ☐

Addition polymers are formed when an alkene (or derivative) uses the electron pair in a π bond to make a new σ bond to the next molecule (Figure 22.29).

Expert tip

The properties of polymers are very varied. Polymeric materials include plastics, elastomers and fibres.

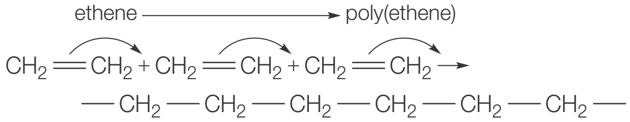


Figure 22.29 A simplified model of addition polymerization

Condensation polymers are formed when a monomer eliminates a small molecule, freeing some bonds to bond to the next molecule.

Structures of addition polymers

The properties of some addition polymers with substituents on a carbon chain depend on the way in which the side-chains are orientated. This is known as tacticity.

In isotactic poly(propene), for example, all the methyl substituents are on the same side of the carbon chain (backbone) (Figure 22.30). The molecules coil into a regular helical shape and pack together to form a crystalline and tough polymer.

There is another form of poly(propene) in which the methyl side groups along the polymer chain (carbon backbone) are randomly orientated. This atactic polymer has an amorphous (non-crystalline) structure and is rubbery.

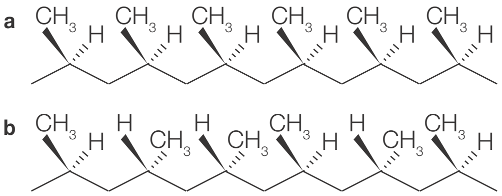
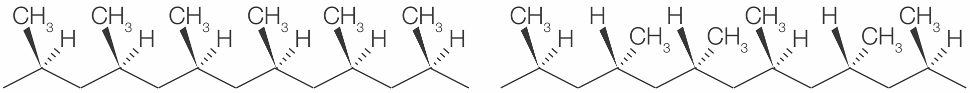


Figure 22.30 a Planar representation of isotactic poly(propene) (with all the methyl groups on the same side of the carbon chain). **b** Part of a chain of atactic poly(propene)

QUICK CHECK QUESTION

26 Poly(propene) can exist in two forms. Identify the two forms below. State and explain which of the two forms of poly(propene) is more crystalline. Explain why the more crystalline form can be used to make strong fibres for carpets.



NATURE OF SCIENCE

Hermann Staudinger's pioneering theories on the polymer structures of fibres and plastics as macromolecules formed the basis for developments in the field of materials science and supported the rapid growth of the plastics industry. For his work in the field of polymers, Staudinger was awarded the Nobel Prize for chemistry in 1953.

Polymerization of 2-methylpropene

2-Methylpropene can undergo addition polymerization to form poly(2-methylpropene), known as butyl rubber or polyisobutylene (Figure 22.31). It is a synthetic rubber and an elastomer.

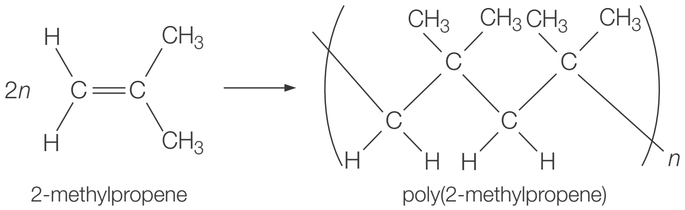


Figure 22.31 Formation of poly(2-methylpropene) from 2-methylpropene

Typically, monomers join head-to-head and the two methyl groups are placed on every alternate carbon atom on the chain. Occasionally, a monomer adds on to the carbon chain the other way round (head-to-tail) and two consecutive carbon atoms have two methyl side groups (Figure 22.32).

QUICK CHECK QUESTIONS

27 Consider the hydrocarbon, $(CH_3)_2C{=}CHCH_3$, which can be polymerized. Name the type of polymerization involved and draw the repeating unit of the polymer. Draw the structure of an isomer of the monomer which shows *cis–trans* isomerism.

28 A polymer's structure influences its physical properties. Describe **two** structural variations that are possible for poly(propene) but not for poly(ethene).

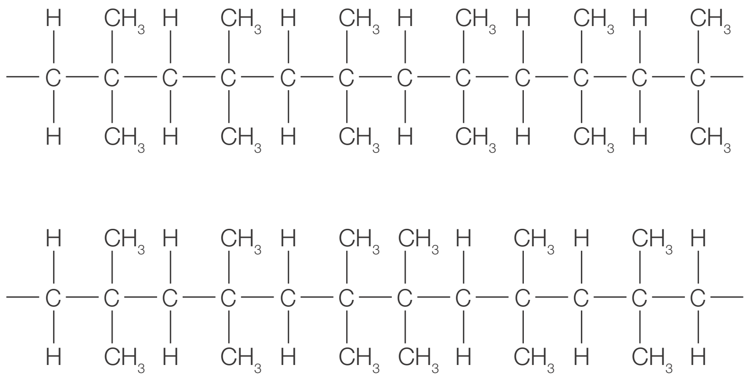


Figure 22.32 Head-to-head and head-to-tail polymers of poly(2-methylpropene)

Classifying plastics

Revised ☐

One possible way of classifying polymers is by the effect that heat has on them (Figure 22.33).

A thermoplastic can be heated until it softens, and then cooled to harden again, repeatedly. Addition polymers, such as nylon and polyesters, are thermoplastics and are often melted in the process of manufacture into some useful material.

A thermoset, once heated, hardens as new covalent bonds form and will not soften again. Thermosets are often formed by the covalent crosslinking of polymer molecules. These are known as prepolymers and are soft solids or viscous liquids. The more the polymer is heated (cured), the greater the extent of crosslinking and the harder the product.

Some polymers, such as natural rubber, are elastomers. Elastomers can be deformed a long way under the application of a force, but will return to their original shape and length once the stress is released (Figure 22.34).

Expert tip

Cross-linking during polymerization is possible if one of the monomers has three functional groups.

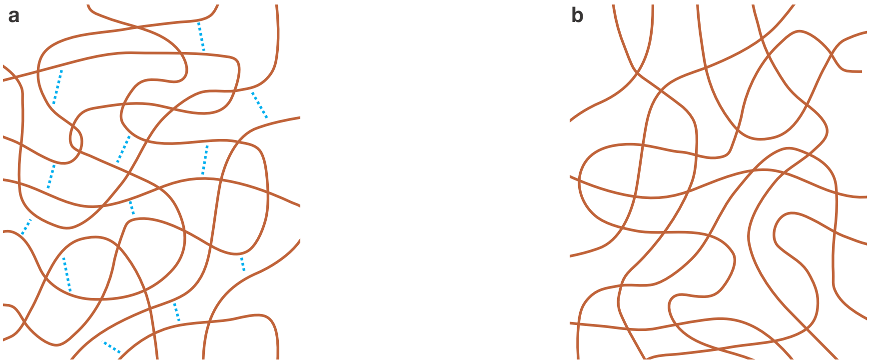


Figure 22.33 **a** Thermosetting and **b** thermoplastic polymers have different properties

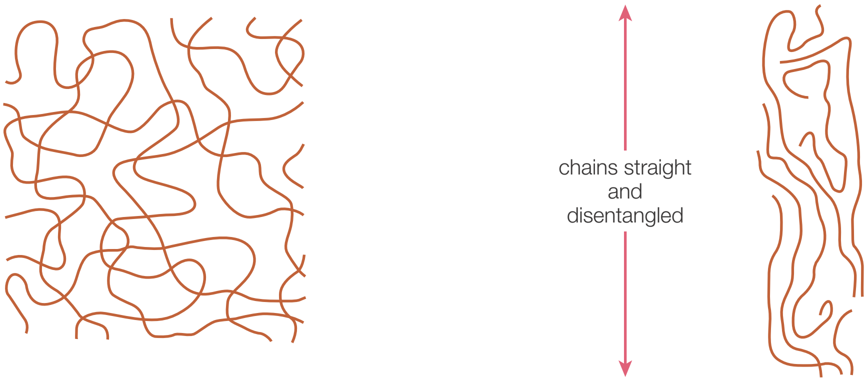


Figure 22.34 Unstretched and stretched rubber chains

■ QUICK CHECK QUESTION

29 Outline how properties of thermosetting polymers differ from those of thermoplastics.

Modification of plastics

Revised ☐

Crystallinity

The greater the extent of intermolecular forces operating between adjacent polymer chains, the stronger the material will be, and the lower the flexibility. The degree of branching (which will limit contact) and the degree of polymer chain alignment (crystallinity) will control the properties of a plastic (Figure 22.35).

Crystallinity can be increased by aligning the crystalline areas through 'cold drawing', stretching the polymer at room temperature (Figure 22.36).

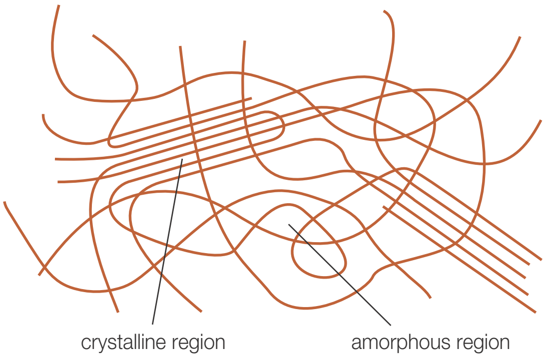


Figure 22.35 Crystalline and amorphous regions of a polymer

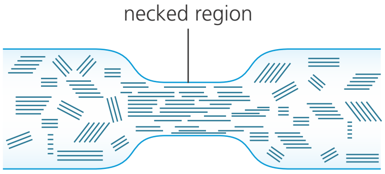


Figure 22.36 The cold drawing of a polymer forms a neck where the polymer chains become aligned

Branching

Depending on the reaction conditions (and hence reaction mechanism), ethene can undergo polymerization to form high-density poly(ethene) (HDPE) or low-density poly(ethene) (LDPE) (Figure 22.37). In HDPE, there is little branching and the long chains can fit together closely. This makes it stronger, more rigid and a higher density than LDPE.

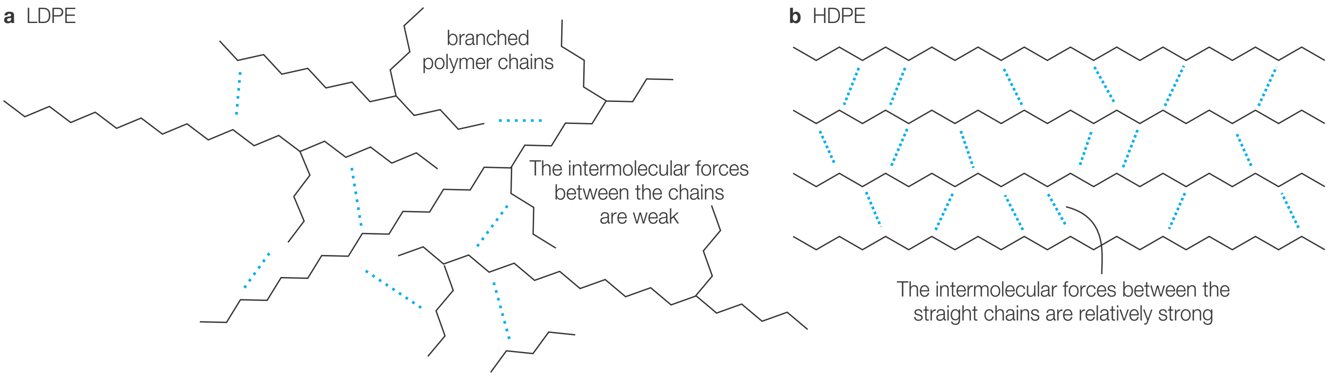


Figure 22.37a The branched nature of the chains in low-density poly(ethene), LDPE, makes for a flexible plastic product. In general, LDPE has about one C_4–C_6 branch per 100 carbon atoms of the chain, with the occasional longer branch. **b** The unbranched chains in high-density poly(ethene), HDPE, make for a more crystalline structure and a more rigid plastic

QUICK CHECK QUESTION

30 Outline the basic differences between the structure and properties of low-density and high-density poly(ethene).

Properties of polymers and structural features

Revised ☐

The physical properties of a polymer, such as its strength and flexibility, are determined by the structural features of its molecules:

- Chain length: in general, the longer the chains the stronger the polymer, but the more viscous it is in the molten state the harder it is to process.
- Side groups: polar side groups result in stronger attraction between polymer chains, making the polymer stronger.

- Branching: straight unbranched chains can pack together more closely than highly branched chains, resulting in polymers that have a higher degree of crystallinity.
- Cross-linking: if polymer chains are covalently linked together (curing), the polymer is harder and more difficult to melt. Thermosetting polymers have extensive cross-linking.

Plasticizers

Another approach to controlling the physical properties of plastics is the use of plasticizers. Polymer chains that might normally have relatively strong attractive intermolecular forces can be kept apart by the introduction of small molecules, giving greater flexibility (Figure 22.38).

QUICK CHECK QUESTIONS

31 Explain, in molecular terms, why poly(chloroethene) (PVC, poly(vinyl chloride)) becomes more plastic when a plasticizer is added.

32 Explain why poly(chloroethene) (PVC, polyvinyl chloride) is less flexible than poly(ethene).

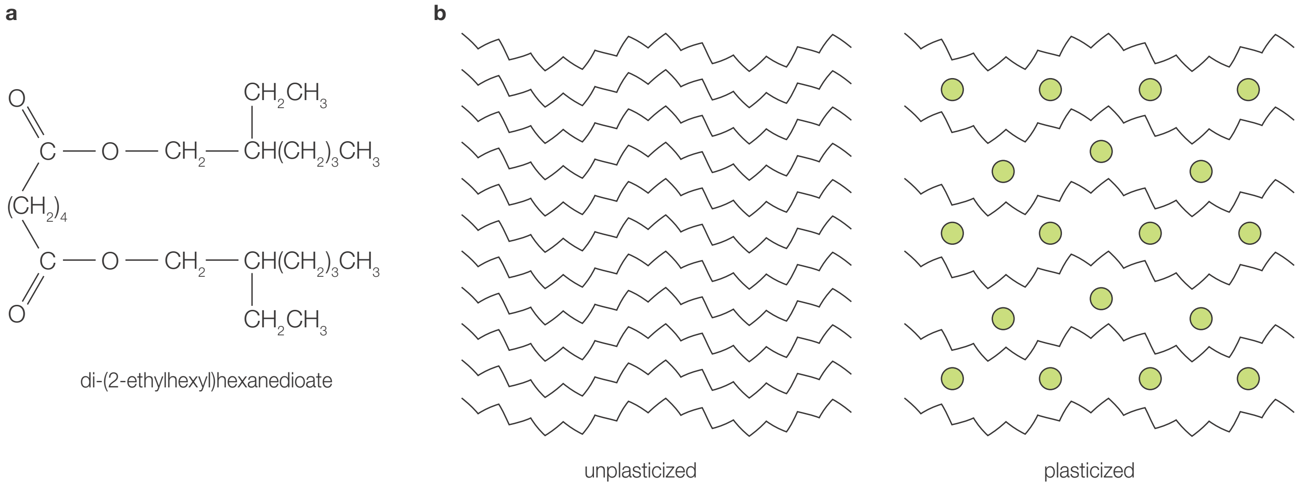


Figure 22.38 a A plasticizer used in the manufacture of poly(chloroethene), PVC, – di-(2-ethylhexyl)hexanedioate. **b** The plasticizer molecules separate the PVC polymer chains, allowing them to move freely past one another

Volatile hydrocarbons

If pentane is added during the formation of poly(styrene) (Figure 22.39) and the product heated in steam the volatile pentane vaporizes producing expanded poly(styrene). This material has a low density and is a good thermal insulator and has good shock-absorbing properties.

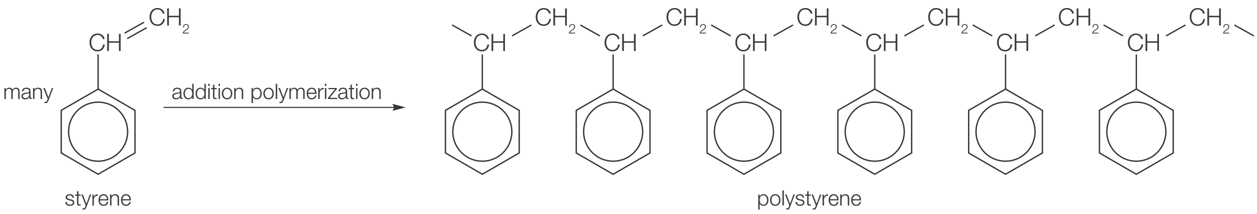


Figure 22.39 Formation of poly(styrene) from styrene

Atom economy

Addition polymers have high atom economies as all the monomer molecules are incorporated into the polymer chain. Condensation polymers will have lower atom economies due to the elimination of small molecules during the polymerization process.

QUICK CHECK QUESTION

33 Plastics have replaced more traditional materials such as metal and wood. Suggest **one** polymer property, different in each case, that makes polymers more suitable than iron and wood.

22.6 Nanotechnology

Revised ☐

Essential idea: Chemical techniques position atoms in molecules using chemical reactions whilst physical techniques allow atoms/molecules to be manipulated and positioned to specific requirements.

Nanotechnology

Revised ☐

- Molecular self-assembly is the bottom-up assembly of nanoparticles and can occur by selectively attaching molecules to specific surfaces. Self-assembly can also occur spontaneously in solution.
- Possible methods of producing nanotubes are arc discharge, chemical vapour deposition (CVD) and high-pressure carbon monoxide (HIPCO).
- Arc discharge involves either vaporizing the surface of one of the carbon electrodes, or discharging an arc through metal electrodes submersed in a hydrocarbon solvent, which forms a small rod-shaped deposit on the anode.

Nanotechnology

Revised ☐

Nanotechnology is the synthesis and study of compounds, devices (Figure 22.40) and structures within the range of 1 to 100 nanometres (1×10^{-9} m to 1×10^{-7} m) in size. The motor (Figure 22.40) is powered by light and the molecule rotates about a carbon–carbon double bond. The groups either side of the double bond are identical and ultraviolet radiation causes them to undergo *cis–trans* isomerization. Because of the large size of the groups, which are chiral, the motor can only rotate in one direction.

Expert tip

At these atomic dimensions, quantum physics determines the behaviour of nano-sized particles. For example, the properties of gold nanoparticles vary with size and are very different from the properties of a bulk sample of gold. Gold particles may be any colour (depending on size and shape) and will react with nitric acid unlike gold (in bulk).

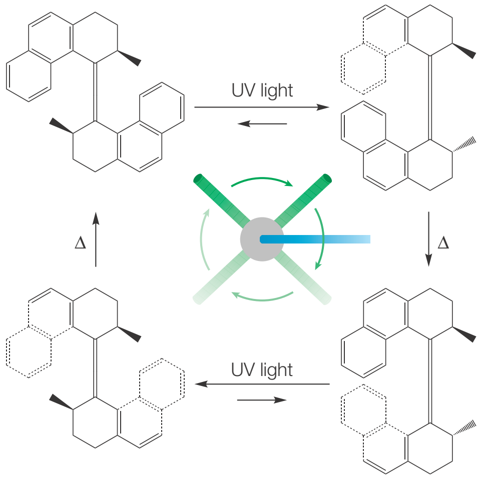


Figure 22.40 The first light driven molecular motor

Nano-sized particles have many useful properties that can be different from bulk materials, due to, for example, different surface area to size ratios, resulting in a higher percentage of atoms at the surface (which enhances their reactivity and catalytic effect) and quantum effects which becomes important at this level.

Approaches to nanotechnology

Revised ☐

There are two main approaches in nanotechnology:

- The 'bottom-up' approach involves synthesizing materials, structure, compounds and devices from individual atoms or molecules. This is also termed molecular nanotechnology and involves building organic and inorganic structures atom-by-atom or molecule-by-molecule. Self-assembly can occur by spontaneous binding of molecules to other molecules or to specific surfaces. Self-assembly can also occur spontaneously in solution. Ribosomes and viruses are examples of biological structures that are formed by self-assembly.
- The 'top-down' approach involves constructing or assembling nano-structures from larger structures. Examples of 'top-down' nanotechnology include lithography and etching. Small features are made by starting with larger materials, for example, semiconductors and patterning to make nanoscale structures with precise patterns.

Physical and chemical techniques

Revised ☐

Physical techniques

Researchers often use physical techniques that allow atoms, ions and molecules to be manipulated and positioned to specific locations, within a nano-structure, or a surface. The atom force microscope (AFM), the scanning tunnelling microscope (STM) and focused electron beam induced processing are all examples of physical techniques used in nanotechnology.

Atomic force microscope

The AFM (Figure 22.41) generates a topological (three-dimensional map) image by moving a sharp tip held at the end of a cantilever across a surface (within air or liquid) which is on top of a piezoelectric block. Small changes in voltage across the block allow tiny but accurate and precise movements that allow very prescise scanning.

As the tip tracks the surface, the force between the tip and surface causes the cantilever to bend. The deflection of the cantilever is measured optically by means of a laser beam and a photo detector, which measures changes in position of the incident laser beam as small as 1 nm. Atomic resolution is possible.

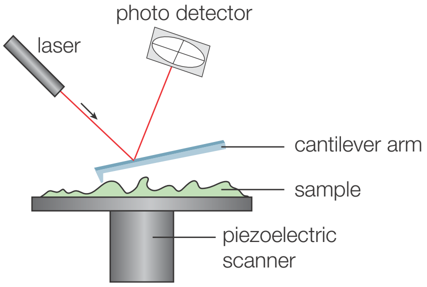


Figure 22.41 Atomic force microscopy (AFM)

Expert tip

As the cantilever approaches the surface, there are weak attractive London (dispersion) forces between the surface and the cantilever. As the cantilever is pushed into the surface they become repulsive forces, since the cantilever is trying to displace atoms on the surface. Both forces displace (move) the cantilever and can be used to measure topography.

Scanning tunnelling microscope

The scanning tunnelling microscope (STM) (Figure 22.42), gives images of individual rows of atoms. Like the AFM, it is based on a fine-tipped probe that scans across a small area of a surface and the probe's scanning movement is controlled to within 0.001 nm by piezoelectric transducers. The probe is held at a small constant potential (voltage), with the tip held at a fixed height of no more than 1 nm above the surface so that electrons 'tunnel' across the gap. If the probe tip moves near a raised atom or across a dip in the surface, the tunnelling current increases or decreases respectively due to a respective decrease or increase of the gap width.

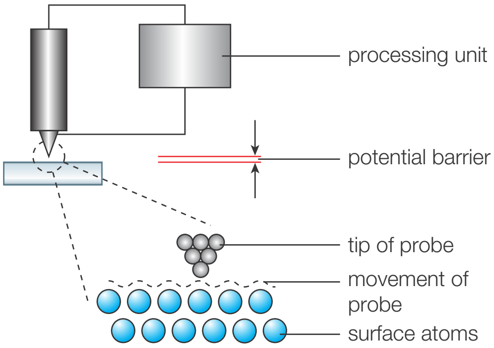


Figure 22.42 Principle of the scanning tunnelling microscope (STM)

Expert tip

In constant height mode, the change of current is used to generate an image of the surface provided the probe's vertical position is unchanged. In constant current mode, the change of current is used to move the probe vertically upwards or downwards respectively until the gap width and the current are the same as before. The vertical resolution is of the order of 0.001 nm, much smaller than the size of the smallest atom. The principle of tunnelling is based on the wave nature of particles.

Chemical techniques

Carefully controlled and specific chemical reactions can also be used to synthesize particular molecules and nanostructures (Figure 22.43). A wide variety of chemical reactions can be used to synthesize and stabilize nanoparticles including chemical reduction, reactions in micelles and emulsions, photochemical reduction, synthesis at low temperatures (cryochemical synthesis) and polymerization reactions.

NATURE OF SCIENCE

The scanning tunnelling microscope (STM) is among a number of instruments that allows scientists to view and manipulate nanoscale particles, atoms and small molecules. Atomic force microscopes (AFMs) gather information by 'feeling' the surface with a mechanical probe. These microscopes make use of tiny but exact movements to enable precise mechanical scanning.

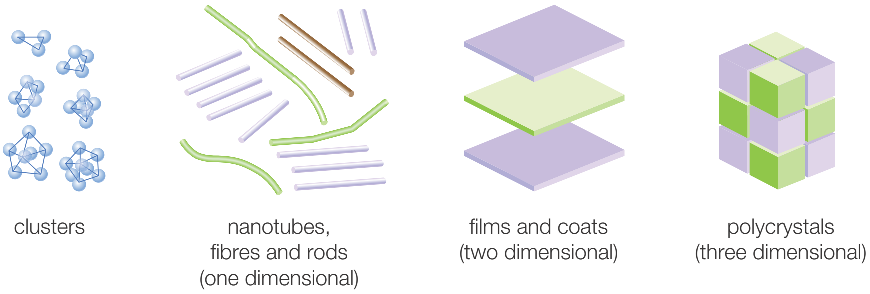


Figure 22.43 Types of nanocrystalline materials classified by size of their structural elements

Carbon-60

Carbon-60 (Figure 22.44) is an allotropic form of carbon. A total of 60 sp^2 hybridized carbon atoms are present, forming a sphere consisting of five-carbon and six-carbon atom rings arranged in the same pattern as the seams on a modern soccer ball. There are 20 hexagons and 12 pentagons, with a carbon atom at the vertices (corners) of each polygon and a bond along each polygon edge.

Expert tip

The presence of pentagonal rings prevents the graphite sheet from being planar (flat).

Figure 22.44 A model showing the geometry of carbon-60

The bonding within a single molecule of buckminsterfullerene is very strong. The carbon-60 molecule is not easily squashed, deformed or broken apart during a collision.

Carbon-60 is a simple molecular substance whose lattice is due to the presence of London (dispersion) forces. It is a soft black solid with a low sublimation point and dissolves in non-polar solvents to form coloured solutions.

In carbon-60 the carbon atoms are all joined by delocalized π bonds, but the delocalization is reduced by the curvature. Transfer of the current (π electrons) from one molecule to the next does not occur because of the large band gap (between the conduction and valence band). Carbon-60 behaves like a semiconductor.

Carbon-60 can be prepared by electrically heating graphite rods in an inert atmosphere of helium at low pressure. The sublimate contains carbon-60, which will dissolve in organic solvents.

Carbon nanotubes

Carbon nanotubes are structurally related to carbon-60. These are cylindrical in structure and resemble a rolled-up sheet of graphene, with the carbon molecules arranged in repeating hexagons. They have a diameter of a few nanometres and can be open at both ends, sealed at one end or sealed at both ends. Both single and multi-walled graphene tubes (Figure 22.45), made from concentric carbon nanotubes, have been prepared.

Expert tip

A carbon nanotube can be closed by the presence of pentagons, which introduce curvature into graphene.

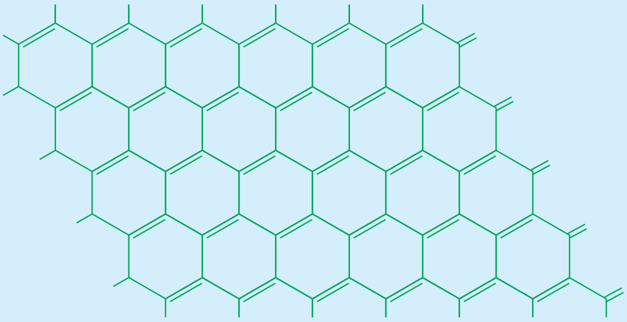


Figure 22.45 Graphene wall of a carbon nanotube

Carbon nanotubes (Figure 22.46) have a very high tensile strength (in bulk), may have very good electrical conductivity and a relatively high thermal conductivity.

The high tensile strength is due to the effective overlap between p orbitals on the small carbon atoms leading to effective π delocalization across the surface of the nanotubes. The large surface area to volume ratio means that there are extensive London (dispersion) forces operating between carbon nanotubes arranged in bundles.

The electrical and thermal conductivity is also due to the presence of delocalized π electrons, but there is a wide range of electrical conductivity depending on the length and width of the carbon nanotube and how the graphene sheet was rolled to form the nanotube.

Carbon nanotubes can be used as semiconductors, 'molecular wires', catalysts and in composite materials. Applications suggested include their use to make tiny mechanical devices, molecular computers as well as extremely strong materials.

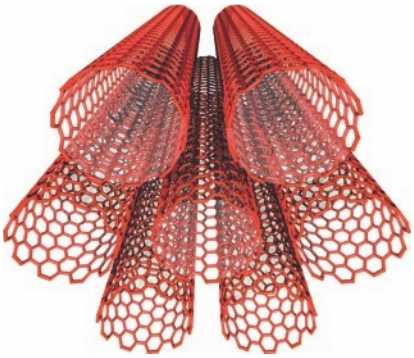


Figure 22.46 Open ended single-walled carbon nanotubes (computer generated)

QUICK CHECK QUESTION

34 Describe the structure and properties of carbon nanotubes.

Graphene

Graphene is a single layer of carbon in the form of graphite, with its layered structure of hexagonal rings of carbon atoms. Graphene can also be considered as a two-dimensional nano-material because it is only one atom thick.

Graphene has a high thermal stability (like graphite, up to 3000 °C if no oxygen present), high electrical conductivity (due to extensive π delocalization), a high optical transparency, high mechanical strength and is chemically relatively inert.

Production of carbon nanotubes

Revised ☐

Carbon nanotubes can be prepared by arc discharge, chemical vapour deposition (CVD) and high-pressure carbon monoxide (HIPCO).

Arc discharge

Graphite electrodes are placed a small distance apart and a large electric current is passed through the electrode which creates an electric arc between the two electrodes. An inert helium or argon atmosphere is present inside the apparatus to prevent formation of oxides of carbon (Figure 22.47).

Alternatively, two metal electrodes are placed a small distance apart in a liquid hydrocarbon solvent (Figure 22.48). A large current creates an arc between the electrodes, causing the hydrocarbon molecules to decompose to release carbon atoms. This is catalysed by iron or nickel. A small rod-shaped structure containing carbon nanotubes is deposited at the anode (negative electrode).

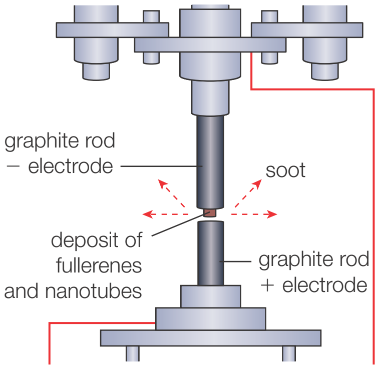


Figure 22.47 Arc discharge method for carbon nanotube production

The oxidation state of carbon in a hydrocarbon is always negative (hydrogen is less electronegative), but in carbon nanotubes (an elemental form) it is zero, therefore this process involves the oxidation of carbon.

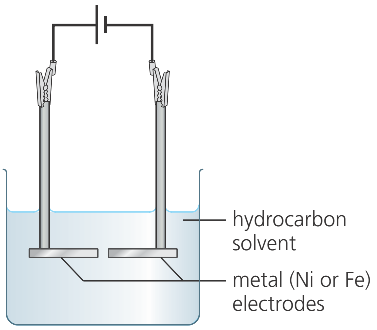


Figure 22.48 Experimental apparatus for arc discharge using metal electrodes and a hydrocarbon solvent

Chemical vapour deposition (CVD)

CVD production of carbon nanotubes involves flowing a hydrocarbon or alcohol gas into a chamber containing a heated inert object (with a transition metal catalyst) to be coated. Chemical reactions occur on and near the hot surfaces, resulting in the deposition of a thin film of nanotubes on the surface, accompanied by the production of chemical by-products that are exhausted out of the chamber along with unreacted precursor gases. Inert nitrogen gas is introduced to ensure the apparatus (Figure 22.49) is free of air and to prevent oxidation of carbon to its oxides. Depending on the precursor and conditions, single-walled and multi-walled carbon nanotubes can be formed.

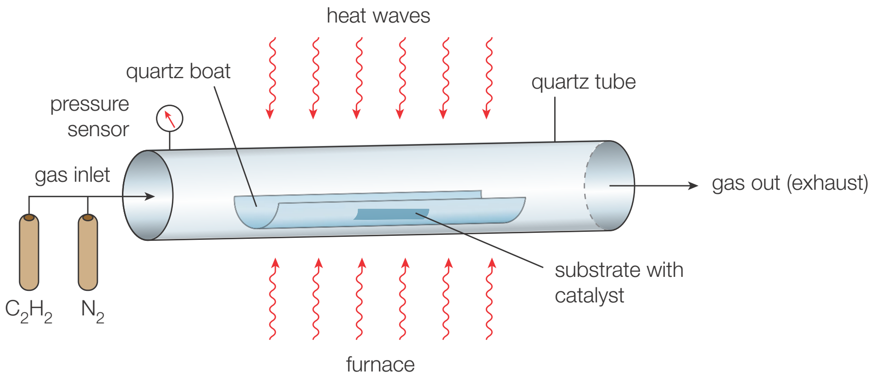


Figure 22.49 Chemical vapour deposition

HIPCO

The high-pressure carbon monoxide method, or HIPCO, results in the rapid synthesis of high-quality single-walled carbon nanotubes. In this process in the continuous-flow gas phase carbon monoxide acts as a feedstock and the iron(0) pentacarbonyl complex, $Fe(CO)_5$, as a catalyst. The HIPCO process runs continuously and allows the reuse of carbon monoxide.

During the HIPCO process the iron complex decomposes to form iron nanoparticles:

$$Fe(CO)_5(g) \rightarrow Fe(s) + 5CO(g)$$

The iron nanoparticles provide a catalytic nucleation site for the conversion of carbon monoxide into carbon atoms during the growth of the carbon nanotubes:

$$xCO(g) \rightarrow C(s) \text{ (of carbon nanotube)} + \frac{1}{2} \times CO_2(g)$$

where x is typically several thousand. This is a disproportionation reaction.

QUICK CHECK QUESTION

35 Identify the catalyst, conditions and product of high-pressure catalytic decomposition of carbon monoxide (HIPCO).

Problems, implications and issues associated with nanomaterials

Revised ☐

There are concerns that nanoparticles may have undiscovered harmful side effects, for example if they are breathed in or orally ingested, so there may be health and safety issues. Any such side effects are not yet fully understood, so these new materials should be tested for possible toxicity and carcinogenicity. Nanoparticles are small enough to be absorbed by the skin so could cause irritation. They may also have unexpected catalytic effects inside the body and there is the possibility that the human immune system may be unable to mount a response against nanoparticles. Self-cleaning windows, sunscreen and modern hard drives are applications that use nanoparticles.

QUICK CHECK QUESTION

36 Outline the concerns over the possible harmful effects of the use of nanotechnology.

22.7 Environmental impact – plastics

Revised ☐

Essential idea: Although materials science generates many useful new products there are challenges associated with the recycling of, and the high levels of toxicity of, some of these materials.

Environmental impact of plastics

Revised ☐

- Plastics do not degrade easily because of their strong covalent bonds.
- Burning of polyvinyl chloride releases dioxins, HCl gas and incomplete hydrocarbon combustion products.
- Dioxins contain unsaturated six-membered heterocyclic rings with two oxygen atoms, usually in positions 1 and 4.
- Chlorinated dioxins are hormone disrupting, leading to cellular and genetic damage.
- Plastics require more processing to be recycled than other materials.
- Plastics are recycled based on different resin types.

Environmental issues with plastics

Revised ☐

Depletion of non-renewable resources

Nearly all artificial polymers are organic (carbon-based) and currently crude oil (petroleum) is the major source of chemicals for the synthesis of plastics. Fossil fuels are in a limited supply, but the bulk is used as fuels, rather than as feedstock for plastics (which currently consumes about 5% of all crude oil extracted).

Disposal and degradation

Because of their lack of chemical reactivity partly due to the presence of relatively strong covalent bonds that resist cleavage, most plastics are not biodegradable. Some plastics can be recycled after plastic waste is sorted and separated. Some plastics are weakened and eventually broken down (degraded) by the action of ultraviolet radiation.

Plastics can be incinerated (combusted), but at low temperatures toxic dioxins, carbon monoxide, hydrogen cyanide (from urethanes) and hydrogen chloride (from chlorine-containing plastics, such as PVC) may be produced.

To help reduce the risk of this occurring during a house fire, many plastics are modified with fire-retarding additives but these have their own environmental impact. Low-smoke zero halogen cabling is often used in electrical wiring in public spaces.

The equations below describe the complete combustion of polythene, PVC and one repeating unit of poly(methylmethacrylate) (PMMA).

$$(CH_2)_n + 1\frac{1}{2}nO_2 \rightarrow nCO_2 + nH_2O$$

$$(CH_2CHCl)_n + 2\frac{1}{2}nO_2 \rightarrow 2nCO_2 + nHCl + nH_2O$$

$$C_5H_8O_2 + 6O_2 \rightarrow 5CO_2 + 4H_2O$$

Biodegradability

The majority of synthetic plastics are not degraded by the action of bacteria and fungi and persist in the environment, including landfills. Biodegradable condensation polymers can be synthesized that are hydrolysed to release lower molecular weight fragments which can cross cell walls and be bio-assimilated.

Expert tip

A variation in the complete combustion reaction is shown by the hydrogen-deficient polymer PTFE ($(C_2F_4)_n$) which requires the addition of water as a reactant in the stoichiometric equation:

$$C_2F_4 + O_2 + 2H_2O \rightarrow 2CO_2 + 4HF$$

QUICK CHECK QUESTIONS

37 Suggest why incomplete combustion of plastics, such as polyvinyl chloride (PVC) is common during house fires.

38 Write equations for the combustion of polyethene and polyvinyl chloride (PVC) and explain why these polymers are first separated before combustion.

39 Suggest a reason, with a reference to bonding, why many adults in developed countries have measurable concentrations of phthalates (used as plasticizers in PVC) in their bodies.

Resin identification code

The resin identification code (RIC) was developed to facilitate plastic sorting and separating by identifying specific plastics with a numbered label to improve the efficiency of plastic recycling (Table 22.2) and disposal. Plastics require more processing to be recycled than other materials, such as metals and paper.

Table 22.2 Plastic resin identification codes

Resin identification code (RIC)	Plastic and properties	Applications	Recycling
1 PET	Poly(ethylene terephthalate) is clear, tough and solvent resistant. Used for rigid sheets and fibres. Good barrier to gases and liquids. Resin can be spun into threads.	Carbonated soft drink bottles, food jars, carpet fibres, microwave trays, fruit juice bottles, pillow and sleeping bag filling, textile fibres	Drinks bottles, clothes, detergent bottles, laminated sheets, carpet fibres, clear packaging films
2 HDPE	High-density polyethylene (HDPE) is hard to semi-flexible and opaque. Relatively impermeable to gas and moisture.	Freezer bags, milk bottles, bleach bottles, hard hats, buckets, 3D printing, milk crates, wire cable covering	Pipes for farms, pallets, bins, extruded sheet, garden edging, household bags, oil containers
3 PVC	Plasticized polyvinyl chloride (PVC) is flexible, clear and elastic; can be solvent welded. Unplasticized PVC is hard and rigid; may be clear and can be solvent welded.	Garden hoses, shoe soles, cable sheathing, car gaskets, shower curtains, gloves, pipes, blood bags and tubing, credit cards, watch straps	Pipe and hose fittings, garden hose, electrical conduit, shoes, road cones, drainage pipes, ducting, detergent bottles
4 LDPE	Low-density polyethylene (LDPE) is soft and flexible; surface is translucent; withstands solvent.	Rubbish (garbage) bags, squeezy bottles, cling wrap, hot and cold drinks cups, flexible container lids, rubbish bins	Concrete lining and bags
5 PP	Polypropylene is hard, flexible and translucent (can be transparent) and has good chemical resistance.	Film, carpet fibre, carts, bottles, caps, furniture, rigid packaging, yoghurt containers, takeaway containers, fishing nets, toilet seats	Crates, boxes, plant pots, compost bins, garden edging
6 PS	Polystyrene is clear, glassy, rigid, brittle, opaque, semi-tough and affected by fats and solvents. Expanded polystyrene is foamed, lightweight and thermally resisting.	Refrigerator bins, stationery accessories, coat hangers, medical disposables, trays, cartons, vending cups, plastic cutlery, yoghurt containers	Industrial packaging, coat hangers, moulded products, office accessories, spools, rulers, video cases, printer cartridges
7 OTHER	Other plastics includes all other resins, laminates, acrylonitrile butadiene styrene, acrylic, nylon, polyurethane and polycarbonates.	Automotive (car), aircraft, boating, furniture, electrical and medical parts	Agricultural piping, furniture fittings, wheels and castors, fence posts, pallets and outdoor furniture, marine structures

Infrared spectroscopy can also be used to identify plastics whose molecules contain specific functional groups that strongly absorb specific infrared radiations. For example, PET can be recognized by strong absorption in the region 1700–1750 cm^{-1}, due to the presence of the carbonyl group, >C=O. PVC shows an absorption due to the stretching of the C–Cl bond between 600 and 800 cm^{-1}.

The use of phthalate esters (Figure 22.50), as plasticizers, is being phased out because of their toxicity and their correlation with birth defects via disruption of the endocrine system.

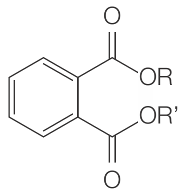


Figure 22.50 Generalized structure of phthalate esters

Dioxins and polychlorinated biphenyls

Dioxins can be formed when polymers are combusted unless the temperature is very high. They can also be released into the air during natural processes, such as forest fires and volcanoes.

They do not decompose in the air and water and are absorbed and stored in fat tissue and, therefore, accumulate (Figure 22.51) and undergo biomagnification as they pass along food chains. More than 90% of human exposure to dioxins is through food.

Expert tip

Some dioxins endure a long time and are extremely resistant to environmental degradation. They are therefore are classified as persistent organic pollutants (POPs).

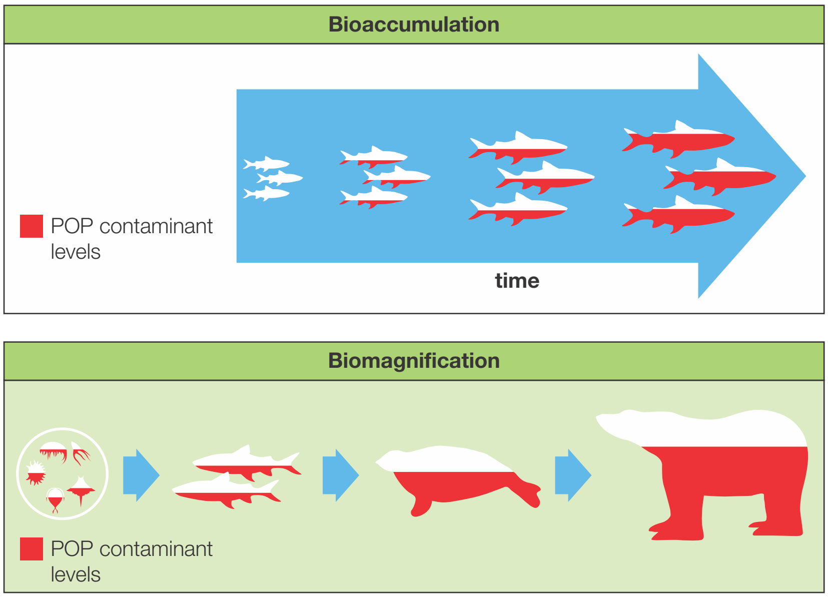


Figure 22.51 Bioaccumulation and biomagnification

The chlorinated dioxins are carcinogenic and can disrupt the endocrine system, which secretes hormones. Dioxins contain a heterocyclic six-membered ring where two carbon atoms have been replaced by oxygen atoms (in positions 1 and 4, or less commonly 1 and 2). Examples of dioxins include polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (Figure 22.52).

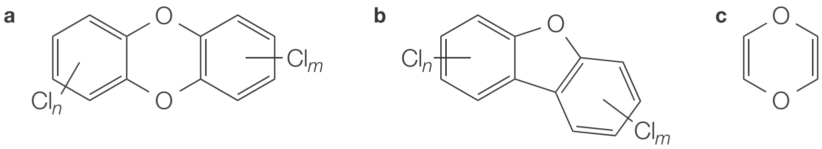


Figure 22.52 The generalized structures of **a** PCDFs, **b** PCDDs and **c** dioxin (where *m* and *n* refer to different numbers of chlorine atoms)

Polychlorinated biphenyls (PCBs) contain two linked benzene rings where more than one hydrogen atom has been substituted by chlorine atoms (Figure 22.53). They do not have a 1,4-dioxin ring in their structure, but have the same toxic effect as dioxins and so can be described as dioxin-like. PCBs were used in transformers and capacitors, as insulators.

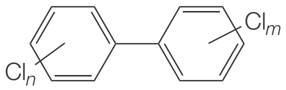


Figure 22.53 Generalized structure of polychlorinated biphenyls (PCBs)

Expert tip

The most toxic PCB is the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, TCDD, also known (inaccurately) as 'dioxin' shown in Figure 22.54. It was a contaminant in some herbicides.

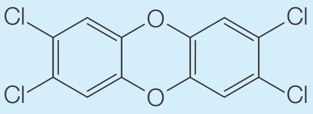


Figure 22.54 Structure of 2,3,7,8- tetrachlorodibenzo-*p*-dioxin

22.8 Superconducting metals and X-ray crystallography

Revised ☐

Essential idea: Superconductivity is zero electrical resistance and expulsion of magnetic fields. X-ray crystallography can be used to analyse structures.

Superconducting metals and X-ray crystallography

Revised ☐

- Superconductors are materials that offer no resistance to electric currents below a critical temperature.
- The Meissner effect is the ability of a superconductor to create a mirror image magnetic field of an external field, thus expelling it.
- Resistance in metallic conductors is caused by collisions between electrons and positive ions of the lattice.
- The Bardeen–Cooper–Schrieffer (BCS) theory explains that below the critical temperature electrons in superconductors form Cooper pairs, which move freely through the superconductor.
- Type 1 superconductors have sharp transitions to superconductivity whereas Type 2 superconductors have more gradual transitions.
- X-ray diffraction can be used to analyse structures of metallic and ionic compounds.
- Crystal lattices contain simple repeating unit cells.
- Atoms on faces and edges of unit cells are shared.
- The number of nearest neighbours of an atom/ion is its coordination number.

Superconductors

Revised ☐

When mercury (purified by repeated distillation) is cooled to 4.2 K (at standard pressure) the electrical resistance drops sharply at 4.5 K to zero (Figure 22.55). The loss of resistance is the result of it entering what we call the superconducting state.

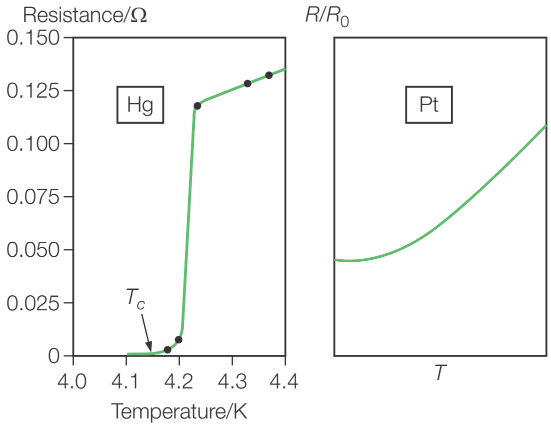


Figure 22.55 Plots of resistance versus temperature for mercury and platinum

Expert tip

When an electric current flows in a conductor, some of the electrical energy is transformed into heat. This is known as the heating effect of an electric current and is due to the resistance of the conductor. As the temperature decreases, the cations vibrate less (smaller amplitude) and resistance drops (Figure 22.56).

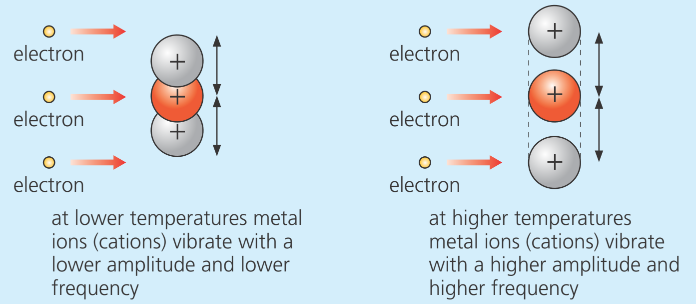


Figure 22.56 The effect of temperature on resistance

Many other elemental metals and alloys were also found to exhibit zero resistance when their temperatures were lowered below a certain characteristic temperature of the material, called the critical temperature, T_c. In addition, these materials lose their superconducting behaviour above a certain temperature-dependent critical magnetic field, H_c.

If a superconductor is cooled below its critical temperature while in a magnetic field, the magnetic field surrounds but does not penetrate the superconductor. The magnet induces current in the superconductor which creates a counter-magnetic force that causes the two materials to repel. This can be seen as the magnet is levitated above the superconductor (Figure 22.57) and is known as the Meissner effect.

A zero internal magnetic field is the result of superconductivity. The Meissner effect can be visualized as involving the expulsion of the applied magnetic field from inside the superconductor, by creating a mirror image of the magnetic field (Figure 22.58). In the superconductor electrons are circulating round the sample and this is what creates an equal and opposite upward magnetic field to counteract the downward magnetic field. Electrons are moving into the paper on the right of the circle of the superconductor and out of the paper on the left. The essential difference between the two cases is the absence of scattering in the superconductor: the reason the electrons in the normal metal have random directions is because they scatter into a random direction (connected with the metal's resistance) before they can get very far.

Type 1 and Type 2 superconductors

Superconductors can be divided into two types: Type 1 and Type 2 (Figure 22.59). Both types of superconductor show a sharp transition in resistance at the critical temperature. Type 1 superconductors exhibit complete diamagnetism unless a certain critical magnetic field is applied – then superconductivity disappears sharply. Type 1 superconductors tend to be metals and metalloids and are likely to show a sharp transition to the superconducting state.

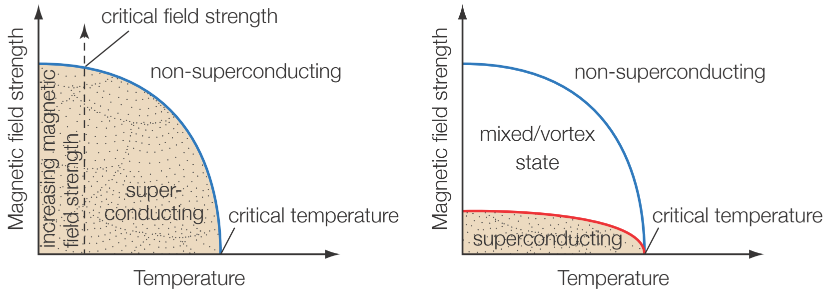


Figure 22.59 The behaviours of Type 1 and Type 2 superconductors (mixed state refers to a phase where some of the material is in the normal state and part still superconducting)

Figure 22.57 The Meissner effect: the floating magnet is only in contact with air

■ **QUICK CHECK QUESTIONS**

40 Outline the cause of electrical resistance in metallic conductors.

41 Describe the Meissner effect.

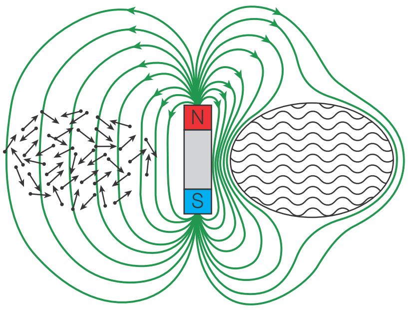


Figure 22.58 An ordinary conductor (left) shows random electron movement because of collisions and so allows magnetic field penetration, but in a superconductor (right) electrons have no collisions and so can circulate so as to exclude any magnetic field penetration, creating a mirror image of an applied magnetic field

Expert tip

The ferromagnetic metals: iron, cobalt and nickel do not show superconductivity.

Type 2 superconductors tend to be metallic compounds, alloys or ceramics. As an applied magnetic field is increased, Type 2 superconductors go into a part-superconducting 'mixed' state, where small parts of the sample are normal but the rest is superconducting. They can stay in this state up to much higher critical fields. This means that they can carry much higher current densities while remaining in a superconducting state.

NATURE OF SCIENCE

Superconductivity (zero electrical resistance and perfect diamagnetism) was discovered in 1911 but an explanation of the behaviour of some types of superconductors was only developed in 1957. BCS theory was a paradigm shift involving a quantum many-body effect, i.e. interactions between electrons were the crucial factor to explain superconductivity.

The first ceramics found to be superconducting are those based on yttrium–barium and copper oxide, $YBa_2Cu_3O_7$ (Figure 22.60). They have a relatively high critical temperature and can be cooled to their critical temperature by liquid nitrogen. Liquid helium is used to cool the more traditional types of superconductors.

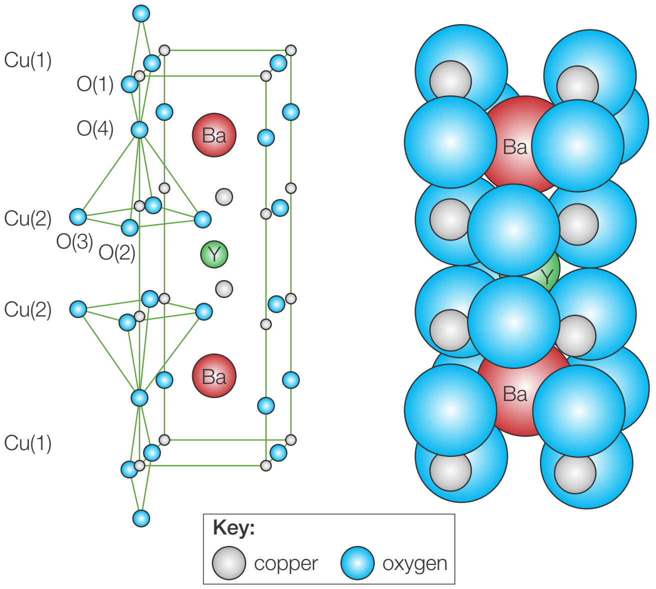


Figure 22.60 Idealized structure of $YBa_2Cu_3O_7$

■ QUICK CHECK QUESTIONS

42 When yttrium(III) oxide, barium carbonate and copper(II) oxide are mixed, heated and cooled in an oxygen atmosphere, $YBa_2Cu_3O_{6.5}$ is formed. Deduce an equation to show its formation. Barium carbonate is decomposed to barium oxide (and carbon dioxide).

43 $YBa_2Cu_3O_{6.5}$ can be converted to $YBa_2Cu_3O_7$ by heating and then cooling it in a stream of oxygen gas. State the name of the structure it adopts in the crystalline state. State the type of superconducting behaviour it exhibits.

■ Bardeen–Cooper–Schrieffer (BCS) theory

A central feature of BCS theory is the formation of a bound two-electron state called a Cooper pair (Figure 22.61). It consists of a pair of interacting electrons with opposite spins. The Cooper pair has a spin of zero. It explains the behaviour of some types of superconductors at temperatures close to absolute zero.

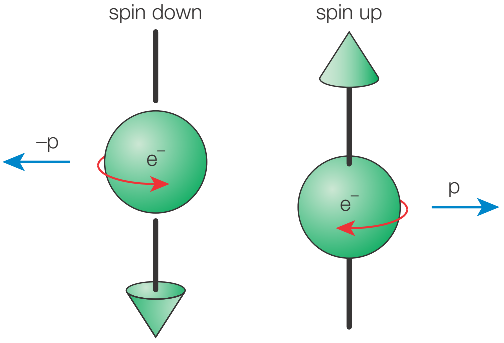


Figure 22.61 A Cooper pair: the arrows represent direction of movement and p represents momentum (*mv*); spin down and spin up can be interpreted as clockwise and anticlockwise directions of spin

Part of the resistance of a metal is due to collisions between free electrons and cations of the metal lattice, and part is due to scattering of electrons from impurities or defects in the metal.

The behaviour of electrons inside a superconductor is very different. The impurities and lattice framework are still there, but the movement of the superconducting electrons is a very different cooperative process.

An overall attraction between two electrons can occur if the electrons interact with each other via the motion of the crystal lattice as the lattice structure is momentarily deformed by a passing electron. Figure 22.62 shows two electrons moving through the lattice of a metallic superconductor, where the cations can move as if attached by 'stiff springs'.

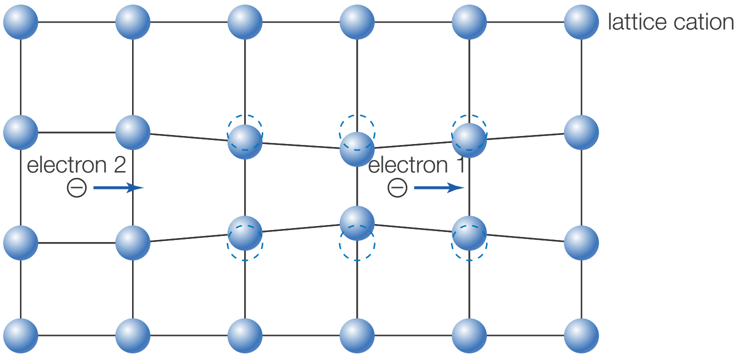


Figure 22.62 The basis for the attractive interaction between two electrons via the lattice deformation in a superconducting metal

The movement of electron 1 causes nearby cations to move inward toward the electron, resulting in a slight increase in the concentration of positive charge in this region. Electron 2 (the second electron of the Cooper pair), approaching before the cations have had a chance to return to their equilibrium positions (dashed circles), is attracted to the distorted (positively charged) region. The overall effect is a weak delayed attractive force between the two electrons, resulting from the movement of the cations.

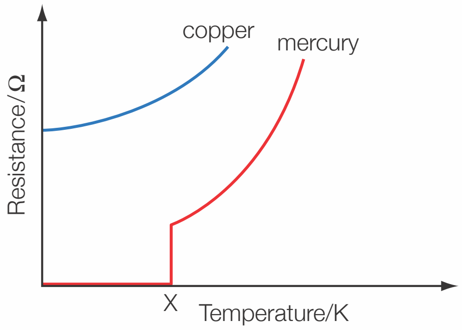
Expert tip

Since the interaction is relatively weak, the Cooper pair exists only at relatively low temperatures. BCS theory does not fully account for the observed properties of the high-temperature superconducting perovskite-based ceramics.

■ QUICK CHECK QUESTIONS

44 State the relationship between spin and momentum of the electrons in a Cooper pair.

45 Explain the behaviour of mercury below temperature X in terms of the Bardeen–Cooper–Schrieffer (BCS) theory.



X-ray crystallography

Revised ☐

Diffraction

X-rays are high-energy electromagnetic radiation whose wavelength is close to 10^{-10} m. They can be diffracted, like all waves. Diffraction occurs whenever a wave meets a barrier that has an opening similar in size to its wavelength (Figure 22.63).

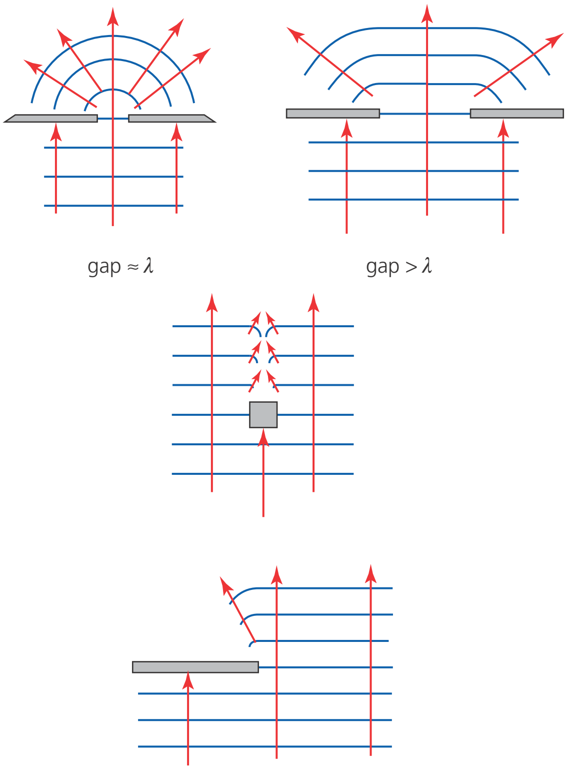


Figure 22.63 Diffraction of plane waves through a single gap

Layers of atoms, ions and molecules in crystals are separated by distances small enough to cause X-rays to diffract.

Atoms are able to produce diffraction patterns because the electric field of the X-ray interacts with the electrons around an atom. Large atoms have more electrons and these atoms produce the strongest patterns.

Expert tip

The small hydrogen atom with its single electron has little effect on X-rays.

When a beam of X-rays falls on a crystal plane composed of a regular arrangement of atoms or ions, the X-rays are diffracted. Waves from the diffracted X-rays may produce constructive interference (waves 'add up') or destructive interference (waves 'cancel out') (Figure 22.64).

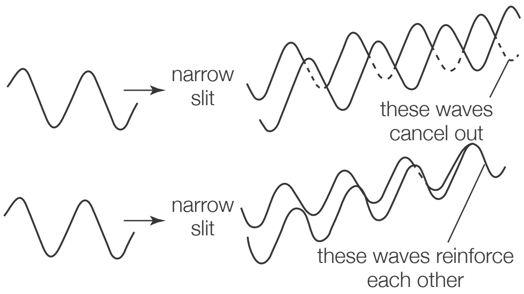


Figure 22.64 After waves pass through a narrow slit there are directions in which they reinforce (constructive interference) and directions in which they cancel out (destructive interference). The overall pattern is a diffraction pattern.

Bragg equation

For constructive interference, the path difference must be equal to an integral (whole number) multiple of the wavelength. $2d \sin \theta = n\lambda$ is known as the

Bragg equation, where d = distance between planes (layers); λ = wavelength of X-rays, n = 1, 2, 3… order of reflection and θ = reflection angle, it increases with increasing order of reflection (Figure 22.65).

Expert tip

IB questions will only involve first order reflections, so n will always be 1.

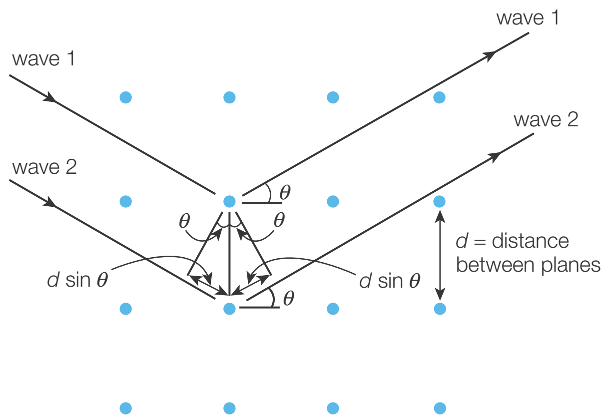


Figure 22.65 The extra distance travelled by X-ray wave 2 is $2 \times 2d \sin \theta$ and for constructive interference $n\lambda = 2d \sin \theta$

Expert tip

You will only be required to apply the Bragg equation to simple cubic structures in which the value of d is equal to the length of the unit cell.

X-ray diffraction patterns can be obtained by directing X-rays at a single crystal or a fine powder made by grinding a crystal. The intensity of the spots on an X-ray diffraction photograph depends on the electron densities of the atoms or ions.

Worked example

X-rays of wavelength 0.154 nm are diffracted from a metal crystal at an angle of 14.17°. Assuming that n = 1, determine the distance (in pm) between layers in the crystal.

$$n\lambda = 2d \sin \theta$$

$$d = \left(\frac{1 \times 154\,\text{pm}}{2 \times \sin 14.17}\right) = 314.54\,\text{pm}$$

QUICK CHECK QUESTIONS

46 a X-rays with a wavelength of 154 pm are used in a diffraction experiment with silver. A first order diffraction beam is observed at an angle of 10.91°. Determine the spacing (in pm) between the planes of silver atoms.

b X-rays from a copper X-ray tube (λ = 154 pm) were diffracted at an angle of 14.22° by a crystal of silicon. Assume first order diffraction (n = 1 in the Bragg equation). Determine the interplanar spacing in silicon (in metres).

47 Explain the principles of operation of an X-ray diffractometer.

Unit cells

The unit cell of a crystal lattice is the basic three-dimensional 'building block' of a crystal (Figure 22.66). Unit cells fit together to make up an entire crystal lattice. They have the full symmetry of the crystal.

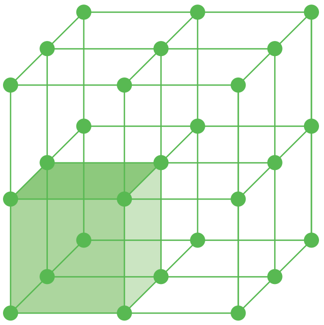


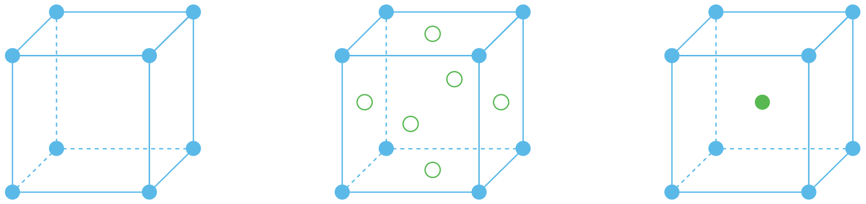
Figure 22.66 A crystal lattice with the shaded portion representing the unit cell (a simple cubic unit cell)

Types of unit cell

There are three cubic unit cells (Figure 22.67):

- simple unit cell in which the atoms are present only at the corners
- face-centred cubic in which atoms are present at the centre of each face in addition to atoms at the corner
- body-centred cubic in which the atoms are present at the centre of the cube in addition to atoms at the corners.

The unit cell adopted by a particular crystal will depend on the radii of the atoms, or ions forming the structure.



simple cubic face-centred cubic body-centred cubic

Figure 22.67 Cubic unit cells

In counting the effective number of atoms or ions in a unit cell (Figure 22.68):

- atoms at each corner count as $\frac{1}{8}$
- atoms on an edge count as $\frac{1}{4}$
- atoms at each face count as $\frac{1}{2}$
- atoms within the unit cell count as 1.

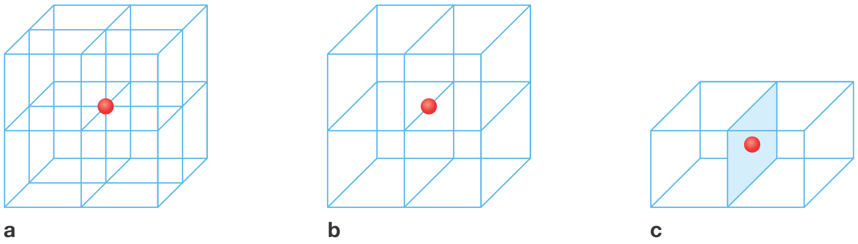


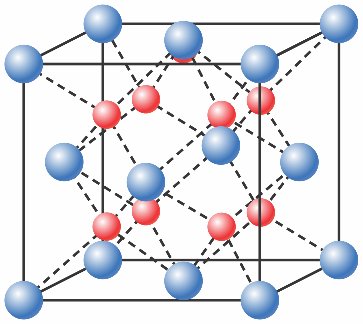
Figure 22.68 Calculating number of particles in a unit cell

QUICK CHECK QUESTIONS

48 Metallic uranium crystallizes in a body-centred cubic lattice, with one uranium atom per lattice point.

- **a** Deduce the number of atoms there are per unit cell.
- **b** If the edge length of the unit cell is found to be 343 pm, deduce the metallic radius of uranium in pm.

49 The unit cell of a compound of uranium and oxygen that crystallizes in a cubic unit cell is shown in the diagram below, where the gray spheres represent uranium ions and the red spheres represent oxide ions. Deduce the chemical formula of the compound. Determine the coordination number of the uranium ions in the crystal.



50 An unknown metal X has a density of 10.5 $\mathrm{g\,cm^{-3}}$. An X-ray diffraction experiment measured the edge of the face-centred cubic unit cell as 4.09×10^{-10} m. Identify X from its molar mass.

Expert tip

In a cube there are 8 corners, 12 edges and 6 faces.

The number of atoms per unit cell are:

- simple cubic, $8 \times \frac{1}{8} = 1$ atom
- face-centred cubic, $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2})$ = 4 atoms
- and in body-centred cubic, $1 + (8 \times \frac{1}{8})$ = 2 atoms.

Worked example

For a unit cell with X at the eight corners of the cubic unit cell, Y at the centre of the cube, and Z at the centre of each face, deduce the formula of the compound.

Each atom at the corner of a cube counts as 1/8 in the unit cell. Each atom on a face counts as ½ in the unit cell. Each atom in the centre of the unit cell counts as 1. The formula for the compound is XYZ_3.

Packing in solids

Revised ☐

Packing in solids refers to the close-packed arrangement of atoms, which behave as hard spheres. Crystals can be generated by stacking one layer over another. In a close-packed structure (Figure 22.69), the atoms stack together occupying maximum space and leaving minimum empty space.

The packing percentage is the percentage of volume occupied in a lattice. It is independent of the radius of the atoms and depends only on the type of packing. There are four types of packing.

Square based or simple cubic

The atoms are arranged so that the centres of all the atoms in any row are in a straight line (Figure 22.70). The coordination number within the layer is four. The packing percentage is 52%.

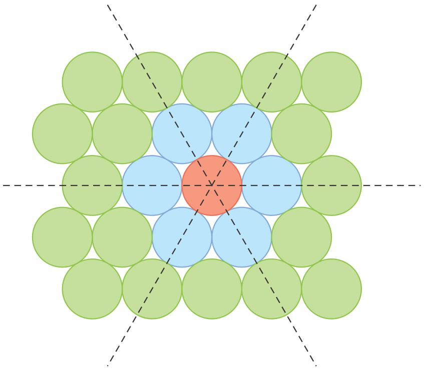


Figure 22.69 Close packing of atoms

Body-centred packing

The coordination number is 8. The atoms of the second layer are placed between the empty spaces of the first layer. The packing percentage is 68%.

Hexagonal close packing and cubic close packing

In both structures, the coordination number is 12. Each atom is in direct contact with six others in its own layer, three other in each layer above and below it. In both structures the packing percentage is 74%.

In hexagonal close packing (Figure 22.71) the packing pattern is ABABABAB and in cubic close packing the packing pattern is ABCABCABC (Figure 22.72).

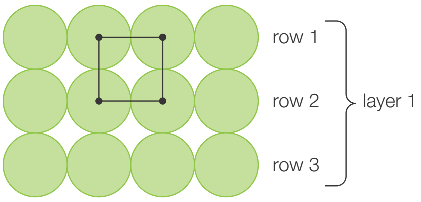


Figure 22.70 Simple cubic packing

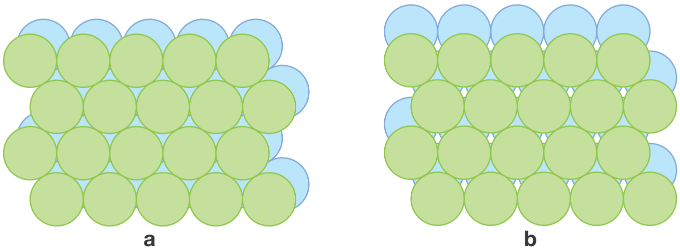


Figure 22.71 Schematic representation of two close packed layers arranged in A (blue) and B (green) positions. The alternative stacking of the B layer is shown in **a** and **b**

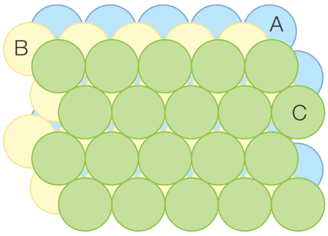


Figure 22.72 Schematic representation of the three close packed layers in a cubic close packed arrangement: A (blue), B (yellow) and C (green)

The spaces enclosed between the packed atoms are known as voids or holes.

Expert tip

In crystals with directional covalent bonds, the coordination number is lower compared to crystals with non-directional bonds in metals and ionic compounds. Table 22.3 summarizes the simple cubic, body-centred and face-centred cubic crystal structures (Figure 22.73).

Table 22.3 Summary of simple cubic, body-centred and face-centred cubic crystal structures for metals

Unit cell	Number of particles involved	Number of particles per unit cell	Coordination number	Percentage of cell volume occupied by atoms
Simple cubic	8;1 at each corner	1	6	52
Body-centred cubic	9;1 at each corner and a central atom	2	8	68
Face-centred cubic	14;1 at each corner and 1 on each face	4	12	74

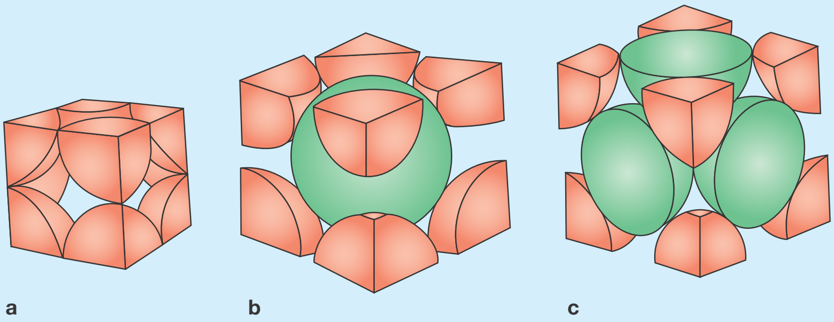


Figure 22.73 Space filling models of simple cubic, body-centred and face-centred cubic crystal structures

QUICK CHECK QUESTION

51 Distinguish between cubic closest packed (ccp) and hexagonal closest packed (hcp) structures.

Determining the density of a metal from X-ray crystallography data

Revised ☐

This type of calculation requires the metallic radius and the type of lattice structure. One approach is:

1. Determine the volume of one atom of the metal. The volume of a sphere is given by the formula $4/3\pi r^3$.
2. Determine the volume of one mole of the metal atoms. Multiply the volume of one metal atom by the Avogadro constant.
3. Determine the volume of a lattice containing one mole of metal atoms. Multiply the volume of one mole of metal atoms by the percentage of available space (for that type of lattice).
4. Determine the density using the molar mass.

Alternatively, the density of the substance/unit cell can be calculated from the following expression:

$$d = \frac{zM}{a^3 N_A}$$

where a = cell edge, z = number of atoms per unit cell, M = molar mass and N_A = Avogadro constant.

Table 22.4 summarizes the calculation of the volume of a unit cell from its crystal structure. These expressions are based on applying Pythagoras's theorem to a three-dimensional drawing of the unit cell.

Table 22.4 Crystal structures and unit cell volume expressions

Crystal structure	Volume of unit cell
Simple cubic	$8r^3$
Face-centred cubic	$16\sqrt{2}r^3$
Body-centred cubic	$\frac{64}{3\sqrt{3}r^3}$

Worked example

Calculate the percentage of cell volume occupied by atoms (packing factor) in the simple cubic structure of polonium.

Atoms contact along unit cell edges. $2R$ atoms along edge length a. Volume of atoms = $\frac{4}{3}\pi R^3$. One atom per unit cell; unit cell volume, $a^3 = 8R^3$. Packing factor = $(\frac{4}{3}\pi R^3)/(8R^3) = \frac{4\pi}{6}$ = 52.3%.

Worked example

Calculate the density (in $g\,cm^{-3}$) of polonium. It has a unit cell dimension of 3.352×10^{-10} m and a molar mass of 209 $g\,mol^{-1}$.

Unit cell edge length = 3.352×10^{-10} m; radius = 1.676×10^{-10} m; 209 $g\,mol^{-1}/6.02 \times 10^{23}\,mol^{-1} = 3.471 \times 10^{-22}$ g atom^{-1}; 1 atom per unit cell, hence 3.471×10^{-22} g/unit cell. Unit cell volume = $(3.352 \times 10^{-10}\,m^3)$. $(3.471 \times 10^{-22})/(37.6627 \times 10^{-24})$ = 9.216 $g\,cm^{-3}$.

QUICK CHECK QUESTION

52 Silver crystallizes with a face-centred cubic lattice. The unit cell edge length is 408.7 pm. Calculate the density of silver (in $g\,cm^{-3}$).

Ionic crystals

Revised ☐

An ionic crystal is made up of two oppositely charged ions; both may have different sizes and charges. Opposite charges attract each other and ions of one type of charge will group around ions of the opposite charge.

The coordination number is the number of nearest oppositely charged ions surrounding a central ion.

In AB type (cation to anion mole ratio is 1:1) solids, there are three types of lattices. The type of lattice is determined by the relative sizes of the cation and anion (ionic radii ratio).

Rock salt structure

Sodium ions, Na^+, are present at the centre of each edge and at the body centre while chloride ions, Cl^-, are present at the corners as well as the centre of each face. This is a simple cubic structure (Figure 22.74).

The number of Na^+ ions per unit cell = $1 + (\frac{1}{4} \times 12) = 4$.

The number of Cl^- ions per unit cell = $(\frac{1}{8} \times 8) + (\frac{1}{2} \times 6) = 4$.

There are four formula units present per unit cell (Figure 22.74). Rock salt has 6:6 coordination, meaning each ion has a coordination number of 6.

The distance between the cation and anion is given by the following expression:

$$r^+ + r^- = \frac{a}{2}$$

where a = cell edge, r^+ = cation radius and r^- = anion radius

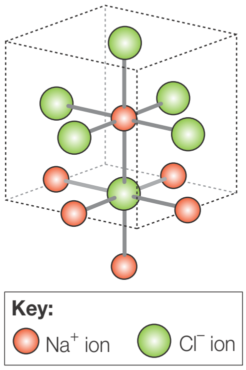


Figure 22.74 The sodium chloride lattice showing 6:6 coordination

Caesium chloride

The caesium chloride lattice is a body-centred cubic structure (Figure 22.75). The chloride ions, Cl^-, are at the corners, while the caesium ion, Cs^+, is at the centre of the cube. The lattice shows 8:8 coordination, the coordination number of each ion is 8.

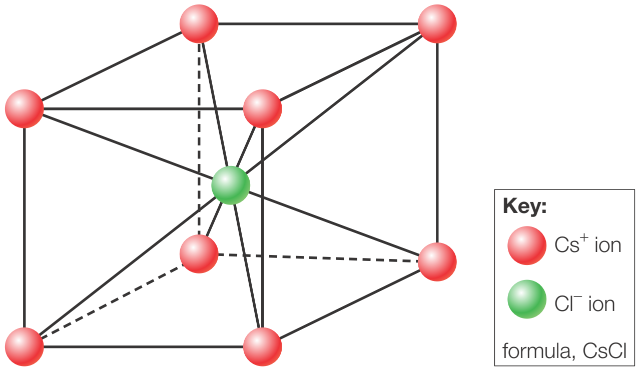


Figure 22.75 Caesium chloride unit cell

Number of Cs^+ ions per unit cell = 1.

Number of Cl^- ions per unit cell = $(\frac{1}{8} \times 8) = 1$.

The ions touch each other along the unit cell diagonal and the distance between the cation and anion is given by the following relationship:

$$r^+ + r^- = \frac{\sqrt{3}}{2}a$$

The sphalerite (zinc blende) structure

This is a 4:4 coordination lattice with four formula units per unit cell. Each sulfide ion is tetrahedrally surrounded by four zinc ions and each zinc ion is surrounded tetrahedrally by four sulfide ions (Figure 22.76).

Fluorite structure

The AB_2 (fluorite) type lattice (Figure 22.77) shows 8:4 coordination with the calcium ions having a face-centred cubic lattice. (The A_2B (antifluorite) is a 4:8 coordination lattice. Each has four formula units per unit cell.)

Perovskite structure

Perovskite (Figure 22.78) is a mineral with the formula $CaTiO_3$. The calcium ions, Ca^{2+}, lie at the corners of a cube. The oxide ions, O^{2-}, lie on the faces of the cube, and the titanium(IV) ion, Ti^{4+}, lies at the centre of the cube. High-temperature type 2 cuprate superconductors have structures based on perovskite.

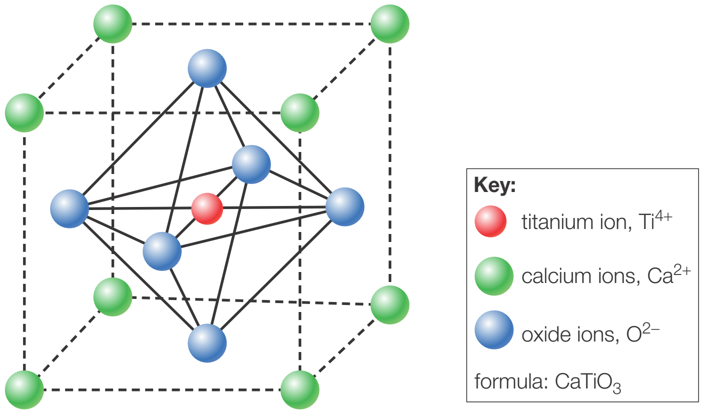


Figure 22.78 Unit cell of the perovskite structure

Expert tip

The CsCl structure can be thought of as two interlocking cubic arrangements of the two ions.

QUICK CHECK QUESTION

53 Depending on temperature, rubidium chloride, RbCl, can exist in either the rock salt or caesium chloride structure. State the coordination number of the anion and cation in each of these structures.

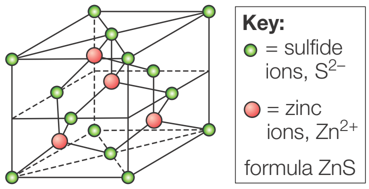


Figure 22.76 Zinc blende structure

Expert tip

The structure of zinc blende is similar to that of diamond. In diamond all the positions are occupied by carbon atoms.

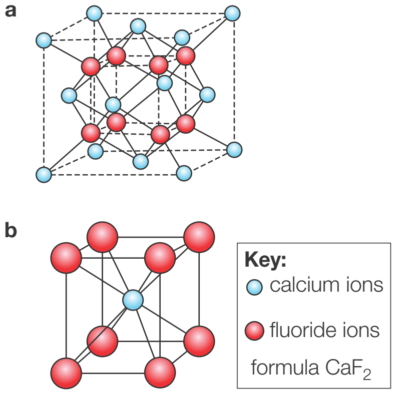


Figure 22.77 The fluorite structure

Expert tip

Perovskite crystalline structures of many superconductors can be analysed by X-ray crystallography but these will not be assessed.

QUICK CHECK QUESTION

54 Confirm that in perovskite the stoichiometry is consistent with the structure shown in Figure 22.78.

22.9 Condensation polymers

Revised ☐

Essential idea: Condensation polymers are formed by the loss of small molecules as functional groups from monomers join.

Polymers

Revised ☐

- Condensation polymers require two functional groups on each monomer.
- NH_3, HCl and H_2O are possible products of condensation reactions.
- Kevlar® is a polyamide with a strong and ordered structure. The hydrogen bonds between O and N can be broken with the use of concentrated sulfuric acid.

Condensation polymers

Revised ☐

Condensation polymers are formed from monomers that contain at least two reactive functional groups within their molecules. A long chain can be formed because bifunctional molecules with reactive sites at each end can link up indefinitely (under appropriate conditions).

Expert tip

Condensation polymers are given this name because when the monomers bond together, water or some other small stable molecule, such as hydrogen chloride or occasionally ammonia is eliminated.

Expert tip

The nylon is numbered depending on how many carbon atoms there are between each amide linkage. The one in Figure 22.79b is formed from two small molecules each with six carbons atoms in it and hence is named nylon 6,6.

Polyamides

Polyamides, such as the nylons (Figure 22.79), are formed when a diamine molecule undergoes a condensation reaction with a dicarboxylic acid molecule. A dimer is initially formed and a water molecule is eliminated. The resulting dimer has an amine group at one end and an acid group at the other so it can keep growing by further condensation reactions.

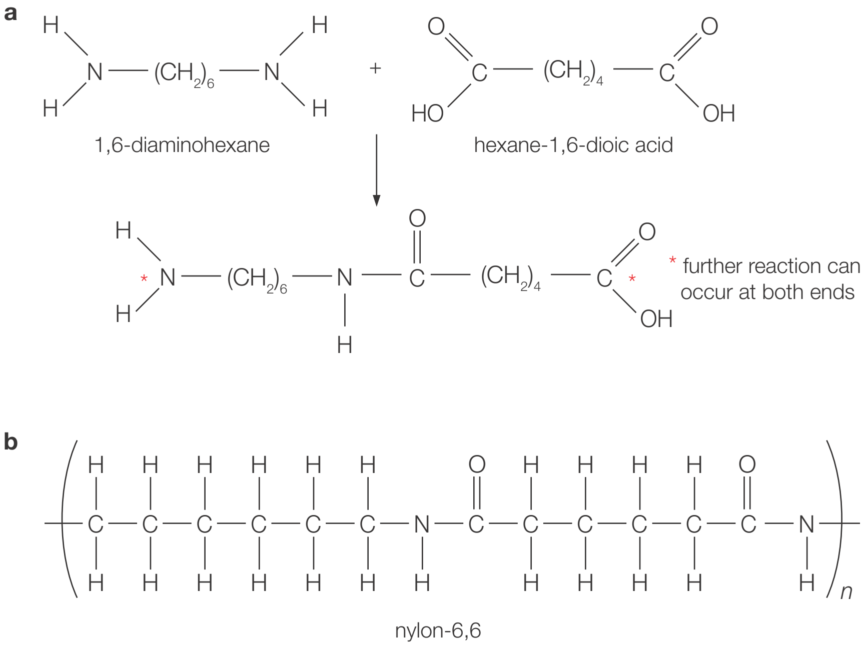


Figure 22.79 a The polymerization of 1,6-diaminohexane and hexane-1,6-dioic acid to form nylon **b** the structure of nylon-6,6

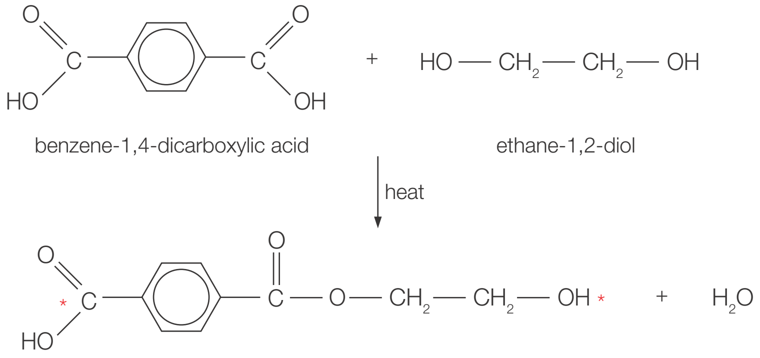
QUICK CHECK QUESTIONS

55 Synthetic polyamides are produced by the reaction of dicarboxylic acids with compounds such as $H_2N(CH_2)_6NH_2$. Name the compound $H_2N(CH_2)_6NH_2$ and draw the repeating unit.

56 Distinguish between addition and condensation polymers in terms of how the monomers react together during the polymerization process.

Polyesters

Polyesters are joined together by ester linkages. The acid commonly used is benzene-1,4-dicarboxylic acid because polyesters made from the alkyl (aliphatic) acids are soluble and have a low melting point. The commonest polyester is Terylene (Figure 22.80) or (poly(ethylene terephthalate)) (PET).



* further reaction can occur at both ends

Figure 22.80 The formation of the condensation polymer PET (Terylene)

Expert tip

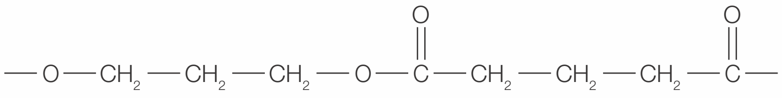
The traditional names for these monomers are terephthalic acid and ethylene glycol. Hence the commercial name Terylene for one brand of polyester in the form of fibres.

Fibres

Fibres are long thin threads that form material such as wool and polyester fabrics. Examples of synthetic polymers used to make fibres are polyesters, polyamides (including Kevlar) and the addition polymer, polypropylene. Synthetic polymers are spun into fibres by forcing the hot molten polymer through small holes or by pushing a solution through small holes into a bath which contains a liquid (often water) which precipitates the polymer as a fibre.

QUICK CHECK QUESTION

57 The repeating unit of a polymer is shown below.



$$-O-CH_2-CH_2-CH_2-O-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-$$

Draw the structures of the monomers used to produce this polymer and state the type of polymerization that has taken place.

Differences between addition and condensation polymers

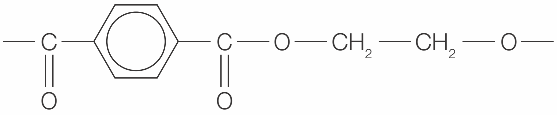
Table 22.5 summarizes the differences between addition polymers and condensation polymers.

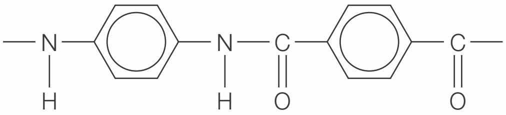
Table 22.5 Differences between addition polymerization and condensation polymerization

Addition polymers	Condensation polymers
Monomers are alkenes or alkene derivatives with a carbon–carbon double bond	Monomers are not alkenes, and typically contain polar functional groups
Monomers undergo polymerization without the loss of small molecules	Each time two monomers bond together a small molecule is eliminated (except polyurethanes)
The empirical formula and percentage composition by mass is the same as that of the monomer (repeating unit) – ignoring end groups	The empirical formula and percentage composition by mass is not the same as that of the monomers (unless polyurethanes)
Typically only one monomer is used (but co-polymerization may involve two addition monomers)	Typically two different monomers are used
Monomer needs a reactive π bond as part of a carbon–carbon double bond	Monomers typically contain two reactive functional groups at the ends of the molecules
Polymer chains contain mostly non-polar groups with strong bonds and usually chemically inert and not usually biodegradable	Polymer chains contain polar groups (typically ester and amide linkages) that may be slowly hydrolysed and may be slowly biodegradable

QUICK CHECK QUESTION

58 The following structures are the repeating units of two different condensation polymers. For each example, name the type of condensation polymer. Give a common name for a polymer of this type. Explain why the second polymer has a higher melting point than the first polymer.

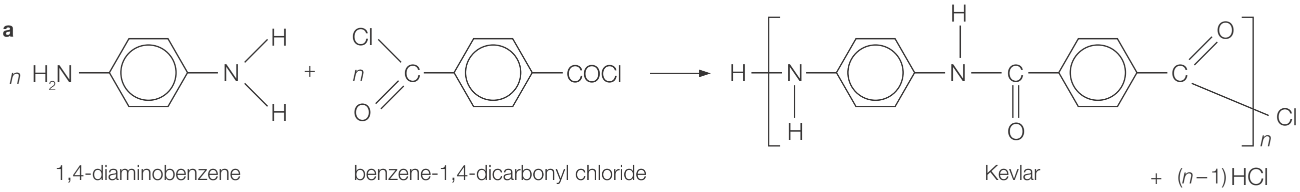




Kevlar

Kevlar is a very strong polyamide made by condensing 1,4-diaminobenzene with benzene-1,4-dicarbonyl chloride. Kevlar forms a strong three- dimensional structure due to hydrogen bonding between the long, rigid chains (Figure 22.81). The molecules are essentially flat due to π delocalization.

a



b

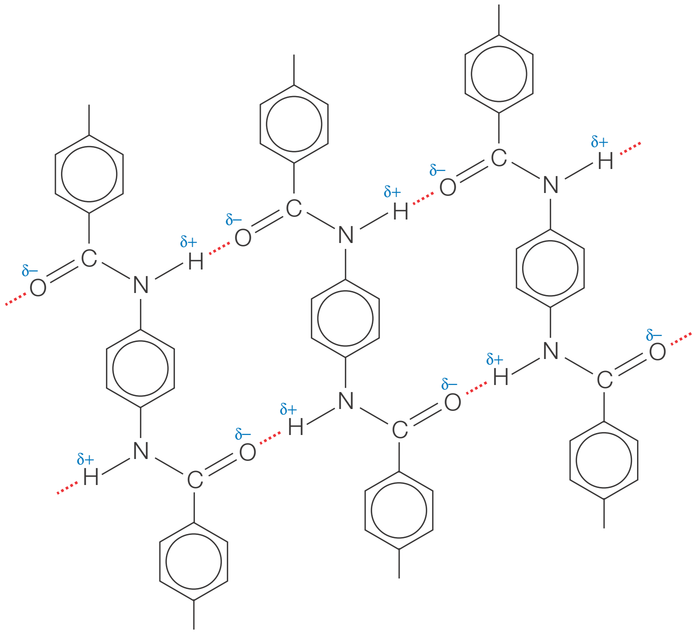


Figure 22.81 a The formation of Kevlar from its monomers. **b** The structure of Kevlar showing the hydrogen bonding between chains

In strongly acidic solution, Kevlar can act as a lyotropic liquid crystal. This means that the alignment of its molecules depends upon the concentration of Kevlar molecules.

In solutions with a very low pH the oxygen and nitrogen atoms in the amide linkage become protonated and this disrupts the hydrogen bonding between the chains (Figure 22.82). The positively charged chains will experience repulsion and the Kevlar will dissolve in the acid solvent. In concentrated sulfuric acid some of the amide linkages can be hydrolysed and Kevlar loses its strength and liquid crystal properties.

Expert tip

Kevlar is an example of an aramid: a polymeric aryl amide, where aryl refers to a benzene ring.

QUICK CHECK QUESTIONS

59 Kevlar is a very tough condensation polymer made from 1,4-diaminobenzene and benzene-1,4-dicarboxylic acid.

- **a** State a use for Kevlar.
- **b** Describe the polymerization reaction that forms Kevlar and state the structural feature that is primarily responsible for its strength.

60 Kevlar is insoluble in most solvents but dissolves in concentrated sulfuric acid.

- **a** Explain how this happens.
- **b** Suggest why Kevlar is less elastic than nylon.

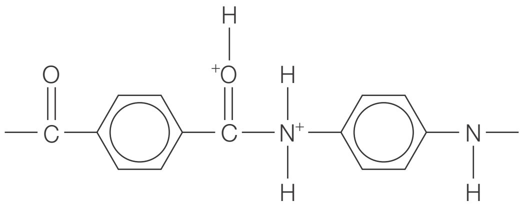


Figure 22.82 Protonated repeating unit of Kevlar

Expert tip

Composites maximize the properties of two separate materials, for example, Kevlar fibres in a matrix of epoxy resin or polyester.

Green polymers

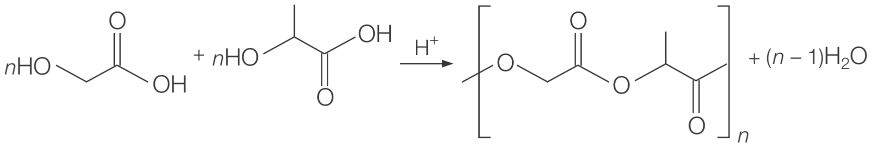
Revised ☐

The major environmental issue with addition polymers is their lack of biodegradability due to the presence of strong and non-polar carbon–carbon single bonds which are not hydrolysed or recognized by enzymes. In polyamides and polyesters, the linkages will hydrolyse slowly in the presence of acid or alkali.

Green chemistry principles can be used to make polymers, such as poly(lactic acid) (Figure 22.83) made from renewable sources, such as starch. The ester linkages between the monomers can be slowly hydrolysed under normal conditions by bacteria.

■ QUICK CHECK QUESTION

61 Explain why polyamides are degraded by sodium hydroxide whereas polymers such as poly(ethene) are not.



Polyester: acid-catalysed hydrolysis degrades the polymer backbone by breaking ester C—O bonds

Figure 22.83 Poly(lactic) acid – a copolymer used for self-dissolving sutures

22.10 Environmental impact – heavy metals

Revised ☐

Essential idea: Toxicity and carcinogenic properties of heavy metals are the result of their ability to form coordinated compounds; heavy metals have various oxidation states and act as catalysts in the human body.

Environmental impact – heavy metals

Revised ☐

- Toxic doses of transition metals can disturb the normal oxidation/reduction balance in cells through various mechanisms.
- Some methods of removing heavy metals are precipitation, adsorption and chelation.
- Polydentate ligands form more stable complexes than similar monodentate ligands due to the chelate effect, which can be explained by considering entropy changes.

Heavy metals

Revised ☐

Heavy metals that exist as ions in polluted water include cadmium, iron, arsenic (a metalloid), mercury, lead, chromium, nickel, copper and zinc; their sources are varied.

The heavy metals affect the cell membrane and membrane bound structures inside cells and some enzymes involved in metabolism, detoxification and damage repair. Heavy metal ions interact with DNA and nuclear proteins, causing DNA damage and changes that may lead to cancer or death of the cell.

Expert tip

Heavy metals are naturally occurring elements that have a high relative atomic mass and a density at least 5 times greater than that of water.

Sources of heavy metals

Revised ☐

Arsenic-containing compounds have been used to manufacture such substances as insecticides, herbicides, fungicides, sheep dips, wood preservatives and dye-stuffs. They have also been used in veterinary medicine for the removal of tapeworms in sheep and cattle. Cadmium is involved in the production of alloys and pigments. It can be found in the effluent (waste water) near zinc mining and in nickel–cadmium rechargeable batteries and certain paints. Mercury is used as a fungicide in seed dressings, utilized in the electrical industry (switches and thermostats) and used as an electrode in the industrial production of chlorine via electrolysis of sodium chloride. Lead used to be used in paints and leaded petrol (to improve engine performance) and is still used as electrodes in lead acid batteries in cars, as an X-ray shield, to make solder and as a roofing material.

Other heavy metals originate from specific industrial processes, for example, chromium(III) sulfate is used for tanning leather and chromium is required for stainless steel making and biocides (e.g. copper(II) compounds used in woodworm treatment).

Removing heavy metals from polluted water

Revised ☐

Adsorption

Various solid substances such as zeolites, waste iron, activated carbon (charcoal), clay minerals and certain transition metal oxides can be added to solution containing heavy metal ions. The metal ions are adsorbed to the surface of the solid and removed from solution. The adsorbed particles can be separated from the water by filtration.

Precipitation

Transition metals tend to form insoluble hydroxides, so the addition of substances like calcium oxide, CaO, which reacts with water to form hydroxide, ($Ca(OH)_2$, causes the heavy metal hydroxides to form and precipitate from the solution. For example

$$Cr^{3+}(aq) + 3OH^-(aq) \rightarrow Cr(OH)_3(s)$$

It is also possible to precipitate certain heavy metals like mercury by bubbling hydrogen sulfide gas through the solution to form insoluble sulfides. This is most effective under alkaline conditions. For example

$$Zn^{2+}(aq) + H_2S(aq) \rightarrow ZnS(s) + 2H^+(aq)$$

These precipitates are dense, settle if the water is still, and can be separated easily by sedimentation and filtration.

QUICK CHECK QUESTIONS

62 Describe the processes of adsorption and chelation of heavy metal ions from waste water.

63 Deduce the structure and shape of the complex ion formed by the reaction of three diaminoethane molecules with a nickel(II) ion.

Solubility equilibria

No ionic substance is totally insoluble; there will always be some small amount in solution. Ionic compounds that have a very limited solubility in water are described as sparingly soluble.

When increasing quantities of a sparingly soluble ionic solid are added to water, a saturated solution is eventually formed. A saturated solution is a solution that contains the maximum possible quantity of dissolved solid (at a given temperature). The solubility can be expressed in grams per cubic centimetre ($g\,cm^{-3}$) or moles per cubic decimetre ($mol\,dm^{-3}$) and interconversion is via the molar mass.

Solubility product

A sparingly soluble ionic solid, in contact with a saturated solution of its own ions is an example of a chemical equilibrium (Figure 22.84).

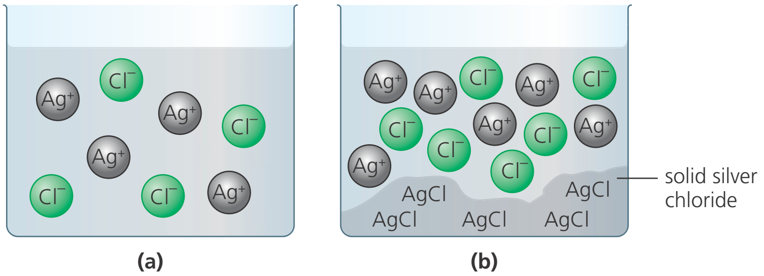


Figure 22.84 a The formation of a dilute (unsaturated) solution of silver chloride and **b** a solution when excess silver chloride has been added to a saturated solution (at constant temperature)

The equilibrium constant for the process is the **solubility product**.

$$AB(s) \rightleftharpoons A^{x+}(aq) + xB^{-}(aq)$$

$$K_{sp} = [A^{x+}(aq)]\,[B^{-}(aq)]^{x}(aq)$$

for example, $K_{sp} = [Ag^+(aq)]\,[Cl^-(aq)]$

The solubility product of an ionic compound can be determined from its solubility, the unit of solubility must be moles per cubic decimetre, mol dm^{-3}. The flow chart in Figure 22.85 shows the steps involved in calculating the solubility for a sparingly soluble ionic compound from its solubility product and vice versa via a balanced dissociation equation and the concentration of ions at equilibrium.

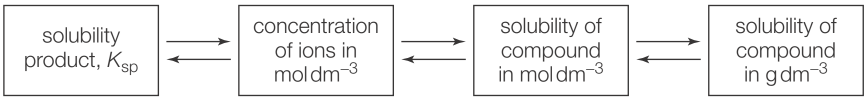


Figure 22.85 The interconversion between solubility product and solubility

The product of ionic concentrations other than those occurring at an equilibrium is called the ionic product. A saturated solution is formed when the ionic product equals the solubility product. Precipitation of a salt will occur when its ionic product exceeds the solubility product (Figure 22.86).

(a) $[Ca^{2+}(aq)] = 10^{-5}\,mol\,dm^{-3}$
$[CO_3^{2-}(aq)] = 10^{-5}\,mol\,dm^{-3}$
$[Ca^{2+}(aq)][CO_3^{2-}(aq)] = 10^{-10}\,mol^2\,dm^{-6}$
this is less than $5.0 \times 10^{-9}\,mol^2\,dm^{-6}$
⟶ no precipitate

(b) $[Ca^{2+}(aq)] = 10^{-4}\,mol\,dm^{-3}$
$[CO_3^{2-}(aq)] = 10^{-4}\,mol\,dm^{-3}$
$[Ca^{2+}(aq)][CO_3^{2-}(aq)] = 10^{-8}\,mol^2\,dm^{-6}$
this is greater than $5.0 \times 10^{-9}\,mol^2\,dm^{-6}$
⟶ precipitate forms

Figure 22.86 The use of K_{sp} to determine whether a precipitate will form a solution of a sparingly soluble ionic compound, (for example, calcium carbonate)

Figure 22.86 shows this principle being applied to calcium carbonate, $K_{sp} = 5.0 \times 10^{-9}$ (at 298 K). Below $[Ca^{2+}(aq)]\,[CO_3^{2-}(aq)] = 5.0 \times 10^{-9}$, no precipitate is formed.

Common ion effect

An ion in common with one of the ions already present in the equilibrium is termed the common ion. For example, when solid sodium fluoride is added to a solution of calcium fluoride, the common ion is the fluoride ion.

Expert tip

The number of ions in the water is the same regardless of how much silver chloride solid is in the beaker.

Key definition

Solubility product [of a sparingly soluble ionic compound] – the product of the equilibrium concentrations of its ions, each raised to the power of its coefficient in the dissociation equation.

QUICK CHECK QUESTION

64 Write the chemical equation showing how the substance dissociates and write the K_{sp} expression for aluminium phosphate, barium sulfate and cadmium sulfide.

Worked example

Silver chloride, AgCl, has a $K_{sp} = 1.77 \times 10^{-10}$. Calculate its solubility in moles per cubic decimetre.

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$; $K_{sp} = [Ag^+]\,[Cl^-]$; $1.77 \times 10^{-10} = [Ag^+][Cl^-]$; $[Ag^+] = x = [Cl^-]$; $1.77 \times 10^{-10} = x^2$; $x = 1.33 \times 10^{-5}\,mol\,dm^{-3}$.

QUICK CHECK QUESTIONS

65 Calculate the solubility product K_{sp} for $Ce(IO_3)_4$, given that its molar solubility is $1.80 \times 10^{-4}\,mol\,dm^{-3}$.

66 Calculate the K_{sp} for $Mg_3(PO_4)_2$, given that its molar solubility is $3.57 \times 10^{-6}\,mol\,dm^{-3}$.

67 Determine the K_{sp} of nickel sulfide (NiS), given that its solubility is 2.97×10^{-10} g/100 cm^3.

The common ion effect reduces the solubility of a sparingly soluble ionic compound when a soluble compound that contains an ion in common is added. The common ion effect operates via Le Châtelier's principle (Figure 22.87).

For example, the presence of either calcium ions, $Ca^{2+}(aq)$ or fluoride ions, $F^-(aq)$ in a solution reduces the solubility of calcium fluoride, CaF_2, shifting the solubility equilibrium of CaF_2 to the left:

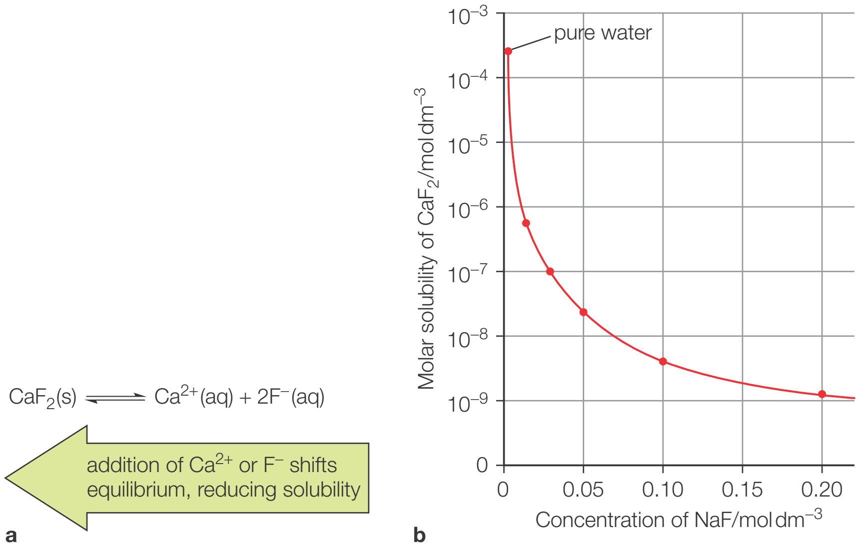


Figure 22.87 a Applying Le Châtelier's principle to the solubilty of calcium fluoride, CaF_2. **b** The effect of the concentration of NaF on the solubility of CaF_2 demonstrates the common-ion effect

Chelation

Chelation occurs when a ligand containing non-bonding (lone) pairs of electrons bonds to a central metal atom or ion forming two or more coordinate bonds. Chelating agents are polydentate ligands and usually organic compounds.

Two important chelating agents are ethane-1-2-diamine (Figure 22.88) and the ethylenediaminetraacetate ion, $EDTA^{4-}$ (Figure 22.89). The ethane-1-2 diamine molecule contains two non-bonding (lone) pairs of electrons, one on each of the nitrogen atoms and so is a bidentate ligand. $EDTA^{4-}$ contains six non-bonding (lone) pairs of electrons, two on nitrogen atoms, and four on charged oxygens, so is a hexadentate ligand forming very stable complexes.

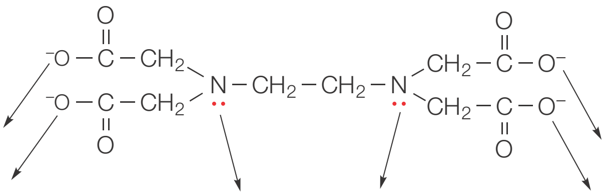


Figure 22.89 EDTA is a hexadentate ligand

Polydentate ligands form much more stable complexes than similar monodentate ligands as measured by the size of the equilibrium constant. From the expression $\Delta G = -RT \ln K$, a high value for the equilibrium constant will give a large negative value for the Gibbs free energy change.

The reaction will be highly spontaneous (under standard conditions). From the Gibbs equation, $\Delta G = \Delta H - T\Delta S$ and hence the large negative value for ΔG is largely due to the large positive entropy change, ΔS, as the system becomes more highly ordered than when monodentate ligands react with the same metal ion or atom.

Worked example

Determine the solubility of silver(I) iodide, AgI, in a 0.274 mol dm^{-3} solution of sodium iodide, NaI. (K_{sp} of AgI = 8.52×10^{-17}).

Dissociation equation:
$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$

K_{sp} expression: $K_{sp} = [Ag^+][I^-]$

Substituting into the K_{sp} expression:

$8.52 \times 10^{-17} = (x)(0.274)$

$[Ag^+] = 3.11 \times 10^{-16}$ mol dm^{-3}

Expert tip

The chelate effect describes the enhanced affinity of chelating ligands for a metal ion compared to the affinity of a collection of similar non-chelating (monodentate) ligands for the same metal ion.

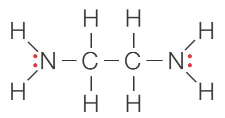


Figure 22.88 Ethane-1-2-diamine is a bidentate ligand

QUICK CHECK QUESTION

68 Explain why a solution of Cu^{2+} in the presence of EDTA is not toxic to phytoplankton.

Consider the reaction where six ammonia ligands (6 nitrogen donor atoms) are replaced with three ethane-1-2-diamine ligands (6 nitrogen donor atoms).

$$[Co(NH_3)_6]^{2+}(aq) + 3H_2NCH_2CH_2NH_2(aq) \rightleftharpoons [Co(H_2NCH_2CH_2NH_2)_3]^{2+}(aq) + 6NH_3(aq)$$

The enthalpy change will be relatively small because there are the same number and similar types of coordinate bonds on both sides (ignoring interactions with solvent molecules). However, the reaction in the forward direction is favoured because it involves an increase in entropy (four particles forming seven particles).

Haber–Weiss and Fenton reactions

A simple mixture of hydrogen peroxide and an iron(II) salt produces hydroxyl radicals. This is known as the Fenton reaction.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {\bullet}OH + OH^-$$

In the presence of trace amounts of iron, superoxide ions can then reduce iron(III) ions to molecular oxygen and iron(II) ions:

$$Fe^{3+} + O_2^- \rightarrow Fe^{2+} + O_2$$

The sum of these two equations produces molecular oxygen, hydroxyl radicals and hydroxide ions from superoxide ions and hydrogen peroxide, in the presence of catalytic amounts of iron(II) ions – the so-called Haber–Weiss reaction:

$$O_2^- + H_2O_2 \rightarrow O_2 + {\bullet}OH + OH^-$$

Iron complexes will catalyse the Fenton reaction if the iron(III) complex can be reduced and the iron(II) complex has a reduction potential that allows it to transfer an electron to a hydrogen peroxide molecule (Figure 22.90).

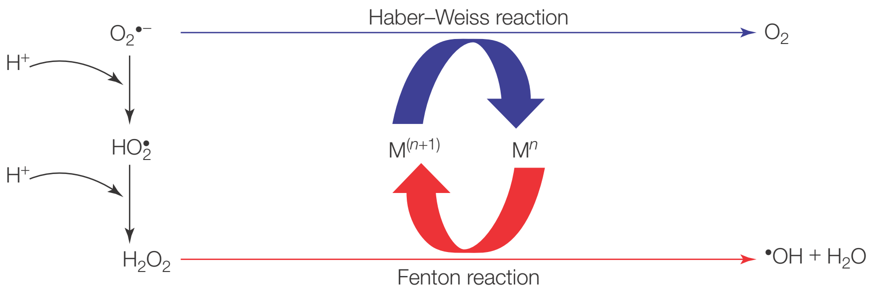


Figure 22.90 Fenton and Haber–Weiss reactions

Fenton's reagent is a solution of hydrogen peroxide and iron(II) sulfate used to treat water with a wide variety of organic pollutants. The iron(II) ions and hydrogen peroxide molecules generate hydroxyl and peroxyl radicals:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {\bullet}OH + OH^-$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {\bullet}OOH + H^+$$

The hydroxyl radicals undergo a variety of reactions involving the organic pollutants which ultimately result in the formation of carbon dioxide and water. The overall process is exothermic and rapid. Fenton's reagent is also used as an oxidizing agent in organic chemistry.

QUICK CHECK QUESTION

69 The iron-catalysed Haber–Weiss reaction may occur in cells. State the equations for this process.

23 Option B Biochemistry

23.1 Introduction to biochemistry

Revised ☐

Essential idea: Metabolic reactions involve a complex interplay between many different components in highly controlled environments.

Introduction to biochemistry

Revised ☐

- The diverse functions of biological molecules depend on their structures and shapes.
- Metabolic reactions take place in highly controlled aqueous environments.
- Reactions of breakdown are called catabolism and reactions of synthesis are called anabolism.
- Biopolymers form by condensation reactions and are broken down by hydrolysis reactions.
- Photosynthesis is the synthesis of energy-rich molecules from carbon dioxide and water using light energy.
- Respiration is a complex set of metabolic processes providing energy for cells.

Metabolism

Revised ☐

Biochemistry is the study of chemical processes in living cells at the molecular level.

Cells are the basic unit of structure and function in all living organisms. Complex organisms contain vast numbers of cells, which together carry out all the life processes. At any one time within the microscopic volume of a living cell, thousands of chemical reactions occur involving a range of biochemically important molecules that have a series of diverse roles. Some metabolic reactions take place in the cytoplasm of the cell, the synthesis of proteins on ribosomes, for example, and some in membrane-bound organelles, such as the chloroplast, the site of all the reactions involved in photosynthesis in green leaves. Many metabolic pathways involve redox reactions, which involve the transfer of electrons.

Living organisms convert energy from one form into another. The enzyme-controlled reactions that place inside living cells are collectively known as **metabolism**. Reactions in which organic molecules are broken down to release energy are catabolic reactions. Reactions that use energy to synthesize larger molecules are known as anabolic reactions. Metabolism involves **anabolism** and **catabolism**.

The biochemical reactions involved in metabolism are organized into *metabolic pathways*, each step of which is catalysed by a specific enzyme in an aqueous environment (within a narrow range of conditions) (Figure 23.1).

Key definitions

Metabolism – the total of all the enzyme-catalysed reactions in a cell or organism. It involves the breakdown of molecules with the release of energy and the synthesis of molecules that are required by the cell.

Catabolism – the breakdown of complex molecules into simpler molecules. Such processes release energy.

Anabolism – the synthesis of more complex molecules from simpler precursor molecules. Such processes require energy.

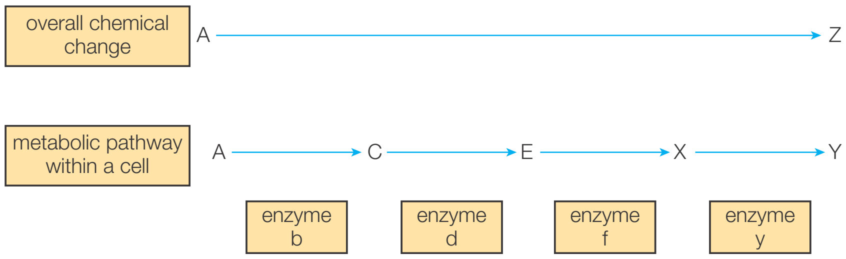


Figure 23.1 A metabolic pathway achieves a chemical conversion in a sequence of enzyme-catalysed steps

Metabolic pathways may be linear or cyclic (Figure 23.2). Compounds taking part in metabolism are known as *metabolites*.

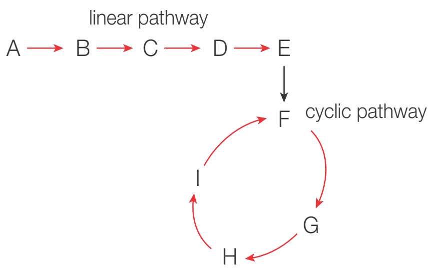


Figure 23.2 Linear and cyclic metabolic pathways

Expert tip

The shape of a molecule determines the way it behaves inside cells and metabolic pathways. The chemical nature of a molecule is dependent upon the shape as well as the distribution of the electron density in its covalent bonds. The shape of a molecule and its polarity influence the physical and chemical properties of the elements involved.

Respiration and *photosynthesis* are two key metabolic processes central to life on the Earth.

- Respiration is a process by which cells generate energy through the breakdown of glucose. As such it is a catabolic process. It is common to the metabolism of all cell types, whether bacterial, fungal, plant or animal.
- Photosynthesis is an anabolic process in which carbon dioxide from the atmosphere is taken in by plants and combined with water to form energy-rich molecules such as glucose.

Photosynthesis

Revised ☐

Photosynthesis (Figure 23.3) is an anabolic process used by plants and some bacteria to synthesize glucose from carbon dioxide and water using light energy absorbed by chlorophyll. During photosynthesis water molecules are 'split' and oxygen is released as a by-product. It is a complex series of enzyme-controlled reactions occurring inside chloroplasts.

Photosynthesis can be summarized by the following overall chemical equation:

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$$

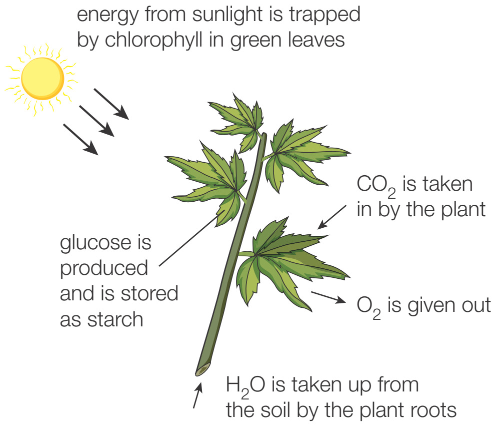


Figure 23.3 An overview of photosynthesis, showing the importance of sunlight as the source of energy

Expert tip

Photosynthesis is responsible for the origin and maintenance of oxygen in the atmosphere. It essentially 'fixes' carbon (in the form of carbon dioxide) into biomass.

Photosynthesis and respiration are largely responsible for the global balance of carbon dioxide and oxygen in the atmosphere, though levels of carbon dioxide are increasing, largely due to emissions of carbon dioxide from the combustion of fossil fuels.

Respiration

Revised ☐

Aerobic respiration

Respiration is a catabolic process operating in all living organisms. Aerobic respiration involves the breakdown of glucose in the presence of molecular oxygen to form carbon dioxide and water. The overall equation is the reverse of the process of photosynthesis, but it is a complex series of enzyme-controlled steps involving a large number of intermediates (in linear and cyclic metabolic cycles) (Figure 23.4).

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

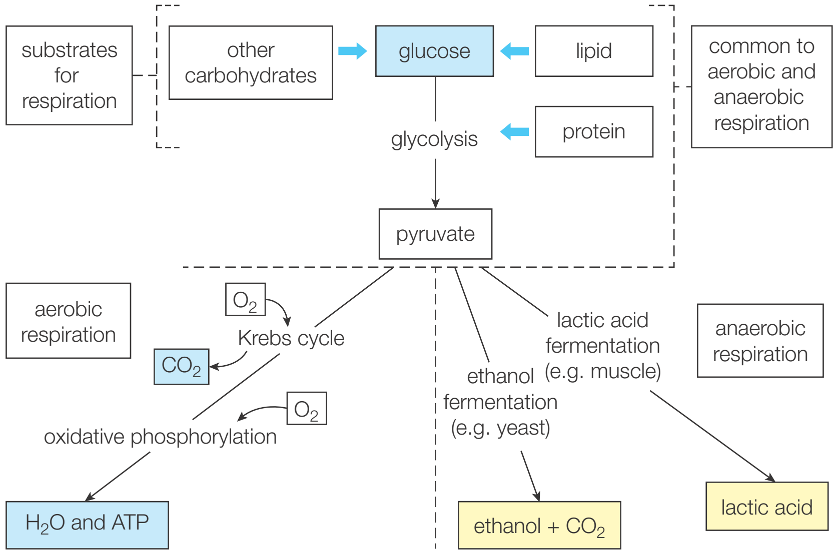


Figure 23.4 The metabolic processes involved in cellular respiration

The overall products of aerobic respiration are carbon dioxide and water, with the generation of a large number of molecules of ATP (**a**denosine **trip**hosphate), the short-term energy store in cells.

Worked example

The blood plasma of a typical human adult contains 20.00 g of glucose. Calculate the mass of oxygen needed to completely oxidize it to water and carbon dioxide.

$$\text{amount of glucose} = \frac{20.00\,\text{g}}{180.16\,\text{g mol}^{-1}}$$

$$= 0.111\,\text{mol}$$

During aerobic respiration:

1 mole of glucose requires 6 moles of oxygen to react with it, so the amount of oxygen required is

$$6 \times 0.111\,\text{mol} = 0.666\,\text{mol}$$

hence the mass of oxygen required is

$$0.666\,\text{mol} \times 32.00\,\text{g mol}^{-1} = 21.3\,\text{g}$$

Anaerobic respiration

Respiration can also occur in the absence of oxygen. In humans, lactic acid (2-hydroypropanoic acid) is formed, but in plants and yeast ethanol is formed (Figure 23.4), which can be used as biofuel (Option C Energy). Anaerobic respiration releases less energy to cells than aerobic respiration as fewer molecules of ATP are formed. Anaerobic respiration in yeast is known as fermentation:

$$C_6H_{12}O_6(aq) \rightarrow 2CO_2(g) + 2C_2H_5OH(l)$$

The two processes of photosynthesis and respiration help to maintain the balance between carbon dioxide and oxygen in the atmosphere.

In addition to carbohydrates, lipids and proteins can be used as energy sources for ATP synthesis. This happens during starvation. After hydrolysis, these large molecules form fatty acids plus glycerol and amino acids. These three types of molecule can also be catabolized to release energy and so produce ATP.

NATURE OF SCIENCE

One of the most important events that happened during 1900s in the history of biochemistry is the experiment done by Buchner. He prepared a cell-free extract of yeast which he called the zymase. It fermented glucose and produced carbon dioxide and ethanol. He introduced the concept of an 'enzyme' and falsified the earlier idea that only cytoplasm could carry out metabolic processes.

Expert tip

The removal of metabolic waste is known as excretion. Excretory products in humans are carbon dioxide and urea.

Condensation and hydrolysis reactions

Revised ☐

Biological macromolecules and polymers (biopolymers), such as proteins, lipids and DNA, are formed by enzyme-controlled condensation reactions (Figure 23.5). These involve the reaction between the functional groups of two smaller molecules to form one large molecule with the release of a water molecule. Condensation reactions are an addition reaction followed by an elimination reaction.

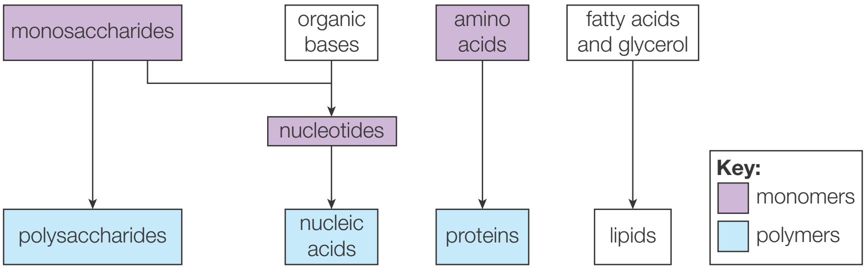


Figure 23.5 The synthesis of macromolecules from smaller monomers

For condensation polymerization (Figure 23.6) to occur each of the reacting molecules must possess at least two reactive functional groups. Examples include the condensation of amino acids to form proteins, the condensation of nucleotides to form DNA, the condensation of propane-1,2,3-triol (glycerol) and fatty acids to form lipids and the condensation of glucose to form starch and cellulose.

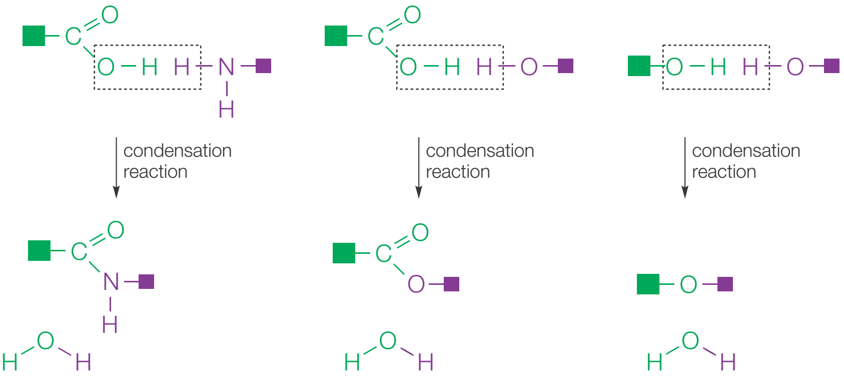


Figure 23.6 The condensation reactions involved in the formation of proteins, lipids and polysaccharides

For example, the two amino acids alanine, $H_2N–CHCH_3–COOH$, and cysteine, $H_2N–CH(CH_2SH)–COOH$, can condense together to form two different possible dipeptides provided each dipeptide contains one of each of two amino acid residues.

Each end of the dipeptides contains a reactive group so can undergo further condensation reactions (in the presence of enzymes) with additional amino acids to produce a polypeptide chain (protein).

Hydrolysis is the reverse of condensation (Figures 23.7 and 23.8). A molecule is hydrolysed when a water molecule reacts with a large molecule to break a specific bond (ester or amide) and form two smaller molecules. The hydrolysis of proteins produces amino acids and the hydrolysis of starch and cellulose (polysaccharide) produces glucose. Sucrose (a disaccharide) can be hydrolysed to form glucose and fructose. The hydrolysis reactions can also occur in the presence of acid without the presence of enzymes.

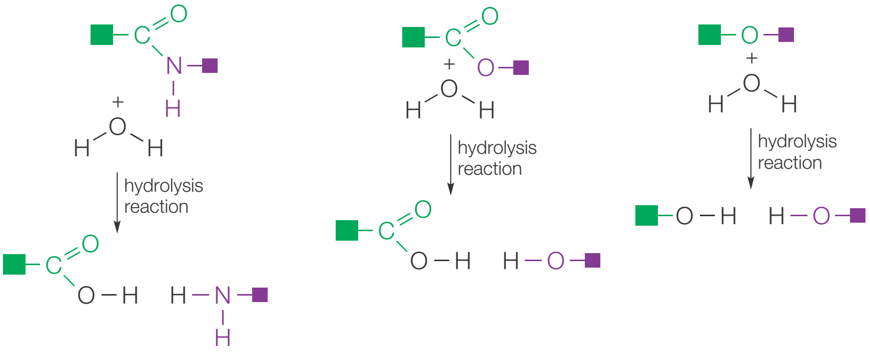


Figure 23.7 Hydrolysis reactions involve the breaking of a covalent bond by the addition of the fragments of water (H– and –OH) across the bond

Figure 23.8 summarizes the interrelationship between condensation and hydrolysis, and the key role of water, in the formation of biopolymers.

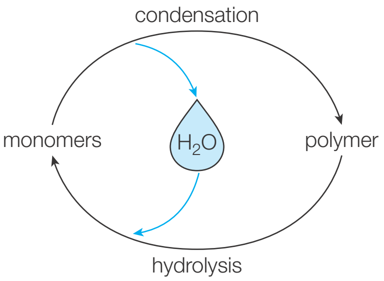


Figure 23.8 Summary of the general interrelationship between condensation reactions and hydrolysis

■ QUICK CHECK QUESTIONS

1. Distinguish between catabolic and anabolic reactions in metabolism. Classify photosynthesis and respiration as one or other of these types of reaction, giving your reasons.
2. Name the product(s) of anaerobic respiration in the following two different biological situations:
   - **a** in yeast
   - **b** in human muscle.
3. Write balanced equations to show the catabolism of glycerol, $C_3H_8O_3$, and oleic acid, $C_{18}H_{34}O_2$, a fatty acid, to carbon dioxide and water.
4. Hydrogen peroxide is broken down to water and oxygen and under the control of the enzyme, catalase.

   Write a balanced equation for the reaction. State and explain what type of metabolic reaction this is an example of.
5. Maltotriose is formed when three molecules of glucose react together to form water. Write a balanced equation to describe this reaction and state what type of reaction it is. Suggest how the trisaccharide can be hydrolysed to form glucose.

Expert tip

Water behaves as a solvent and hydrates all biological molecules, as a reactant (during hydrolysis), and as a product (during condensation reactions). These all rely on its polar nature and its ability to form intermolecular hydrogen bonds.

23.2 Proteins and enzymes

Revised ☐

Essential idea: Proteins are the most diverse of the biopolymers responsible for metabolism and structural integrity of living organisms.

Proteins and enzymes

Revised ☐

- Proteins are polymers of 2-amino acids, joined by amide links (also known as peptide bonds).
- Amino acids are amphoteric and can exist as zwitterions, cations and anions.
- Protein structures are diverse and are described at the primary, secondary, tertiary and quaternary levels.
- A protein's three-dimensional shape determines its role in structural components or in metabolic processes.
- Most enzymes are proteins that act as catalysts by binding specifically to a substrate at the active site.
- As enzyme activity depends on the conformation, it is sensitive to changes in temperature and pH and the presence of heavy metal ions.
- Chromatography separation is based on different physical and chemical principles.

Amino acids

Revised ☐

Amino acids contain an amine and a carboxyl group bonded to a central common atom. Figure 23.9 shows the generalized molecular formula of amino acids.

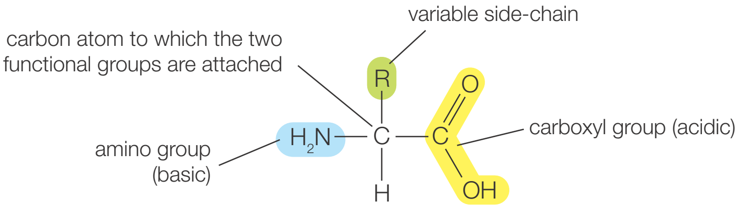
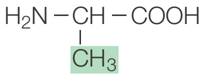
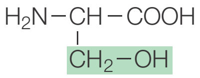
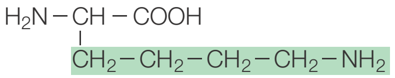
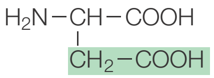


Figure 23.9 Generalized structure of amino acids

There are 20 amino acids. Each a different variable side-chain (a full table is available in the IB Chemistry *data booklet*). Amino acids can be classified based on their polarity and their acid–base properties (Table 23.1).

With the exception of glycine (2-aminoethanoic acid), all of the 2-amino acids contain a chiral carbon atom and therefore exhibit optical isomerism.

Table 23.1 Some examples of the different types of variable side-chains, R, in amino acids

Type of amino acid	R group contains	Example	Structure
Non-polar/hydrophobic	Hydrocarbon chain	Alanine, Ala	 $H_2N-\underset{CH_3}{CH}-COOH$
Polar, uncharged	Hydroxyl (–OH), sulfhydryl (–SH) or amide (–CONH$_2$) groups	Serine, Ser	 $H_2N-\underset{CH_2-OH}{CH}-COOH$
Basic (positively charged at pH 6.0–8.0)	Amino group (–NH$_2$)	Lysine, Lys	 $H_2N-\underset{CH_2-CH_2-CH_2-CH_2-NH_2}{CH}-COOH$
Acidic (negatively charged at pH 6.0–8.0)	Carboxyl group (–COOH)	Aspartic acid, Asp	 $H_2N-\underset{CH_2-COOH}{CH}-COOH$

Amino acids are white crystalline solids under standard conditions. They exist in the solid state and in neutral aqueous solution as zwitterions (Figure 23.10). This is due to an internal acid–base reaction. A hydrogen ion is released from the carboxyl group and protonates the amine group.

The presence of zwitterions leads to ionic bonding in crystalline amino acids involving electrostatic forces of attraction between oppositely charged ends of the zwitterions. This results in high melting (or decomposition) points and good solubility in water.

Expert tip

They are referred to as 2-amino acids as the amine group is attached to the first carbon after that of the carboxyl functional group in the chain.

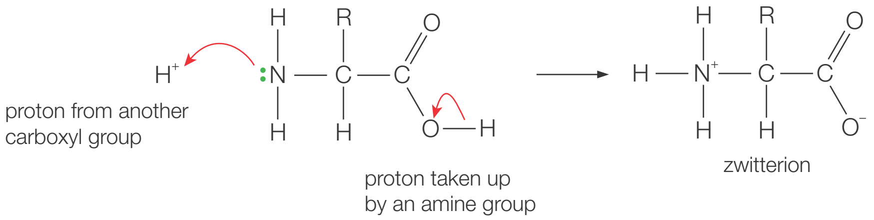


Figure 23.10 Zwitterion formation in amino acids

During protein synthesis in cells, amino acids condense (in the presence of enzymes) through the formation of the amide link (–CONH–), or peptide bond, to form a polypeptide chain (Figure 23.11), which then folds to form a biologically active protein.

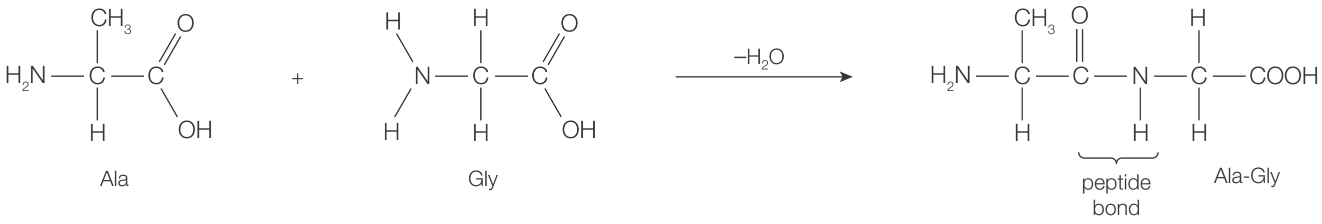


Figure 23.11 Peptide formation between two amino acids

Peptide bonds experience restricted rotation (Figure 23.12) due to resonance (π delocalization), giving rise to two possible conformations: the *trans* conformation is generally more stable.

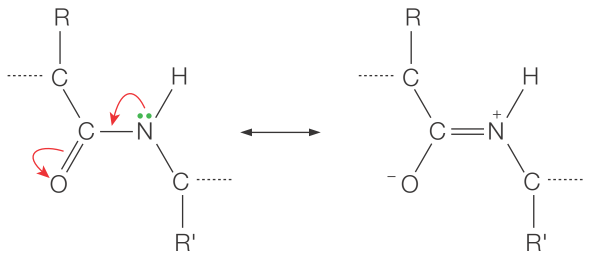


Figure 23.12 Resonance structures of the peptide bond (in the *trans* conformation)

Common mistake

Figure 23.11 shows the formation of a dipeptide, Ala-Gly, formed by condensation of the two amino acids, alanine and glycine. If this reaction is carried out in a test tube then remember that this is just one of two possible options. Gly-Ala is equally likely to be formed. When writing, or drawing, an equation for the reaction, do not forget the molecule of water eliminated in the condensation reaction.

Each particular protein has a specific number of amino acid residues bonded in a specific sequence between an amine group and a carboxyl group. This is known as the primary structure (see Figure 23.13). A small change in a primary structure can result in a large change in biological function.

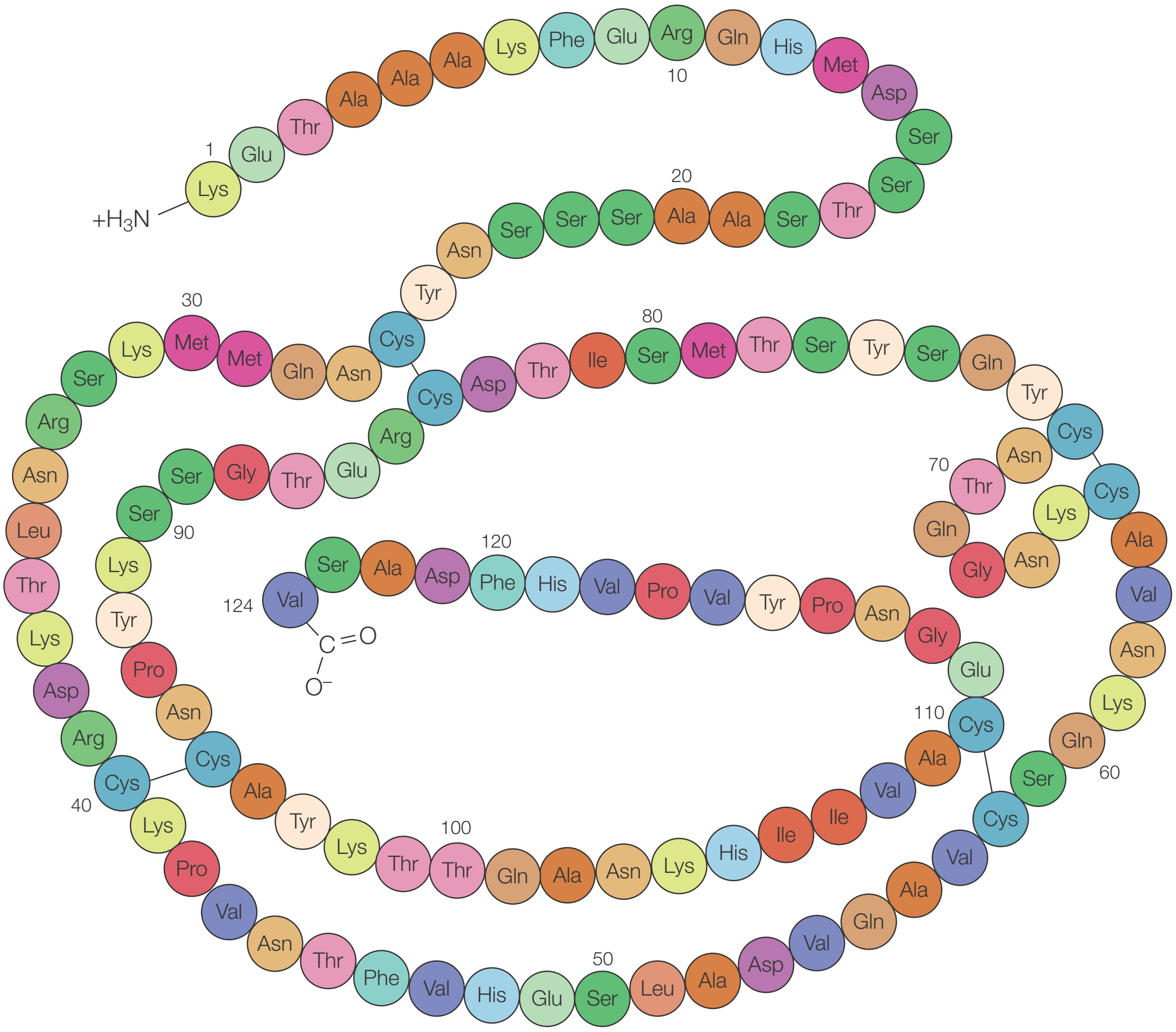


Figure 23.13 The primary sequence of the enzyme ribonuclease A (bovine pancreatic ribonuclease). Note the four disulfide bridges between cysteine residues

Ribonuclease A is a relatively short polypeptide of 124 amino acid residues and it illustrates the key features of the primary chain structure of polypeptides. The sequence is written with the $–NH_2$ group which has not been converted into a peptide link at the left-hand end. The unchanged –COOH group is written at the right-hand end. The end of the peptide chain with the $–NH_2$ group is known as the amino(N)-terminal end, and the end with the −COOH group is the carboxyl(C)-terminal end. This reflects the fact that in biological cells the synthesis of a protein in cells is directional, with the protein chain being synthesized from the N-terminal end to the C-terminal end.

Expert tip

The term amino acid residue has to be used since a peptide chain is not made up of amino acids. When the amino acids chemically combine together, a water molecule is lost. The peptide chain is made up from what is left after the water is eliminated. Relatively short chains of amino acid residues are called peptides.

In order to sequence an entire protein, the polypeptide chain is broken down into smaller fragments using either chemicals (concentrated acid or alkali), or proteases (Figure 23.14). The resulting smaller fragments are then sequenced. The complete sequence is assembled by analysing overlapping fragments generated by cleaving the polypeptide chain with different reagents.

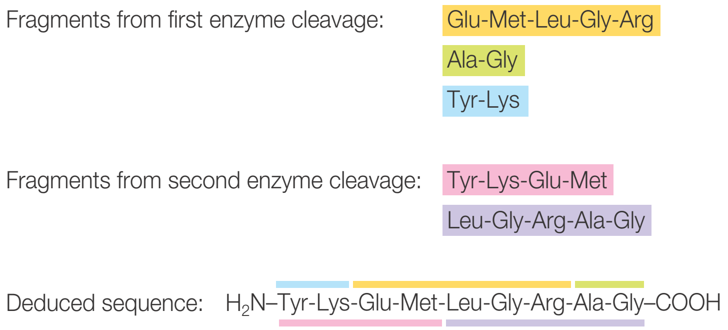


Figure 23.14 Establishing the primary structure of a protein by partial hydrolysis

Amino acids are amphoteric or, more specifically, amphiprotic, because, depending on pH, they can act as either an acid (via proton loss at the carboxyl group), or as a base (via protonation at the amino group). Amino acids have two pK_a values, one for the carboxyl functional group and one for the amine functional group. Amino acids with basic or acidic side-chains will have a third pK_a value.

The isoelectric point (pI) of an amino acid is the pH at which the concentrations of the zwitterionic form reaches its maximum value (Figure 23.15). During electrophoresis, amino acids are separated based on their pI values.

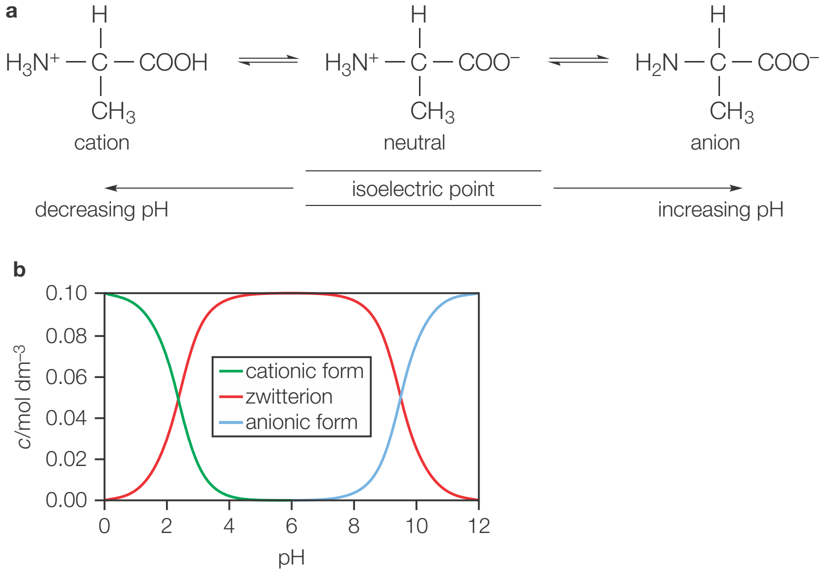


Figure 23.15 The isoelectric point (pI) of alanine: **a** the ionic forms at different pH and **b** the acid–base equilibria in a 0.1 mol dm^{-3} solution (pI = 6.0)

Expert tip

When working with enzymes it is important to buffer the pH of the solution. This prevents denaturation and hence loss of activity.

Structure of proteins

The secondary structure of a protein refers to three-dimensional conformations of localized regions of the protein, in particular, an α-helix (Figure 23.16) or a β-pleated sheet (Figure 23.17). The tertiary structure of a protein is the arrangement of the α-helix or β-pleated sheet into a configuration characteristic of the protein.

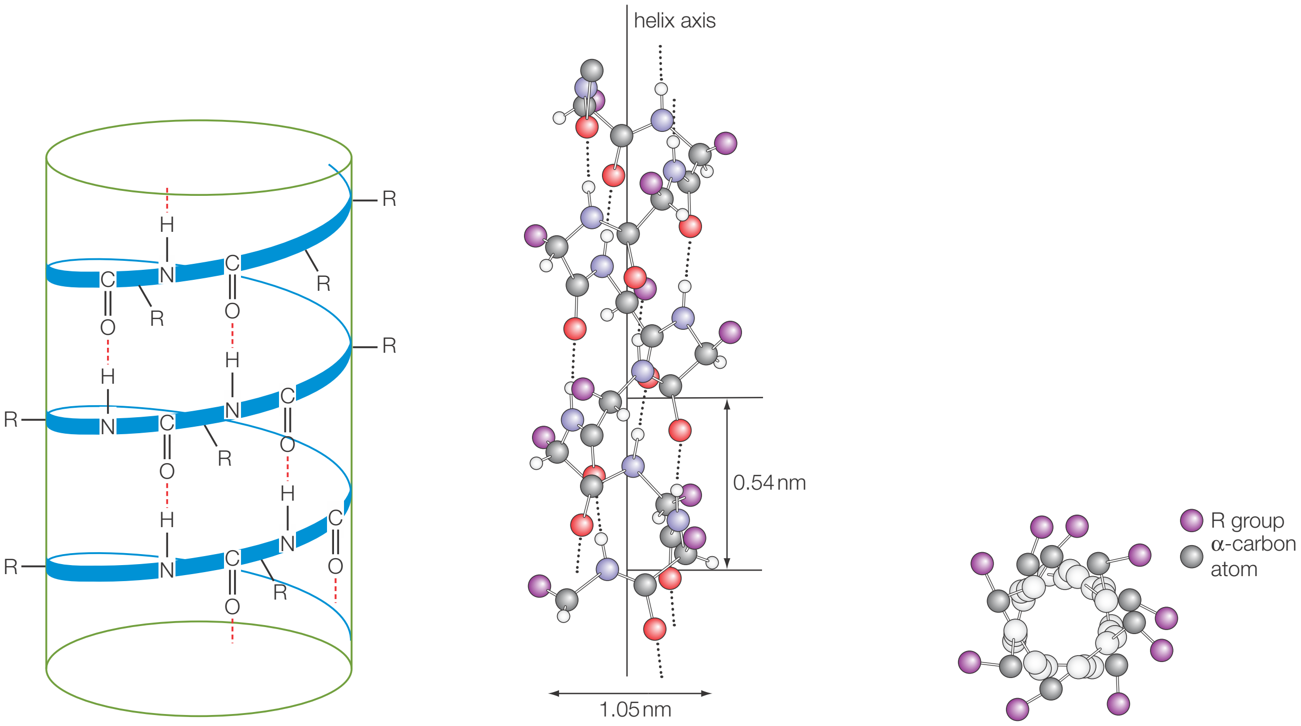


Figure 23.16 An α-helix

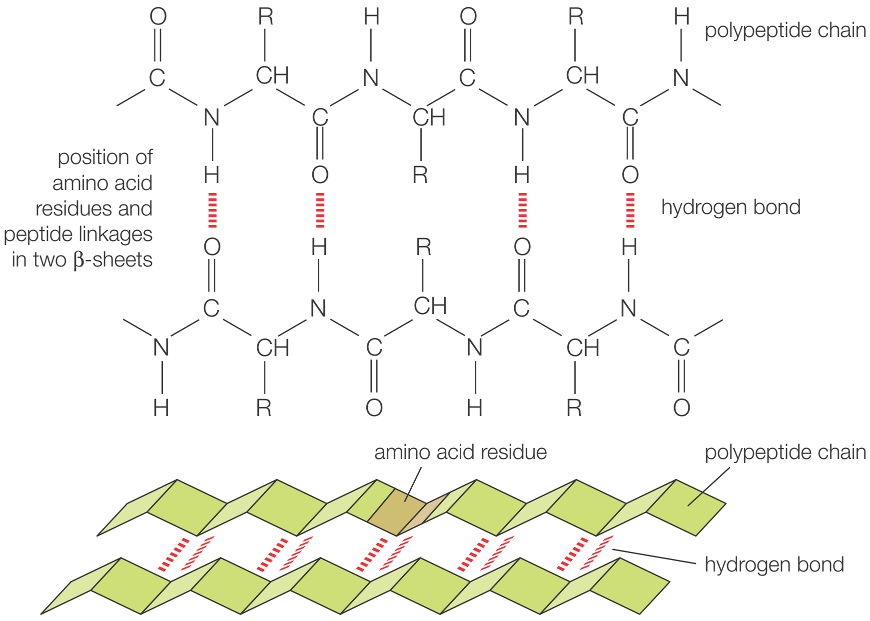


Figure 23.17 A β-sheet

Expert tip

In a parallel β-pleated sheet the hydrogen bonds run in the same direction; in an antiparallel β-pleated sheet the hydrogen bonds run in the same direction.

A variety of bonds and intermolecular forces are involved in maintaining tertiary structure (Figure 23.18). The quaternary structure of a protein is the grouping of two or more tertiary structures into a unit (the functional protein). Thus, myoglobin is an oxygen-carrying protein that consists of a single chain and has a conformation defined up to the tertiary level, whereas hemoglobin, consisting of four sub-units, has quaternary structure too.

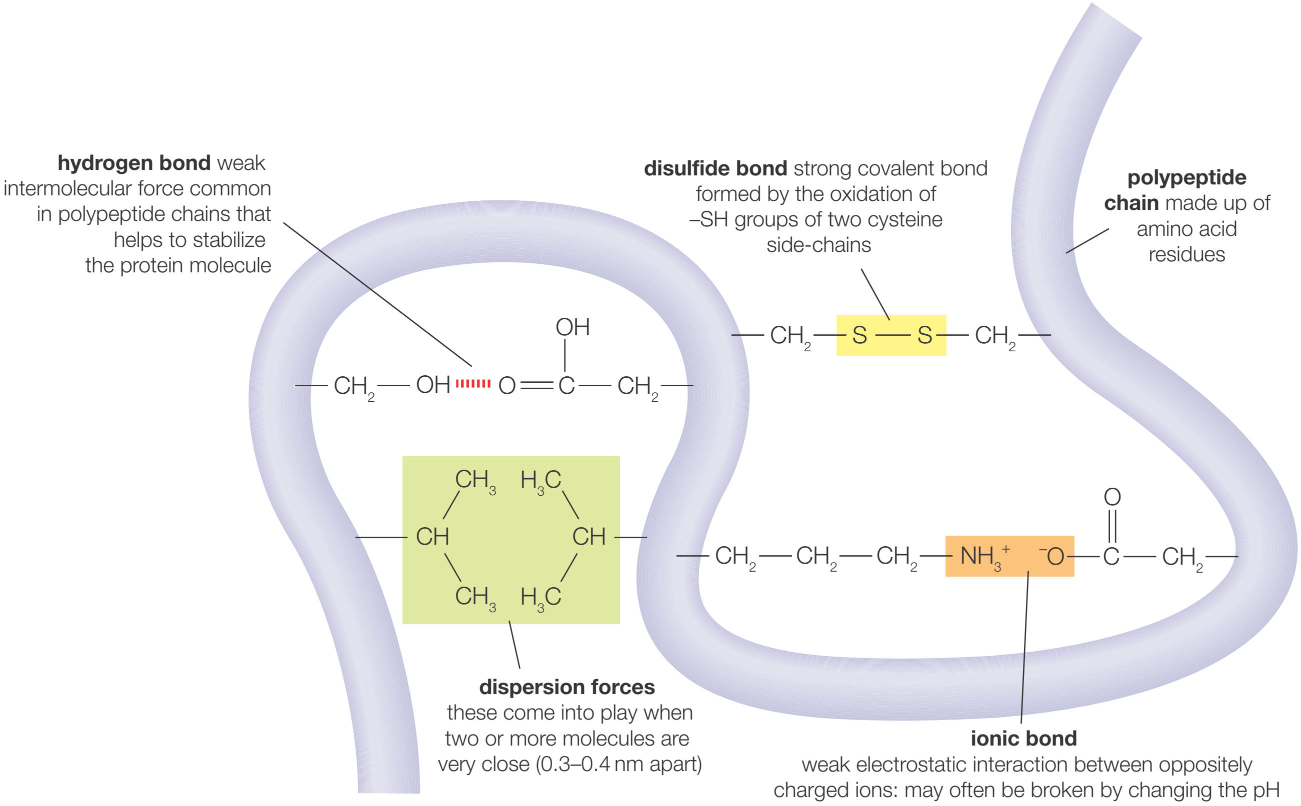


Figure 23.18 Interactions maintaining protein tertiary structure

Expert tip

The position of covalent disulfide bonds between cysteine residues is also included in the primary structure.

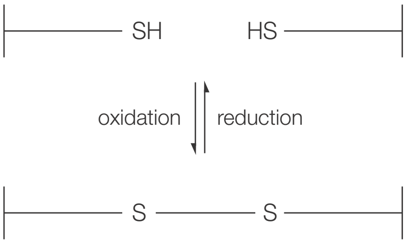


Figure 23.19 The formation of a disulfide bridge

Cysteine residues are capable of being covalently bonded to another (under enzyme control) via the formation of disulfide bridges (Figure 23.19). Their formation contributes to the stability of the secondary and tertiary structures of a protein.

Table 23.2 summarizes the key features of the different levels of protein structure.

Table 23.2 A summary of the bonds and forces involved in protein structure

Level of protein structure	Nature of interactions
Primary	Sequence of amino acids linked by covalent bonds (peptide/amide links)
Secondary	Folding of chain involving hydrogen bonding between the peptide link regions of the chain (α-helix and β-pleated sheet)
Tertiary	Folding of the polypeptide chain involving interactions between the R-groups of the amino acid residues: London dispersion forces, hydrogen bonds, ionic interactions and disulfide bridges
Quaternary	Folding and assembly of multiple sub-units of a protein, involving the same interactions as tertiary structure

QUICK CHECK QUESTIONS

6 Alanine is a white crystalline solid that readily dissolves in water. State the special features about the structure of the molecule that account for:

a its crystalline nature

b its solubility in water.

7 The following diagram represents the two ends of the primary structure of a myoglobin molecule:

X-Val-Leu-Ser-Glu-Gly---------Gly-Tyr-Gln-Gly-COOH

where Val, Leu, Ser, etc. are the shorthand forms referring to the different amino acids in the chain.

a Which functional group is represented by **X**?

b Name the covalent bond formed between **each** pair of amino acids in the chain.

c Draw a diagram of this link region showing clearly the atoms present and the bonds present.

d Describe the bonding responsible for the secondary structure of myoglobin and other proteins.

e Explain what is meant by the *secondary*, *tertiary* and *quaternary* structure of a protein.

8 Polypeptides and proteins are formed by the condensation reactions of amino acids.

a Give the general, condensed structural formula of a 2-amino acid.

b Give the condensed structural formulae of the two dipeptides formed by the test tube reaction of alanine and glycine.

State the other inorganic substance formed during this reaction.

c How many different tripeptides can be formed from glycine, serine and alanine if each tripeptide molecule contains one residue from each of these three amino acids?

Fibrous and globular proteins

Biological molecules, especially proteins, are very diverse in nature and their functions depend upon their chemical structures and overall molecular shape (conformation).

Fibrous proteins, for example, collagen (Figure 23.20), consist of linear polypeptide chains that are bundled and associated together. Globular proteins, for example, hemoglobin (Figure 23.21) are polypeptide chains that are coiled into compact shapes. Structural proteins, such as keratin, are fibrous proteins that provide structural rigidity in nails and hair.

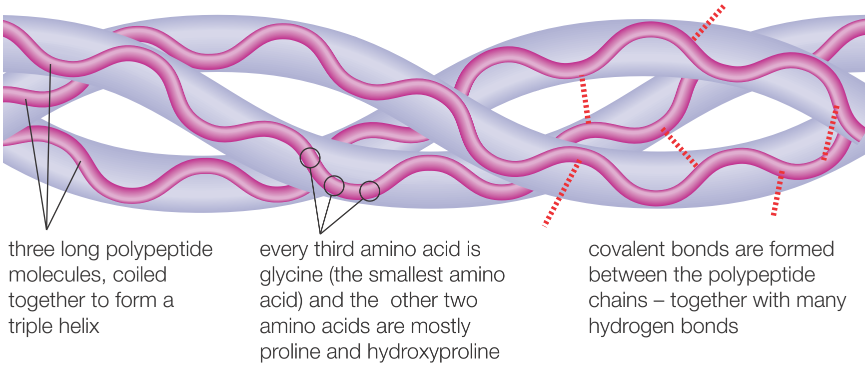


Figure 23.20 The structure of collagen, a fibrous protein

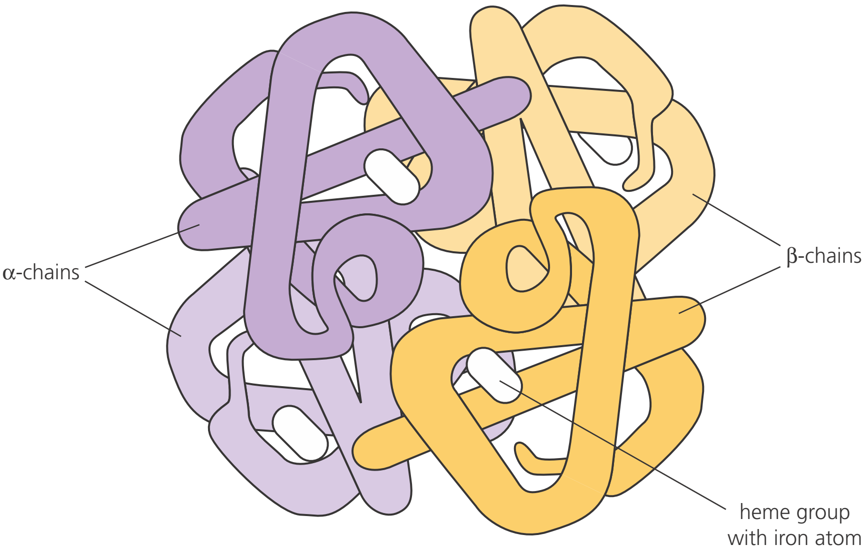


Figure 23.21 Structure of hemoglobin

Transport proteins, such as hemoglobin, are used to transport molecules or ions from one location to another. Hemoglobin consists of a protein unit covalently bonded to a non-protein prosthetic group which contains an iron(II) ion that reversibly bonds to an oxygen molecule. It is an oxygen transport protein.

Expert tip

Some enzymes require of the presence of cofactors, small non-protein units, to function. Cofactors may be inorganic ions or complex organic molecules called coenzymes. A cofactor that is covalently bonded to the enzyme is called a prosthetic group.

Table 23.3 The roles of different proteins

Protein	Function	Where found in body
Collagen	Structural protein, giving strength and elasticity	Skin, tendon, bone
Keratin	Structural	Hair, nails
Myosin	Muscle contraction	Muscle tissue
Actin	Muscle contraction	Muscle tissue
Chymotrypsin	Digestive (proteolytic) enzyme, breaks down proteins in food	Small intestine
Pepsin	Digestive (proteolytic) enzyme, breaks down proteins in food	Stomach
Insulin	Peptide hormone, enables use of glucose for energy through respiration	Blood, pancreas
Immunoglobulin	Antibodies	Blood, lymph
Hemoglobin	Oxygen transport from lungs to other tissues	Blood

Enzymes

Enzymes are biological catalysts and greatly accelerate biochemical reactions without being altered by the reaction. This effect is achieved by providing an alternative reaction pathway that has a lower activation energy than the uncatalysed reaction (Figure 23.22). Enzymes achieve their catalysis via the stabilization of the transition state (activated complex) formed by the reactants (substrate) during the reaction.

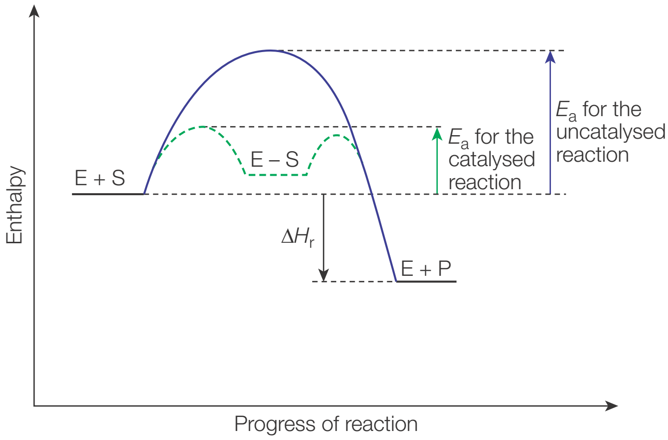


Figure 23.22 The enthalpy profile of an enzyme-catalysed reaction (ΔH_r, E_a, S, E and P represent enthalpy change of reaction, activation, substrate, enzyme and product, respectively)

Table 23.4 Differences between enzymes and inorganic catalysts

Enzymes	Inorganic catalysts
Enzymes are complex globular proteins	Inorganic catalysts are generally ions or simple molecules
Enzymes are synthesized by living cells	Inorganic catalysts are not produced by living cells
Enzymes are usually highly specific in action	Inorganic catalysts are usually less specific in action
Enzymes are sensitive to changes in pH and temperature	Inorganic catalysts are usually less sensitive to changes in pH and temperature
Enzymes only function in aqueous solution	Some inorganic catalysts function in aqueous solution

Enzymes are globular proteins and are able to catalyse in aqueous solution under mild conditions of temperature and pH (unless the enzymes have evolved to function at extremes of temperature or pH). Although very specific compared with inorganic catalysts (see Table 23.4), enzymes vary considerably in their degree of specificity. Some are absolutely specific for a particular substrate, and will not bind and attack even the enantiomer (optical isomer), whereas others will react with a whole class of molecules but at widely differing rates. The function of an enzyme depends on its three-dimensional shape (conformation), in particular the precise shape of the active site. This region of the enzyme's surface recognizes and binds (via non-covalent interactions) the specific substrate of the enzyme.

The chemical basis of enzyme catalysis involves the stabilizing of the transition state of the reaction by helping to orient the substrate(s) in the active site. This brings together functional groups on the enzyme and the substrate so that enzyme functional groups can participate in the chemical catalysis events, which may involve covalent bond formation or acid–base catalysis.

The process of enzyme–substrate recognition and binding is often referred to as the 'lock and key' model (Figure 23.23). The active site of an enzyme is the binding site for the substrate and a catalytic site which completes the enzyme-catalysed reaction.

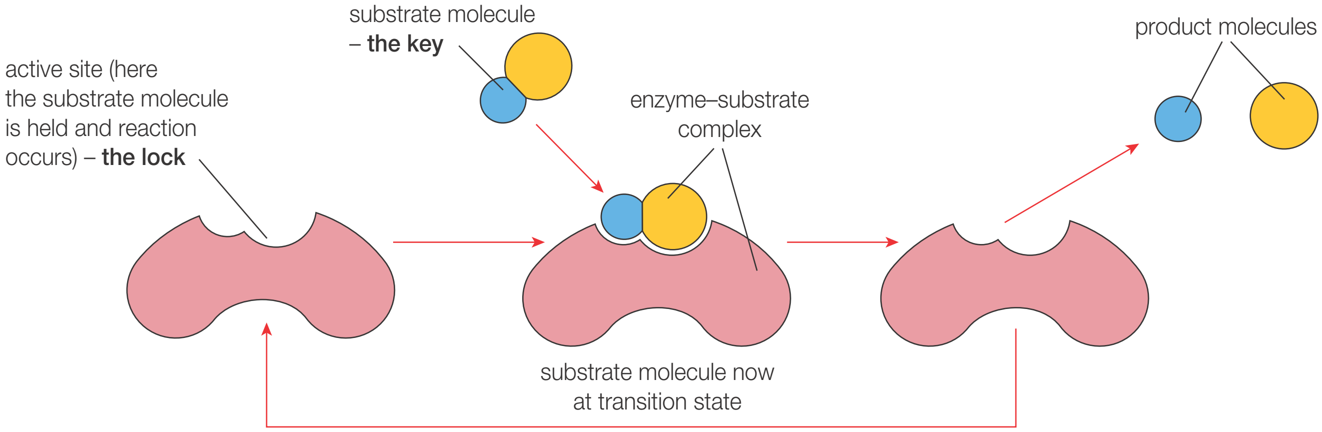


Figure 23.23 The lock and key model of enzyme action

Expert tip

The catalytic rate of an enzyme can be lowered by inhibitor molecules. Many inhibitors exist, including normal body metabolites, foreign drugs and toxins.

Enzyme-catalysed biochemical reactions are sensitive to conditions of temperature and pH. They are usually active within a narrow range and show characteristic temperature and pH optima (Figures 23.24 and 23.25, respectively).

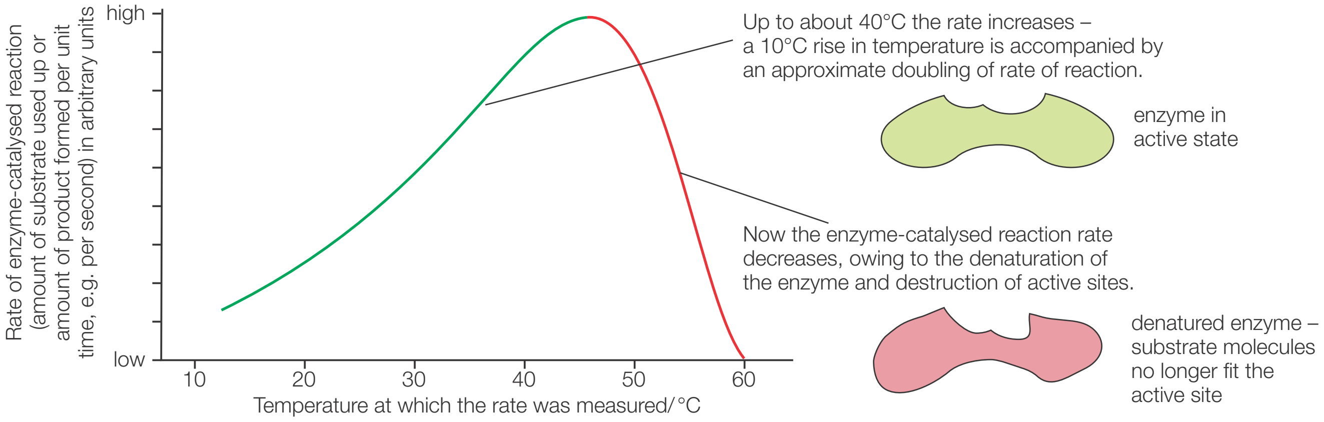


Figure 23.24 The effect of temperature on enzyme shape and activity

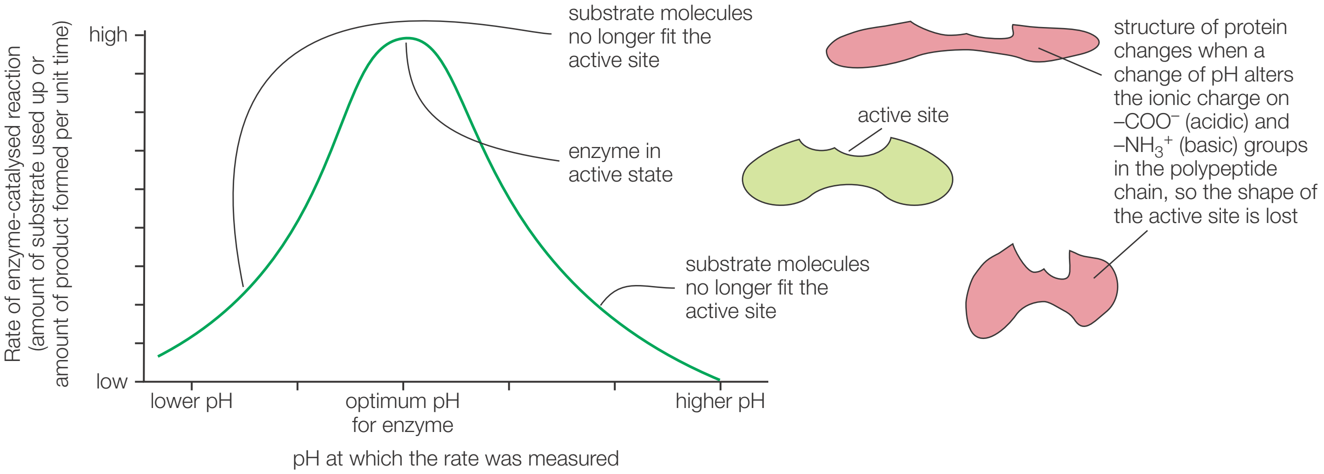


Figure 23.25 The effect of pH on enzyme shape and activity

Temperature affects the rate of enzyme-catalysed reaction by increasing the average kinetic energy of the substrate molecules. This increases the proportion of molecules with sufficient kinetic energy to overcome the activation barrier and hence increases the rate of the reaction.

In addition, the kinetic energy of the component molecules of the enzyme is increased, which leads to an increased rate of denaturation of the enzyme protein due to the disruption of the non-covalent interactions holding the structure together.

Large deviations in pH lead to denaturation of the enzyme due to changes in the ionization of amino acid residues and the disruption of non-covalent interactions, especially hydrogen bonds.

Inhibitors which bind irreversibly to an enzyme often form a covalent bond to an amino acid residue at or near the active site, and permanently inactivate the enzyme. Susceptible amino acid residues include serine and cysteine residues which have reactive –OH and –SH groups, respectively. Heavy metals and their ions react with the side-chain of cysteine residues (Figure 23.26).

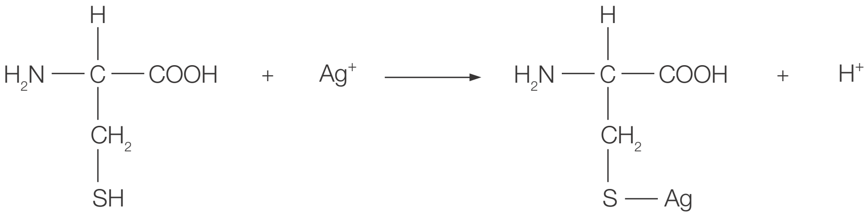


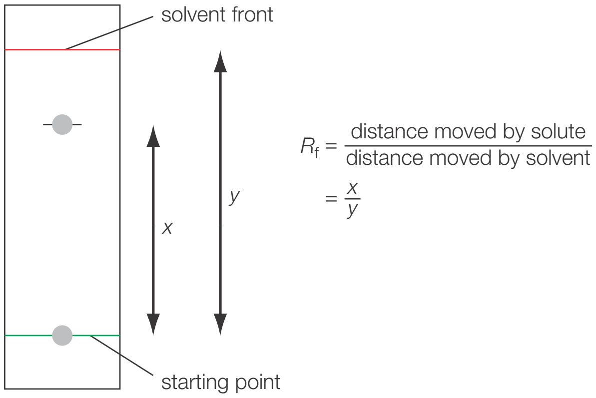
Figure 23.26 The action of silver ions on the –SH functional group of cysteine

Analysis of proteins

The primary structure of a small protein can be determined by paper chromatography or, more efficiently, by gel electrophoresis. Chromatography and electrophoresis both separate and identify substances in complex mixtures. The protein is hydrolysed to amino acids by boiling with concentrated hydrochloric acid in a sealed tube for six hours. The three-dimensional tertiary structure of the protein can be confirmed by X-ray analysis of the crystalline protein.

Paper chromatography

In paper chromatography, the mobile phase (a solvent mixture) moves the amino acids over the stationary phase (hydrated cellulose). Separation occurs by the transfer of amino acids to the stationary phase by portioning between the two liquids. The amino acids are identified by their retention values (R_f) (Figure 23.27) after they have been made visible by reaction with the locating agent ninhydrin.



$$R_f = \frac{\text{distance moved by solute}}{\text{distance moved by solvent}} = \frac{x}{y}$$

Figure 23.27 Calculating the retention factor, R_f, from a paper chromatogram

Common mistake

Remember when measuring distances to calculate R_f values to start from the pencil line (origin) not the bottom of the paper.

Two-dimensional chromatography consists of two successive acts of chromatographic separation, done with different solvents, in directions at 90° to each other. It operates on the principle that amino acids left unseparated by one solvent will be resolved by the second.

Electrophoresis

In gel electrophoresis (Figure 23.28) the mixture of amino acids is supported on a semi-solid gel. The amino acids molecules are charged and move in an applied electric field, where they separate according to their charge and the shape and size of their molecules.

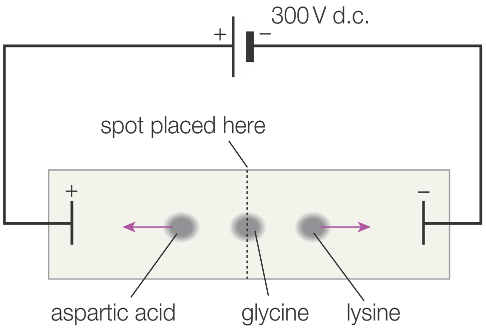


Figure 23.28 Electrophoresis of a mixture of glycine, lysine and aspartic acid

Expert tip

A buffer solution is used as the electrolyte in electrophoresis. For amino acids (and protein fragments), the net charge on the molecule depends on the pH of the medium.

Remember that an amino acid or protein will be positively charged if the pH of the running buffer is below its isoelectric point, and negatively charged if the pH is above its isoelectric point.

QUICK CHECK QUESTIONS

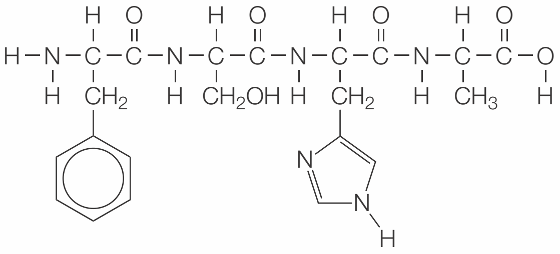
9 Electrophoresis can be used to identify the amino acids present in any given protein. To carry out this analysis the protein must first be hydrolysed.

  a State the reagent and conditions needed to hydrolyse the protein, and identify the bond that is broken during hydrolysis.

  b Explain how the amino acids could be identified using electrophoresis.

10 The isoelectric point (pI value) of the amino acid serine (2-amino-hydroxypropanoic acid) is 5.7. Draw the main structural formula of serine, in the solid state and in an aqueous solution at pH values of 1, 14 and 5.7.

11 Name and give the structures of the amino acids that would be formed by the hydrolysis of the polypeptide below. Use the information on their structures given in Section 33 of the IB Chemistry *data booklet* to help identify them.



12 **a** Sketch the energy profile of an uncatalysed exothermic reaction, showing:

  i the activation energy (E_a)

  ii the enthalpy change of reaction (ΔH_r).

  b Sketch a similar energy profile for the reaction in part **a** when the reaction is enzyme catalysed.

23.3 Lipids

Revised ☐

Essential idea: Lipids are a broad group of biomolecules that are largely non-polar and therefore insoluble in water.

Lipids

Revised ☐

- Fats are more reduced than carbohydrates and so yield more energy when oxidized.
- Triglycerides are produced by condensation of glycerol with three fatty acids and contain ester links. Fatty acids can be saturated, monounsaturated or polyunsaturated.
- Phospholipids are derivatives of triglycerides.
- Hydrolysis of triglycerides and phospholipids can occur using enzymes or in alkaline or acidic conditions.

- Steroids have a characteristic fused ring structure, known as a steroidal backbone.
- Lipids act as structural components of cell membranes, in energy storage, thermal and electrical insulation, as transporters of lipid-soluble vitamins and as hormones.

Fats and oils

Revised ☐

Fats and oils and steroids are collectively termed lipids. Lipids are a structurally diverse group of biological compounds that are grouped together due to their poor solubility in water and excellent solubility in organic solvents. Lipids can be extracted from cells, using non-polar solvents, such as ethers and hydrocarbons.

Lipids act as structural components of cell membranes (as phospholipids), in energy storage (as adipose tissue), thermal and electrical insulation (around nerves) and as transporters of lipid-soluble vitamins and as hormones (vitamin D).

Lipids are a concentrated chemical energy source of carbon and hydrogen. They are more reduced than carbohydrates (owing to the presence of fewer oxygen atoms). Lipids release more energy per gram during respiration (oxidation) than do carbohydrates. Animal fats and vegetable oils contain a mixture of lipids.

Fats and oils are triglyceryl esters (Figure 23.29), esters of glycerol (propane-1,2,3-triol) with fatty acids, aliphatic acids with 16–22 carbon atoms. They are formed by enzyme-controlled reactions between three fatty acid molecules and glycerol (propane-1,2,3-triol) (Figure 23.30). The resulting triglyceride is said to contain three fatty acid residues.

Expert tip

Fats are semi-solid at room temperature; oils are liquids.

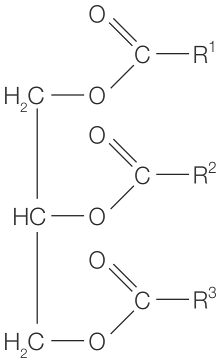


Figure 23.29 The generalized formula of a triglyceride, where R^1, R^2 and R^3 represent fatty acid chains, which may be the same or different

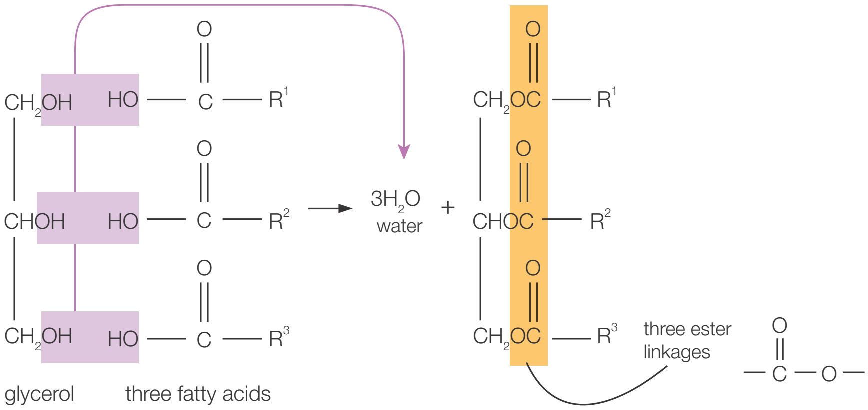


Figure 23.30 Formation of a triglyceride from fatty acids and a glycerol molecule by condensation reactions

The chemical difference between fats and oils is that oils contain unsaturated fatty acid chains and fats contain saturated fatty acid chains (Figure 23.31). Many oil molecules contain one or several carbon–carbon double bonds and are described as polyunsaturated.

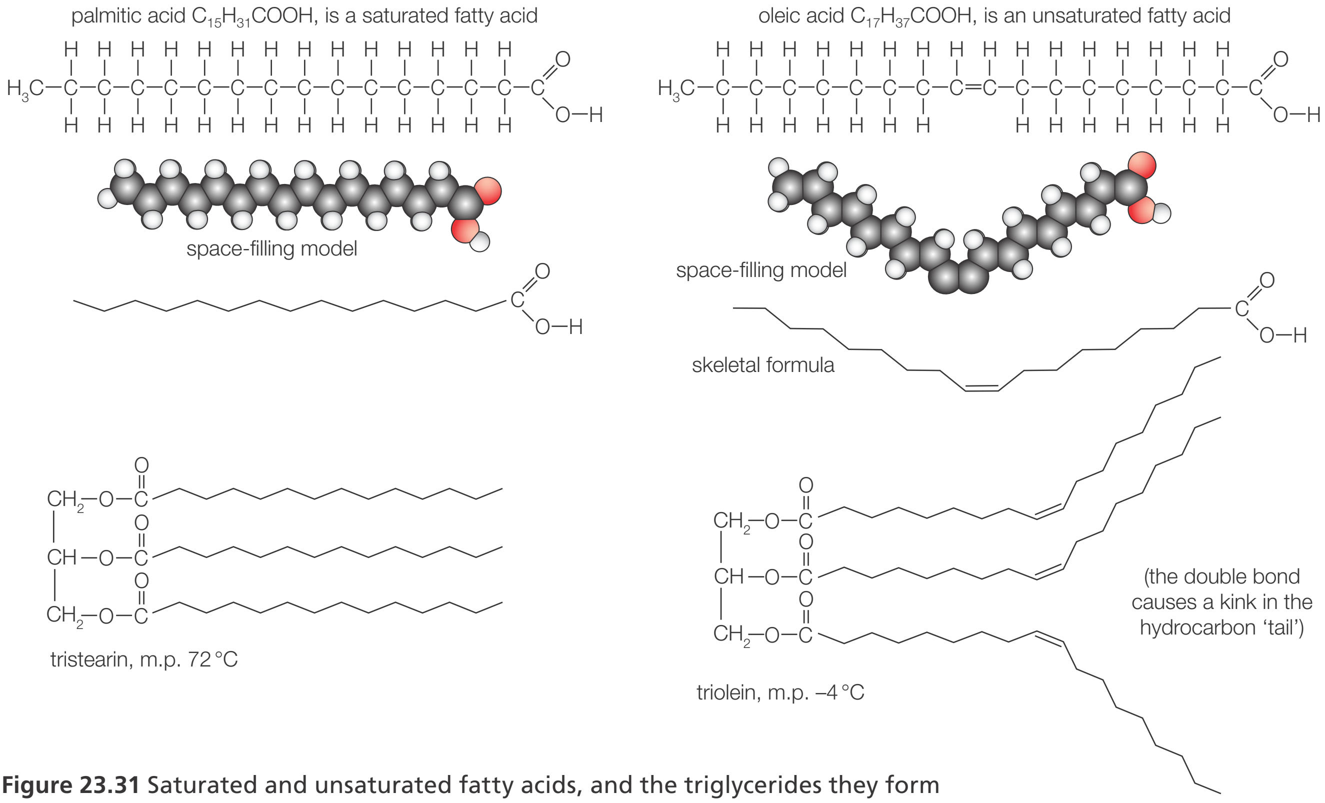


Figure 23.31 Saturated and unsaturated fatty acids, and the triglycerides they form

The melting points and other properties of lipids depend on the identity of the fatty acid groups. Fats containing unsaturated fatty acids melt at lower temperatures than those with saturated fatty acids (Table 23.5).

Table 23.5 The melting points of selected saturated and unsaturated fatty acids

Name of fatty acid	Number of carbon atoms	Number of C=C double bonds	Melting point/°C
Saturated fatty acids			
Lauric acid $CH_3(CH_2)_{10}COOH$	12	0	44.2
Myristic acid $CH_3(CH_2)_{12}COOH$	14	0	54.1
Palmitic acid $CH_3(CH_2)_{14}COOH$	16	0	62.7
Stearic acid $CH_3(CH_2)_{16}COOH$	18	0	69.6
Arachidic acid $CH_3(CH_2)_{18}COOH$	20	0	75.5
Unsaturated fatty acids			
Palmitoleic acid $CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	16	1	–0.1
Oleic acid $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	18	1	10.5
Linoleic acid $CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	18	2	–5.0
Linolenic acid $CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$	18	3	–11.9
Arachidonic acid $CH_3(CH_2)_4(CH=CHCH_2)_4(CH_2)_2COOH$	20	4	–49.0

This trend is a steric effect and occurs because the introduction of a carbon–carbon double bond prevents the triglyceride molecules from approaching each other closely and hence interacting via London dispersion forces. Long-chain saturated fatty acids have a regular tetrahedral arrangement of carbon atoms and so can pack closely together. The dispersion forces between chains are strong because of their extended surface area.

In unsaturated fatty acids the bond angle in the chains changes around the double bond and the structure becomes rigid at that point. This introduces a kink in the chain (Figure 23.31) and they are unable to pack so closely together.

Expert tip

Where two lipids have similar degrees of unsaturation, the one with the higher molecular mass will tend to have the higher melting point.

Phospholipids

Phospholipids are formed by the condensation of two fatty acid molecules and a phosphate group (or a derivative of a phosphate group). The simplest type of phosphoglyceride is a phosphoric acid monoester, called a phosphatidic acid. Phosphoglycerides that contain choline are called lecithins.

Phospholipid molecules are amphipathic, having hydrophobic (non-polar) hydrocarbon chains and a hydrophilic (polar) phosphate group (Figure 23.32). Phospholipid bilayers form as molecules line up with the phospholipids hydrophilic 'heads' on the outside and hydrophobic 'tails' on the inside of the double layer of the cell membrane.

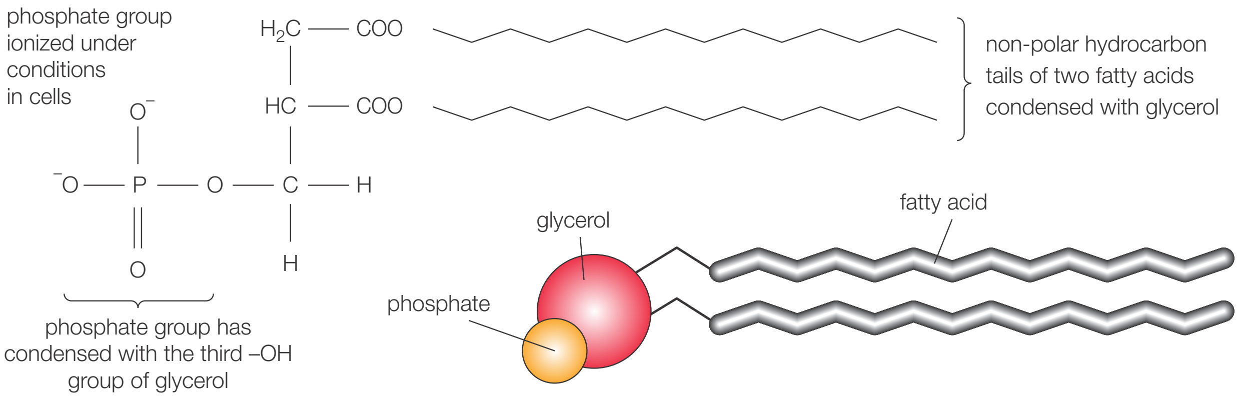


Figure 23.32 Generalized structure of a simple phospholipid

Reactions of lipids

Hydrolysis of lipids occurs slowly to produce fatty acids and other products with a rancid smell. This is termed hydrolytic rancidity.

The alkaline hydrolysis of fats and oils by sodium hydroxide produces soaps: the sodium salt of fatty acids. The process is called saponification (Figure 23.33).

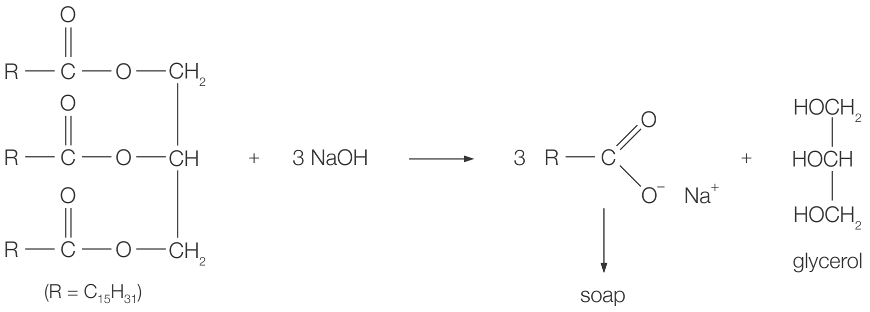


Figure 23.33 Production of soap

The saponification value of a lipid is a measure of the amount of fatty acids that is formed when one gram of lipid is completely hydrolysed by a strong base. This technique can be used to find the fatty acid composition of food.

Unsaturated oils can be hydrogenated, for example, in the production of margarine. Oils contain *cis*-unsaturated fatty acids which are 'healthier' than saturated fats as they increase levels of HDL cholesterol. However, during the hydrogenation process partial hydrogenation may occur, leading to the production of *trans*-unsaturated fats (Figure 23.34). These increase the formation of LDL cholesterol which raises the risk of heart disease.

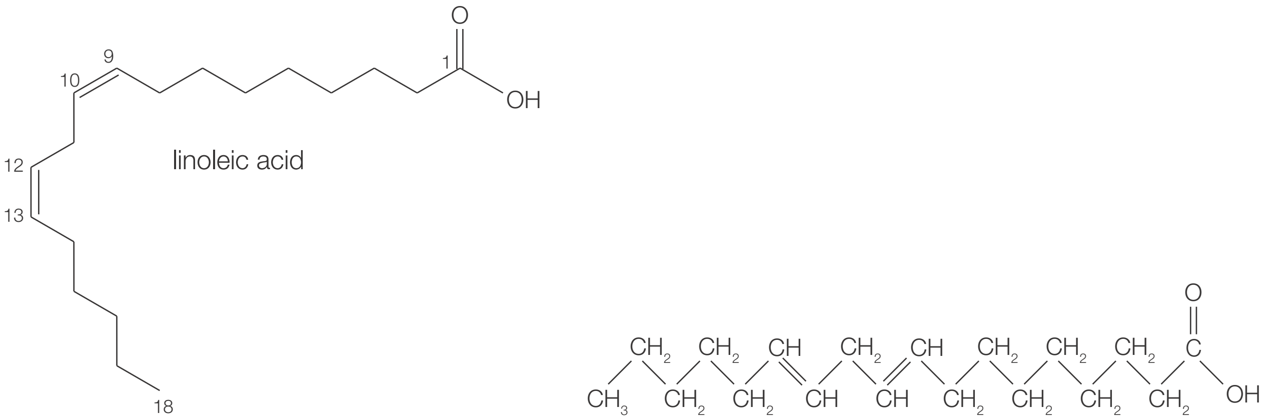


Figure 23.34 a The structures of the *cis,cis* form of linoleic acid and **b** the straightening of the *trans,trans* form of linoleic acid

Fats and oils can undergo addition reactions with iodine (in the presence of a non-polar solvent). The iodine value is a measure of the degree of unsaturation.

The iodine number is the mass of iodine in grams that reacts with 100 g of an unsaturated lipid. A moles calculation can be used to deduce the number of carbon–carbon double bonds since each mole reacts with 1 mole of iodine molecules (Figure 23.35).

Transesterification of triglycerides can be achieved via either acid or base catalysis to produce biodiesel (Option C Energy).

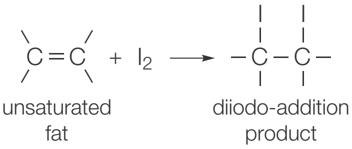


Figure 23.35 Addition reaction between carbon–carbon double bond (in fatty acid) and iodine molecule

Worked example

Oleic acid, [$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$], is present in many animal and vegetable fats and oils. Calculate the iodine number.

It is monounsaturated and hence each carbon–carbon double bond reacts with one molecule of iodine.

$$\text{molar mass of oleic acid} = (18 \times 12.01) + (34 \times 1.01) + (16.00 \times 2)$$

$$= 282.52\,\text{g mol}^{-1}$$

$$\text{molar mass of iodine} = (126.90 \times 2)$$

$$= 253.80\,\text{g mol}^{-1}$$

282.52 g of lipid reacts with 253.80 g of iodine; by ratios, 100 g of fat reacts with $\frac{(253.80 \times 100)}{282.52}$ = 90 g of iodine, and hence the iodine number is 90.

Expert tip

Similar addition reactions occur with the more reactive iodine monochloride, ICl, which was referred to in Topic 20 Organic chemistry.

Rancidity

Lipids become rancid as a consequence of hydrolytic or oxidative processes.

- *Hydrolytic rancidity* occurs where ester links are broken by water, producing glycerol and unpleasant smelling/tasting fatty acids. This condition is favoured by high water content, acidic or alkaline conditions, high temperature and the presence of lipase enzymes.
- *Oxidative rancidity* occurs where fatty acid chains are broken down when oxygen reacts with the C=C bonds of unsaturated lipids. Unpleasant smelling and tasting ketones, alcohols and aldehydes are produced. This condition is favoured by a high proportion of unsaturated fatty acids, high temperature, a high oxygen availability, high light intensity and the presence of metals such as copper and nickel.

Expert tip

You will need to know the conditions that favour rancidification.

QUICK CHECK QUESTIONS

13 State **three** functions of lipids (fats and oils) in the human body.

14 Glycerol can react with three molecules of stearic acid, $C_{17}H_{35}COOH$, to form a triglyceride.

- **a** Deduce the number of carbon atoms in one molecule of the triglyceride formed.
- **b** An oil sample containing 0.0100 mol of oil was found to react with 7.61 g of iodine, I_2, in a test to determine the degree of unsaturation of the oil.

  Determine the number of double bonds present in each molecule of the oil.

15 Fats and oils are made from a molecule of propane-1,2,3-triol bonded to three molecules of fatty (alkanoic) acids.

- **a** Give the structural formula of propane-1,2,3-triol.
- **b** Give the name and formula of the functional group present in all alkanoic acids and draw the structural formula of the saturated fatty acid containing eight carbon atoms per molecule.
- **c** Explain the difference between saturated and unsaturated fats in terms of their molecular structures.
- **d** Explain briefly how the degree of unsaturation of lipids can be determined experimentally.

16 A sample of vegetable oil (2.50 g) reacted completely with 19.00 cm^3 of a 0.50 mol dm^{-3} solution of iodine.

- **a** Calculate the iodine number of the oil.
- **b** Estimate the average number of carbon–carbon double bonds per molecule of this oil if its average molecular mass is 865 g mol^{-1}.
- **c** Explain why is the figure in **b** necessarily an average figure for the number of double bonds per molecule.

17 **a** Predict and explain which fatty acid in each group has the highest melting point:

  - **i** butanoic acid, palmitic acid and stearic acid
  - **ii** linoleic acid, oleic acid and linolenic acid.

- **b** Chocolate is a food made from cocoa, sugars, unsaturated vegetable fats, milk whey and emulsifiers. Chocolate bars sold in hot climates are made with a different blend of vegetable fats from those sold in colder climates.
  - **i** Explain why fats with different structures, and hence physical properties, are used for making chocolate in different climates.
  - **ii** Suggest how the fat molecules used in a hot climate differ chemically from those used in a cold climate.

18 The average figures for the percentage fatty acid composition of some common fats and oils are presented in the table below.

Source of fat/oil	Saturated fatty acids/%	Monounsaturated fatty acid (oleic acid)/%	Unsaturated fatty acids/%	
			Linoleic acid	**Linolenic acid**
Beef fat	59	38	3	–
Corn oil	25	26	47	2
Olive oil	15	78	7	–
Soya bean oil	14	28	50	8
Coconut oil	90	8	2	–

- **a** Deduce which of these fats/oils has the highest iodine number. Give a reason for your answer.
- **b** The 'P/S index' is sometimes used to compare the relative health benefits of different lipids in the diet. It is the ratio of polyunsaturated fat to saturated fat present in the fat or oil. Calculate the P/S index of soya bean oil, olive oil and beef fat.
- **c** Which of the fats or oils listed above is most likely to turn rancid when exposed to the air? Explain your choice.

Steroids

Cholesterol (Figure 23.36) is present in animal cell membranes (where it controls fluidity) and has the characteristic fused four ring structure possessed by all steroids (Figure 23.37). This is a tetracyclic system, involving three six-membered rings and one five-membered ring that form a rigid system.

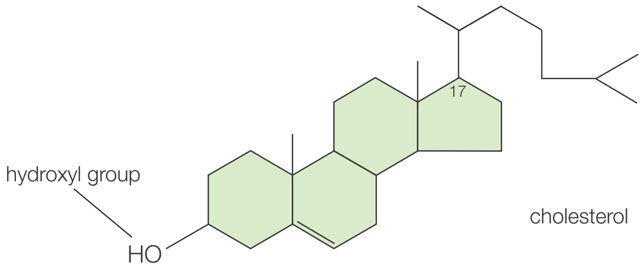


Figure 23.36 The skeletal structure of cholesterol. This is the most abundant steroid in humans

The presence of cholesterol in mammalian cell membranes has the effect of disturbing the close-packing of the phospholipids, influencing the flexibility and fluidity of the membrane, and controlling its permeability to some solutes. Cholesterol molecules have a hydroxyl (–OH) group and a hydrocarbon chain either side of the carbon ring structures. Each cholesterol's hydroxyl group aligns with the phosphate heads of the phospholipids, and the hydrocarbon chain with the fatty acid chain on the nearest adjacent phospholipid (Figure 23.38). This helps maintain a stable structure on the outer surface of the membrane, making it less permeable to very small water-soluble molecules that could otherwise easily pass through.

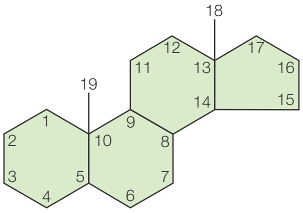


Figure 23.37 The steroid 'nucleus' of four fused rings

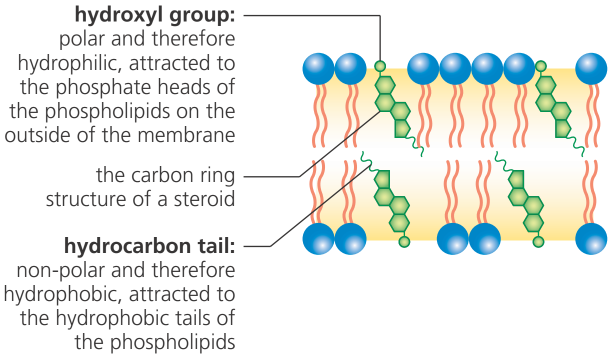


Figure 23.38 The interaction of cholesterol with the phospholipids of animal cell membranes

Cholesterol is transported around the body in the blood plasma by lipoproteins. Low-density lipoproteins (Figure 23.39) (LDL) transport cholesterol through the arteries, where it can line the walls of the arteries as plaque, leading to heart diseases. Smaller lipoproteins, known as high-density lipoproteins (HDL), can remove the plaque (mainly cholesterol) from the arteries and transport it back to the liver to be metabolized.

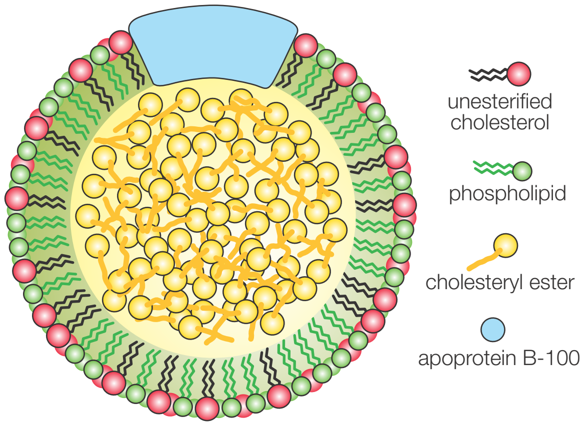


Figure 23.39 Structure of LDL

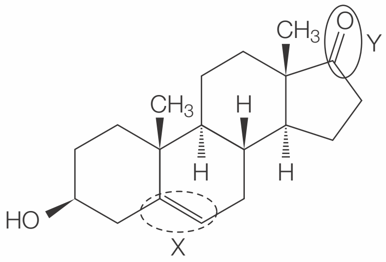
Human sex hormones are steroids that regulate tissue growth and reproductive processes.

Expert tip

You need to be able to describe the use and abuse of steroids.

QUICK CHECK QUESTION

19 The prohibited list of the World Anti-Doping Agency (WADA), which manages drug testing for the Olympics and other sports, includes the steroid hormone dehydroepiandrosterone (DHEA). The structure of DHEA is given below:



a State the name of the functional groups circled in the DHEA molecule shown above.

b Identify the characteristic region of this structure that means that this molecule is classified as a steroid.

c The production of banned synthetic steroids has ethical implications. Suggest a reason why steroid research might be supported.

23.4 Carbohydrates

Revised ☐

Essential idea: Carbohydrates are oxygen-rich biomolecules, which play a central role in metabolic reactions of energy transfer.

Carbohydrates

Revised ☐

- Carbohydrates have the general formula $C_x(H_2O)_y$.
- Haworth projections represent the cyclic structures of monosaccharides.
- Monosaccharides contain either an aldehyde group (aldose) or a ketone group (ketose) and several –OH groups.
- Straight chain forms of sugars cyclize in solution to form ring structures containing an ether linkage.
- Glycosidic bonds form between monosaccharides forming disaccharides and polysaccharides.
- Carbohydrates are used as energy sources and energy reserves.

Monosaccharides

Carbohydrates are important in nutrition and have the general formula $C_x(H_2O)_y$. The simplest carbohydrates are monosaccharide sugars: trioses (C3 sugars), for example, ribose, $C_5H_{10}O_5$, pentoses (C5 sugars), and hexoses (C6 sugars), for example, glucose and fructose, $C_6H_{12}O_6$ (see Table 23.6). Monosaccharides are used to release energy during respiration or act as precursors for other biomolecules.

Table 23.6 Examples of different monosaccharides

Value of n in $C_nH_{2n}O_n$	Example	Formula	Type of sugar
3	Glyceraldehyde (2,3-dihydroxypropanal)	$C_3H_6O_3$	Triose
4	Erythrose	$C_4H_8O_4$	Tetrose
5	Ribose	$C_5H_{10}O_5$	Pentose
6	Glucose	$C_6H_{12}O_6$	Hexose

Expert tip

Deoxysugars contain less oxygen; there is one less hydroxyl group attached to the chain. For example, 2-deoxyribose ($C_5H_{10}O_4$), which is present in DNA, contains one less oxygen atom than ribose ($C_5H_{10}O_5$), the sugar present in RNA.

Monosaccharides are classified as aldoses (containing a terminal aldehyde group), for example, glucose (Figure 23.40), or as ketoses (containing a ketone group) (Figure 23.41). Monosaccharides contain chiral carbon atoms and two or more hydroxyl groups.

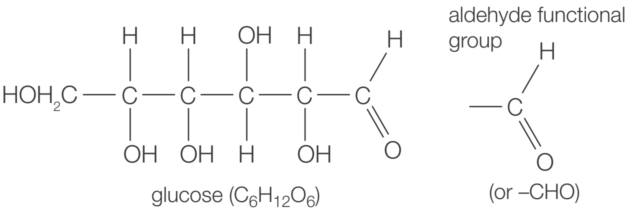


Figure 23.40 The structure of D-glucose, an aldose

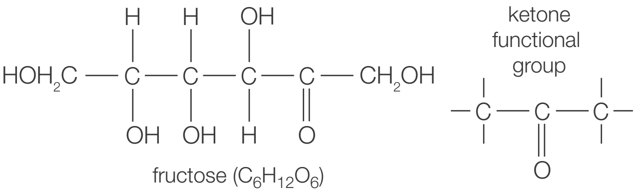


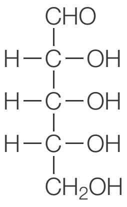
Figure 23.41 The structure of D-fructose, a ketose

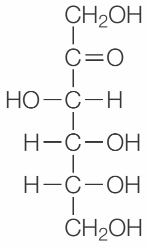
Expert tip

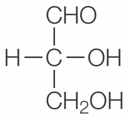
Monosaccharides are known as simple sugars because they cannot be hydrolysed. You'll note that in the monosaccharides the values of *x* and *y* in the general molecular formula $C_x(H_2O)_y$ are the same.

QUICK CHECK QUESTIONS

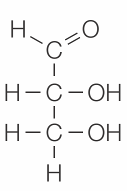
20 Which of the following is (or are) a ketone, an aldehyde, a triose, a pentose and a hexose?

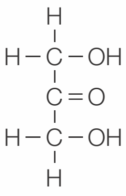
A


B


C


21 The structures of two molecules, **P** and **Q**, having the same formula, $C_3H_6O_3$, are shown below.

P


Q


a Explain why both these molecules are classed as carbohydrates.

b Distinguish between these molecules on the basis of the carbonyl functional group present in each molecule.

22 Glucose, $C_6H_{12}O_6$, is a monosaccharide that our bodies can use as a source of energy.

a Give the equation for the cellular respiration of glucose.

b Calculate the energy, in kJ, produced from 15.0 g of glucose given that its enthalpy of combustion, is –2803 kJ mol^{-1}.

Disaccharides

Monosaccharides condense (in the presence of enzymes) by the formation of glycosidic bonds (ether linkages) to form dimers known as disaccharides, for example, sucrose (Figure 23.42), lactose and maltose (Figure 23.43) ($C_{12}H_{22}O_{11}$). Disaccharides condense (in the presence of enzymes) to form polysaccharides, for example, amylose and amylopectin, (starch) glycogen and cellulose.

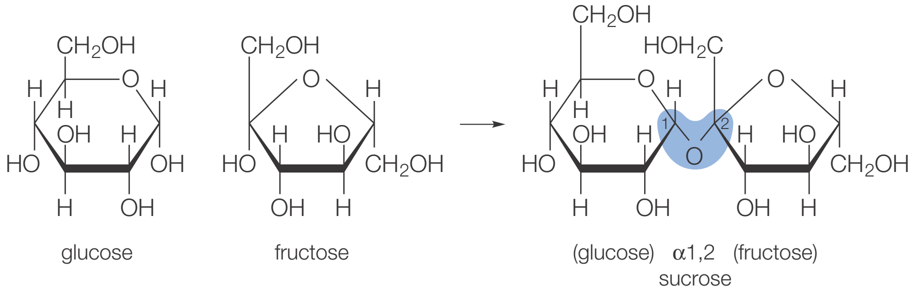


Figure 23.42 The formation of sucrose from glucose and fructose

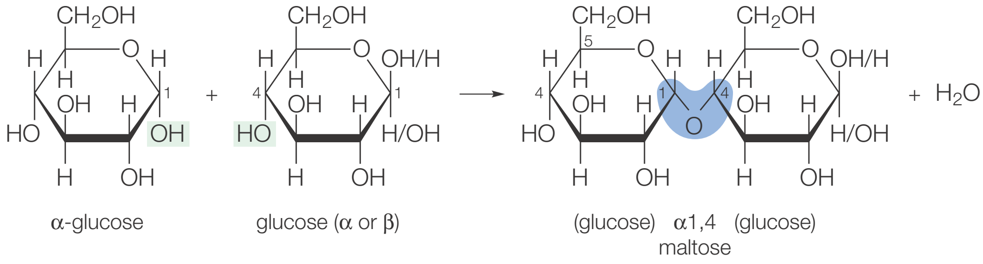


Figure 23.43 The formation of maltose from glucose

Monosaccharides and disaccharides are very soluble because their hydroxyl groups form hydrogen bonds with water molecules. Polysaccharides, such as starch and glycogen, have limited solubility and therefore make better food storage materials.

Polysaccharides

Starch is the food storage material of plants. It is a polysaccharide, which occurs in two forms: amylose and amylopectin. Both are condensation polymers of glucose and poorly soluble in water.

Amylose is an unbranched polymer of glucose molecules linked by α-1,4-glycosidic bonds. Amylopectin is a branched polymer of glucose, but has many branches arising from α-1,4-glycosidic bonds. Starch contains variable amounts of amylose and amylopectin (Figure 23.44).

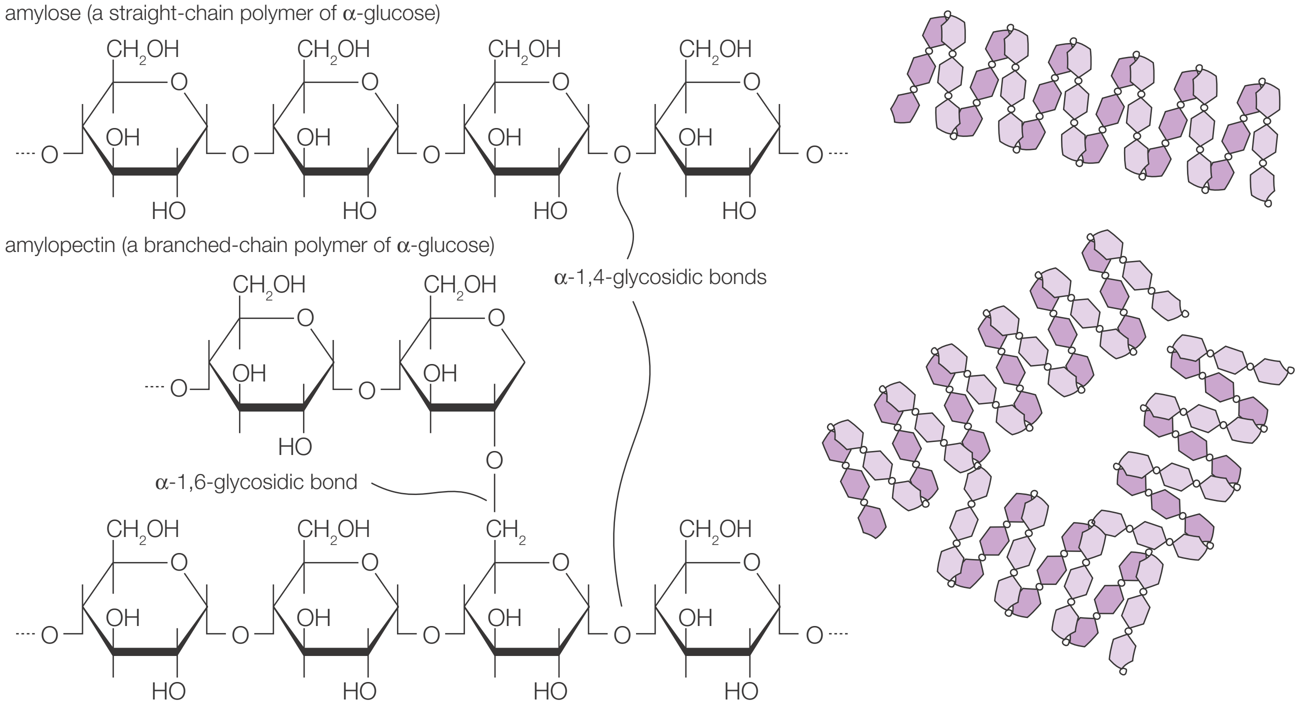


Figure 23.44 Structures of amylose and amylopectin

Glycogen, the food storage material in an animal, is a polysaccharide which is similar in structure to amylopectin (a component of starch), but more branches occur. Glycogen is stored in the liver and muscles.

Cellulose (Figure 23.45) is the structural component of plant cell walls. It is a polysaccharide consisting of glucose units joined by 1, β-4-glycosidic linkages. Few animals have the cellulose enzyme that can hydrolyse these linkages, so allowing them to digest cellulose.

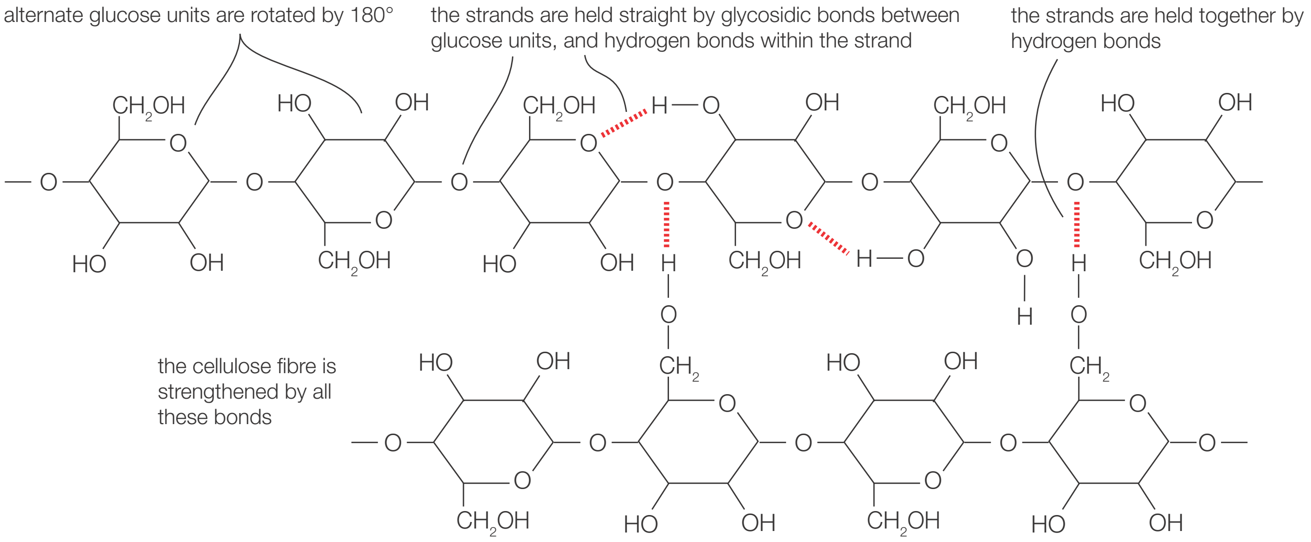


Figure 23.45 Structure of cellulose

Cellulose molecules are linear because of the orientation of the glucose residues. The molecules are held together by hydrogen bonds between hydroxyl groups and are assembled into cellulose fibres which give tensile strength to plant cell walls.

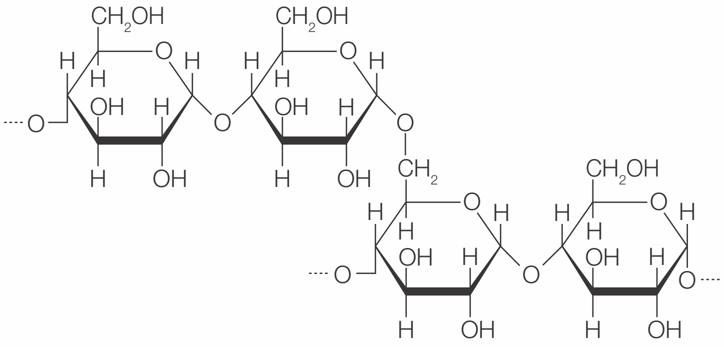
Polysaccharides can be hydrolysed by heating with dilute hydrochloric acid. Polysaccharides can also be hydrolysed by specific enzymes, which convert polysaccharides to monosaccharides when required by the cell. Hence the chemical energy stored in these molecules is available to the organism. Table 23.7 presents the major features and roles of the different polysaccharides.

Table 23.7 A summary of the major features of polysaccharides

Polysaccharide		Monomer	Type of glycosidic link	Shape of macromolecule	Function
Starch	Amylose	α-Glucose	α-1,4	Unbranched chains wound into a helix	Carbohydrate storage in plants
	Amylopectin	α-Glucose	α-1,4 and also α-1,6 at branches	Tightly packed branched chains	Carbohydrate storage in plants
Glycogen		α-Glucose	α-1,4 and also α-1,6 at branches	Very branched, compact molecules	Carbohydrate storage in animals
Cellulose		β-Glucose	β-1,4	Linear	Structural component in plant cell walls

QUICK CHECK QUESTIONS

23 The diagram below shows a part of the structure of a carbohydrate storage polymer which can be broken down by enzyme action.

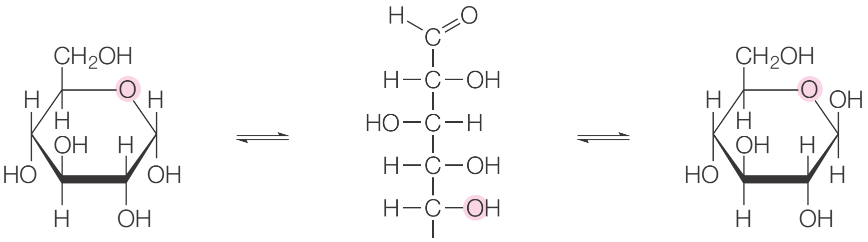


- **a** What types of glycosidic linkages are present in this structure?
- **b** Name this type of breakdown reaction.
- **c** Draw the structure of the monomer unit produced.
- **d** Suggest which carbohydrate polymer this drawing represents.
- **e** Suggest why the polymer functions as an energy store but the monomer does not.

24 Describe the difference in structure between starch and cellulose. How does this difference affect human nutrition?

The structure of glucose

Glucose is one of 16 stereoisomers, 8 pairs of enantiomers, which include fructose and galactose. The glucose molecule exists in solution as an equilibrium between a straight chain form (with a free aldehyde group) and the more favourable six-membered pyranose ring, which exists in α and β forms and can be represented by Haworth projections (Figure 23.46).



-glucose: 36% at equilibrium

open-chain form: very small amounts at equilibrium

-glucose: 64% at equilibrium

Figure 23.46 The equilibrium composition of an aqueous solution of glucose

Expert tip

A pyranose is a six-membered cyclic (ring) form of a monosaccharide. They can exist in chair and boat conformations (see Topic 20 Organic chemistry). The rings can open and re-close, allowing rotation to occur about the carbon with the carbonyl group allowing the formation of alpha and beta isomers, known as anomers.

NATURE OF SCIENCE

The stereochemistry of the cyclic (ring) forms of sugars is often represented by their Haworth projections. These are standardized ways of showing the position of hydroxyl groups in space. Haworth projections show the stereochemistry of sugars. The plane of the ring is attached is tilted to the plane of the paper. The attached groups are above or below the plane of the ring. The ring oxygen is always placed in the back right-hand corner of the ring, with the anomeric carbon (C-1) on the right-hand side and the primary alcohol group drawn up from the back left-hand corner (C-5).

Tests for carbohydrates

Aldoses, such as glucose, are reducing sugars in solution because they contain a terminal carbonyl (aldehyde) group and are easily oxidized under relatively mild conditions. Benedict's solution and Fehling's solution (both of which contain copper(II) ions) are used to test for reducing sugars with an aldehyde, –CHO, group. A red-brown precipitate of copper(I) oxide is formed. The presence of starch (even at low concentrations) can be detected using iodine: an intense blue-black complex is formed.

23.5 Vitamins

Revised ☐

Essential idea: Vitamins are organic micronutrients with diverse functions that must be obtained from the diet.

Vitamins

Revised ☐

- **Vitamins** are organic micronutrients which (mostly) cannot be synthesized by the body but must be obtained from suitable food sources.
- The solubility (water or fat) of a vitamin can be predicted from its structure.
- Most vitamins are sensitive to heat.
- Vitamin deficiencies in the diet cause particular diseases and affect millions of people worldwide.

Key definition

Vitamins – organic micronutrients that cannot (except for vitamin D) be synthesized in the body and must be obtained from appropriate food sources.

Vitamins and micronutrients

Revised ☐

Micronutrients are substances required in tiny amounts by the body unlike protein, carbohydrates and lipids, which are termed macronutrients. They mainly function as co-factors for enzyme activity and include not only vitamins but trace minerals such as iron (Fe), iodine (I_2) and zinc (Zn).

NATURE OF SCIENCE

The term vitamin was derived from '*vitamine*', a combination of *vital* and *amine*, because it was originally suggested that the organic micronutrient food factors which prevented beri beri and perhaps other similar dietary deficiency diseases, might be amines. This proved incorrect for the micronutrient class, and the word was shortened.

Vitamins can be classified as either fat soluble or water soluble

Non-polar groups such as hydrocarbon rings (cycloalkenyl groups, for instance) and long alkyl chains decrease water solubility but increase fat solubility (Table 23.8). Fat-soluble vitamins include vitamins A, D, E and K. They can accumulate in the fatty tissues of the body; sometimes an excess of a fat-soluble vitamin can be as detrimental to good health as a deficiency.

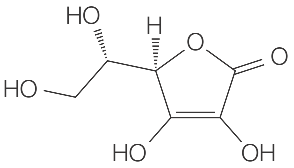
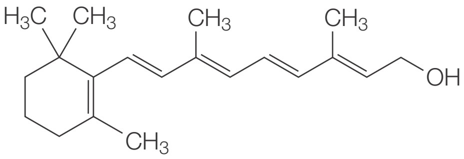
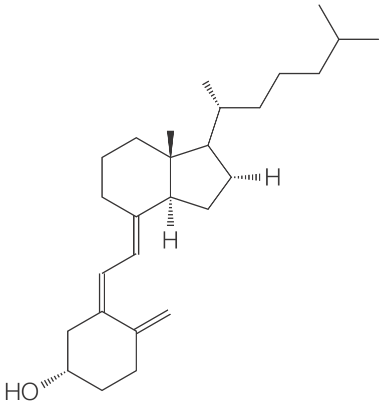
The presence of functional groups capable of taking part in hydrogen-bonding promotes water solubility; these include hydroxyl, carboxyl, amine and amide groups. Vitamin B group members (of which there are eight) and vitamin C are water-soluble molecules. As a result of their solubility, these vitamins are excreted readily in the urine, they do not accumulate in the body and so require regular daily intake from the diet.

Expert tip

You need to be able to identify the key functional groups present in each vitamin molecule and explain how the structures affect water and/or fat solubility.

- Vitamins containing many hydroxyl (–OH) groups and/or several very electronegative atoms (such as nitrogen or oxygen) are generally water-soluble.
- Those that consist almost entirely of carbon and hydrogen are fat-soluble.

Table 23.8 The solubility and function of certain vitamins in relation to functional groups present

	Vitamin C	Vitamin A	Vitamin D
Skeletal structural formula			
Functional groups	alkenyl hydroxyl ester	alkenyl cycloalkenyl alkanyl hydroxyl	alkenyl cycloalkenyl alkanyl cycloalkanyl hydroxyl
Solubility	Contains four hydroxyl groups, interaction with water through hydrogen bonding; highly soluble in water	Predominantly hydrophobic hydrocarbon chains; hydroxyl group has minimal effect; fat soluble, virtually insoluble in water	
Function	Acts as a co-factor in some enzyme reactions; important in tissue regeneration and wound healing; can act as an antioxidant	Involved in the visual cycle of the eye; particularly important for night vision (low light intensity)	Stimulates the absorption of calcium from the gut; important in whole body calcium homeostasis and the health of bones and teeth

Sensitivity to heat

Some vitamins, particularly those that are water soluble, vitamin C and thiamin (vitamin B1), are highly sensitive to heat; they decompose or are chemically altered at temperatures involved in food processing and cooking, causing them to lose their biological effect. Note also that water-soluble vitamins may leach into cooking water and be lost.

The hydrocarbon backbones of the fat-soluble vitamins A and D are relatively stable to heat and do not decompose significantly when food is steamed or boiled. Over-cooked or fried food can lose more than 50 per cent of its fat-soluble vitamin content and virtually all its vitamin C.

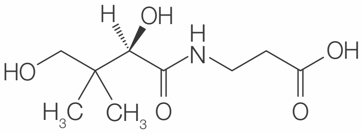
Vitamins A and C, containing carbon–carbon double bonds and –OH groups, are more sensitive to light and air than vitamin D as they are susceptible to free radical and redox reactions.

QUICK CHECK QUESTIONS

25 a Draw out these vitamin structures, **X** and **Y**, and identify the following functional groups in each by circling the appropriate grouping.

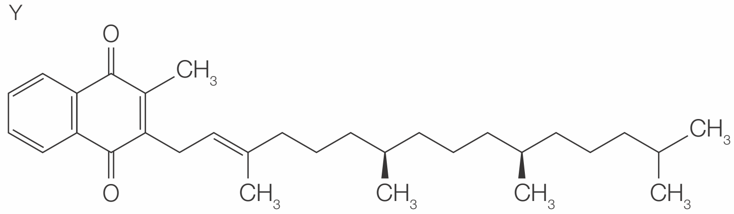
i Identify **A** an ester group, **B** an amide group and **C** a hydroxyl group.

X



➜

ii Identify **A** a ketone group, **B** a phenyl group and **C** an alkenyl group.



b State whether vitamin molecules X and Y are fat-soluble or water-soluble.

26 State two reasons why the vitamin C content of vegetables and fruits decreases when they are left in the open and then boiled in water.

Vitamin deficiencies

An inadequate intake of vitamins is termed *vitamin deficiency*. Severe vitamin deficiencies may lead to diseases or conditions that, if left untreated, can cause significant harm or, in the most severe cases, death, e.g. beri beri caused by vitamin B1 deficiency. The World Health Organization (WHO) has identified vitamin A as the most important vitamin deficiency in global health terms.

The causes of vitamin deficiency vary from country to country. Typical reasons include:

- harsh agricultural conditions
- famine
- poverty
- lack of prolonged periods sunlight for part of year (vitamin D only)
- poor access to or supply of vitamin supplements.

Scurvy, which involves a deficiency of vitamin C, is one of the accompanying diseases of malnutrition and thus is still widespread in areas of the world depending on external food aid. Though rare, there are also documented cases of scurvy due to poor dietary choices by people living in industrialized nations.

Programmes involving the biofortification of diet using crops rich in pro-vitamin A have shown the complexity of the dietary situation where people are under-nourished. Vitamin A is fat soluble, so if the level of body fat is low then the vitamin is not absorbed. An adequate fat intake is essential for the β-carotene from golden rice – a variety of rice rich in provitamin A – to be absorbed.

There are several ways to combat these causes.

- **Addition of vitamins to food-stuffs:** Fortification of foods with vitamin A has proved a successful strategy for combating this deficiency. Programmes also exist to encourage farmers to grow varieties of foods richer in β-carotene (provitamin A; which can be converted into vitamin A in the body) – this is called *biofortification*. For instance, the introduction of orange-fleshed sweet potato into Uganda to replace the indigenous white-fleshed variety has met with some success in reducing vitamin A deficiency. The provision of golden rice should also help with reducing vitamin A deficiency.

  Many foods, such as breakfast cereals, are fortified with niacin and thiamin (vitamin B), and deficiency is rare in developed countries.

  Mandatory vitamin D fortification is increasing; fortification is usually applied to milk and margarine, as the vitamin is fat soluble. Fortification of dairy products with vitamin D means that deficiency is now rare in some industrialized countries; though not all European countries do this and vitamin D tablets may need to be prescribed to some individuals.
- **Genetic modification of crops:** A more controversial form of biofortification involves genetic modification (GM) of foodstuffs to make them richer in a

Expert tip

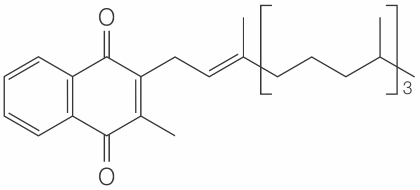
Vitamin deficiencies: note that the guidance in the syllabus explicitly says that you will not be expected to know names of particular deficiency diseases. However, the discussion of such deficiencies does raise certain key issues relating to health and the interplay of general and specific dietary well-being and overall lifestyle.

particular vitamin. Genetic modification has been used to produce golden rice, fortified with vitamin A. It is hoped that the use of golden rice will make a significant difference to vitamin A deficiency in countries such as India, Bangladesh and Vietnam.

- **Education:** Debate is widespread on the extent to which a balanced diet can provide sufficient quantities of vitamins, or whether supplementation is necessary for optimum health. The existence of conflicting information and advice, and the pressure of advertising, can make it difficult for individuals to make an informed choice. Apart from vitamin D, there is little need for supplements for people with a good mixed diet – but there are problems of low vitamin A intake in many developing countries, as well as iron and iodine. Results from intervention trials with antioxidant supplements (especially β-carotene and vitamin E) in developed countries are mixed, with many studies showing increased all-cause mortality among those taking antioxidant supplements.
- **Medical programmes:** Scientists have a duty to share their findings with the public in ways that help people to understand the issues and make valid judgements.
- **Spend more time outdoors:** Vitamin D deficiency it is still a problem in some developing countries where intake of dairy products may be low or where religious or social customs or climatic conditions prevent an adequate exposure to sunlight. More widespread use of sunscreen lotions during the summer months seems to have resulted in greater concern over an increase in vitamin D deficiency even in affluent populations. Current recommendations for vitamin D intake are greater than can be achieved readily from diet, especially in winter above about 40°N or S.

QUICK CHECK QUESTION

27 Vitamin K_1 is required for the synthesis of certain proteins necessary for blood clotting. Its structure is shown below.



a Define the term vitamin.

b State and explain whether vitamin K is classified as a water-soluble or fat-soluble vitamin.

c It is present in green leafy vegetables. Some meal replacement bars and shakes are *fortified* with vitamin K. Explain this term.

23.6 Biochemistry and the environment

Revised ☐

Essential idea: Our increasing knowledge of biochemistry has led to several environmental problems, while also helping to solve others.

Biochemistry and the environment

Revised ☐

- Xenobiotics refer to chemicals that are found in an organism that are not normally present there.
- Biodegradable/compostable plastics can be consumed or broken down by bacteria or other living organisms.

- Host–guest chemistry involves the creation of synthetic host molecules that mimic some of the actions performed by enzymes in cells, by selectively binding to specific guest species, such as toxic materials in the environment.
- Enzymes have been developed to help in the breakdown of oil spills and other industrial wastes.
- Enzymes in biological detergents can improve energy efficiency by enabling effective cleaning at lower temperatures.
- Biomagnification is the increase in concentration of a substance in a food chain.
- Green chemistry, also called sustainable chemistry, is an approach to chemical research and engineering that seeks to minimize the production and release to the environment of hazardous substances.

Host–guest chemistry

Revised ☐

Host–guest chemistry involves the design, synthesis and investigation of simpler organic compounds that imitate the working features of naturally occurring compounds: molecular recognition, transport, regulation and catalysis.

A molecular recognition process can be described as a specific interaction between two molecules through multiple non-covalent contacts (via intermolecular forces). Molecular recognition forms basis for many processes in biology: receptor–substrate binding; enzyme catalysis (e.g. lock and key principle); assembly of multi-protein complexes, e.g. ribosomes; and transport across cell membranes.

The host is an organic molecule containing convergent binding sites. These are synthetic counterparts to receptor sites in enzymes, genes and antibodies. The guest is a molecule or ion containing divergent binding sites. The binding sites are the counterparts to substrates, inhibitors, cofactors and antigens.

The host and guest components of a complex are held together in solution (Figure 23.47) by an enthalpy contribution and an entropic contribution to their combination.

- The enthalpy contribution: consists of electrostatic forces of interaction such as ion-pairing, hydrogen bonding, metal ion-to-ligand attraction, ring-stacking, dipole–dipole interaction, and London (dispersion) forces.
- The entropic contribution: results from the process of desolvation – an increase in entropy due to the freeing up of solvent molecules as the host and guest associate.

The host–guest complex is also known as a *supramolecule*.

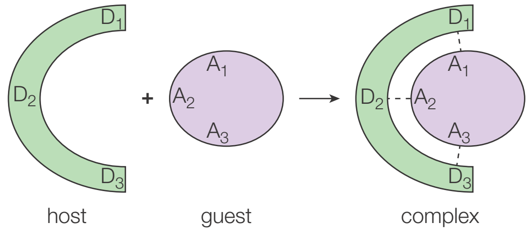


Figure 23.47 Host–guest complex formation

Expert tip

A 'supramolecule' literally means a structure 'beyond the molecular'; the key being that the association is brought about by non-covalent interactions, which distinguishes these structures from complex ions.

A well-studied class of host molecules is that of the crown ethers whose guests are group 1 cations (Figure 23.48). They selectively bind group 1 cations whose size matches that of the cavity. The cavity is polar; but the outside is non-polar.

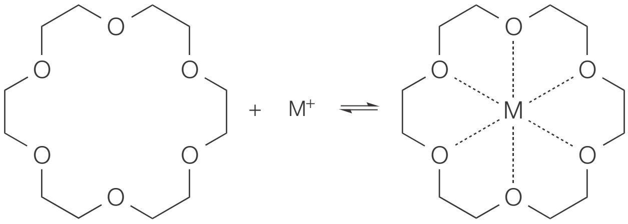
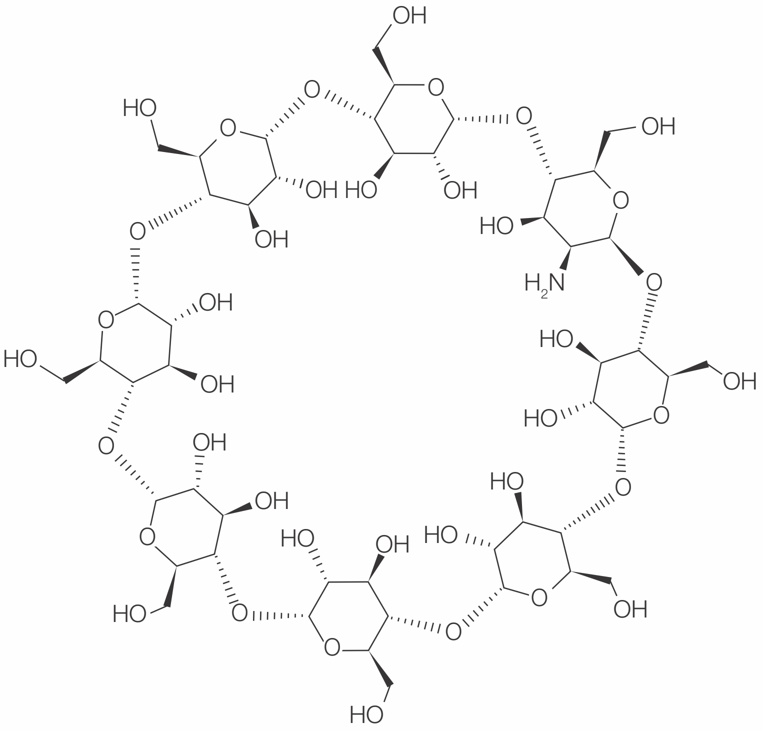


Figure 23.48 The coordination of a group 1 metal ion by a crown ether (here 18-crown-6 ether)

Host–guest complexes have been used to deliver poorly soluble drug molecules more effectively in patients by increasing the solubility and bioavailability of the drug. Cyclodextrins are chemically stable, water-soluble oligosaccharide hosts derived enzymatically from starch. Because their interiors are relatively lipophilic and their exteriors hydrophilic, cyclodextrins can complex hydrophobic guests to form inclusion complexes in aqueous solution.

Worked example

Gamma cyclodextrin consists of eight glucopyranose units joined together in a ring. Deduce an equation for the complete hydrolysis of gamma cyclodextrin. Cyclodextrins can be used to carry drugs, such as ibuprofen.



Cyclic polymers do not have terminal groups, so the formula of gamma cyclodextrin is $(C_6H_{10}O_5)_8$. Because each glucose residue needs one oxygen and two hydrogen atoms to produce glucose, the number of water molecules in the equation will also be eight:

$$(C_6H_{10}O_5)_8 + 8H_2O \rightarrow 8C_6H_{12}O_6$$

Host–guest systems have been utilized to remove hazardous substances from the environment. They can be made in different sizes and different shapes to trap a variety of chemical guests. One application is the ability of BOBCalix6 to trap a caesium ion (Figure 23.49).

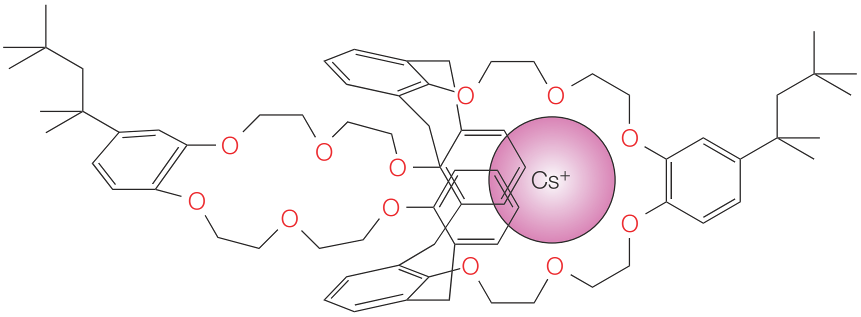


Figure 23.49 Host molecule (BOBCalix6) shown with a positively charged caesium ion held inside one of its cavities

Caesium-137 is radioactive and there is a need to remove it from nuclear waste in an efficient manner. Host–guest chemistry has also been used to remove carcinogenic aromatic amines, and their N-nitroso derivatives from water. These waste materials are used in many industrial processes and found in a variety of products such as pesticides, drugs and cosmetics.

Expert tip

You will need to be able to give a named example of host–guest chemistry – the calixarenes are such an example: used to remove radioactive caesium-137 from waste water by forming ion–dipole interactions.

■ QUICK CHECK QUESTIONS

28 Explain why 18-crown-6 is unable to bind calcium ions, but has a high affinity for oxonium ions (H_3O^+). Draw a diagram of the complex between 18-crown-6 and an oxonium ion.

29 Small molecules, such as nitrogen, methane and argon, can be trapped within the spaces of the ice lattice when it forms under high pressure. This is an example of a structure known as a clathrate; it is not a true compound, but an example of supramolecular chemistry.

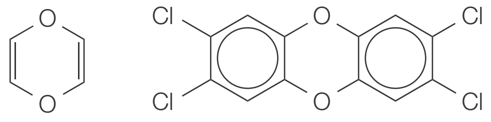
- **a** Suggest **one** way that the ice clathrate could be made to release its gas molecules.
- **b** Suggest why helium is unable to form a clathrate.
- **c** Identify the interaction between the gas particle and the water molecules.

Xenobiotics

Revised ☐

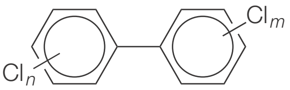
Xenobiotics are chemicals found in organisms which are not normally present or are present in higher than usual concentrations. They are chemical compounds, often drugs (including antibiotics which enter the water supply and those given to livestock), pesticides or carcinogens that are foreign to the living organism.

Some xenobiotics may be natural compounds, but most are pollutants. Three well-studied classes of xenobiotics are dioxins, dioxin-like substances, such as polychlorinated dibenzodioxins (PCCDs, Figure 23.50), and polychlorinated biphenyls (PCBs, Figure 23.51).



1,4-dioxin 2,3,7,8-tetrachlorodibenzodioxin

Figure 23.50 The structure of 1,4-dioxin and 2,3,4,8-tetrachlorobenzodioxin (an example of a PCCD)



polychlorinated biphenyl

Figure 23.51 The generalized formula of PCBs

Dioxins are produced as by-products in the manufacture of some chlorinated organic compounds and the incineration of plastics. They are highly carcinogenic, especially the chlorinated dioxins, and they can disrupt the endocrine system (hormone action) and lead to cellular and genetic damage.

PCBs contain one to ten chlorine atoms attached to a biphenyl molecule (Figure 23.51). They are highly stable, with high electrical resistance and were used as coolants, plasticizers, lubricants and insulating liquids.

A major issue with xenobiotics is **biomagnification,** which involves an increase in concentration as a substance passes up the food chain via digestion and assimilation. DDT (Figure 23.52) (dichlorodiphenyltrichloroethane) is an insecticide (now banned in many countries) against the malaria mosquito which accumulates in birds of prey and makes their eggs non-viable (Figure 23.53). Heavy metals, such as mercury compounds, can also be involved in biomagnification in marine environments.

Key definition

Biomagnification – the increase in the concentration of the pollutant as it moves up through the food chain.

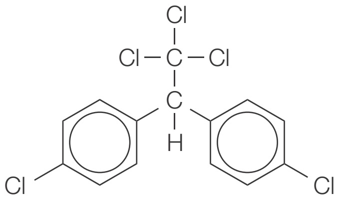


Figure 23.52 The structure of DDT

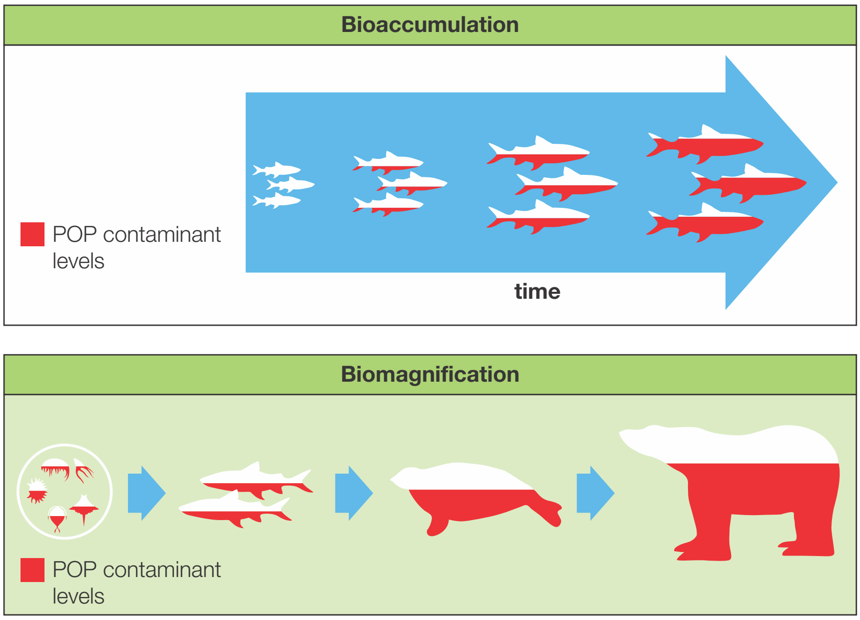


Figure 23.54 The processes of **bioaccumulation** and biomagnification of POPs (**P**ersistent **O**rganic **P**ollutants)

Worked example

A 500.0 cm^3 water sample is analysed for DDT using chromatography and mass spectrometry. The water sample undergoes chromatography and is then rinsed with 20.0 cm^3 of water. The DDT-containing fraction is removed with 20.0 cm^3 of methanol, evaporated and then transferred to a 2.00 cm^3 volumetric flask using methanol. A 20 μdm^3 aliquot is injected for analysis and the concentration of DDT in this extract is found to be 27.1 $ng\,cm^{-3}$.

Determine the concentration of DDT in $ng\,dm^{-3}$ in the water sample, assuming 100% transfer efficiency.

mass isolated in DDT extract = $(27.1\,ng\,cm^{-3})(2.00\,cm^3) = 54.2\,ng$

(note that $2.00\,cm^3$ = final extract volume)

initial water volume = $500.0\,cm^3 = 0.500\,dm^3$

$$\text{initial water concentration} = \frac{\text{mass of DDT isolated}}{\text{water volume}}$$

$$= \frac{54.2\,ng}{0.500\,dm^3}$$

$$= 108\,ng\,dm^{-3}$$

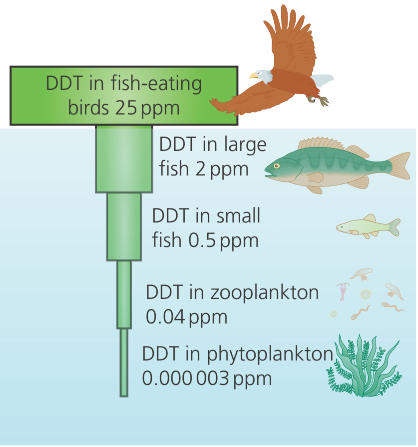


Figure 23.53 The biomagnification of DDT concentration as it passes up the food chain

Key definition

Bioaccumulation – the increase in the concentration of a pollutant in an organism as it absorbs or it ingests it from its environment (Figure 23.54).

Expert tip

Persistent Organic Pollutants (POPs) are a group of chemicals that are very toxic and can cause cancer and other adverse health effects. POPs are persistent in the environment and travel vast distances via air and water. POPs are organic chemical compounds which bioaccumulate in animals and humans.

Green chemistry

Revised ☐

Green chemistry promotes the design and application of chemical products and chemical processes that are compatible with human health and preserve the environment. The areas in which green chemistry can operate to improve environmental quality include choices of solvents and reagents for chemical reactions, development of alternative processes and improvements in existing chemical processes or practices.

Some of the major principles of green chemistry are:

- It is better to avoid producing waste than to clean or treat it after it has been created.
- When synthesizing new substances, the method used should generate as little waste as possible. The substances generated should have little or no toxicity to human health or towards the environment.
- Catalysts that allow the use of common and safe chemical reagents should be used whenever possible.
- The raw materials for chemical processes should be renewable feedstock when it is technologically and economically feasible.
- Auxiliary substances, such solvents, should be eliminated or made as harmless as possible.
- Chemical processes should be designed to be as energy efficient as possible, avoiding high temperatures and pressures.

Expert tip

You are not expected to learn this list, or the 12 principles of green chemistry, but you will be expected to be able to discuss the broad issues and apply them in a discussion of the 'greenness' of a particular product.

A further key component of green chemistry is the assessment of *atom economy* (see Topic 1 Stoichiometric relationships and worked example).

Worked example

An ultrasound imaging agent can be made by the reaction of butane and fluorine as shown in the following equation.

$C_4H_{10} + 10F_2 \rightarrow C_4F_{10} + 10HF$

Calculate the atom economy for the formation of decafluorobutane, C_4F_{10}, to three significant figures.

$$\text{atom economy (\%)} = \frac{\text{molecular mass of atoms in useful products}}{\text{molecular mass of atoms in reactants}} \times 100$$

$$= \frac{(238 \times 100)}{438} = 54.3\%$$

Biodegradability

Revised ☐

Synthetic plastics are organic and usually based on hydrocarbons. Thus they are generally not biodegradable and cause pollution in the sea and in landfills. Biodegradable plastics are plastics capable of being decomposed by bacteria and fungi, ultimately to carbon dioxide and water. They are based on naturally occurring polymers usually with ester functional groups, such as PLA (polylactic acid) or glycosidic (ether) linkages, such as starch.

Bacterial and fungal enzymes can be used to degrade biological pollutants, such as the hydrocarbons released in crude oil spills, a process known as bioremediation. Proteases, lipases and other enzymes are used in biological washing powders. Biological detergents allow for use at lower temperatures than non-biological ones and so save energy. Immobilized enzymes (enzymes attached to a solid support) have been used in the clean-up of industrial waste water.

■ QUICK CHECK QUESTIONS

30 Corn starch is made up of two carbohydrate polymers, amylose and amylopectin. It can be used to make replacements for plastics derived from petroleum, especially for packaging. Discuss **one** potential advantage and **one** disadvantage of this use of starch.

31 The organic compound 1-phenylethanone ($C_6H_5COCH_3$) is being investigated as a potentially useful enzyme inhibitor. There are two possible ways of synthesizing 1-phenylethanone from 1-phenylethanol under consideration.

Method 1:

$3C_6H_5CH(OH)CH_3 + 2CrO_3 + 3H_2SO_4 \rightarrow C_6H_5COCH_3 + Cr_2(SO_4)_3 + 6H_2O$

Method 2 (using a catalyst):

$C_6H_5CH(OH)CH_3 + \frac{1}{2}O_2 \rightarrow C_6H_5COCH_3 + H_2O$

a Calculate the atom economy of both these methods.

b Identify **two** other considerations which would need to be borne in mind, besides the atom efficiencies, when deciding which method is 'greener' and therefore the preferred option.

23.7 Proteins and enzymes

Revised ☐

Essential idea: Analyses of protein activity and concentration are key areas of biochemical research.

Proteins and enzymes

Revised ☐

- Inhibitors play an important role in regulating the activities of enzymes.
- Amino acids and proteins can act as buffers in solution.
- Protein assays commonly use UV–Vis spectroscopy and a calibration curve based on known standards.

Enzyme activity

At the active site of the enzyme, the amino acid side-chains of the folded protein are precisely positioned so they favour the formation of the high-energy transition states that the substrate(s) must pass through to be converted to product.

NATURE OF SCIENCE

The 'lock and key model' explains enzyme specificity, but it does not explain X-ray diffraction data indicating that the active site of some enzymes change shape when the substrate binds. This finding led to the development of the induced-fit model of enzyme activity (Figure 23.55).

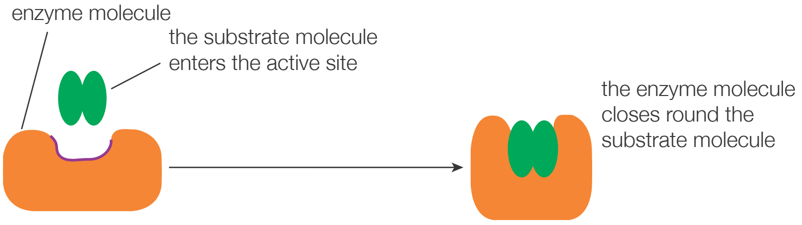


Figure 23.55 The induced fit model of enzyme action

Enzyme kinetics

When reaction rate is plotted against substrate concentration, a hyperbolic curve with an asymptotic plateau is reached. This is known as saturation kinetics (Figure 23.56) and occurs when the rate at which substrate enters active sites is equal to the rate at which products leave active sites.

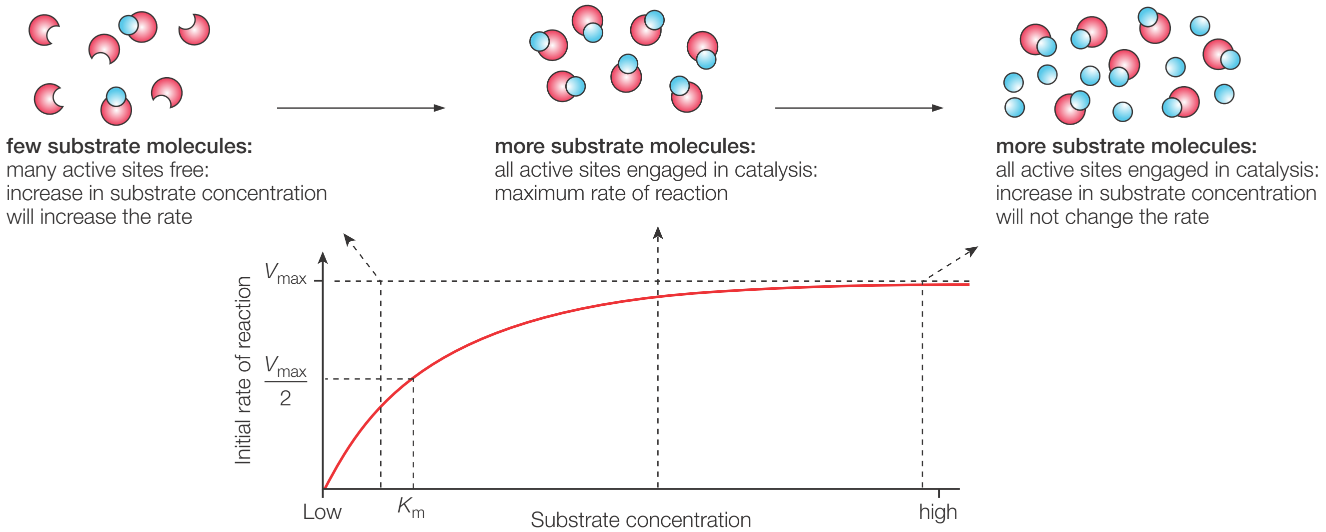


Figure 23.56 Interpreting the change in initial reaction rate with substrate concentration of an enzyme-catalysed reaction

The kinetics of enzyme-controlled reactions (known as Michaelis–Menten kinetics) identifies two important parameters: V_{max} and K_m (the Michaelis constant), the concentration of substrate that results in half the maximum rate.

A low value of the Michaelis constant, K_m, indicates that the enzyme works efficiently even if the concentration of the substrate is low, while a high value of the Michaelis constant indicates that the enzyme requires a high concentration of the substrate before being relatively active.

An enzyme assay measures the conversion of substrate to product, under conditions when the enzyme is optimally active. High substrate concentrations are used so that the initial rate is proportional to the enzyme concentration. Either the rate of appearance of product or the rate of disappearance of substrate is measured, often by following changes in absorbance using a spectrophotometer.

Expert tip

The maximum reaction rate for given a concentration of enzyme at a specified temperature and other conditions, e.g. pH, is referred to as V_{max}.

Inhibition

There are two common types of reversible inhibition of enzymes, **competitive** and **non-competitive inhibition** (Figure 23.57). They can be distinguished by their effects on enzymes.

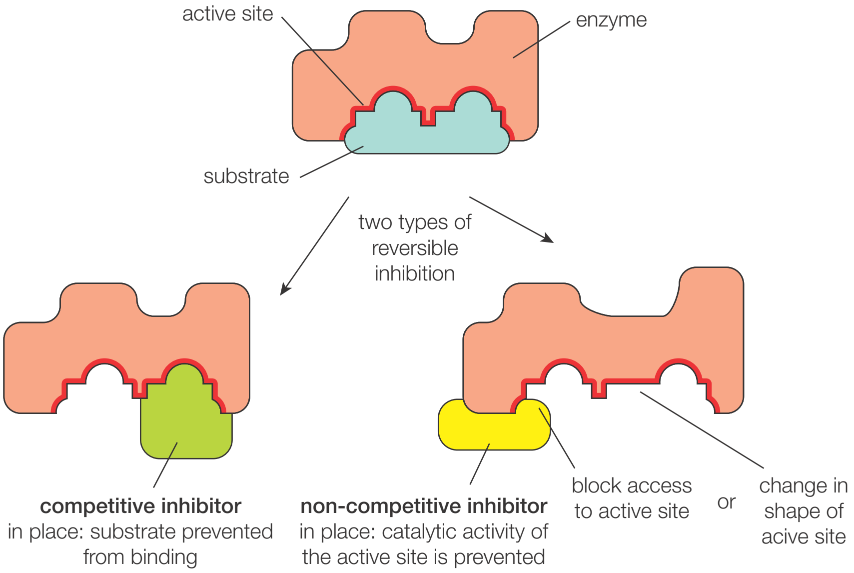


Figure 23.57 The principles of competitive and non-competitive inhibition

In competitive inhibition the inhibitor has a similar shape to the substrate and competes with the substrate to bind with the active site. In non-competitive inhibition the inhibitor does not bind to the active site but another binding site. This binding alters the shape (conformation) of the enzyme and prevents the catalysed reaction occurring.

Key definitions

Competitive inhibition – involves a molecule binding to the active site of an enzyme and thus preventing substrate from binding. The inhibitor has a similar structure to the substrate. Competitive inhibition does *not* affect the value of V_{max} but increases K_m.

Non-competitive inhibition – involves a molecule binding to the enzyme at a site distinct from the active site. This alters the shape of the enzyme, affecting the active site so that it no longer binds the substrate. Non-competitive inhibition *decreases* the value of V_{max} but has no effect on the value of K_m.

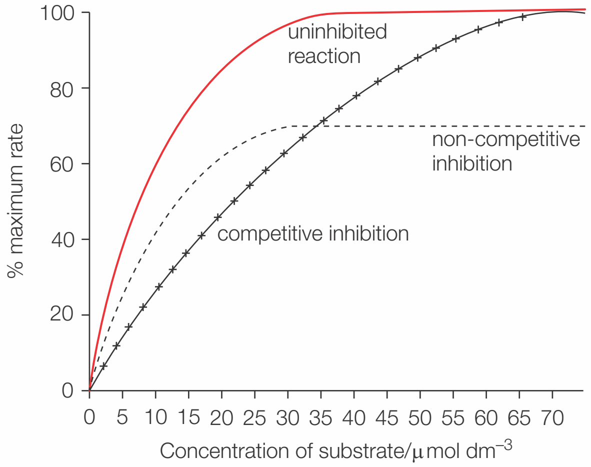
Expert tip

The rates of enzyme reactions are often so fast they are limited by diffusion. Rates can be increased if the enzymes are part of a multi-enzyme complex or if confined within a membrane.

QUICK CHECK QUESTIONS

32 Outline the general principle that describes how enzymes work as catalysts. Describe the effect, if any, that the enzyme has on the free energy difference between the initial and the final states of the reaction. What is the major source of free energy required for the catalytic power of enzymes?

33 The graphs show how the rate of an enzyme-catalysed reaction varies with substrate concentration for the uninhibited enzyme, for competitive inhibition and for non-competitive inhibition.



a Explain in both energy and structural terms how enzymes are able to catalyse specific biological reactions.

b Describe the difference in the way that competitive and non-competitive inhibitors interact with the enzyme.

The activities of most enzymes within cells are strictly regulated. One of the most common forms of inhibition is feedback inhibition (Figure 23.58), in which an enzyme early in a metabolic pathway is inhibited by its binding to one of the metabolic pathway's end products.

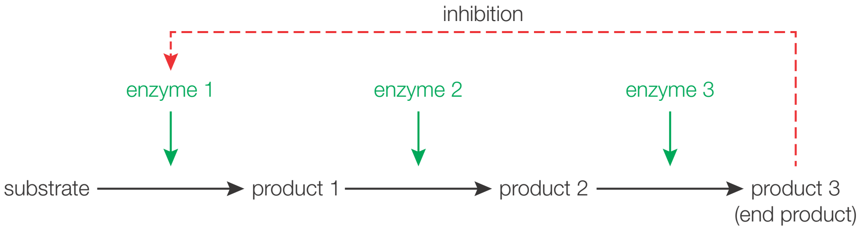


Figure 23.58 Feedback control of a metabolic pathway. The rate of reaction of the whole sequence is controlled by the concentration of the end product

Uses of enzymes

Proteases are widely used in biological washing powders to destroy organic material in stains and to condition fabrics. The enzymes are selected for their activity at high temperatures. Most of the enzymes used in industry are extracellular and secreted by bacteria into the growth medium. The main methods of immobilizing enzymes are cross-linking, entrapment and adsorption (Figure 23.59).

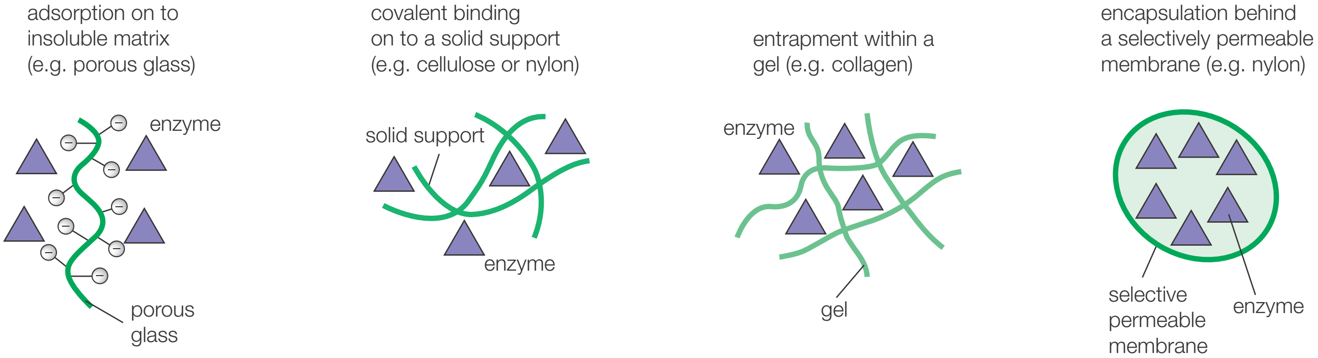


Figure 23.59 Methods of immobilizing enzymes

Isolated enzymes are used commercially and their effectiveness is increased if the enzyme is immobilized. Immobilized enzymes can be readily removed from a reaction mixture to avoid feedback inhibition by products. Immobilization of an enzyme can also improve its thermal stability. Immobilized enzymes are important in biosensor and diagnostic tests.

Buffers

Biological fluids including the cytoplasm and fluids, such as blood, are buffered. The major components in most biological fluids are the dihydrogen phosphate ion ($H_2PO_4^-$, pK_a 6.82) and the hydrogencarbonate ion (HCO_3^-, pK_a 6.35).

However, many biological molecules, including amino acids, proteins, nucleic acids and lipids have multiple acid–base groups that are effective at buffering in the physiological pH range (pH 6–8).

The carboxyl and amino groups bonded to the central carbon-2 atom of an amino acid act as acid–base groups, donating or accepting a proton as the pH is changed (Figure 23.60). At low pH, both groups are fully protonated, but as the pH is increased first the carboxylic acid group and then the amino group lose a hydrogen ion (H^+). Those amino acids with an ionizable side-chain with an additional side-chain have an additional acid–base group with a distinctive pK_a.

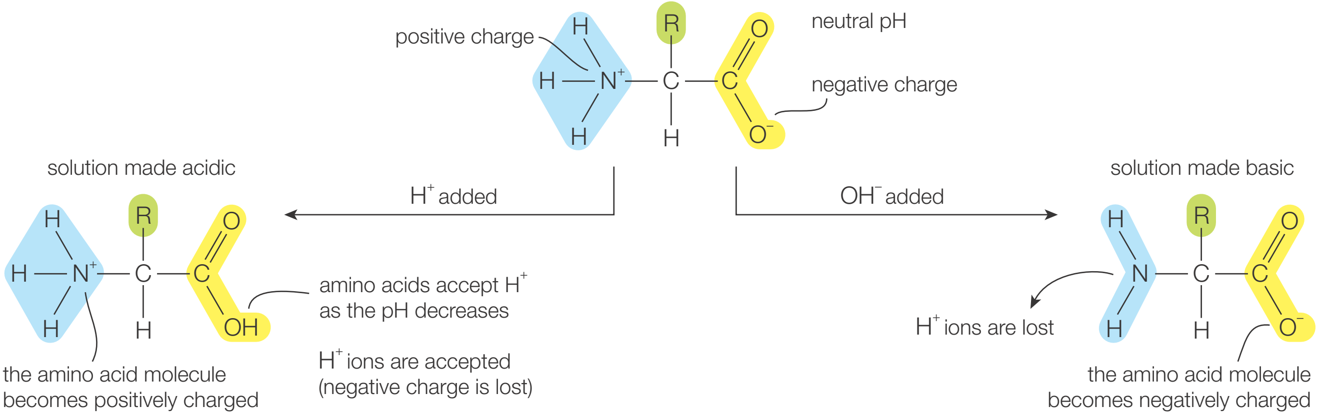


Figure 23.60 The buffering action of amino acids in aqueous solution

An acid–base conjugate pair can act as a buffer, resisting changes in pH. It is important to realize that an amino acid does not act as a buffer around its isoelectric point because there is only one species present. The titration curve for alanine (isoelectric point = 6.0) is shown in Figure 23.61, with the buffering regions being the almost horizontal regions of the curve (around pK_{a1} and pK_{a2}). The buffering capacity of the acid–base pair is in the range of the pK_a ± 1.

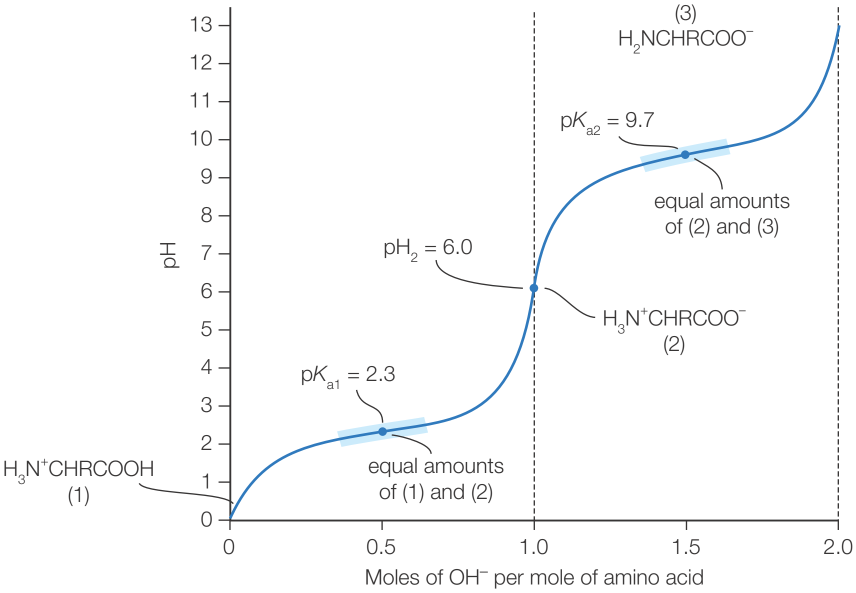


Figure 23.61 Titration curve for alanine

Solutions with an acidic pH (pH < pI) contain a mixture of the zwitterion and the cation, while alkaline solutions (pH > pI) contain zwitterions and anions. The exact ratio of these forms depends on the solution pH and the pK_a value of the conjugate acid present in the solution. Since pH = $-\log_{10}[H^+]$, the pK_a expression can be modified into the *Henderson–Hasselbalch* equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{conjugate acid}]}$$

For amino acid buffers this can be adapted as follows:

acidic pH (pH < pI)

$$\text{pH} = \text{p}K_{a1} + \log \frac{[\text{zwitterion}]}{[\text{cationic form}]}$$

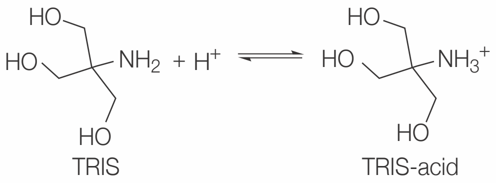
alkaline solutions (pH > pI)

$$\text{pH} = \text{p}K_{a2} + \log \frac{[\text{anionic form}]}{[\text{zwitterion}]}$$

QUICK CHECK QUESTIONS

34 The following buffer systems are used in working with biochemical systems:

- **a** Calculate the pH of a solution containing 0.200 mol dm^{-3} ethanoic acid ($K_a = 1.74 \times 10^{-5}\,\text{mol dm}^{3}$) and 0.250 mol dm^{3} sodium ethanoate.
- **b** Phosphate buffers are routinely used in biochemical experiments, particularly for buffering around neutral pH. Calculate the pH of a buffer solution containing 0.055 mol dm^{3} $H_2PO_4^-$ (pK_a = 7.21) and 0.045 mol dm^{-3} HPO_4^{2-}.
- **c** TRIS is a buffer system used frequently in biochemistry. A buffer solution is prepared by adding hydrochloric acid to TRIS to form a mixture of TRIS and its protonated form (TRIS–acid). The equilibrium that exists in the buffer solution is:



Calculate the pH of a buffer solution containing 0.650 mol dm^{-3} TRIS–acid (pK_a = 8.30) and 0.750 mol dm^{-3} TRIS.

35 Calculate the pH of an aqueous solution that contains 0.8 mol dm^{-3} zwitterionic and 0.2 mol dm^{-3} anionic forms of serine. (For serine, pK_{a1} = 2.2 and pK_{a2} = 9.1.)

Expert tip

When calculating the pH of a buffer solution, you can check whether or not your answer is reasonable. If the solution contains a higher concentration of acid than base, the pH of the solution will be lower than the pK_a of the acid; if there is a higher concentration of base than acid, the pH will be higher than the pK_a.

Protein assay by ultraviolet–visible spectroscopy

The concentration of a protein in solution can be determined by UV–Vis spectroscopy (Figure 23.62). Proteins are colourless and only weakly absorb UV radiation so the protein is complexed with a dye or redox reagent to form a highly coloured complex.

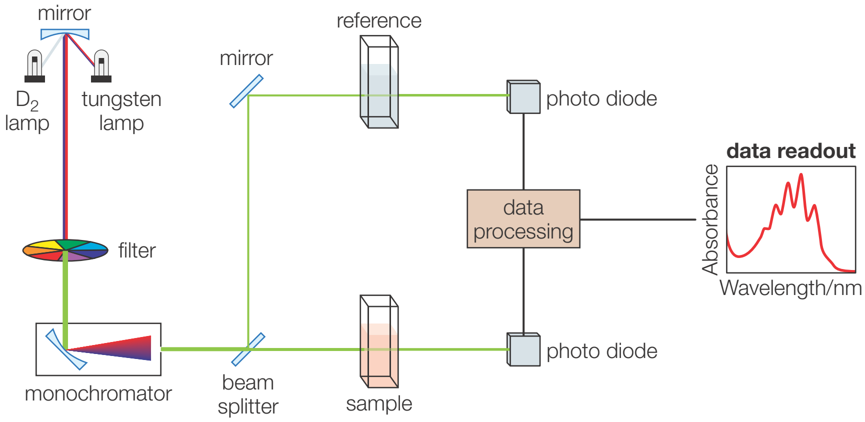


Figure 23.62 A schematic diagram of a UV–Vis spectrophotometer. The combination of the filter and monochromator ensures that only light of a particular wavelength is shone through the sample

One common approach known as the Bradford assay is to add a dye called Coomassie Brilliant Blue to bind to the protein in solution. The intensely coloured complex with the dye absorbs light with maximum absorption at a wavelength of 595 nm.

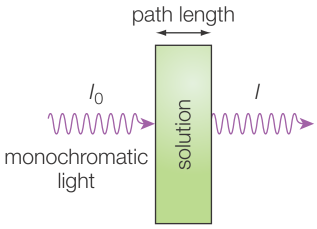


Figure 23.63 The Beer–Lambert law relates the absorbance of light by a solution to the path length and concentration

The principle of quantitative spectroscopy depends on the Beer–Lambert law (Figure 23.63). This states that for dilute solutions at a fixed wavelength absorbance is directly proportional to concentration:

$$\log_{10}\left(\frac{I}{I_0}\right) = \varepsilon lc$$

where I_0 is the intensity of the incident radiation, I is the intensity of the transmitted radiation, ε the molar absorption coefficient ($\text{cm}^{-1}\,\text{mol}^{-1}\,\text{dm}^3$), l is the path length (in the cuvette) of the absorbing solution (usually 1 cm) and c is the concentration (mol dm^{-3}) of the solution.

Ultraviolet spectrometers measure $\log_{10}\left(\frac{I}{I_0}\right)$ directly as absorbance if the path length is kept the same by using the same cuvette sample tube and all the readings are taken at the wavelength of maximum absorption, λ_{max}.

The Beer–Lambert Law describes the behaviour of solutions of proteins complexed with Coomassie Brilliant Blue covering the range of protein concentrations from 0 to approximately 1500 μg cm^{-3}.

To determine the concentration of the solution of the protein with an unknown concentration, it is necessary to obtain a calibration curve (line) by using a range of known concentrations of a specific purified soluble protein (such as serine albumin from a cow) and measuring the associated absorbance values.

A line of best fit (Figure 23.64) is constructed and once the absorbance of the unknown sample has been measured its concentration can be determined by interpolation of the graph.

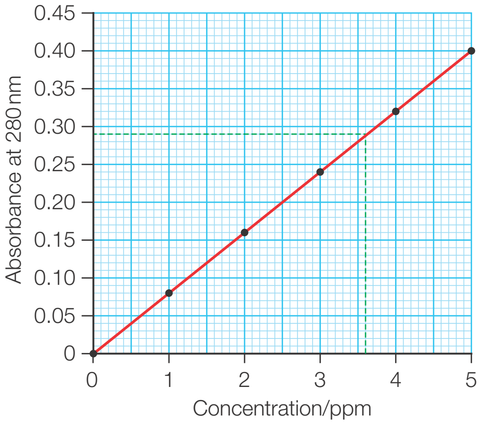


Figure 23.64 A calibration curve for the UV assay of proteins using absorbance at 280 nm (note that 1.00 mg dm^{-3} is the same concentration as 1 ppm)

Expert tip

You should note that absorbance has no units since it is a logarithmic scale.

QUICK CHECK QUESTION

36 Using the Beer–Lambert law, calculate the concentration of each of the following protein solutions. All absorbance values were measured at 280 nm in a cuvette of path length 1.0 cm.

a The molar absorptivity at 280 nm for a particular protein solution is 500 cm^{-1} mol^{-1} dm^{3} and the absorbance = 0.31.

b The molar absorptivity at 280 nm for a particular protein solution is 63.5 cm^{-1} mol^{-1} dm^{3} and the absorbance = 0.23.

23.8 Nucleic acids

Revised ☐

Essential idea: DNA is the genetic material that expresses itself by controlling the synthesis of proteins by the cell.

Nucleic acids

Revised ☐

- Nucleotides are the condensation products of a pentose sugar, phosphoric acid and a nitrogenous base – adenine (A), guanine (G), cytosine (C) and thymine (T) or uracil (U).
- Polynucleotides form by condensation reactions.
- DNA is a double helix of two polynucleotide strands held together by hydrogen bonds.
- RNA is usually a single polynucleotide chain that contains uracil in place of thymine, and a sugar ribose in place of deoxyribose.
- The sequence of bases in DNA determines the primary structure of proteins synthesized by the cell using a triplet code, known as the genetic code, which is universal.
- Genetically modified organisms have genetic material that has been altered by genetic engineering techniques, involving transferring DNA between species.

Nucleic acids

Revised ☐

There are two forms of nucleic acid: DNA (deoxyribonucleic acid), in which the sugar is deoxyribose, and RNA (ribonucleic acid), where the sugar is ribose. Both these sugars are pentose sugars containing five carbon atoms.

DNA and RNA are condensation polymers consisting of: two chains of sugar–phosphate backbone (the sugar is 2-deoxyribose in DNA and ribose in RNA), nitrogen-containing bases attached to each sugar; the bases are adenine (A), guanine (G), cytosine (C) and thymine (T) (in DNA only) and uracil (in RNA only) (Figure 23.65).

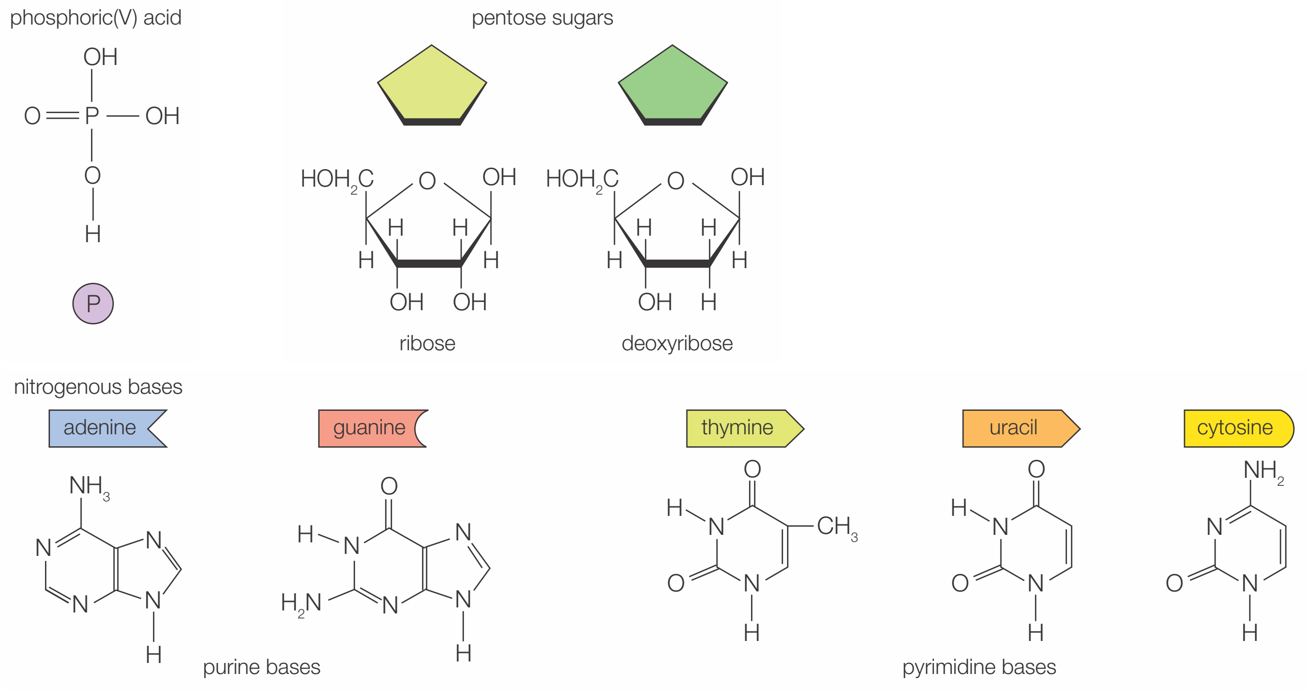


Figure 23.65 Components of DNA and RNA nucleotides

Nucleotides are the monomers from which the nucleic acids are synthesized by enzyme-controlled condensation reactions (Figure 23.66). The nucleotides themselves are made from a pentose sugar, a nitrogen-containing base and a phosphate group (which is ionized and negatively charged under physiological conditions).

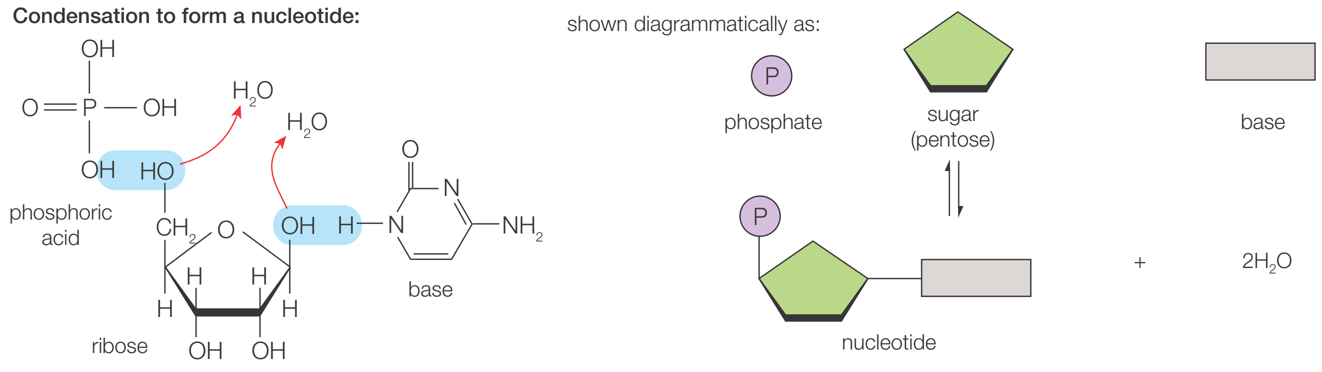


Figure 23.66 Condensation to a base, phosphate and pentose sugar to form a nucleotide

Expert tip

The nitrogenous bases present in RNA and DNA nucleotides are heterocyclic ring structures classified as purines or pyrimidines. The *pyrimidines* (thymine, uracil and cytosine) contain just a single ring (Figure 23.65), whereas the *purines* (guanine and adenine) contain two fused rings (Figure 23.65).

The two sugar–phosphate chains run in opposite directions in double-stranded DNA (they are anti-parallel) with the two chains twisted round each other to form a right-handed double helix (Figure 23.67). The sugar–phosphate backbone is on the outside and the bases are in the centre.

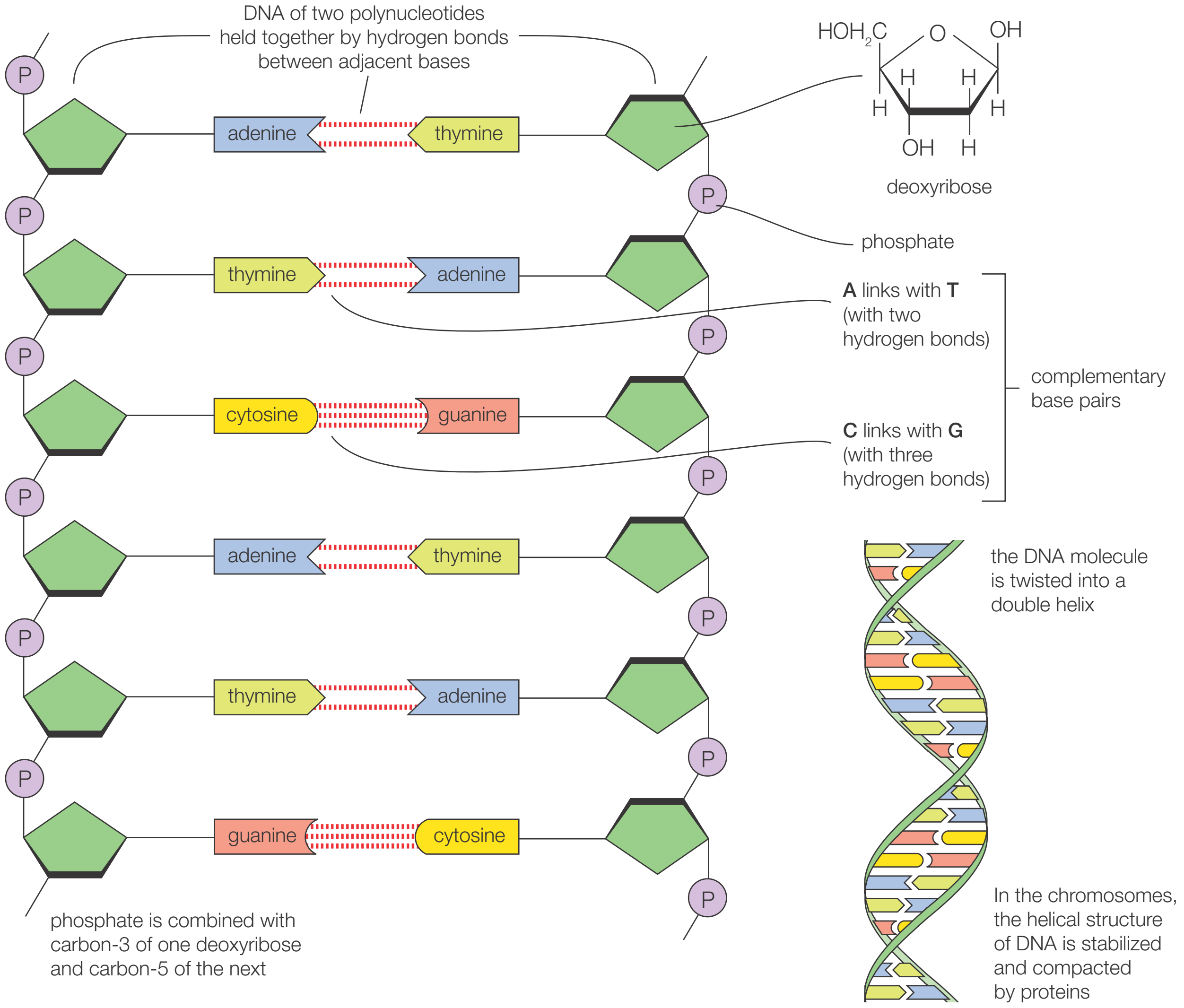


Figure 23.67 The double helix formed from two DNA strands

Pairs of bases (complementary base pairs) are stacked at right angles to the long axis of the helix. A always pairs with T, while C always pairs with G. The pairing is mediated through hydrogen bonding which stabilizes the double helix structure; note that the AT pairing involves two hydrogen bonds, whereas the GC pairing involves three such bonds. London (dispersion) forces due to the presence of the flat-ringed bases stacked above and below each other also contribute to maintaining the secondary structure of DNA.

NATURE OF SCIENCE

During the early 1950s a number of scientists were studying crystals of proteins and other large molecules by irradiating them with X-rays and examining the photographic evidence produced by the X-rays after they had been diffracted by the layers of molecules in the crystal. Rosalind Franklin and Raymond Gosling, working in London in association with Maurice Wilkins, found that one crystalline form of DNA produced a cross-like pattern characteristic of a helical structure. However, Franklin focused on another DNA form which she felt would yield more information but did not give a diffraction pattern characteristic of a helix. James Watson and Francis Crick realized the importance of the X-ray results from Franklin's group, which they coupled with crucial chromatographic data on base pairing (from Erwin Chargaff) and accurate model building to propose a double helical structure for DNA.

Worked example

If a given sample of double-stranded DNA is analysed for its base composition and shown to contain 40% cytosine, what is the expected percentage of adenine?

By Chargaff's ratios, 40% cytosine means the sequence must have 40% guanine as C always pairs with C. That leaves 20% of the bases as being A and T. Again, by Chargaff's pairing ratios, the %A must equal %T (A always pairs with T). Therefore, A and T split the remaining 20%, and there must be 10% adenine and 10% thymine in the DNA.

RNA (Figure 23.68) has an almost identical structure to DNA, except that the sugar is ribose, thymine is replaced by uracil, and it is single stranded and less chemically stable than DNA.

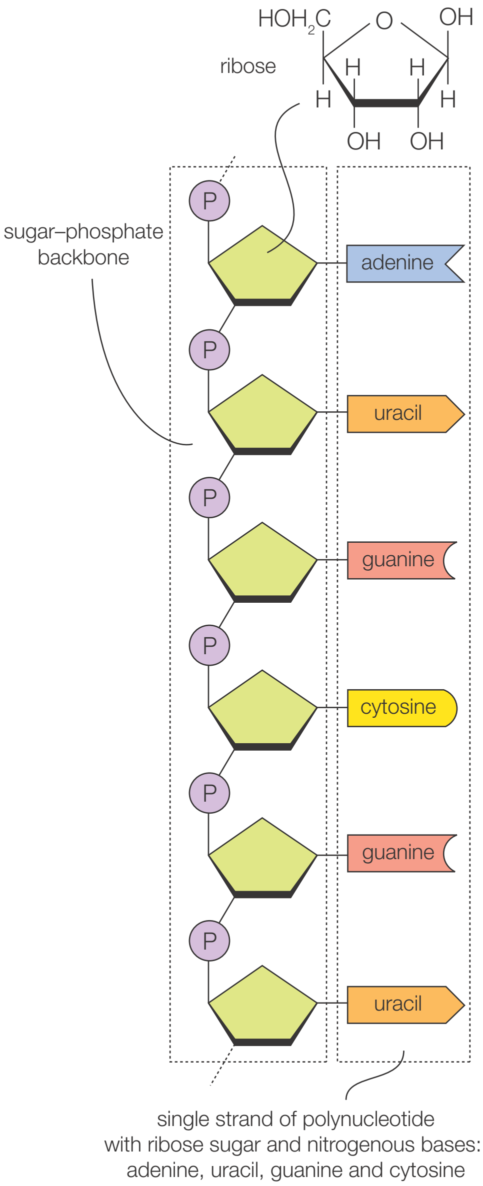


Figure 23.68 Structure of RNA

Replication

DNA produces new copies of itself (under enzyme control) during cell division. This is called replication (Figure 23.69). When DNA replicates itself identical copies of the base sequence are produced.

After cell division the new DNA molecules consist of one parent DNA strand and one 'new' strand. Complementary base pairing is the molecular basis for DNA replication.

The process of replication is semi-conservative; after cell division the new DNA molecules consist of one parent strand and one daughter strand (Figure 23.70).

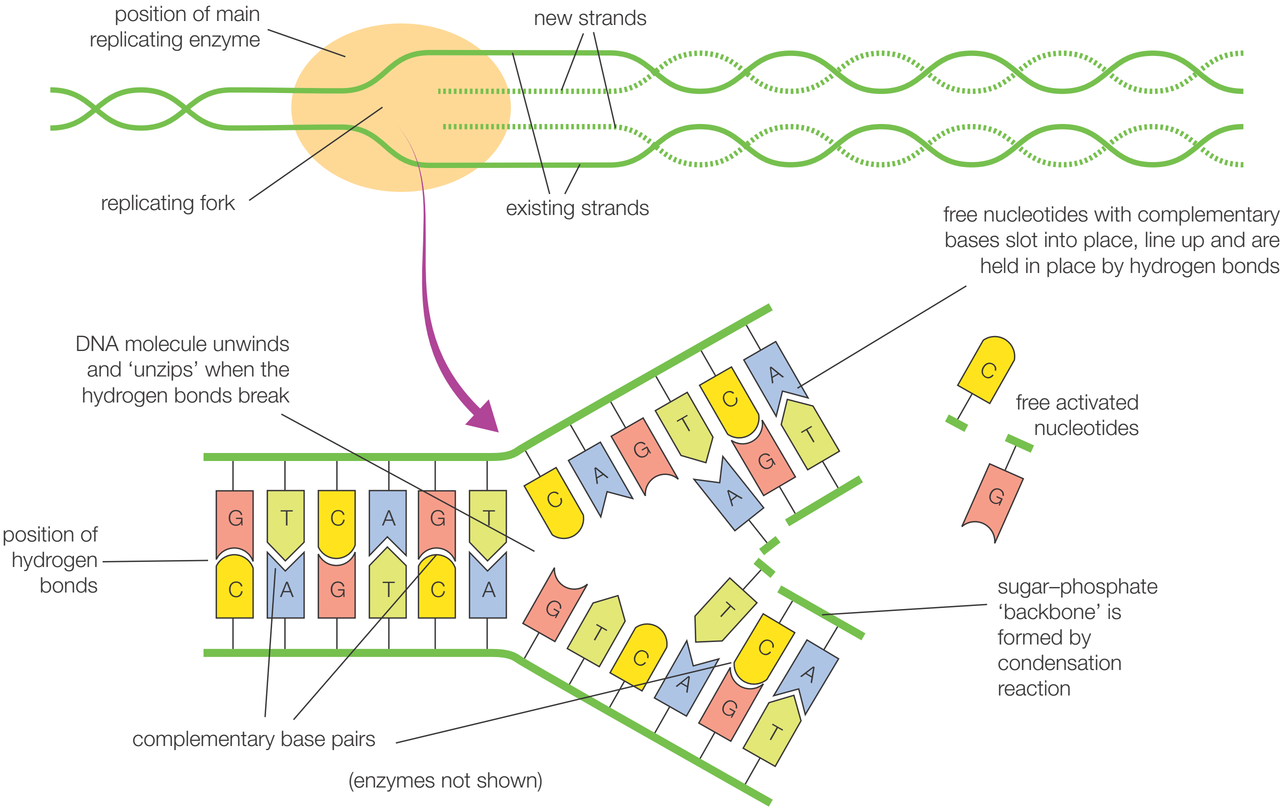


Figure 23.69 Simplified summary of the replication of DNA

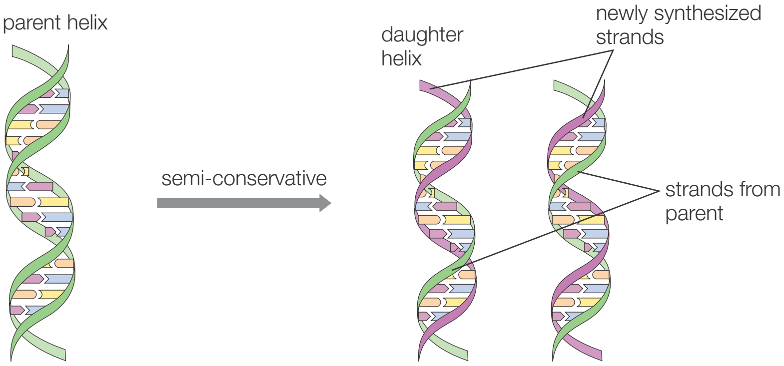


Figure 23.70 The outcome of semi-conservative replication

QUICK CHECK QUESTIONS

37 DNA (deoxyribonucleic acid) molecules and their fragments have been analysed in a variety of ways, one of which is by polyacrylamide gel electrophoresis. State the name of the component of DNA responsible for the migration of its fragments to the positive electrode in gel electrophoresis.

38 **a** What role do hydrogen bonds play in the accurate replication of DNA?

b DNA is replicated semi-conservatively. What is meant by this term?

c **i** What type of interaction takes place between the bases in the two DNA strands?

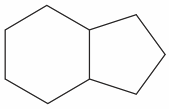
ii Condensation reactions are involved in the formation of DNA. What is the name given to the links which form the backbone of a DNA strand?

➜

39 **a** State two consistent differences between the structure of DNA and that of RNA.

b i Name two nitrogenous bases present in DNA, one a purine and the other a pyrimidine.

ii Suggest the most appropriate name for each of the following outline structures: purine or pyrimidine.



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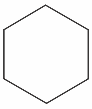


II

40 DNA is the molecule that carries genetic information in nearly all cells. Two months before Watson and Crick published their paper describing the double helical nature of DNA in 1953, Linus Pauling published a suggested structure for DNA based on a triple helix. Pauling's model soon proved to be incorrect; it had the phosphate groups facing into the core of the helix and the nitrogenous bases facing out.

a Suggest why Pauling's model would not have been a stable structure for DNA.

b DNA has the unusual property of being able to replicate. State the type and position of the bonds that break at the start of the replication process.

Transcription and translation

DNA stores the genetic information for the production of proteins. Each gene stores the information for a single polypeptide chain (protein). The flow of information in all living cells is DNA → RNA → protein. This is known as the central dogma (Figure 23.71). The conversion of the genetic code in DNA into RNA and proteins is termed gene expression.

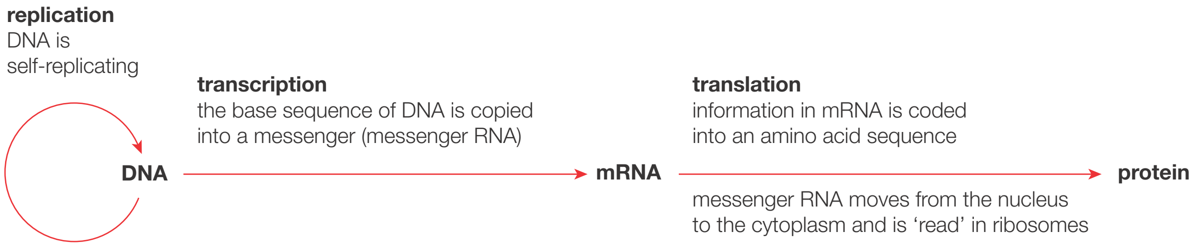


Figure 23.71 The central dogma

Using the genetic code to synthesize proteins involves several types of RNA: messenger RNA (mRNA), synthesized in the nucleus, transfer RNA (tRNA) to interact with amino acids and ribosomal RNA (rRNA) to catalyse the formation of a polypeptide chain from amino acids.

The enzyme-controlled processes involved in synthesizing proteins based on the genetic code in DNA of a gene are known as *transcription* and *translation* (Figure 23.72). Transcription involves the copying of the gene from the DNA into an mRNA molecule within the nucleus. The RNA molecule is then translated into the polypeptide chain in a complex process involving the ribosomes (composed of proteins and rRNA molecules) of a cell.

The mRNA molecules contain a triplet code in which three successive bases (a triplet) in the RNA sequence code for one amino acid in the polypeptide chain. The correspondence between the amino acids and the mRNA codons is specified by the genetic code. The possible combinations of the four different nucleotides in mRNA give 64 different codons ($4^3 = 64$) in the genetic code. Most amino acids are specified by more than one codon (Figure 23.73); for this reason the genetic code is described as being redundant.

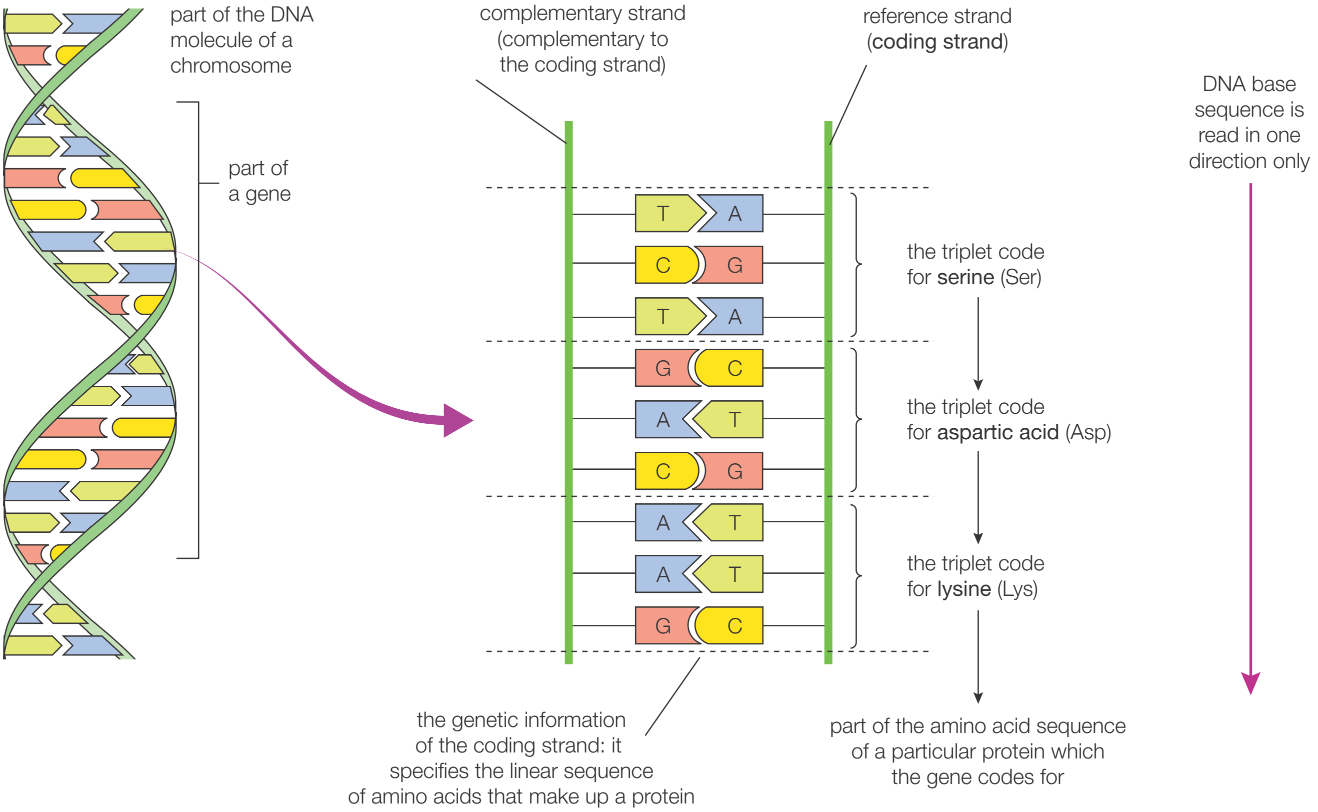
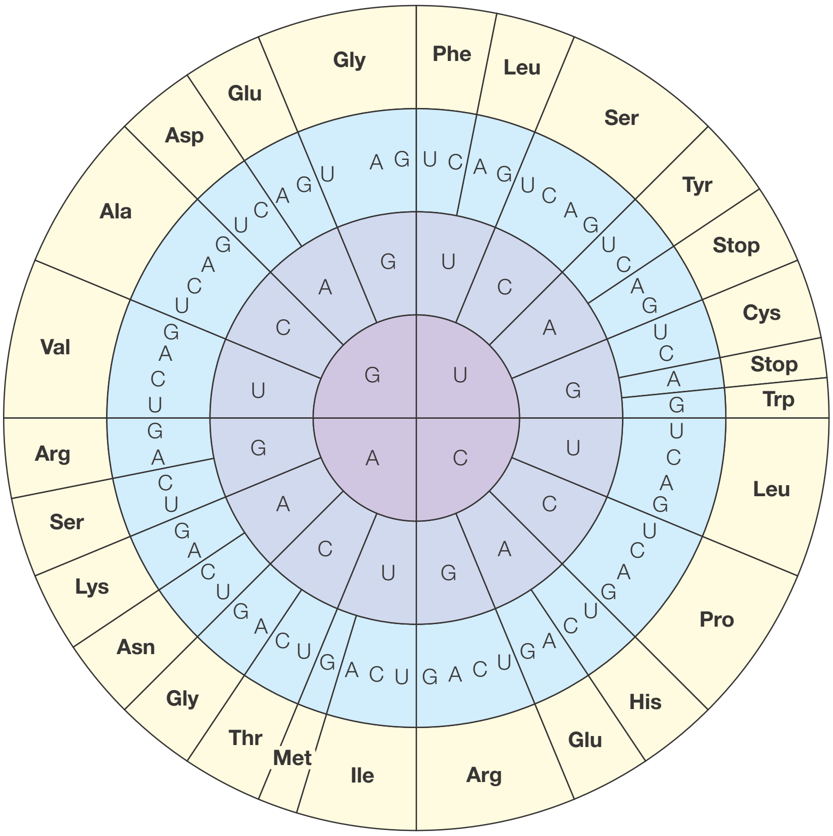


Figure 23.72 Part of a gene and how its DNA codes for amino acids

The genetic code in circular form
The codons are those of the DNA complementary strand and of messenger RNA (where uracil, U, replaces thymine, T).

Read the code from the centre of the circle outwards along a radius. For example, serine is coded by UCU, UCC, UCA or UCG, or by AGU or AGC.



In addition, some codons stand for **stop**, signalling the end of a polypeptide/protein chain.

Figure 23.73 The genetic code

Specific tRNA molecules bring specific amino acids from the cytoplasm to the ribosomes and bind to specific codons (via complementary base pairing) in the mRNA molecules. Protein synthesis (Figure 23.74) then takes place in three stages within the ribosome: initiation, elongation (amino acid polymerization) and termination (release and folding of the polypeptide to form a protein).

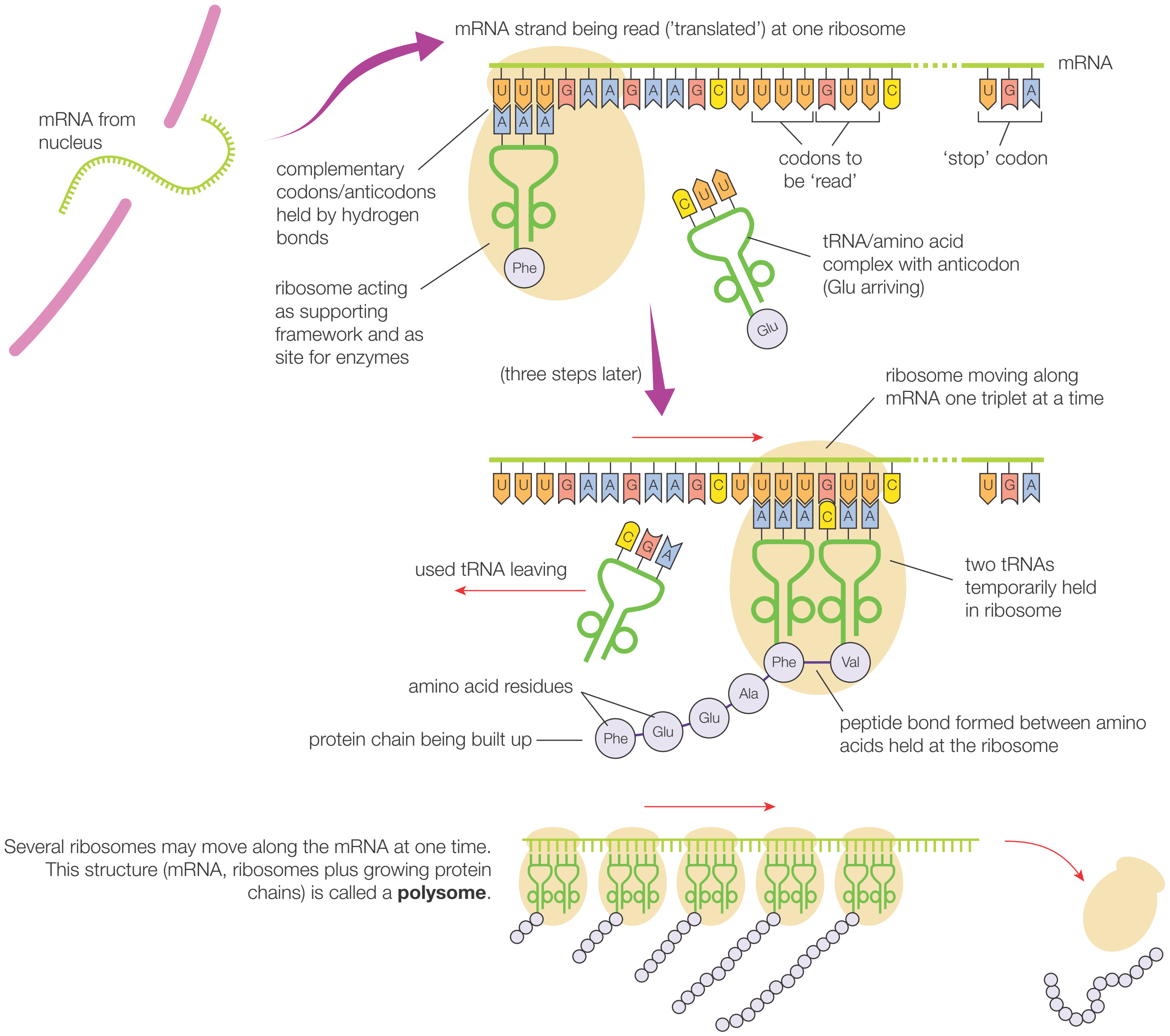


Figure 23.74 Translation: protein synthesis

The genetic material of cells with nuclei is contained in a set of paired chromosomes, each formed from a long DNA molecule with many genes. *Chromosomes* consist of DNA bound to specialized, highly basic proteins which help fold the DNA into a compact form. These basic proteins are known as histones and they have a high content of amino acid residues with basic positively charged R-groups. The first level of association between the DNA strand and histones is the formation of *nucleosomes*. A nucleosome consists of a length of DNA of about 150 base pairs, wrapped around a core of eight histones. These nucleosomes are spaced along the DNA, and thus form a 'string of beads' referred to as *chromatin*. Nucleosomes help to *supercoil* the DNA while still ensuring appropriate access to it. Figure 23.75 shows the relationship between the DNA strand, the nucleosomes, and a chromosome.

Expert tip

Details of transcription and translation are not required for the examination. For the examination limit your revision of the expression of DNA to the concept of a 4-unit base code determining a 20-unit amino acid sequence.

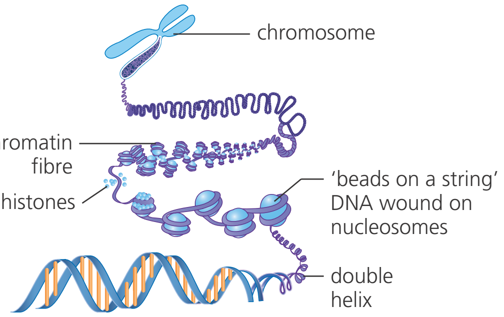


Figure 23.75 The packaging of DNA into a chromosome

The human genome contains approximately 3×10^9 nucleotide base pairs divided among 23 pairs of chromosomes (in humans). Only a small percentage of the DNA codes for proteins and RNA. The remainder is a mixture of 'junk' and sections that regulate the decoding, or expression, of the genes themselves. The functional regions of DNA are known as *genes*.

Individual humans differ from each other by an average of 1 nucleotide pair in every 1000; this variation is the basis for our genetic individuality and is the basis for identifying individuals by DNA 'fingerprinting'.

■ QUICK CHECK QUESTIONS

41 Human blood is recovered from a knife found at a crime scene. Outline briefly the stages in preparing a DNA profile from the blood sample.

42 The base composition of a virus was found to be 11% A, 32% G, 18% U and 39% C.

a i Deduce whether this a DNA or RNA virus. Explain how you reached your conclusion.

ii Deduce whether this genetic material is single-stranded or double-stranded. Explain your suggestion.

b A fragment of DNA strand that is used as a template for mRNA synthesis has the following sequence: 5′-ACTGTCGCACAGT-3′.

Write the sequence of the mRNA molecule (starting from the 5′-end) synthesized from this DNA. Can this mRNA adopt a 3-dimensional structure by itself?

Expert tip

Certain viruses (retroviruses such as HIV) have been discovered which function initially in the opposite direction to the 'central dogma'. The genetic information of these viruses is coded in viral RNA which is then copied into DNA using a reverse transcriptase enzyme. Such enzymes have proved immensely useful in research into the isolation and identification of genes for specific protein chains.

Expert tip

You will note that the majority of the terms used in connection with this section are words that are associated with language and coding; terms such as transcription and translation. The overall term for the reading of the information contained in the genetic information is gene expression – the information contained within the genes is expressed in the proteins generated, and ultimately in the organisms that make up the living world.

Recombinant DNA technology

Revised ☐

The universal nature of the genetic code makes it possible for DNA from one organism to be expressed by directing protein synthesis when it is transferred into the DNA of a different species. This is the basis of *genetic engineering* which gives rise to **genetically modified organisms (GMOs)**.

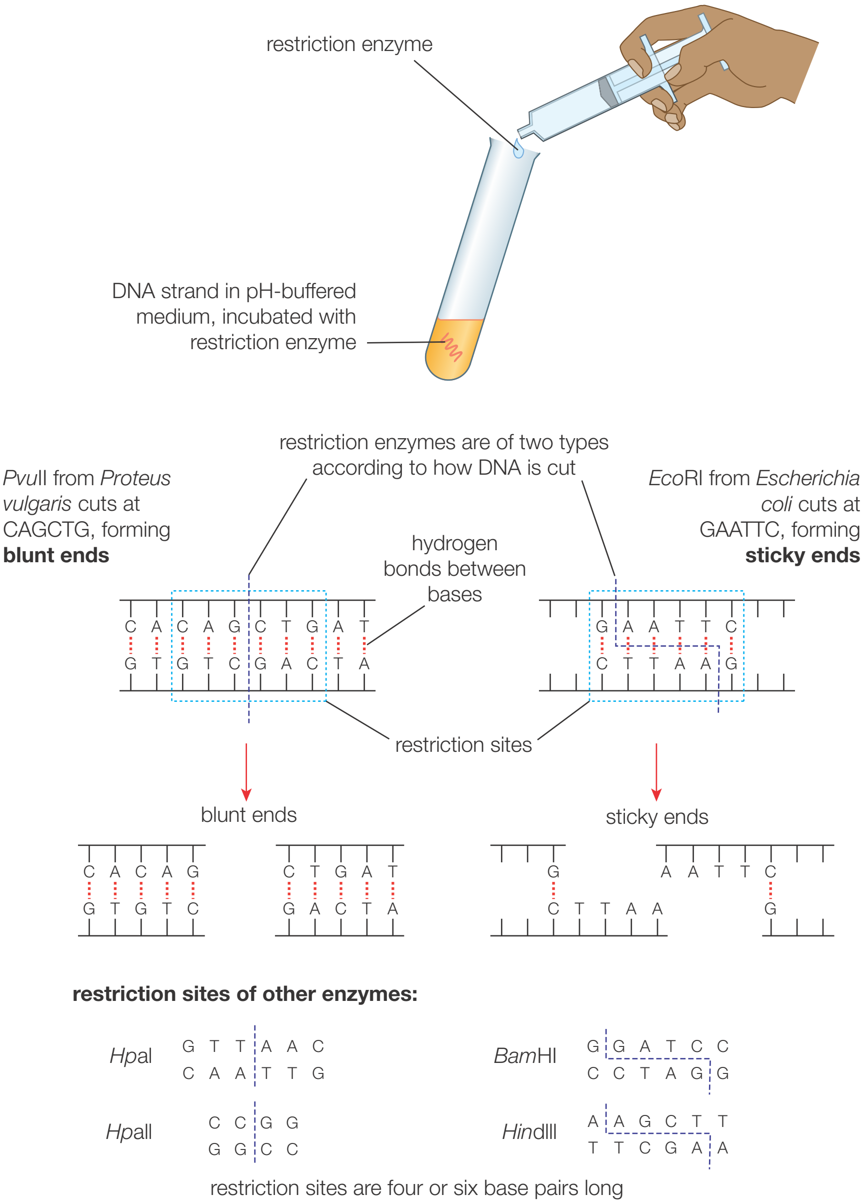
The DNA sequences used in the construction of **recombinant DNA (rDNA)** molecules can originate from any species. For example, plant DNA may be joined to bacterial DNA, or human DNA may be joined with fungal DNA. In addition, DNA sequences that do not occur anywhere in nature may be created by the chemical synthesis of DNA and incorporated into recombinant molecules. Using recombinant DNA technology and synthetic DNA, literally any DNA sequence may be created and introduced into any of a very wide range of living organisms.

Recombinant DNA technology allows biochemists to pick out a specific gene from a cell's genome and determine the molecular structure of the gene. An important technique is the ability to cut a long DNA molecule into a specific and reproducible set of fragments using restriction enzymes (Figure 23.76), each of which cuts the DNA double helix only at a particular nucleotide sequence.

Key definitions

Genetically modified organisms (GMOs) – organisms that have genetic material that has been changed in some way by genetic engineering. This can often be the result of the insertion of DNA from a different species.

Recombinant DNA (rDNA) – these molecules are DNA molecules formed by laboratory methods of genetic recombination which bring together genetic material from multiple sources, creating sequences that would not otherwise be found in the genome.



Restriction enzymes are named after the microorganisms they are found in. Roman numbers are added to distinguish different enzymes from the same microorganism.

Figure 23.76 The role of restriction endonucleases (restriction enzymes)

DNA fragments can be separated from one another on the basis of size by gel electrophoresis. Nucleic acid hybridization (Figure 23.77) can detect any specific RNA or DNA sequence in a mixture of nucleic acid fragments. This technique relies on the fact that a single strand of DNA or RNA will form a double helix only with another nucleic acid strand of the complementary nucleotide sequence.

Genetic engineers isolate, cut out and transfer genes between organisms. In order to transfer DNA in a living cell the DNA is introduced by a vector, usually a plasmid (circular DNA from bacteria). Once the foreign DNA is inside the host cell it may be incorporated by the host cell. Genes in the foreign DNA are expressed using the host cell's ribosomes. The foreign DNA is replicated (copied) each time the cell divides.

Molecular cloning and PCR are two techniques for the rapid replication of modified DNA. The fundamental difference between the two methods is that molecular cloning involves replication of the DNA within a living cell (often a bacterial cell), while PCR replicates DNA in the test tube, free of living cells. Recombinant DNA is widely used in biotechnology, medicine and research. The most common application of recombinant DNA is in basic research, but many additional practical applications of recombinant DNA are found in industry, food production, human and veterinary medicine, agriculture and bioengineering. Some specific examples are listed below.

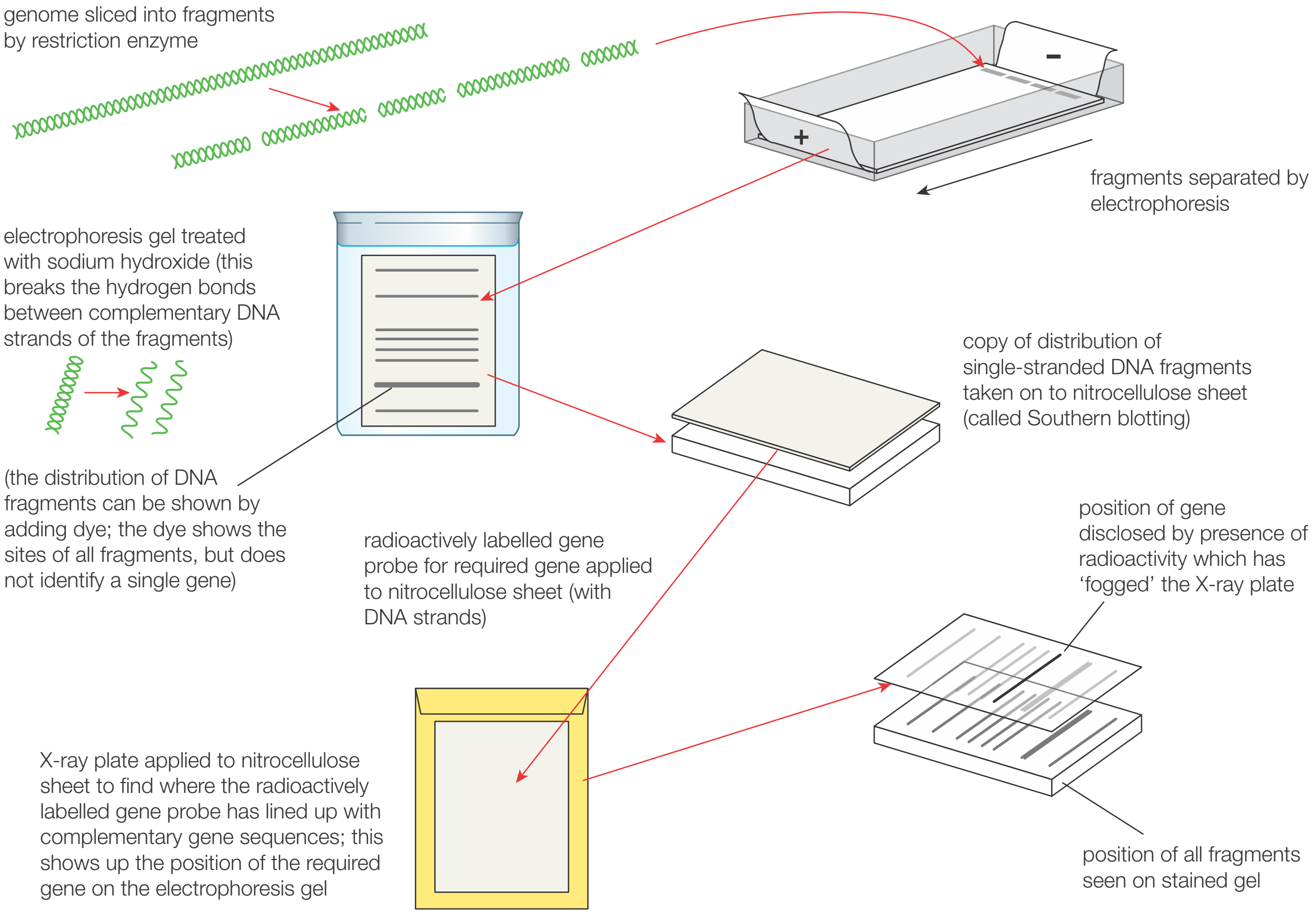


Figure 23.77 Gene probe technology

- **Recombinant human insulin:** This form of insulin has almost completely replaced insulin obtained from animal sources for the treatment of insulin-dependent diabetes. Recombinant insulin is synthesized by inserting the human insulin gene into *E. coli*, or yeast (*Saccharomyces cerevisiae*), which then produces insulin for human use. This example is of importance because of its impact on patients and the fact that it was essentially the first successful application of this ground-breaking technique. A similar approach has been taken in the following cases.
- **Recombinant human growth hormone (HGH, somatotropin):** Recombinant HGH is now administered to patients whose pituitary glands generate insufficient quantities to support normal growth and development. The use of the recombinant protein eliminated problems associated with HGH from cadavers (dead corpses), which had been the previous source.
- **Recombinant hepatitis B vaccine:** Recombinant hepatitis B vaccine contains a form of the hepatitis B virus surface antigen that is produced in yeast cells. The development of this recombinant vaccine was an important and necessary development because hepatitis B virus, unlike other common viruses such as the polio virus, cannot be grown *in vitro*.

These examples indicate the importance of recombinant DNA techniques using rapidly growing organisms such as bacteria or yeast. However, a number of GMOs have been developed for commercial use involving animals and plants that produce pharmaceuticals or other compounds. Within the field known as *pharming*, intensive research has been conducted to develop transgenic animals that produce biotherapeutics. The first human biological drug produced from such an animal, a goat, is the drug anti-thrombin (ATryn), which is an anticoagulant that reduces the probability of blood clots during surgery or childbirth. The anticoagulant is extracted from the goat’s milk.

Genetically modified crops

Biotechnology is the manipulation of organisms and cells for the benefit of people in agriculture, medicine and food production. Biotechnology is used to modify plants used in food production (Figure 23.78). Techniques of inter-species DNA transfer are now advanced, and a wide range of genetically modified foods, known as GM *foods*, are marketed in many countries. The genetic modification may:

- add a gene to yield a new product
- inactivate a gene to remove undesired an undesired property
- modify a gene for higher yields of its protein.

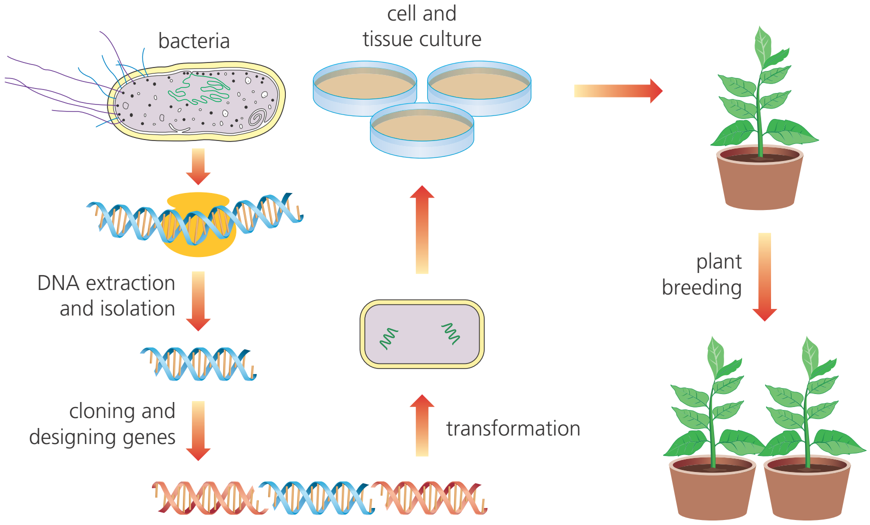


Figure 23.78 The process of genetic modification through isolation of a gene and insertion into the genetic sequence of a host organism (a plant)

Examples include corn which contains a bacterial gene that produces a natural pesticide, herbicide-resistant crops, rice which produces higher concentrations of vitamin A ('golden rice'), and tomatoes that remain fresh for longer.

While genetically modified foods such as these promise certain benefits, their development also raises many issues and is the subject of ongoing debate. Some aspects of both sides of this debate are summarized here.

Benefits of GM foods: Some GM foods and GMOs have the following qualities:

- longer shelf-life
- improved flavour, texture and nutritional value
- increased resistance to diseases and pests, reducing the use of pesticides
- produce a supply of substances such as vitamins and vaccines
- increased crop yields
- tolerance of a wider range of growing conditions, such as drought resistance.

Concerns over GM food: Many people, however, express the following concerns:

- lack of information about long-term effects
- changes to the natural ecosystem through cross-pollination
- possible links to increased allergies
- risk of altering natural composition of food
- concerns of breeding species that are resistant to control
- in some cases lack of information through food labelling.

QUICK CHECK QUESTION

43 Many modern food items contain genetically modified components.

a Explain what is meant by the term *genetically modified food.*

b Describe **two** advantages and **one** concern about the use of genetically modified food.

23.9 Biological pigments

Revised ☐

Essential idea: Biological pigments include a variety of chemical structures with diverse functions which absorb specific wavelengths of light.

Biological pigments

Revised ☐

- Biological pigments are coloured compounds produced by metabolism.
- The colour of pigments is due to highly conjugated systems with delocalized electrons, which have intense absorption bands in the visible region.
- Porphyrin compounds, such as hemoglobin, myoglobin, chlorophyll and many cytochromes are chelates of metals with large nitrogen-containing macrocyclic ligands.
- Hemoglobin and myoglobin contain heme groups with the porphyrin group bound to an iron(II) ion.
- Cytochromes contain heme groups in which the iron ion interconverts between iron(II) and iron(III) during redox reactions.
- Anthocyanins are aromatic, water-soluble pigments widely distributed in plants. Their specific colour depends on metal ions and pH.
- Carotenoids are lipid-soluble pigments, and are involved in harvesting light in photosynthesis. They are susceptible to oxidation, catalysed by light.

Biological pigments

Revised ☐

Biological pigments are coloured compounds which are produced by metabolism (enzyme-controlled reactions inside cells). Melanin is a biological pigment responsible for the colour of skin, hair and eyes. The colour of pigments results from the absorption of certain wavelengths of visible light. All pigment molecules have intense absorption bands in the visible region of the spectrum. The colour seen is the light that is not absorbed but instead is reflected (Figure 23.79).

White light can be described as a mixture of red, green and blue light. These are known as the primary colours and when mixed together (in equal intensities) produce white light. All the colours can be generated from the three primary colours.

The colour that we see is white light minus the colour being absorbed. The colour we see is called the complementary colour to the colour being absorbed. A colour wheel (Figure 23.80) illustrates the approximate complementary relationship between the wavelengths of light absorbed and the wavelengths transmitted or reflected.

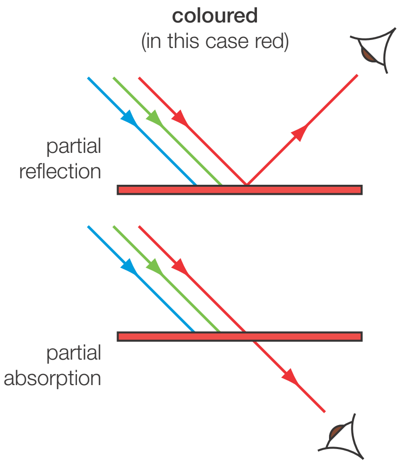


Figure 23.79 Perception of a red coloured pigment

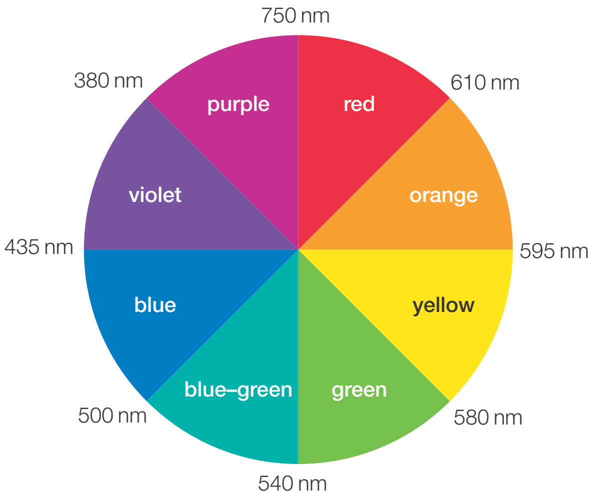


Figure 23.80 A simple colour wheel

Examples of naturally occurring coloured organic compounds include the anthocyanins, carotenoids (e.g. β-carotene) and the porphyrins (e.g. chlorophyll, hemoglobin, cytochromes and myoglobin).

NATURE OF SCIENCE

A study of the interaction of light (or other electromagnetic radiation) with matter is an important tool for chemists. Much of our knowledge of chemical substances comes from their specific absorption or emission of light. In recent years spectrophotometric methods have become the most frequently used and important methods of quantitative analysis. They are applicable to many industrial and clinical problems involving the quantitative determination of compounds that are coloured or that react to form a coloured product.

Chromophores

Groupings within organic molecules that cause colour are chromophores. They are typically delocalized electron systems, often benzene rings or with functional groups with lone pairs, such as >C=O, –N=N– and $-NO_2$. A common chromophore is an arrangement of alternating single and double carbon–carbon bonds (Figure 23.81). The more extensive the conjugation, the lower the energy (longer the wavelength) of the light (photons) absorbed.

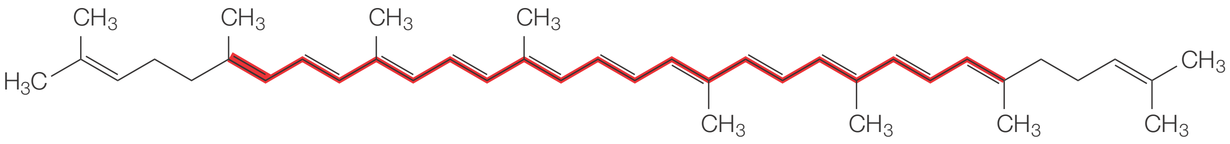


Figure 23.81 Lycopene, the red pigment in tomatoes, has 11 conjugated double bonds (highlighted). Note that not all the >C=C< bonds in lycopene are part of the conjugated system

The absorption of light (of specific energy) causes electrons in π-bonds or lone pairs (*n*) being excited and undergoing a transition to a molecular orbital of higher energy, usually an anti-bonding orbital (Figure 23.82).

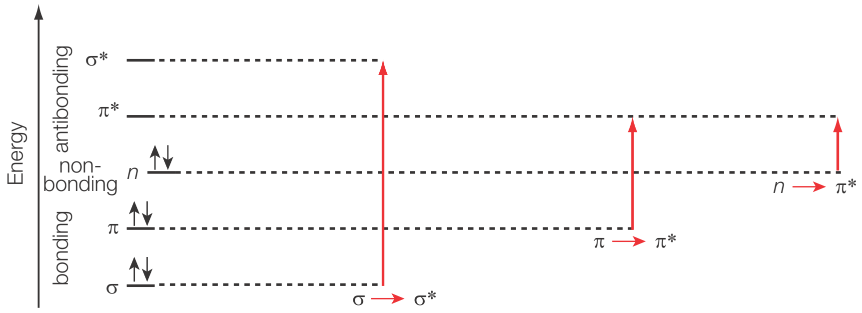


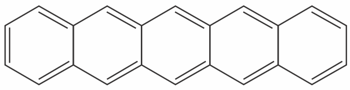
Figure 23.82 Possible electron transitions: only π to π* transitions and *n* to π* transitions that occur in the UV–Vis region are observed

QUICK CHECK QUESTIONS

44 Lycopene (Figure 23.81) is a carotenoid and is responsible for the red colour in tomatoes. When bromine is slowly added to some tomato juice, the colour of the juice gradually changes from red to yellow.

Explain this colour change in terms of changes in bonding in lycopene.

45 Pentacene (structure below) is purple while benzene is colourless. Both molecules are conjugated. Explain these observations.



Expert tip

Conjugation occurs when three or more p orbitals overlap. This can be achieved via π–σ–π bonds or can be achieved by an atom (such as nitrogen or oxygen) with a lone pair that is sp^2 or sp^3 hybridized.

Anthocyanins

Anthocyanins are aromatic, water-soluble polyphenol pigments found in fruits, vegetables and flowers. Their structures are based on the hydrocarbon flavan structure (Figure 23.83) which has a C_6–C_3–C_6 skeleton with two benzene rings (conjugated systems) isolated by an oxygen-containing pyran ring.

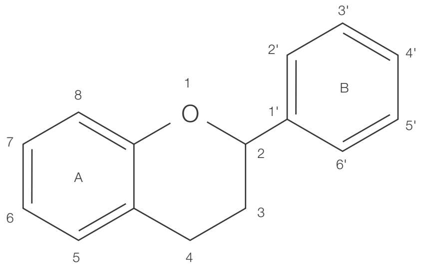


Figure 23.83 The central flavan structure of the anthocyanins

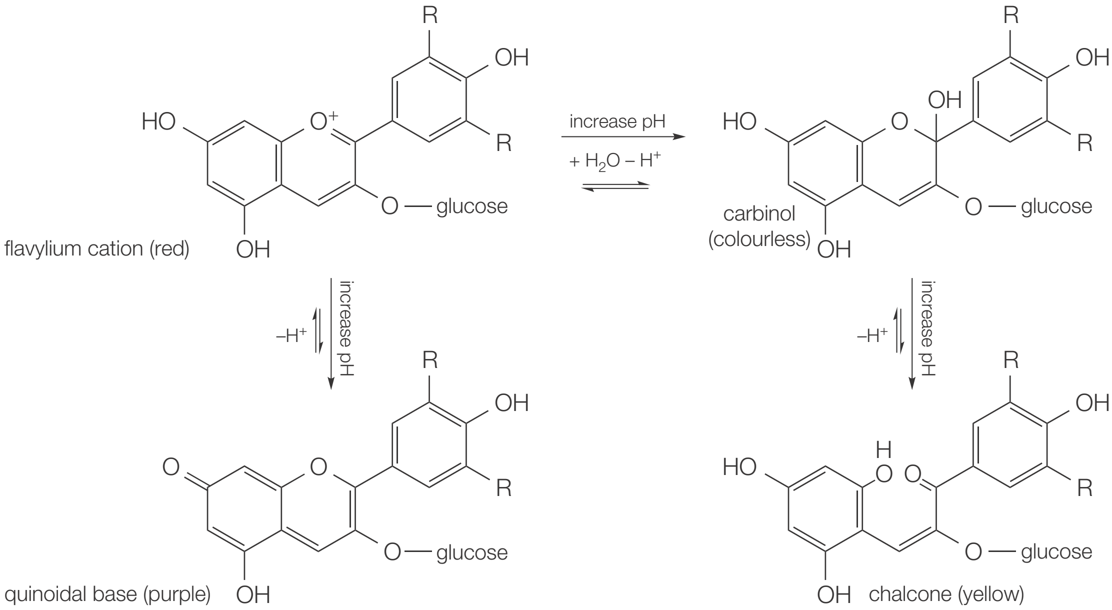
The colour of anthocyanin molecules is affected by the presence of cations, pH and temperature. They can act as acid–base indicators.

Anthocyanin molecules can act as ligands (Lewis bases) via their oxygens and can coordinate to cations, such as aluminium, iron(II) and iron(III) to form intensely coloured complexes.

A complex equilibrium exists in aqueous solution (Figure 23.84) with four different structural forms with different extents of conjugation:

A $\rightleftharpoons$ AH^+ $\rightleftharpoons$ B $\rightleftharpoons$ C
quinoidal base $\rightleftharpoons$ flavylium cation $\rightleftharpoons$ carbinol $\rightleftharpoons$ chalcone
purple/red $\rightleftharpoons$ red $\rightleftharpoons$ colourless $\rightleftharpoons$ yellow

Low values of pH favour the red flavylium form; high values of pH favour the yellow chalcone form. At intermediate pH values the purple quinoidal base and colourless carbinol form are at high concentrations in the equilibrium mixture. At low temperatures the red flavylium form predominates; at high temperatures the yellow chalcone form predominates.

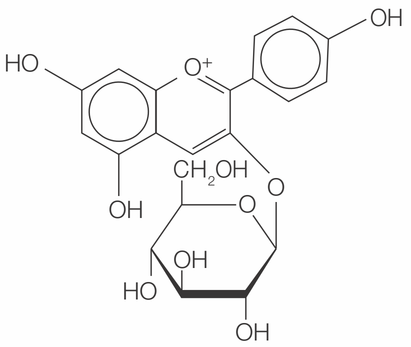


shorter conjugated chain – absorbs only UV light – colourless

Figure 23.84 A complex equilibrium, which is very sensitive to pH, exists in an anthocyanin solution

■ QUICK CHECK QUESTIONS

46 The colour of many flowers and fruits is due to the presence of anthocyanin pigments. The red colour of ripe strawberries is largely due to the anthocyanin pigment having the structure below.



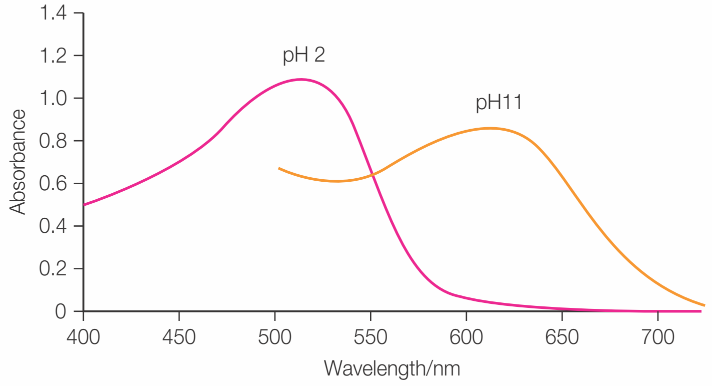
a Explain why this molecule absorbs visible light.

b By referring to its chemical structure, outline whether this pigment is found in aqueous solution in the cells or in the lipid-based membranes.

➜

47 Anthocyanins can act as pH indicators. An extract from blackberry juice produced the following absorption spectra at different pH values when analysed using a UV–Vis spectrophotometer:

Using information from section 17 of the IB Chemistry *data booklet*, deduce the colour of the extract at each of the pH values shown.



Carotenoids

Carotenoids are lipid-soluble plant pigments involved in the absorption of blue light during photosynthesis. The conjugated system in carotenoids is due to the presence of a long hydrocarbon chain consisting of an alternating series of single and double carbon–carbon bonds.

Many carotenoids, such as beta-carotene (Figure 23.85), are derived from a polyene chain containing 40 carbon atoms, which may have terminal cyclic groups and oxygen-containing functional groups.

β-Carotene (a precursor to vitamin A) is found in carrots and has a characteristic orange colour. It has a conjugated π-system involving 11 conjugated carbon–carbon double bonds. It appears orange when viewed in white light since its molecules absorb strongly in the violet-blue (400–510 nm region) of the electromagnetic spectrum.

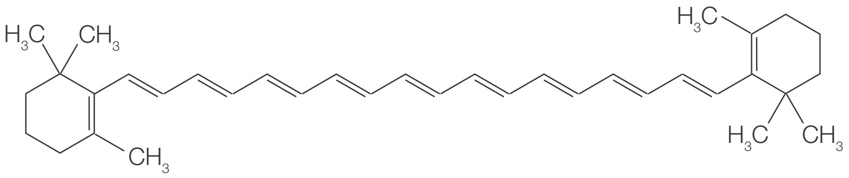


Figure 23.85 The structure of β-carotene

Owing to their polyunsaturated nature, carotenoids are susceptible to oxidation. This is a complex free radical reaction catalysed by light, transition metal cations and hydroperoxides (ROOH). At high temperatures carotenoids isomerize from the all-*trans* form into a mixture of *cis* isomers.

Expert tip

The carotenoids are divided into two groups: the carotenes, which are hydrocarbons, and the xanthophylls, which contain oxygen.

Porphyrins

The porphyrins are a series of related nitrogen-containing macrocyclic (large single ring with multiple donor sites) conjugated ligands that are able to strongly coordinate a specific metal cation. Examples of porphyrins and their cations are chlorophyll (Mg^{2+}), hemoglobin (Fe^{2+}), myoglobin (Fe^{2+}) and the cytochromes (Fe^{2+} and Fe^{3+}, depending on their oxidation state).

Hemoglobin

Hemoglobin is a protein found in mammals that transports molecular oxygen in the red blood cells. Oxygen binds cooperatively to hemoglobin, resulting in a sigmoidal (S-shaped) oxygen dissociation curve. It is a tetrameric protein – four protein molecules associated together. Each of the four globin proteins contains a heme group with an iron(II) ion at the centre (Figure 23.86).

Expert tip

This effect is due to small changes that occur in the quaternary structure as oxygen binds. A conformational shift caused by the binding of oxygen at one heme group makes the other heme groups have a higher affinity for oxygen.

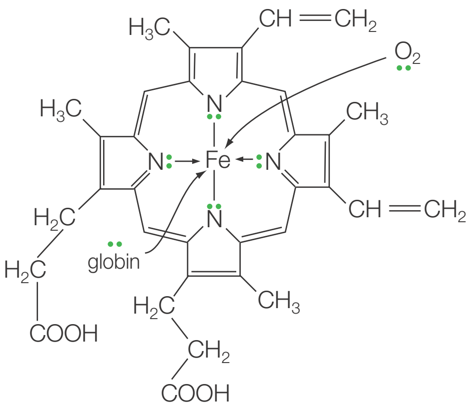


Figure 23.86 The structure of the heme group in hemoglobin

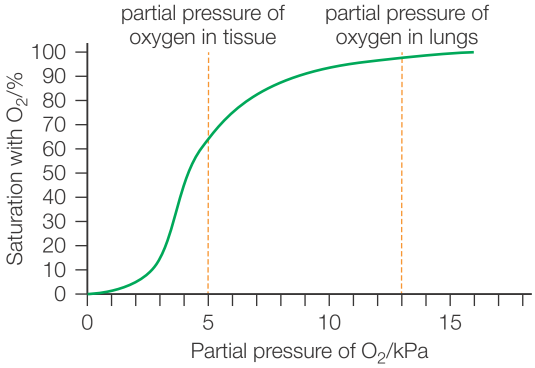


Figure 23.87 The oxygen binding or dissociation curve for hemoglobin. The partial pressure of oxygen is the pressure of the oxygen in a mixture of gases

The oxygen saturation of hemoglobin (Figure 23.87) is influenced by the following factors.

Common mistake

Do not confuse oxygen pressure with blood pressure. Oxygen pressure, oxygen partial pressure and oxygen tension are the same concept and are simply a measure of the concentration of oxygen in the blood.

pH

Hemoglobin can be protonated (at an amino acid side-chain) at a low value of pH (high concentration of protons), resulting in the dissociation (release) of oxygen as the protein undergoes a conformational change:

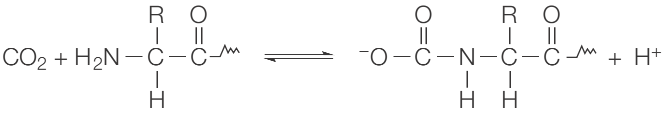
$$HbO_2 + H^+ \rightleftharpoons HbH^+ + O_2$$

Carbon monoxide

Carbon monoxide is a competitive inhibitor of oxygen at the iron(II) ion in the heme group. Hemoglobin has a higher affinity for carbon monoxide than oxygen. A strong coordinate bond is formed between the iron(II) ion and the lone pair of electrons on the carbon atom of carbon monoxide.

Carbon dioxide

Carbon dioxide reacts reversibly with water to form carbonic acid (H_2CO_3), which dissociates to form hydrogen carbonate, HCO_3^-(aq) and hydrogen ions, H^+(aq). This lowers the pH so that more H^+ binds to hemoglobin and causes a release of oxygen. Hemoglobin also binds carbon dioxide, but not at a different site from oxygen. This carbon dioxide reacts with the $-NH_2$ group on the terminal amino acid of each polypeptide chain that makes up hemoglobin (Figure 23.88) which releases H^+ and also changes the shape of the protein; both of these reduce the affinity of hemoglobin for oxygen.



$$CO_2 + H_2N-\underset{H}{\overset{R}{C}}-\overset{O}{\overset{\|}{C}}-\!\sim \rightleftharpoons {}^-O-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\underset{H}{\overset{R}{C}}-\overset{O}{\overset{\|}{C}}-\!\sim + H^+$$

Figure 23.88 The reaction of carbon dioxide with the terminal amino acid of a polypeptide chain

Common mistake

A frequent source of confusion is in distinguishing 'carboxyhemoglobin' from 'carbaminohemoglobin'. The first is hemoglobin combined with CO and the second is hemoglobin carrying CO_2.

Temperature

The dissociation of oxyhemoglobin ($HbO_2 \rightarrow Hb + O_2$) is an endothermic process. Hence, the position of equilibrium will shift to the right as the temperature is increased and less oxygen binds to hemoglobin.

Expert tip

When muscles are metabolically active they release heat and the hemoglobin provides with the increased oxygen required for respiration.

Fetal hemoglobin and myoglobin

Fetal hemoglobin is a different form of hemoglobin only present in the blood of the developing fetus. It has a higher affinity for oxygen than maternal hemoglobin (which replaces it after birth) (Figure 23.89). This adaptation allows the efficient transfer of oxygen from the mother's blood to the fetal blood in the placenta.

Myoglobin also has an oxygen dissociation curve to the left of that of hemoglobin, which means it has a greater affinity for oxygen and can accept oxygen from hemoglobin for storage (in the striated muscles).

QUICK CHECK QUESTION

48 Hemoglobin contains a heme group with an iron(II) ion.

a Outline how the oxygen saturation of hemoglobin is affected by changes in the blood plasma

b Explain why fetal hemoglobin has a greater affinity for oxygen than adult hemoglobin.

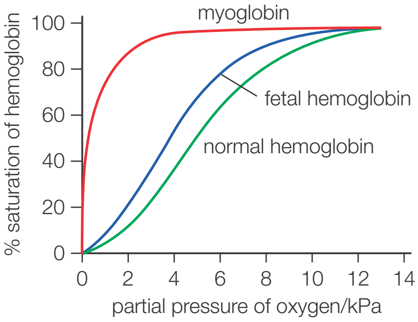


Figure 23.89 Dissociation curves for fetal hemoglobin and myoglobin

Expert tip

The dissociation curve for myoglobin is not sigmoidal in shape as there can be no cooperative binding within its one heme structure.

Cytochromes

Cytochromes are a varied group of electron transport proteins that contain a heme group which has an iron ion that alternates between iron(II) and iron(III). It is able to accept electrons from one substance and donate them to another (with a less negative electrode potential), functioning as part of the electron transport chain which is involved in the last step of the aerobic respiration of glucose. Cytochrome c passes its electrons to the terminal acceptor oxygen with the formation of water:

$$4Fe^{2+}_{(cytochrome\ c)} + 4H^+ + O_2 \rightarrow 4Fe^{3+}_{(cytochrome\ c)} + 2H_2O$$

Expert tip

Cyanide ions are a very effective poison because they block this reaction and prevent respiration.

Chlorophyll

Chlorophylls are the main photosynthetic pigments in leaves and are involved in absorbing the light needed in the process of photosynthesis. Chlorophyll molecules ionize and donate an electron to the electron transport chain.

Chlorophyll (Figure 23.90) occurs in plants in two closely related forms: chlorophyll a (blue green) and chlorophyll b (yellow green).

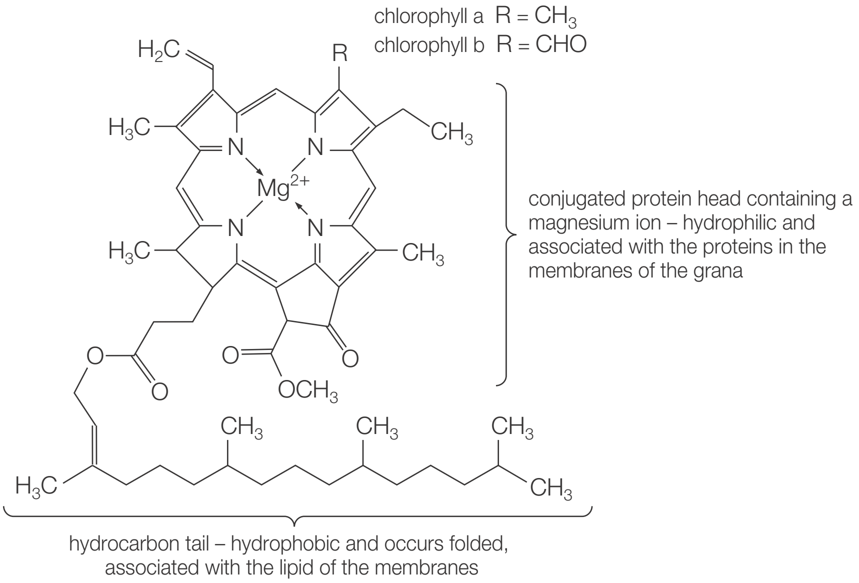


Figure 23.90 The structure of chlorophyll

Chlorophyll absorbs light strongly in the blue part of the spectrum and to a lesser extent in the red (see Figure 23.91) and hence leaves appear green (when viewed in white light). The chromophore is the conjugated porphyrin ring system.

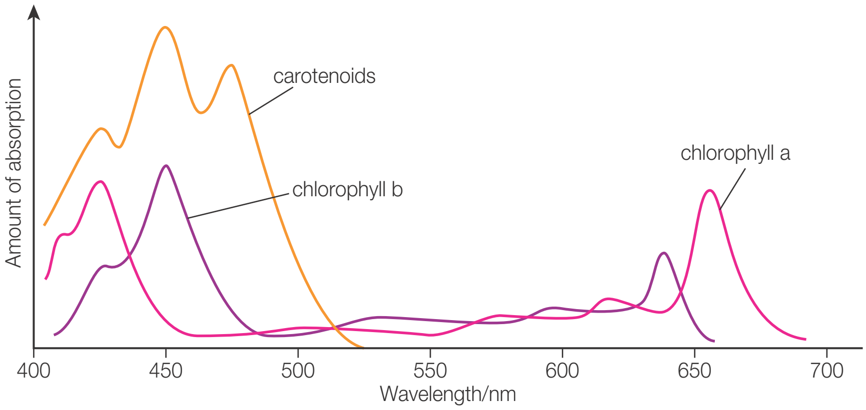


Figure 23.91 Ultraviolet spectrum of chlorophyll a, chlorophyll b and carotenoids

The stability of chlorophyll is affected by pH: in highly acidic conditions (pH < 3) the central magnesium ion, Mg^{2+}, is replaced by a proton (H^+). Chlorophyll will undergo decomposition at high temperatures and in the presence of high intensity ultraviolet radiation.

Chromatography

Chromatography is based upon the differential retention of compounds in a mobile phase as they pass through or across a stationary phase. It can be used to separate, identify, identify and quantify the component pigments (or dyes) in a mixture.

In paper chromatography, the stationary phase is a liquid adsorbed onto the surface of the paper. The paper has many pores that can adsorb and strongly hold hydrogen bond water molecules to form the stationary phase. The water can be displaced by other liquids to give different stationary phases.

Pigments that are more soluble in the solvent than they are in the water molecules of the stationary phase move rapidly up the paper, while those that are more soluble in the water are not carried as far up the paper (Figure 23.92).

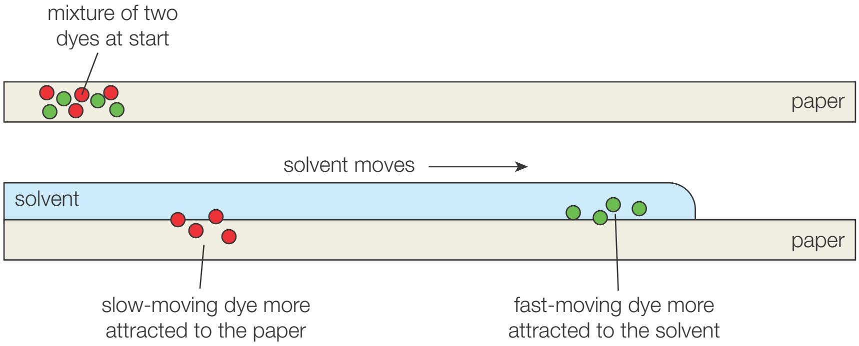


Figure 23.92 The principles of paper chromatography

Thin layer chromatography (TLC) uses a stationary phase of silica or alumina particles bonded to a thin layer of glass or plastic. TLC (Figure 23.93) separates a mixture of pigments based on how strongly they are adsorbed on the stationary phase and dissolved in the mobile phase (a liquid or mixture of liquids). This equilibrium is known as partitioning. The greater the affinity of the pigment for the stationary phase, the more slowly it moves along the surface of the TLC plate.

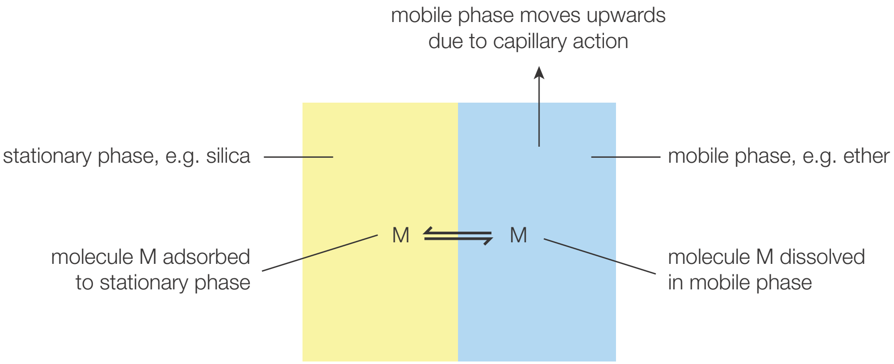


Figure 23.93 Principles of TLC

Expert tip

TLC is faster, more sensitive and has better resolution than paper chromatography.

23.10 Stereochemistry in biomolecules

Revised ☐

Essential idea: Most biochemical processes are stereospecific and involve only molecules with certain configuration of chiral carbon atoms.

Stereochemistry in biomolecules

Revised ☐

- With one exception, amino acids are chiral, and only the L-configuration is found in proteins.
- Naturally occurring unsaturated fat is mostly in the *cis* form, but food processing can convert it into the *trans* form.
- D and L stereoisomers of sugars refer to the configuration of the chiral carbon atom furthest from the aldehyde or ketone group, and D forms occur most frequently in nature.
- Ring forms of sugars have isomers, known as α and β, depending on whether the position of the hydroxyl group at carbon 1 (glucose) or carbon 2 (fructose) lies below the plane of the ring (α) or above the plane of the ring (β).
- Vision chemistry involves the light-activated interconversion of *cis-* and *trans-* isomers of retinal.

Chirality

Revised ☐

Enantiomers are a pair of molecules related as non-superimposable images ('mirror images'). Molecules with sp^3 hybridized carbon atoms bonded to four different atoms/ groups show chirality due to their tetrahedral shape. Figure 23.94 shows the enantiomers ('optical isomers') of the amino acid, alanine. All amino acids can exist as a pair of enantiomers except glycine (2-amino ethanoic acid).

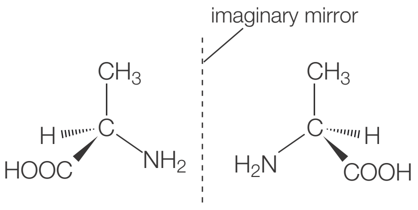


Figure 23.94 Enantiomers of alanine

Fischer projections

Fischer projections (Figure 23.95) attempt to show three-dimensional structure using a two-dimensional framework of vertical and horizontal bonds. The main carbon chain is drawn as a vertical line, and bonds to all substituents (atoms or groups of atoms) are drawn as horizontal lines. All vertical lines represent bonds behind the plane of the page, and horizontal lines bonds coming out of the plane towards the viewer.

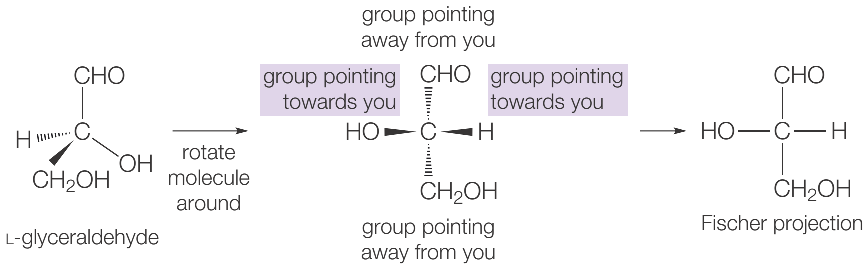


Figure 23.95 Deriving a Fischer projection for glyceraldehyde, starting from a tetrahedral model and moving to a line drawing

When shown in Fischer projection, if the –OH group on the highest numbered chiral carbon is on the right, the molecule is assigned the label D; if the –OH group is on the left, it is given the label L. These notations are known as absolute configurations and often used to describe amino acids and monosaccharides.

Expert tip

The amino acids that make up the majority of proteins exist in the L configuration; most naturally monosaccharides exist in the D configuration.

Stereoisomerism in monosaccharides

Fischer projections are a method of representing the structure of any straight-chain forms of a sugar by projection on to a plane. In a Fischer projection, the sugar molecule is shown with the carbon numbered 1 at the top – according to the normal naming rules the aldehyde/ketone group will be given the lowest possible number (Figure 23.96).

In sugars, such as ribose or glucose (see Figure 23.97), the tetrahedral centres are simply stacked on top of each other, with the aldehyde group at the top.

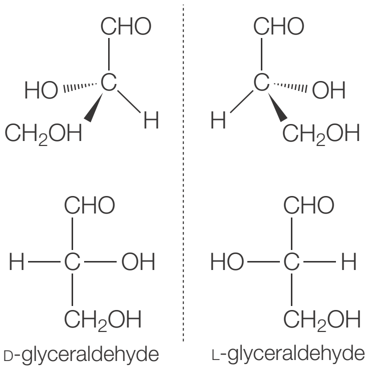


Figure 23.96 The structures of D- and L-glyceraldehyde (a C_3 monosaccharide), showing the Fischer projections

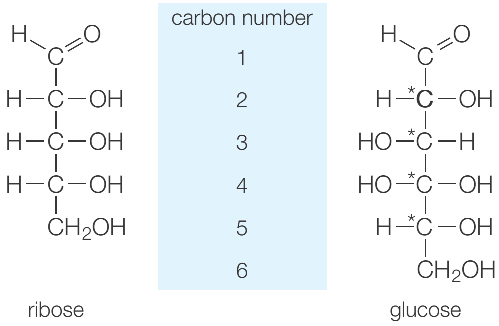


Figure 23.97 Open-chain structures of ribose and glucose. These structures are drawn as Fischer projections, which enables stereoisomers to be compared easily

Cyclic forms of monosaccharides

The conversion of sugars in the straight-chain form to the ring form creates α- and β-isomers (Figure 23.96) known as anomers. These differ by the relative position of the hydroxyl substituent attached to the carbon atom derived from the aldehyde or ketone carbon in the open chain form of the sugar.

When a sugar cyclizes from the straight-chain (linear) form, an extra chiral carbon is formed (Figure 23.98). The lone pair of electrons on the oxygen atom on carbon 5 can attack the carbonyl group (>C=O) from either above the plane of the group or below. Two cyclic molecules can therefore be formed: α- and β-forms. If the –OH on the new chiral carbon (anomeric carbon) is above the ring when the structure is drawn with the ring oxygen at the rear then it has β configuration (the –OH is on the same side of the ring as carbon-6), and if it is beneath then it is α.

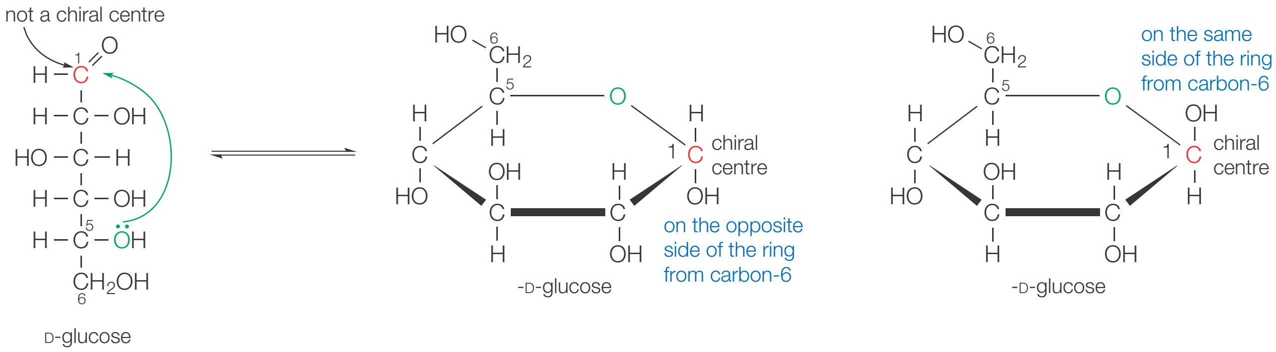
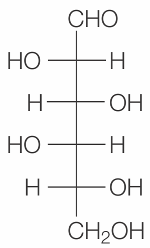


Figure 23.98 The structures of glucose in aqueous solution; the formation of the cyclic (ring) structures

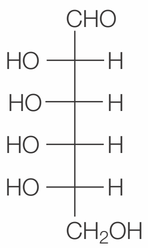
QUICK CHECK QUESTIONS

49 Examine the structures of monosaccharides **A**, **B** and **C** and determine whether each of the sugars shown below is the D-form or the L-form:

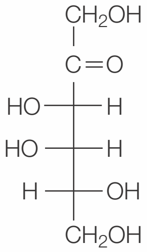
A



B

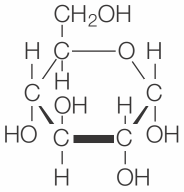


C

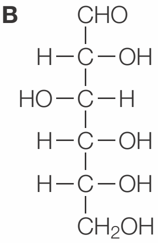


50 Glucose is an example of an aldohexose sugar which dissolves in water. In aqueous solution, glucose exists in three different structures which are in equilibrium with each other. The three structures are shown below:

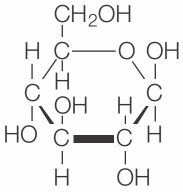
A



B



C



a What chemical term is used to describe the different forms shown above?

b Explain why glucose is very soluble in water.

c Which of the two cyclic forms of glucose can be described as α-glucose?

Vision chemistry

The visual cycle (Figure 23.99) is a process by which light (photons) are converted into an electrochemical signal in the cells of the retina lining the eye. Rhodopsin consists of the protein opsin and a covalent bonded co-factor retinal, which is synthesized from vitamin A. Retinal acts as the chromophore.

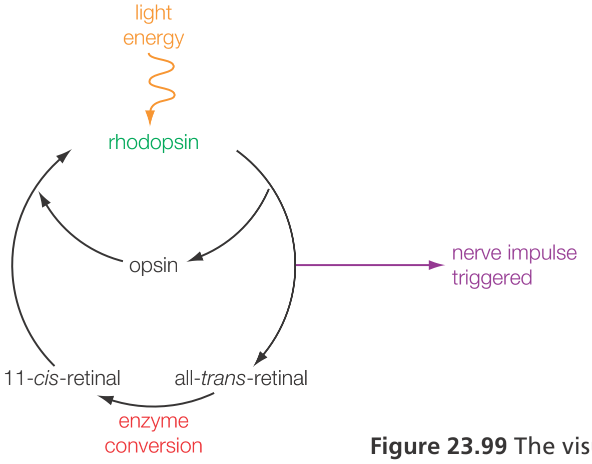


Figure 23.99 The visual cycle

The absorption of light converts the *cis* form of retinal (11-*cis*-retinal) to the *trans* form (all *trans*-retinal) (Figure 23.100). This causes the all-*trans*-isomer to dissociate from the opsin, which ultimately causes a nerve impulse to the brain. Rhodopsin is regenerated from opsin and 11-*cis*-retinal after the all-*trans* form has isomerized back to the 11-*cis* form in a series of steps catalysed by enzymes.

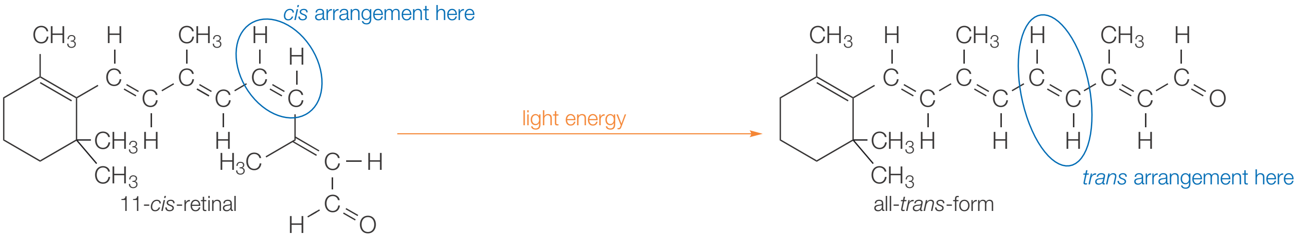
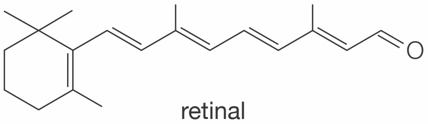


Figure 23.100 The light-induced transformation of 11-*cis*-retinal to all-*trans*-retinal

■ QUICK CHECK QUESTIONS

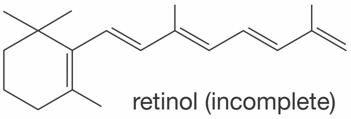
51 a The rod cells in the retina at the back of the eye contain a primary alcohol called retinol which is responsible for their sensitivity to visible light. Retinol is oxidized by an enzyme-catalysed reaction to the aldehyde retinal.



retinal

i Deduce the molecular formula of retinal from its skeletal formula shown above.

ii Suggest the structure of the alcohol retinol by completing the skeletal formula below.



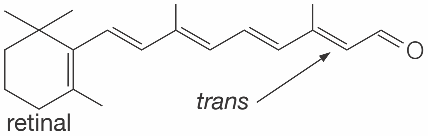
retinol (incomplete)

iii Identify a functional group which is present in both the retinol and retinal molecules.

iv Outline the reagents and conditions could be used to convert an alcohol to an aldehyde in a laboratory.

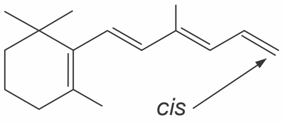
v Deduce how many moles of hydrogen molecules you would expect to react with one mole of retinol (in the presence of a heated nickel catalyst).

b When light enters the rod cells of the eye, an enzyme-catalysed reaction occurs. This changes the arrangement around the double bond at position 11 from *trans* to *cis*, as indicated in the following structure.



retinal

i Suggest the structure of *cis*-retinal by completing the skeletal formula below.

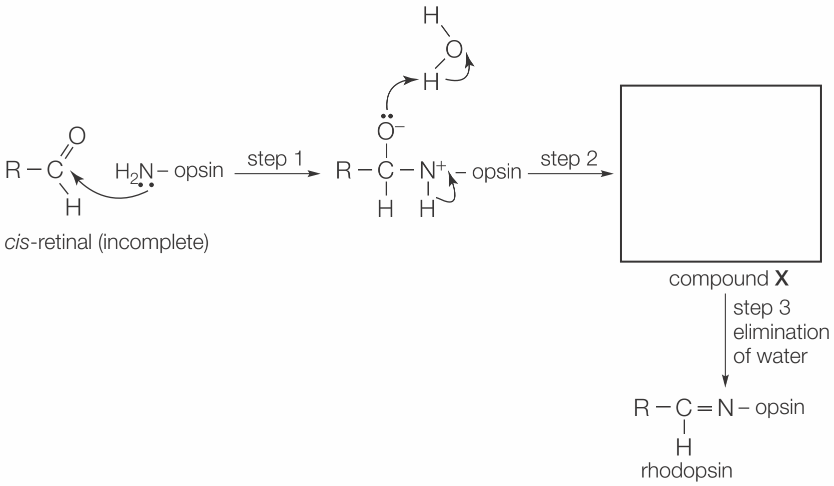


cis-retinal (incomplete)

ii The *cis*-retinal bonds covalently to the protein opsin to form rhodopsin. Part of the mechanism of this reaction is shown below. State the name of the functional group on opsin which is reacting with the aldehyde group on the *cis*-retinal molecule.

iii State the type of reaction mechanism which starts in step 1 and is completed in step 2.

iv Deduce a structure for compound **X** that would be drawn in the box below.



24

Option C Energy

24.1 Energy sources

Revised ☐

Essential idea: Societies are completely dependent on energy resources. The quantity of energy is conserved in any conversion but the quality is degraded.

Energy sources

Revised ☐

- A useful energy source releases energy at a reasonable rate and produces minimal pollution.
- The quality of energy is degraded as heat is transferred to the surroundings. Energy and materials go from a concentrated into a dispersed form. The quantity of the energy available for doing work decreases.
- Renewable energy sources are naturally replenished. Non-renewable energy sources are finite.

$$\text{Energy density} = \frac{\text{energy released from the fuel}}{\text{volume of fuel combusted}}$$

$$\text{Specific energy} = \frac{\text{heat energy released from fuel}}{\text{mass of fuel consumed}}$$

$$\text{The efficiency of an energy transfer} = \left(\frac{\text{useful output energy}}{\text{total input energy}}\right) \times 100$$

Introduction

Revised ☐

Energy is the ability to do work. In thermodynamics the most common form of work is expansion work, the work due to the change in volume of a gas. This occurs in power stations that use expanding steam to drive turbines.

The global society depends on various renewable and non-renewable energy sources. Energy is transferred from sunlight (solar energy), moving water (tides), moving air (wind), fuels (biomass and fossil fuels) and nuclear ‘fuel’ and converted to a more useful form: heat or electricity (from photovoltaics or power stations).

A primary energy source refers to a source which occurs naturally and has not been processed. When a primary source is converted into another, more useful resource it is then a secondary energy source.

For example, crude oil (petroleum) refined into petrol, processing uranium into plutonium, or the generation of electricity. The original source of most of the energy consumed on the Earth is the Sun.

However, no energy transfer is 100% efficient and with each conversion the quality is degraded as some of the available energy is dispersed (spread out) – increasing the entropy of the surroundings – or converted to thermal energy (heat).

NATURE OF SCIENCE

Converting energy from one form to another is due to potential and kinetic changes at the molecular, atomic, electronic or nuclear level. Exothermic reactions, such as combustion, and exothermic changes of state, such as condensation, release thermal energy which can increase the kinetic energy of the surrounding molecules. The usefulness of the energy decreases as it is more dispersed.

Thermodynamics is the study of the transfer of heat between a chemical system and its surroundings when a chemical reaction or change of state takes place within the system. Thermodynamics is based on two fundamental laws.

The first law states that energy cannot be created or destroyed, only changed from one form to another. Another expression is that the energy of an isolated system remains constant. The second law of thermodynamics states that the entropy of the universe is increasing. Another expression of this law is that it is not possible for heat energy to flow spontaneously from a cold object to a hot object.

Quality of energy

Revised ☐

The available energy is the energy that can be used to do work. A good example of a thermodynamic system is gas confined by a piston in a cylinder. If the gas is heated, it will expand, doing work on the piston.

For example, water has a relatively large specific heat capacity, so a large body of water contains a large amount of heat. The major problem in getting some of this heat from a body of water in order to do work is that usually there is a small temperature difference between the upper part of the body of water and the atmosphere. The quality of this heat is low. However, if you take some of this water and put it into a boiler, converting it to steam, you have made a high-quality source of energy.

Hence, in many cyclical processes designed to convert thermal energy to do work, some energy is degraded, that is, it is no longer available to do useful work, so the quality of the energy has decreased. The steam engine, in very basic terms, is a heat engine and flow of heat from one region to another produces useful work. Carnot proposed the heat engine concept (Figure 24.1).

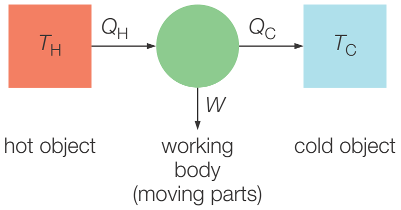


Figure 24.1 Carnot's heat engine. The thermal energy flows (Q_H, Q_C) from the hot body (T_H) to the cold body (T_C) via the working body (the circle). This working body does useful work (W) on the surroundings

Availability

Revised ☐

In many parts of the world, availability of fuel is the most important factor. About half the world's population (3 billion people) burns solid fuels (usually very inefficiently) that are easily obtainable locally: wood, coal, charcoal, crop waste, dried dung, all examples of biomass, or coal.

In developed countries, natural gas (mainly methane), liquid hydrocarbons and electricity are common, but these energy sources require more infrastructure to bring them to the population. Liquefied natural gas (e.g. propane or butane) can be piped into homes, or provided in portable pressurized bottles for cooking. Liquid hydrocarbons (petrol and diesel) are provided at filling stations by the roadside for easy filling of motor vehicle fuel tanks.

Electricity is provided by a power grid, which typically extends across the entire country via overhead or underground cables. However, the electricity not a source of energy in itself – it must be generated.

Energy sources

Revised ☐

Crude oil (petroleum) is the source of the majority of chemical fuels used in power stations (to generate electricity) and vehicles. Fuels derived from crude oil (petroleum) include: petrol (gasoline), paraffin (kerosene) and diesel fuel, which are all hydrocarbon mixtures. Other chemical fuels include alcohols and hydrogen gas.

These fuels, natural gas (mainly methane) and coal (mainly carbon) are all fossil fuels and contain stored chemical energy from photosynthesis. These are all non-renewable energy resources since the formation of fossil fuels from plant and animal remains takes hundreds of millions of years. Energy from nuclear fission is also non-renewable since it relies upon a limited supply of fissionable uranium.

Renewable energy sources include hydroelectric, wind, geothermal, tidal, solar and wave power as well as biofuels (such as ethanol produced by fermentation) and photovoltaics, the conversion of solar (light) energy to electrical energy.

All of these energy sources can be used to generate electricity via the boiling of water to form steam and use of turbines and a generator (dynamo). None of these processes are 100% efficient, energy is transferred to the surroundings as heat and heat is also generated (because of electrical resistance) when electricity is transmitted via power lines.

Choice of fuel

Revised ☐

The choice of fuel depends on a number of factors: economic factors, such as abundance and cost of extraction, ease and cost of transport and a range of chemical and physical properties.

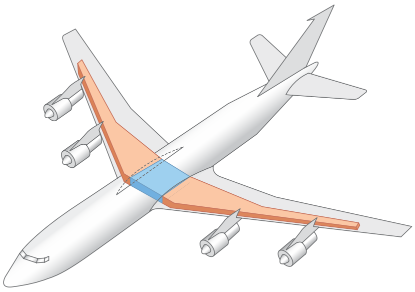


Figure 24.2 Layout of a modern airliner's main fuel tanks; specific energy of Jet-A1 fuel is 43.15 MJ kg^{-1}; energy density is 34.7 MJ dm^{-3}

Important properties include:

- Enthalpy of combustion, the amount of heat released when one mole of the fuel undergoes complete combustion. In real-life applications it is more useful to consider the energy that can be provided by the combustion of a certain volume or mass of the fuel, as this will influence the ease of transporting the fuel (Figure 24.2).

  $$\text{Energy density} = \frac{\text{energy released from the fuel}}{\text{volume of fuel combusted}}$$

  $$\text{Specific energy} = \frac{\text{heat energy released from fuel}}{\text{mass of fuel consumed}}$$

- **Energy density** is defined as the energy released from a fuel per unit of volume consumed (combusted). An energy density is usually quoted in megajoules per cubic metre, MJ m^{-3}.

  $$\text{Energy density} = \frac{\text{energy released from fuel}}{\text{volume of fuel consumed}}$$

  A higher energy density means more thermal energy (heat) is released per volume of fuel consumed and a smaller fuel tank is required. A lower energy density means a larger fuel tank. Thus the energy density in MJ m^{-3} is a very useful concept for identifying the space or volume requirements for the storage of a liquid fuel.
- **Specific energy** is defined as the energy released from a fuel per unit mass of fuel combusted (consumed), often quoted as megajoules per kilogram, MJ kg^{-1}:

  $$\text{Specific energy} = \frac{\text{energy released from fuel}}{\text{mass of fuel consumed}}$$

  A higher specific energy means more thermal energy (heat) is released per kilogram of fuel combusted (consumed) and a smaller mass of fuel is required, and hence less fuel has to be carried.

  A lower specific energy means more fuel has to be carried. Hence the specific energy in megajoules per cubic kilogram, MJ kg^{-3}, is a very useful concept for identifying the mass of fuel that has to be carried. It is also an indication of how much fuel has to be transported which requires fuel and thus decreases its overall efficiency.

Expert tip

One issue with problems dealing with solving problems on energy density and specific energy are unit conversions. Recall that 1 litre is one cubic decimetre; $1000\,\text{cm}^3 = 1\,\text{dm}^3$. In addition, $1\,\text{kg} = 1000\,\text{g}$ and $1\,\text{m}^3 = (10\,\text{dm} \times 10\,\text{dm} \times 10\,\text{dm}) = 1000\,\text{dm}^3$, hence $1\,\text{g dm}^{-3} = 1\,\text{kg m}^{-3}$. $1\,\text{m}^3 = 10^6\,\text{cm}^3$.

■ QUICK CHECK QUESTIONS

1. Calculate the specific energy and energy density of undecane, $C_{11}H_{24}$. It has a density of 0.740 g cm^{-3} and its enthalpy of combustion is −7434 kJ mol^{-1}. The molar mass of undecane is 156.31 g mol^{-1}.
2. Propan-1-ol is a solvent which may be used as a fuel. It has a density of 0.803 g cm^{-3} and its enthalpy of combustion is −2.02106 MJ mol^{-1}. It is produced by the hydration of propene, but trace amounts are formed during fermentation.
   - a Calculate the energy density and specific energy for propan-1-ol. The molar mass of propan-1-ol is 60.11 g mol^{-1}.
   - b Write a balanced equation for the complete combustion of propan-1-ol. State the amount (in mol) of carbon dioxide produced per mole of propan-1-ol combusted.
3. Explain why the production of ethanol by fermentation is regarded as being ‘green’ or environmentally friendly.

Table 24.1 shows energy data for a range of alcohols.

Table 24.1 Values of energy density and specific energy for alcohols

Alcohol	Molar mass/g mol^{-1}	Molar mass/ kg mol^{-1}	Enthalpy of combustion/ kJ mol^{-1}	Enthalpy of combustion/ MJ mol^{-1}	Density/ g cm^{-3} or kg dm^{-3}	Molar volume/ dm^{3}	Energy density/ MJ dm^{-3}	Specific energy/ MJ kg^{-1}
CH_3OH	32.05	0.03205	726	0.726	0.792	0.0405	17.9	22.7
C_2H_5OH	46.1	0.0461	1367	1.367	0.789	0.0584	23.4	29.7
C_3H_7OH	60.1	0.0601	2021	2.021	0.803	0.0748	27.0	33.6
C_4H_9OH	74.1	0.0741	2676	2.676	0.81	0.0915	29.3	36.1

Note that, as the enthalpy of combustion increases with molar mass in Table 24.1, so does the specific energy. Also, since an increase in density decreases the volume of liquid (density = mass/volume) and volume appears in the denominator in the energy density equation, then an increase in density produces a higher specific energy for the fuel (if all other factors are constant).

Table 24.2 Energy density and specific energy of hydrogen gas, natural gas (methane), propane and butane

Gaseous fuel	Molar mass/ g mol^{-1}	Molar mass/ kg mol^{-1}	Enthalpy of combustion/ kJ mol^{-1}	Enthalpy of combustion/ MJ mol^{-1}	Density/g cm^{-3} or kg dm^{-3}	Molar volume (at STP)/dm^{3}	Energy density/ MJ dm^{-3}	Specific energy/ MJ kg^{-1}
H_2	2.02	0.00202	286	0.286	0.0902	22.7	0.0128	141.6
CH_4	16.05	0.01605	891	0.891	0.717	22.7	0.0398	55.5
C_3H_8	44.10	0.0441	2219	2.219	1.968	22.7	0.0990	50.3
C_4H_{10}	58.14	0.05814	2878	2.878	2.596	22.7	0.1285	49.5

Consider the energy density and specific energy of gaseous fuels such as hydrogen gas, natural gas (methane) and propane (Table 24.2). The calculation of energy density is more relevant in these cases since the gases occupy much larger volumes compared with liquid fuels, even when the gases are compressed.

Hence hydrogen gas has a high specific energy per mass compared with hydrocarbons and alcohols. However, the energy density comparison per volume is quite low, suggesting that much larger volumes of gas would be required for similar energy densities.

Even though 1 kg of hydrogen gas contains approximately 2.55 times the energy of methane (141.6 5 MJ kg^{-1} compared to 55.5 MJ kg^{-1}) and even more compared with fossil fuels, it is inefficient in terms of its production and use, not to mention issues with its delivery and use of larger, heavier tank storage, relative to the same amount of energy for use in automobiles (cars) or fuel cells.

A comparison of energy density and specific energy values for an alcohol and a hydrocarbon of similar molar masses show that the hydrocarbon has higher values (Table 24.3). This is due to the partial oxidation state of the alcohol compared to the hydrocarbon.

Table 24.3 Energy density of ethanol, gasohol and gasoline (petrol)

Fuel	Energy density/MJ dm^{-3}	Specific energy/MJ kg^{-1}
Ethanol	23.4	29.7
Gasohol	28	43
Petrol	Approximately 35	Approximately 47

Gasohol is a mixture of 10% ethanol and 90% petrol by mass. Gasohol is widely used in cars as fuel in South American countries with limited crude oil supplies. The alcohol is made by fermentation (see Section 24.4).

Efficiency

Revised ☐

The efficiency of an energy transfer is defined as the useful output of energy divided by the total input of energy quoted as a percentage.

$$\text{Efficiency} = \left(\frac{\text{useful output energy}}{\text{total input energy}}\right) \times 100$$

A higher percentage efficiency of an energy transfer means more useful output of energy is available from the total energy input.

The concept of efficiency can also be displayed graphically by means of a Sankey diagram (Figure 24.3). Consider the example of an incandescent light bulb in which a large proportion of the electrical energy is wasted as heat energy to the surroundings instead of light energy. Efficiency = (10 J / 100 J) × 100 = 10% efficiency.

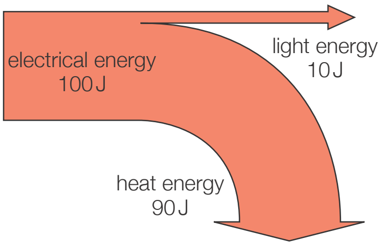


Figure 24.3 Sankey diagram for an incandescent light bulb

In the last 60 years, the efficiency of solar or photovoltaic cells (see Section 24.8) has been increased from about 2% to 45%. Photovoltaic cells convert light energy (solar energy) into electrical energy.

Electricity is generated in the same way in power plants including a nuclear power plant. Heat is used to boil water and convert it into steam; this turns turbines, which generates electricity using a generator (dynamo). The energy losses are approximately 65% in each case; only 35% of the chemical (potential) energy present in the fuel is converted to electrical energy. The energy efficiency of various devices and applications is given in Table 24.4.

Table 24.4 Energy transfers and efficiencies of various devices and processes

Device	Energy transfer	Efficiency
Electric heater	Electrical → thermal	nearly 100%
Battery	Chemical → electrical	90%
Hydroelectric	Kinetic → electrical	90%
Home gas furnace (boiler)	Chemical → thermal	85%
Home oil furnace (boiler)	Chemical → thermal	65%
Nuclear reactor (fission; boiling water)	Nuclear → thermal	32%
Home coal furnace (boiler)	Chemical → thermal	55%
Wind power	Kinetic → electrical	26%
Geothermal power	Thermal → electrical	16%
Photovoltaic cell	Light (solar energy) → electrical	15%
Incandescent light bulb	Electrical → light	5%
Photosynthesis (in a leaf)	Light (solar energy) → chemical	1%

Discussion of advantages and disadvantages of energy sources

Revised ☐

The advantages and disadvantages of several different energy sources are summarized and discussed in Table 24.5.

Table 24.5 Summary of the advantages and disadvantages of energy sources

Source	Where does it come from?	Renewable or non-renewable?	Advantages	Disadvantages
Coal	Fossilized plants found in seams between layers of rock in the Earth. Mostly made up of carbon with some inorganic impurities such as sulfur. Mined by drilling shafts into the Earth.	Non-renewable	Cheap to extract. High specific energy. Large infrastructure already exists for transport and burning. Coal reserves will last much longer than crude oil reserves.	Releases carbon dioxide when burned – a greenhouse gas. Sulfur impurities release sulfur dioxide when burned, which leads to acid rain – power station emissions must be scrubbed to remove this.
Oil	Fossilized animal remains in liquid form, found soaked into layers of porous rock in the Earth. A layer of non-permeable rock above the oil reservoir prevents it from escaping. Pipes are sunk into the Earth to release the oil and it is pumped to the surface.	Non-renewable	Cheap to extract. High specific energy. Large infrastructure already exists for transport and burning. Different crude oil fractions have various physical properties making them suitable for many different fuel applications. Also a chemical feedstock for plastics industry and pharmaceutical industry.	Releases carbon dioxide when burned – a greenhouse gas. Will run out quite soon – conventional reserves may have already peaked.
Natural gas	Usually associated with crude oil. Natural gas consists of lighter molecules (mostly methane, CH_4) which are gaseous at surface pressure and temperature. Pipes are sunk into the Earth to release the oil and it is pumped to the surface.	Non-renewable	Cheap to extract. High specific energy. Energy is easily released – simply burn it. Large infrastructure already exists for transport and burning. Can be piped directly into homes.	Releases carbon dioxide when burned – a greenhouse gas. Will run out quite soon.
Nuclear	Uranium is mined and refined. Nuclear 'chain reaction' involving fission of uranium nuclei generates large amounts of heat. Heat used to generate steam which can then generate electricity via turbines.	Non-renewable	Uranium is cheap to mine. Enormous specific energy. Fission process itself generates no carbon dioxide or other greenhouse gases.	Uranium reserves are finite, although some reactor types can regenerate nuclear fuel. Nuclear waste is highly radioactive, long-lasting, and difficult to dispose of safely. Danger of weapons proliferation.
Wind	Wind turns turbines that generate electricity.	Renewable	In order to produce a useful amount of electricity large numbers of turbines are placed together in a 'wind farm'.	Some people object to wind farms on the grounds that the noise and appearance spoil the landscape. The wind does not always blow – wind farms are more effective in some regions than others.
Solar	Sunlight falls on a solar panel which captures its energy and converts it into electricity.	Renewable	In theory, solar power could offer infinite supplies of energy, especially in very hot, sunny countries.	Currently, solar panels are inefficient and too costly to be adopted widely.

Source	Where does it come from?	Renewable or non-renewable?	Advantages	Disadvantages
Tidal/wave	Energy from water moving back and forth is captured by underwater turbines and used to generate electricity (Figure 24.4).	Renewable	Countries with long coastlines could potentially benefit from tidal or wave power.	Only suitable for countries with long coastlines. Infrastructure is costly and technology is undeveloped. Tidal or wave generators need to be very robust and reliable to resist conditions at sea.
Hydroelectric power (HEP)	Flow of water from high ground towards oceans is used to generate electricity. A river is dammed, and the flow of water through the dam is used to turn turbines.	Renewable	In suitable geographical locations, HEP offers a clean, cheap electricity supply.	Limited to mountainous areas. Building dams often requires flooding of surrounding areas which may displace populations and lead to loss of biodiversity. Dammed rivers also lead to build-up of silt and affects the river ecosystem.
Biofuels	Plant or animal material is used to make a liquid or gaseous fuel. Bio-diesel is an oil extracted from plants such as palm trees. Ethanol can be made from corn (maize), sugar cane, or the inedible cellulose from grasses or plant waste. Biogas is made by fermenting plant or animal waste.	Renewable	In theory, biofuels are 'carbon-neutral' – the carbon that is released when they are burned is the same carbon that they absorbed during photosynthesis. Liquid biofuels allow existing fuel infrastructure and technology to be retained as they are a direct replacement for fossil fuels.	Only renewable if plants are replanted. In some countries tropical rainforest has been replaced with palm oil and sugar cane plantations, leading to loss of biodiversity. Some methods of extraction of biofuels are very energy inefficient. Economic demand for biofuels leads to countries displacing food crops. This could lead to lack of food for population.
Wood/charcoal	Trees can be cut and burned for energy. Slowly roasting wood in the absence of oxygen drives off water and forms charcoal, which has a higher energy density.	Renewable	Wood is widely available to most of the Earth's population and is a convenient source of energy for cooking and heating.	Wood is only renewable if trees are replanted. Often, wood is burned in highly inefficient open fires and stoves, with particulate emissions.
Geothermal	Water is pumped into the Earth where the natural heat turns it into steam. The steam can be used directly for heating, or used to generate electricity.	Renewable	Geothermal energy is most practical in regions where there is a lot of volcanic activity.	Infrastructure can be difficult to engineer, and is costly.

One example of a renewable energy source mentioned in Table 24.5 is tidal power. This tidal electricity generation works as the tide comes in and again when it goes out (Figure 24.4). The turbines are driven by the power of the sea in both directions.

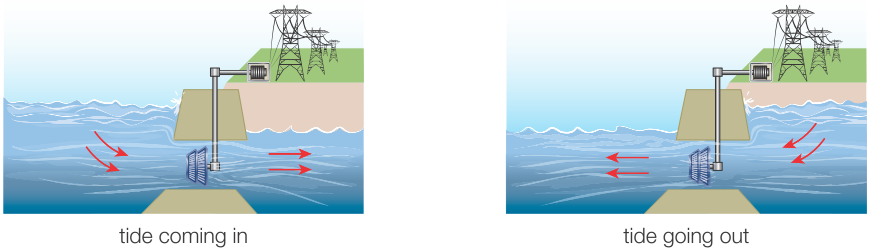


Figure 24.4 Tidal power captures the energy of tidal water moving backwards and forwards.

■ QUICK CHECK QUESTION

4 Outline why it is important for scientists to collaborate internationally when conducting research into alternative energy sources to fossil fuels.

24.2 Fossil fuels

Revised ☐

Essential idea: The energy of fossil fuels originates from solar energy which has been stored by chemical processes over time. These abundant resources are non-renewable but provide large amounts of energy due to the nature of chemical bonds in hydrocarbons.

Fossil fuels

Revised ☐

- Fossil fuels were formed by the reduction of biological compounds that contain carbon, hydrogen, nitrogen, sulfur and oxygen.
- Petroleum is a complex mixture of hydrocarbons that can be split into different component parts called fractions by fractional distillation.
- Crude oil needs to be refined before use. The different fractions are separated by a physical process in fractional distillation.
- The tendency of a fuel to auto-ignite, which leads to ‘knocking’ in a car engine, is related to molecular structure and measured by the octane number.
- The performance of hydrocarbons as fuels is improved by the cracking and catalytic reforming reactions.
- Coal gasification and liquefaction are chemical processes that convert coal to gaseous and liquid hydrocarbons.
- A carbon footprint is the total amount of greenhouse gases produced during human activities. It is generally expressed in equivalent tons of carbon dioxide.

Formation of fossil fuels

Revised ☐

Fossil fuels are chemical fuels that were formed by the anaerobic decay (in the absence of molecular oxygen) of biological material, which was buried and acted upon by bacteria over hundreds of millions of years.

Fossil fuels are rich stores of chemical energy, because they are stores of solar energy, which powered the photosynthetic processes in plants. During photosynthesis plant leaves absorb carbon dioxide from the atmosphere and water from the soil and convert it into glucose. The plants then use some of the glucose to form starch and cellulose, the major component of cell walls. Plant matter contains carbon along with hydrogen and oxygen. Protein molecules found in plants and animals contain nitrogen and sulfur in significant quantities.

Photosynthesis (see also section 24.4) is an endothermic and endergonic process (the reaction is non-spontaneous and the Gibbs free energy change is positive). Photosynthesis requires an energy input to drive the reaction. This solar energy input from the Sun becomes ‘locked up’ within the biological molecules synthesized by the plants. Animals eat, digest and assimilate the plant material and the chemical energy passes into them (where it is used to provide energy for the metabolism of the organism).

Over geological time, prehistoric plant and animal matter is compressed and becomes highly concentrated. Fossil fuels have chemical energy highly concentrated within them, which can be released by combustion (oxidation). The three major categories of fossil fuels are coal, crude oil (petroleum) and natural gas

Coal and crude oil

Coal is fossilized plant material containing mainly carbon together with hydrogen, nitrogen and sulfur. The action of pressure and heat in the absence of oxygen slowly converted the plant material in stages from peat to lignite (brown coal) to bituminous soft coal to hard black coal (anthracite). At each stage the percentage of carbon increased up to about 90% in the most abundant form, soft coal.

Crude oil was formed from the remains of marine organisms by a similar process. Thick sediments built up on top of the organic layers and under the action of high pressure and bacterial activity crude oil was formed.

The crude oil (Figure 24.5) migrated through rocks due to earth movement and collected in traps. Crude oil is a complex mixture of straight-chain, branched, cyclic and aromatic hydrocarbons, although it consists mainly of alkanes.

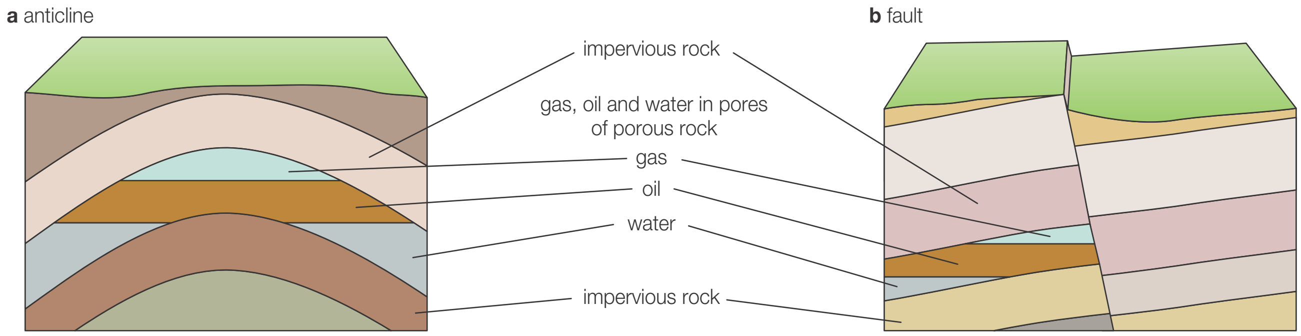


Figure 24.5 Crude oil is found in underground reservoirs in certain geological situations. It permeates the rock in these reservoirs and is usually found in association with natural gas

Crude oil remains one of the most important raw materials in the world today. It is a complex mixture of hydrocarbons and via fractional distillation provides fuels for a range of transport types and for electricity generation. In addition it is an important chemical feedstock for the production of important organic polymers, pharmaceuticals, dyes and solvents.

■ QUICK CHECK QUESTION

5 The combustion of coal produces a number of gases in addition to the major product of carbon dioxide.

  a Write an equation for the combustion of an element in coal to form one of these gases.

  b State **two** advantages of a liquid fuel compared to a solid fuel.

Fossil fuels store reduced carbon

Revised ☐

The formation of fossil fuels from decaying organisms under anaerobic conditions is an example of reduction. Many fossil fuels contain saturated alkanes. Carbon atoms become increasingly saturated with hydrogen and have fewer covalent bonds to nitrogen, sulfur and/or oxygen than existed in the molecules in the plant or animal.

Worked example

Calculate the oxidation numbers of carbon in methane and methanol and show that carbon in methane is in a more reduced form.

The oxidation numbers are deduced as follows: CH_4: oxidation numbers: 1C + 4H = 0; C + 4(+1) = 0; C = −4. CH_3OH: oxidation numbers: 1C + 4H + 1O = 0; C + 4(+1) + (−2) = 0; C = +2. The oxidation number for carbon is −4 in methane and −2 in methanol, showing that carbon is in a more reduced state in methane.

Physical properties of hydrocarbons

Revised ☐

The hydrocarbons in crude oil have different properties depending on their molecular structures. Short chain molecules (small numbers of carbon atoms) have low boiling points, because they have small molar masses and relatively few electrons in each molecule. The instantaneous or temporary dipoles generated during polarization are relatively weak, as are the induced dipoles in neighbouring molecules. Very short chain molecules (1–4 carbon atoms) are gases under standard conditions as the London (dispersion) forces are very weak. Low boiling point hydrocarbons are more volatile, meaning that they release more vapour into the surrounding air. When the surrounding air is saturated with fuel–oxygen mixture the vapour ignites easily.

As the carbon chains get longer, the molar masses increase, along with the number of electrons in the molecules. In addition, the contact area between adjacent molecules in the liquid state will also increase. This leads to stronger London (dispersion) forces, and higher boiling points. When the boiling point is higher, the volatility is lower. There is less vapour in the air surrounding the fuel, and the fuel is more difficult to ignite.

Expert tip

Stronger London (dispersion) forces means that longer hydrocarbon molecules are more viscous and a liquid sample will flow more slowly (less 'runny').

Separating the compounds in crude oil

Revised ☐

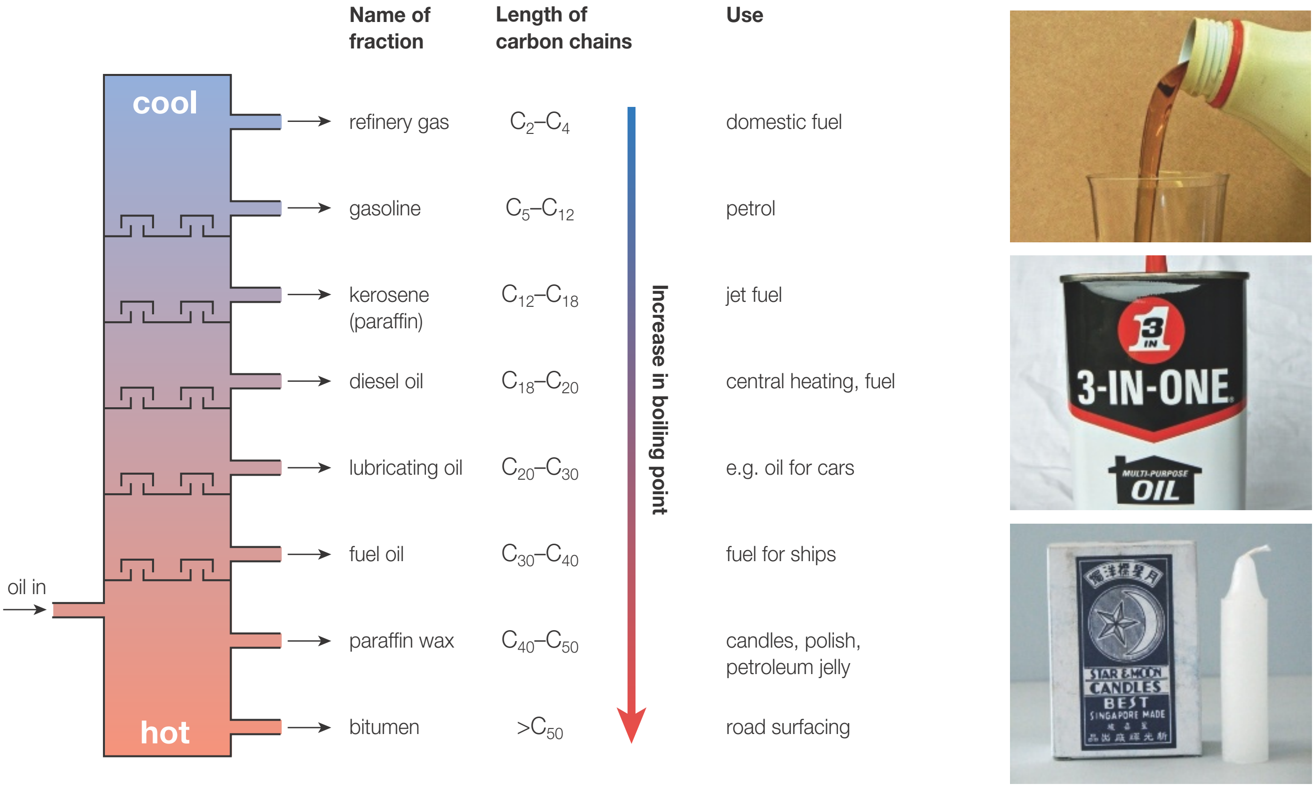
This process of separating out the molecules in crude oil by boiling point involves fractional distillation. The crude oil (petroleum) is heated to a high temperature so that almost all the compounds within it become vapour. This vapour is injected into the base of a vessel called the fractionating column (Figure 24.6).

The vapours rise up the column and as they get further from the heat source at the bottom of the column, the temperature falls. Gradually, each fraction condenses out of the vapour mixture. Heavy fractions, with high boiling points, condense first, close to the bottom of the column. As they move up the column, lighter, shorter-chain fractions condense. At the top of the column some very short-chain molecules are still in the vapour phase and are collected as refinery gas.

QUICK CHECK QUESTION

6 **a** Describe and explain how crude oil (petroleum) is converted into several fractions in a fractionating column.

b Deduce which fraction from the fractional distillation of crude oil would be most likely to contain the following hydrocarbons (alkanes): $C_{35}H_{72}$, C_4H_{10}, $C_{20}H_{42}$, C_8H_{18}



Name of fraction	Length of carbon chains	Use
refinery gas	C_2–C_4	domestic fuel
gasoline	C_5–C_{12}	petrol
kerosene (paraffin)	C_{12}–C_{18}	jet fuel
diesel oil	C_{18}–C_{20}	central heating, fuel
lubricating oil	C_{20}–C_{30}	e.g. oil for cars
fuel oil	C_{30}–C_{40}	fuel for ships
paraffin wax	C_{40}–C_{50}	candles, polish, petroleum jelly
bitumen	$>C_{50}$	road surfacing

Figure 24.6 The fractions obtained industrially from crude oil (petroleum) using a fractionating tower

The petrol engine in a car

Revised ☐

In the internal combustion engine, hydrocarbon fuels are mixed with air, injected into a cylinder and ignited with a spark. The resultant explosion forces a piston to move. The movement of a series of pistons is converted to the rotation of a crankshaft, which in turn drives the wheels of the vehicle.

If we consider a mole of octane (a major component of petrol, or gasoline), for complete combustion to occur, with full oxidation of one mole of octane, we require 12.5 moles of molecular oxygen for each mole of octane:

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

This is a mass ratio (mass of air/mass of fuel) of approximately 15:1 (20% of the air (by volume) is oxygen). If the air/fuel ratio is lower, the mixture is said to be 'rich' and the amount of oxygen is insufficient for complete combustion. This will result in the formation of some carbon monoxide. In this example only 10 moles of oxygen is available for each mole of octane:

$$C_8H_{18}(l) + 10O_2(g) \rightarrow 3CO_2(g) + 5CO(g) + 9H_2O(l)$$

A rich mixture may also lead to the emission of unburned hydrocarbon molecules (called 'volatile organic compounds' or VOCs) from the exhaust. If the air–fuel ratio is increased, the mixture is said to be 'lean'. A lean mixture will not produce carbon monoxide.

A disadvantage of a lean mixture is that the mixture may 'pre-ignite' while under compression. Pre-ignition means that the rapid compression of the fuel–air mixture in the cylinder leads to some of the fuel igniting before the spark, causing a sudden pressure increase in the cylinder. This causes a metallic 'knocking' sound. This inefficient combustion actually increases the proportion of unburned hydrocarbons in the exhaust gases.

Knocking

An automobile (car) engine is designed to operate optimally by using the maximum value for the fuel to air ratio (Figure 24.7) so that the piston is pushed down with the largest possible force from combustion of the hydrocarbon as the spark plug fires.

When an engine is going up a steep hill, the combustion reaction may start prematurely under the condition of high pressure and temperature before the spark plug 'fires'. This tendency of a fuel to auto-ignite leads to 'knocking' in a car engine. This is the sound of small explosions in the cylinders. The ability of a fuel to cause 'knocking' is related to molecular structure and is measured by the octane number.

Octane number (or rating)

The ability of a petrol (gasoline) to perform in an internal combustion engine is measured by its octane number or rating. This is based on how a fuel auto-ignites under pressure. It is a measure of the ability of a fuel to resist knocking when burnt in a standard test engine. The more knocking a fuel causes, the poorer the fuel and the lower its octane rating.

A straight-chain hydrocarbon such as heptane is a poor fuel and has an octane rating of zero, but the highly branched 2,2,4-trimethylpentane is a very efficient fuel and is assigned a value of 100 (Figure 24.8). Aromatic compounds have high octane ratings. The shorter the carbon chain, the higher the octane number. The smaller alkanes are more easily vaporized and are more useful fuels.

It can also be seen from the octane numbers of the isomers of octane and heptane (Table 24.6) that these increase with carbon chain branching, since a compound fragments preferentially at branches. The more branched the alkane is the higher the octane number.

Table 24.6 Selected octane numbers of alkanes

Alkane	Octane number
Heptane	0
2-Methylhexane	42
3-Methylhexane	55
3-Ethylpentane	65
2,3-Dimethyl pentane	91

The combustion of hydrocarbons is not a simple molecular process but a complex free radical reaction. The anti-knocking agents reduce the activity of free radicals in the burning mixture, either by eliminating them, or by converting them to radicals that are relatively stable (and thus unreactive).

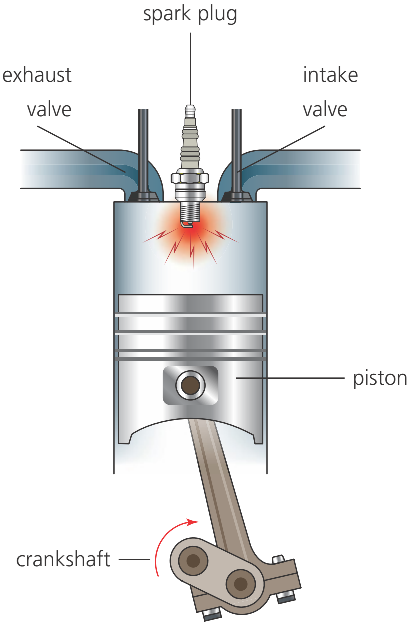


Figure 24.7 An internal combustion piston engine in which a very rapidly burning mixture of air and fuel drives a piston downward during the power stroke and this motion is converted to rotary mechanical motion by the crankshaft

QUICK CHECK QUESTION

7 Suggest why petrol companies make different blends for different times of the year in a country that has a hot summer and a cold winter.

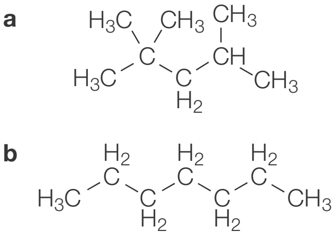


Figure 24.8 Octane numbers: **a** 2,2,4-trimethylpentane: octane rating 100, and **b** heptane: octane rating 0

QUICK CHECK QUESTION

8 **a** Calculate the octane rating of a fuel mixture with 90% 2,2,4-trimethylpentane, 5% heptane and 5% toluene (methyl benzene), which has an octane number of 114.

b Suggest why ether compounds (oxygenates) may be added to petrol mixtures.

Cracking and reforming

Revised ☐

Cracking

The supply of hydrocarbon fractions from the fractional distillation of crude oil does not match the industrial demand for those fractions. Typically, the larger or heavier fractions are more plentiful, whereas the highest demand is for the C_5–C_{10} fractions.

Cracking is a chemical process that breaks down (decomposes) large long chain hydrocarbon molecules into smaller ones using heat. The heavier fractions are heated and passed over a catalyst, which 'cracks' them into shorter chains. The original alkane, having the general formula C_nH_{2n+2}, usually results in two products: a shorter alkane (also C_nH_{2n+2}, and an alkene, C_nH_{2n}).

Expert tip

It is not possible to crack an alkane into two shorter alkanes – there are not enough hydrogen atoms present. For example: the cracking of heptane into pentane and ethene (Figure 24.9). $C_7H_{16} \rightarrow C_5H_{12} + C_2H_4$.

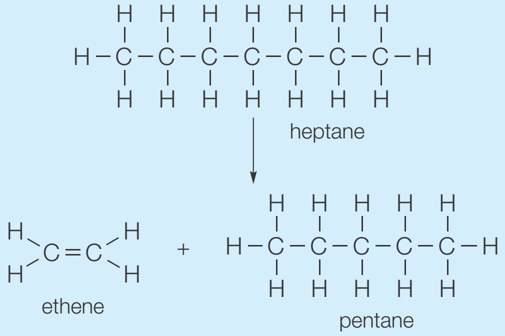


Figure 24.9 Cracking a long-chain saturated hydrocarbon molecule

The reaction shown in Figure 24.9 is starting from a relatively short alkane to illustrate the type of reaction being discussed. Note that the alkene splits off the end of the molecule. The process is not a highly specific one. Ethene is not always the alkene product; it is possible to obtain propene and butene as products. In certain circumstances hydrogen can also break off the end of the alkane molecule.

The different types of cracking are summarized below:

- **Thermal cracking:** Very long chain alkanes found in the heavy fractions are heated to temperatures of 800–850 °C at a pressure of 70 atmospheres, and then cooling the mixture rapidly. A mixture of products is produced that includes shorter chain alkanes, alkenes (often ethene) and coke (an impure form of carbon), e.g. $C_{18}H_{38} \rightarrow C_8H_{18} + 2C_3H_6 + 2C_2H_4$.
- **Steam cracking:** The mixture of ethane, butane and alkanes up to eight carbon atoms long is preheated, vaporized and mixed with steam at 1250–1400 °C. The steam dilutes the feedstock and the reaction produces a higher yield of ethene and other short chain alkenes. The addition of steam also reduces the amount of coke produced, e.g. $C_8H_{18} \rightarrow 4C_2H_4 + H_2$.
- **Catalytic cracking:** Using a catalyst in the cracking process allows the reaction to occur at lower temperatures, around 500 °C, and produces a mixture of alkanes, alkenes and molecules containing the benzene ring (arenes). Large and intermediate sized alkanes are passed over a zeolite or mixed alumina (Al_2O_3) and silica (SiO_2) catalyst, e.g. $C_{16}H_{34} \rightarrow C_7H_{16} + C_7H_{14} + C_2H_4$.
- **Hydrocracking:** The feedstock is mixed with hydrogen at a pressure of about 80 atmospheres and cracked over a platinum or silica/alumina catalyst. This gives a high yield of branched alkanes, cyclic alkanes and aromatic compounds for use in unleaded petrol (gasoline). The presence of hydrogen ensures that no alkenes are produced in this type of cracking, e.g. $C_{16}H_{34} + H_2 \rightarrow 2C_8H_{18}$.

QUICK CHECK QUESTION

9 Write equations to illustrate the following reactions:
  a an alkane with 16 carbon atoms forming an alkane with 11 carbon atoms, ethene and propene
  b an alkane with 12 carbon atoms to form octane and butane
  c an alkane with 10 carbon atoms to form octane and ethene.

Reforming

More useful branched alkanes can be obtained from straight-chain hydrocarbons by mixing them with hydrogen gas, heating them to 500 °C and passing them at high pressure over a platinum catalyst on an aluminium oxide support. The initial reaction is known cyclization (a form of reforming) and under these conditions hexane is converted to cyclohexane and then benzene (aromatization) (Figure 24.10). Straight-chain alkanes, such as hexane, can also be converted to branched isomers, for example, 2-methylpentane.

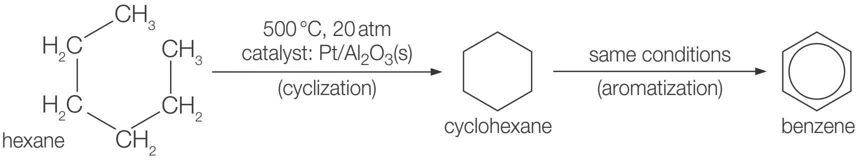


Figure 24.10 The cyclization and aromatization of hexane through to benzene via cyclohexane

QUICK CHECK QUESTION

10 a State how the products of catalytic and thermal cracking differ.

b Write a balanced equation showing the reforming of heptane to methyl cyclohexane and then benzene and molecular hydrogen.

Coal gasification

Revised ☐

Coal is a more abundant fossil fuel than crude oil, and can be converted to more complex hydrocarbons, which may be more useful.

One method is coal gasification in which synthesis gas, also called coal gas or syngas, is produced by reacting coal with oxygen and steam in a gasifier. Inside the gasifier the oxygen reaching the coal is limited so that complete combustion hardly occurs.

Synthesis gas is a mixture consisting of hydrogen and carbon monoxide, with some carbon dioxide. It can be used as a fuel, though it is usually involved in the production of methanol (both components are used) and ammonia (hydrogen gas is used).

Coal gasification may occur in a cavity underground (Figure 24.11), giving plants low costs as no gasifier needs to be built, the coal does not have to be transported to the surface, and the carbon dioxide formed can be stored underground rather than being released to the atmosphere.

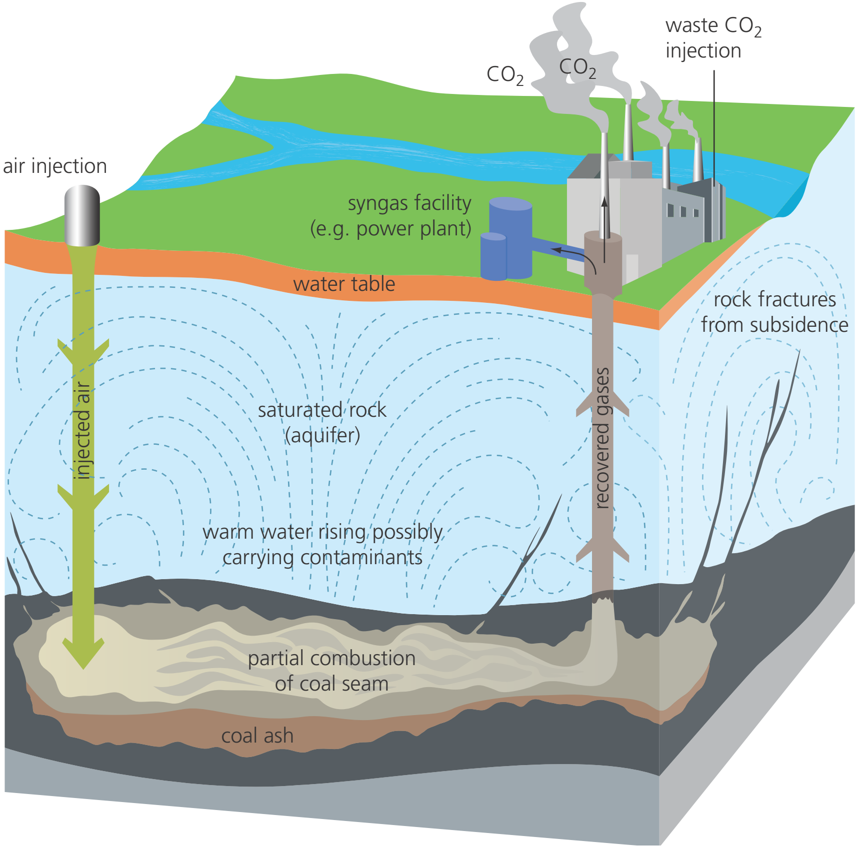


Figure 24.11 The underground coal gasification process

Expert tip

Underground coal gasification converts coal to synthesis gas while still in the coal seam (*in situ*). The technique can be applied to coal resources that are unprofitable or difficult to mine.

Compared with traditional coal mining, the underground coal gasification process eliminates surface damage and solid waste discharge, and reduces emission of sulfur dioxide (SO_2) and oxides of nitrogen (NO_x). Hydrogen sulfide (H_2S) present is oxidized to sulfur.

Pollutants are 'washed out' of the synthesis gas leaving a relatively clean efficient fuel. Wet scrubbers are used to remove acidic gases and particulate matter. The tar is removed via decomposition by subjecting the synthesis gas to a high temperature.

The process of coal gasification (Figure 24.12) is summarized in Table 24.7. Gasification produces other products including slag which is used in roofing materials or for road construction, methanol and nitrogen-based compounds for fertilizers (via ammonia).

The main reactions that occur during coal gasification are listed in Table 24.7.

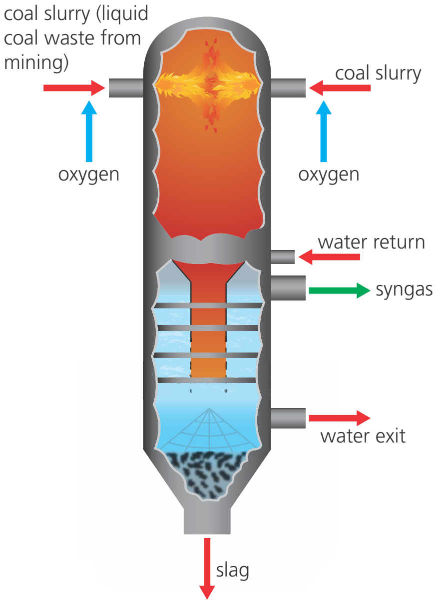


Figure 24.12 Coal gasification; note that syngas is a mixture of carbon monoxide, hydrogen and carbon dioxide

Table 24.7 The main reactions that occur during coal gasification

Reaction	Conditions	Comments
Coal (C,H) $\rightarrow CH_4 + H_2O + C + H_2 + CO + CO_2$ + various gaseous hydrocarbons	Some oxygen, at a temperature that will not allow complete combustion	The first step is pyrolysis. Coal is dried and degraded into several gases and char, a charcoal-like substance. This is partial oxidation and generates oxidized compounds including carbon monoxide, CO, and carbon dioxide, CO_2 (complete combustion product).
$C + H_2O \rightarrow CO + H_2$ $C + CO_2 \rightarrow 2CO$ (reverse Boudard reaction) $CO + 3H_2 \rightarrow CH_4 + H_2O$ (methanation reaction) $CO + H_2O \rightarrow CO_2 + H_2$ (water gas shift reaction)	Increased temperature, decreased oxygen, steam	This is reduction. Here synthesis gas (mainly CO and H_2) is produced which can be burnt to generate electricity. The steam gasification reaction is endothermic. Usually, an excess amount of steam is used.
$C + O_2 \rightarrow CO_2$	Synthesis gas and other wanted substances are passed through a cooling chamber and removed. Remaining char is burnt off and carbon dioxide and impurities can be removed.	Gas clean-up in which the desired products are purified and removed.

■ **QUICK CHECK QUESTION**

11 Write an equation to describe the reaction between coal, C(s), and steam to form methane and an oxide of carbon.

Methods of coal liquefaction

Revised ☐

Coal is mostly carbon, but hydrogen is also present. The proportion of hydrogen in liquid hydrocarbon fuels is much higher than coal. Coal liquefaction relies on increasing the hydrogen : carbon ratio in the fuel. This is done by increasing the amount of hydrogen in the coal or decreasing the amount of carbon in the coal which results in the formation of a mixture of hydrocarbons.

Direct hydrogenation of coal

Coal is crushed, mixed with a solvent (often heavy fuel oil) and heated in the presence of an iron-based catalyst. Hydrogen gas is added to the mixture. This is known as Fischer–Tropsch synthesis (FTS): $nC + (n + 1)\ H_2 \rightarrow C_nH_{2n+2}$. The products are typically heavy hydrocarbons that require significant further refining (cracking, reforming) before they are of use as motor fuels.

Distillation of coal

Some coals contain large amounts of hydrocarbons, so the liquefaction process involves separating the hydrocarbons from the solid carbon. Bituminous coal is saturated with heavy hydrocarbon molecules. These coals are heated (a process called destructive distillation, or pyrolysis) which produces a mixture of tar (containing mostly cyclic or aromatic hydrocarbons), heavy oil and a solid residue of carbon. The tar and heavy oil can be further refined by cracking and reforming in order to make them useful as motor fuels.

Liquid fuels from coal gas

A third approach to coal liquefaction is to use the coal gas produced in the gasification process outlined previously to produce liquid hydrocarbons.

The process of coal liquefaction takes filtered and cleaned synthesis gas and adds steam or carbon dioxide over a catalyst. This process is known as indirect coal liquefaction. In direct coal liquefaction hydrogen gas is added to heated coal in the presence of a transition metal catalyst (Fe, Co, Ru). Both methods adjust the carbon-to-hydrogen ratio and produce synthetic liquid fuels via a process known as the Fischer–Tropsch process, shown by the general equation:

$$\text{Alkanes: } n\text{CO} + (2n + 1)\,\text{H}_2 \rightarrow \text{C}_n\text{H}_{(2n+2)} + n\text{H}_2\text{O}$$

where n is typically 10–20. The formation of methane ($n = 1$) is unwanted. Most of the alkanes produced tend to be straight-chain, suitable as diesel fuel. If the reaction is allowed to continue then the value of n increases. Alcohols and other oxygenated organic compounds can be formed, for example, $CO(g) + H_2(g) \rightarrow H_2CO(g)$; methanal and $H_2CO(g) + H_2(g) \rightarrow CH_3OH(l)$; methanol.

The relative advantages and disadvantages of fossil fuels are itemized in Table 24.8.

QUICK CHECK QUESTION

12 Deduce equations for the production of nonane by

a direct hydrogenation of coal

b liquefaction of coal gas, carbon monoxide, CO(g).

Table 24.8 The relative advantages and disadvantages of fossil fuels

Fossil fuel	Advantages	Disadvantages
Coal	Present in large quantities and distributed throughout the world. Simple to mine. Can be converted into synthetic liquid fuels and gases, e.g. coal gas gasification and liquefaction. Feedstock for organic chemicals. Could yield large quantities of energy compared with renewable sources and safer than nuclear power. Larger reserves compared with oil or gas.	Contributes to acid rain and global warming. Not so readily transported as a liquid or gas (no pipelines). Coal waste (slag heaps) lead to ground acidity and chemical pollution (heavy metal ions). Mining and strip mining is dangerous – cave-ins, explosion and long-term effect of coal dust on miners. Dirty (produces dust, smoke and particulates).
Oil	Easily transported in pipelines or by tankers. Convenient source of fuel for use in cars, lorries, aircraft, etc. Feedstock for organic chemicals.	Contributes to acid rain and global warming. Limited lifespan (30–50 years) and uneven distribution worldwide. Risk of marine pollution associated with transportation by oil tankers on the sea.
Natural gas	Natural gas burns cleaner than other fossil fuels, producing half the carbon dioxide as coal and about a third less than fuel oil. Easily transported in pipelines and stored in pressurized containers. Does not contribute to acid rain. Releases a higher quantity of thermal energy per kilogram than coal or oil. Currently cheapest source of electrical energy.	Contributes to global warming. Limited reserves (30 years) and uneven distribution worldwide. Greater risk of explosion due to leaks. Methane is a very powerful greenhouse gas, up to 20 times more effective than carbon dioxide. If improperly extracted, methane can be released into the atmosphere, or burnt off as flaring at oil fields.

Various developments have been explored to make the use of fossil fuels more environmentally friendly ('greener') and these are listed in Table 24.9.

Table 24.9 Developments explored to make the use of fossil fuels more environmentally friendly

Aim	Examples	Advantages
Remove sulfur and sulfur compounds from fossils fuels, such as coal	Scrubbing, filters and engineered polymers with receptor sites for sulfur compounds.	Reduce sulfur dioxide emissions which could cause acid rain (unless removed from the combustion products); the sulfur extracted can be used in sulfuric acid production (Contact process).
Produce fuels with lower environmental impact	Remove lead; benzene and sulfur from petrol; use of catalytic convertors in cars.	Reduces emission of oxides of nitrogen (NO_x), carbon monoxide, CO, oxides of lead and benzene (toxic and carcinogenic).
Produce alternative or blended petrochemical fuels	Mix ethanol with petrol (gasohol) (see 24.4 Solar energy); develop engines that run on LPG (liquefied petroleum gas, or compressed natural gas (CNG).	Reduces carbon dioxide ('carbon') emissions, lowers the carbon footprint of the vehicle (see below) and reduces emissions of NO_x and CO.
Develop renewable and alternative resources and technologies	Bioethanol, biodiesel, electric cars, hybrid cars, fuel cells and hydrogen cars.	Reduce dependence on crude oil, make existing supplies last longer, move towards carbon-neutral fuels, for example, biodiesel, which are renewable and sustainable.

Carbon footprint

Revised ☐

The carbon footprint is a measure of the total carbon dioxide emissions resulting from a given activity or process. However, most of these involve the emission of other gases, such as methane (CH_4), which has a global warming potential 25 times greater than carbon dioxide, for a given mass, so emissions of methane must be multiplied by this factor.

To simplify the overall emissions are quoted as 'tonnes of carbon dioxide equivalent'. In order to calculate the carbon footprint, it is necessary to know the mass of each greenhouse gas emitted by the particular activity and the global warming potential of each.

Worked example

Calculate the carbon footprint for a car journey of 500 kilometres if the car consumes 44.0 dm^3 (litres) of petrol (gasoline). Assume petrol is pure octane and its density is 0.703 $g\,cm^{-3}$). (1 dm^3 = 1000 cm^3).

Mass of octane consumed = density × volume

= $0.703\,g\,cm^{-3} \times 44\,000\,cm^3 = 30\,932\,g$

Amount of octane consumed = $30\,932\,g/114.26\,g\,mol^{-1} = 270.7\,mol$

The equation for the complete combustion of one mole of octane (under standard conditions) is:

$$C_8H_{18}(l) + 12.5O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)$$

1 mole of octane reacts with 1.25 moles of oxygen molecules to form 8 moles of carbon dioxide molecules and nine moles of water molecules.

Amount of carbon dioxide produced = amount of octane × 8 = 2166 mol

Mass of carbon dioxide produced = $2166\,mol \times 44.01\,g\,mol^{-1} = 95.31\,kg$

QUICK CHECK QUESTION

13 A coal-fired power station uses 4000 tonnes of coal a day. The carbon factor of the coal is 0.746 tonnes of carbon per tonne of coal. Calculate the mass of carbon dioxide in tonnes produced daily by the coal-fired power plant.

24.3 Nuclear fusion and fission

Revised ☐

Essential idea: The fusion of hydrogen nuclei in the Sun is the source of much of the energy needed for life on Earth. There are many technological challenges in replicating this process on Earth but it would offer a rich source of energy. Fission involves the splitting of a large unstable nucleus into smaller stable nuclei.

Nuclear fusion and fission

Revised ☐

Nuclear fusion

- Light nuclei can undergo fusion reactions as this increases the binding energy per nucleon.
- Fusion reactions are a promising energy source as the fuel is inexpensive and abundant, and no radioactive waste is produced.
- Absorption spectra are used to analyse the composition of stars.

Nuclear fission

- Heavy nuclei can undergo fission reactions as this increases the binding energy per nucleon.
- ^{235}U undergoes a fission chain reaction:

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{236}_{92}U \rightarrow X + Y + \text{neutrons}$$

- The critical mass is the mass of fuel needed for the reaction to be self-sustaining.
- ^{239}Pu, used as a fuel in 'breeder reactors', is produced from ^{238}U by neutron capture.
- Radioactive waste may contain isotopes with long and short half-lives.
- Half-life is the time it takes for half the number of atoms to decay.

Introduction

Revised ☐

Nuclear chemistry is concerned with nuclear stability and the process of nuclear changes. Examples of nuclear changes are: radioactivity, artificial transmutation, nuclear fission and nuclear fusion.

Nuclear reactions

Revised ☐

The most important characteristics of a nucleus are its charge (protons) and its mass (neutrons and protons). The charge on the atomic nucleus is determined by the number of protons (positive charges) it contains. Protons and electrons have opposite elementary charges. The properties of the fundamental particles are summarized in Table 24.10.

Table 24.10 Properties of the proton, neutron and electron

	Proton	Neutron	Electron
Mass (kg)	1.672622×10^{-27}	1.674927×10^{-27}	9.109383×10^{-31}
Charge (C)	1.602189×10^{-19}	0	1.602189×10^{-19}

A particular atom with a specific atomic (proton) number and mass (nucleon) number is termed a nuclide, $^{A}_{Z}X$. The number of neutrons is given by $A - Z$. Isotopes are nuclides of the same element but different mass (nucleon) numbers. They have identical chemical properties, but slightly different physical properties, for example, diffusion rates in the gaseous state.

It is usual to measure the mass of an atom in atomic mass units, abbreviated amu. The atomic mass unit (Figure 24.13) is equal to $\frac{1}{12}$ th of the mass of the neutral $^{12}_{6}C$ atom. 1 amu = 1.66×10^{-27} kg.

Elements which emit ionizing or nuclear radiation are termed radioisotopes. Radioactivity is a property of an unstable nucleus and is independent of its physical state, chemical state or temperature. Radioactive decay is the process by which a nucleus of an unstable atom loses energy by emitting radiation.

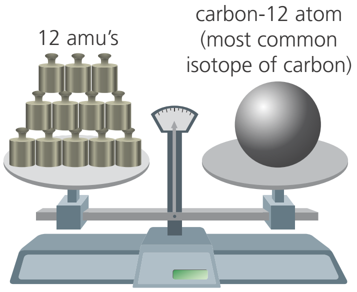


Figure 24.13 Concept of the atomic mass unit

The three types of radiation emitted by radioactive elements are: alpha particles, beta particles and gamma rays. The characteristics of the three common types of radiation are given in Table 24.11.

Table 24.11 Properties of alpha, beta (minus) and gamma radiations

	Alpha particle	**Beta (minus) particle**	**Gamma ray**
Relative charge and relative mass	+2 and 4	−1 and 0	0 and 0
Nature	Helium nucleus or helium ion	High-speed electron	Electromagnetic wave with very short wavelength $< 10^{-10}$ m
Notation	${}^{4}_{2}\text{He}$ or ${}^{4}_{2}\alpha$	${}^{0}_{-1}\text{e}$ or ${}^{0}_{-1}\beta$	${}^{0}_{0}\gamma$
Action of magnetic field	Deflected towards cathode (negative)	Deflected towards anode (positive)	Not deflected
Velocity	$\frac{1}{10}$ speed of light	Up to $\frac{9}{10}$ speed of light	Speed of light ($3.00 \times 10^{8}\,\text{m s}^{-1}$)
Ionizing power	Very high, nearly 100 × that of beta particles	Low	Low
Penetrating power	Low; easily stopped by air	100 × that of alpha particles	10 × that of beta particles
Kinetic energy	High	Considerably less than alpha particles	Zero

Positrons (${}^{0}_{+1}\text{e}$ or ${}^{0}_{+}\beta$) are particles with the same mass as an electron, but the opposite charge. They can also be produced when a radioisotope decays.

Expert tip

For every particle there is an antiparticle that has the same mass as the particle, but the opposite charge (if it is charged) (and the opposite quantum number). If antimatter comes into contact with matter, they will annihilate, converting all the mass into energy. For example, in a collision of an electron and a positron, a pair of high-energy photons (gamma rays) are created.

■ QUICK CHECK QUESTION

14 List the three forms of radiation in order of decreasing penetrating power (the most penetrating first).

Nuclear equations

Revised ☐

The emission of an alpha particle decreases the mass (nucleon) number of a daughter nucleus by 4 and atomic (proton) number by 2. The daughter nucleus shifts two places to the left of the parent in the periodic table.

The generalized equation for alpha decay is:

$${}^{A}_{Z}\text{X} \rightarrow {}^{A-4}_{Z-2}\text{X} + {}^{4}_{2}\text{He} + \text{energy}$$

parent nuclide daughter nuclide alpha particle

For example:

$${}^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$$

$${}^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$$

Expert tip

The totals of the mass (nucleon) numbers on both sides of the nuclear equation are equal; the totals of the atomic (proton) numbers on both sides are also equal.

The emission of beta (minus) particle does not change the mass (nucleon) number of the daughter nucleus but increase the atomic (proton) number by 1. The daughter nucleus shifts one place to the right of the parent in the periodic table. The loss of a beta particle (high-speed electron) converts a neutron to a proton.

The generalized equation for beta decay is:

$${}^{A}_{Z}\text{X} \rightarrow {}^{A}_{Z+1}\text{X} + {}^{0}_{-1}\beta + \text{energy}$$

parent nuclide daughter nuclide beta particle

For example:

$${}^{234}_{90}\text{Th} \rightarrow {}^{234}_{91}\text{Pa} + {}^{0}_{-1}\text{e}$$

$${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\text{e}$$

In nuclear equations, reactant (parent) and product (daughter) nuclei are represented by their mass (nucleon) numbers and atomic (proton) numbers, as well as their chemical symbols.

■ QUICK CHECK QUESTION

15 Write nuclear equations for the following nuclear reactions:

- **a** radon-222 produces an alpha particle
- **b** scandium-49 produces a beta (minus) particle and a neutron
- **c** carbon-14 produces a beta (minus) particle.

During gamma decay no new element is formed: there are no changes to the proton or nucleon number of the parent nuclide. Gamma rays are released from the excited nucleus as an excited nucleus relaxes to the ground state. Gamma decay may occur on its own, or accompany alpha or beta decay.

Decay series

Revised ☐

Radioactive heavy nuclei decay by a series of alpha and beta emissions, until lead (atomic number 82) is obtained. The series which includes the elements formed from the initial to the final stable element is known as a decay series.

Radioactive decay

Revised ☐

The radioactive decay of a radioisotope of an element is a random and spontaneous process. Radioactivity is a random process – it is not possible to predict when a particular nuclide will decay. Radioactivity is a spontaneous process which means a particular nuclide will undergo decay independently of what is happening outside that nuclide.

It is a first order process and for a large number of radioactive nuclides follows an exponential law: $N_t = N_0e^{-kt}$, where N_0 = initial number of radioactive nuclei at time = 0.

Each radioisotope has a characteristic half-life, $t_{\frac{1}{2}}$, which is the time it takes for half of the radioactive atoms in the sample to decay. The half-life is independent of the amount of the radioisotope. The half-life can be determined graphically from a decay curve graph (Figure 24.14) which plots activity (number of radioactive nuclides remaining) against time.

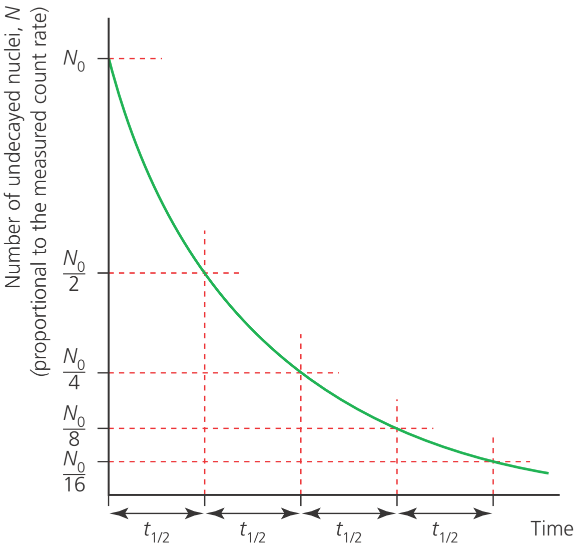


Figure 24.14 Generalized radioactive decay curve

If N_0 is the initial number of radioactive nuclides, then after a period of one half-life t only ½N_0 radioactive nuclides are left in the sample. After two half-lives $2t$, then there will be only ¼N_0 radioactive nuclides left in the sample, etc.

The amount after n half-lives can be calculated from the equation

$$N_t = N_0\left(\frac{1}{2}\right)^n$$

and radioactive decay also obeys the logarithmic equation:

$$t = \frac{2.303}{k}\log\left(\frac{N_0}{N_t}\right)$$

and

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

where *k* is the rate or decay constant. The decay constant is defined as the probability of decay per unit time of a nucleus. Activity is the rate of decay, i.e., the number of disintegrations per second.

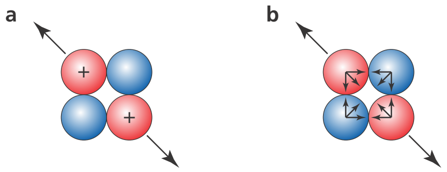
Expert tip

It is meaningless to refer to the half-life of a single atom of a radioisotope because decay could take at any time; it is impossible to predict.

Forces acting in the nucleus

Revised ☐

There are two main interactions within a nucleus of an atom or ion: electrostatic repulsion between protons (Coulomb repulsion) and a short-range attractive force known as the strong nuclear force which operates between neighbouring nucleons (Figure 22.15).



Coulomb forces push the protons apart

there must also be strong nuclear forces between the nucleons pulling them together

Figure 24.15 Repulsive and attractive forces in a helium nucleus

Stable nuclei have larger attractive forces than repulsive forces. Stable small nuclides with a low value of proton number have approximately the same number of protons and neutrons in the nucleus. In heavy or large nuclei, such as uranium or plutonium, there are more neutrons than protons, giving a neutron to proton ratio greater than 1. The strong nuclear force decrease rapidly with distance and it extends effectively only to its immediate neighbouring nucleons.

Transmutations

Revised ☐

A transmutation is a nuclear reaction involving the formation of a new daughter nuclide. Artificial (induced) transmutations occur when one or more nucleons is captured by or transferred onto another nucleus. For example, bombardment of 14-nitrogen atoms by alpha particles:

$$^{14}_{7}\text{N} + ^{4}_{2}\text{He} \rightarrow ^{17}_{8}\text{O} + ^{1}_{1}\text{H}$$

QUICK CHECK QUESTION

16 A hydrogen-1 nucleus reacts with a nitrogen-15 nucleus to produce an alpha particle, gamma ray and another nuclide.

- **a** Write a balanced nuclear equation.
- **b** Outline how transmutation is different from radioactive decay.

Background radiation

Revised ☐

All living organisms are exposed to cosmic radiation from the Sun and space, and terrestrial radiation. It is important that background radiation and artificial radiation from nuclear medicine and the nuclear industry are monitored. Some of the natural background radiation is due to radon released from radioactive rocks (granite) and fall out from the nuclear bombs dropped during World War 2 and the testing of nuclear bombs after the war.

Mass defect

Revised ☐

The mass of a hydrogen-1 atom is simply the mass of a proton. For all other atoms (and isotopes of hydrogen), the atomic mass is less than the sum of protons and neutrons. The difference in mass is known as the mass defect (Figure 24.16).

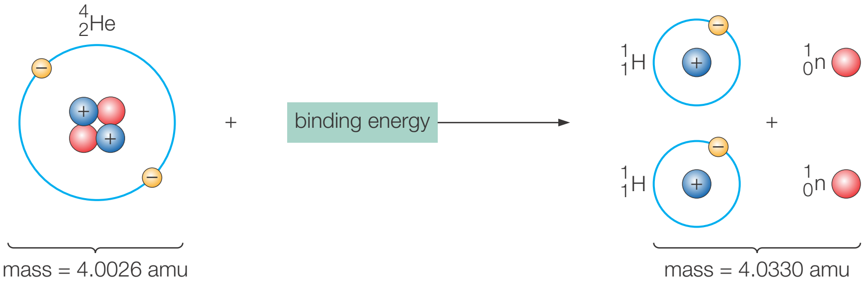


Figure 24.16 The mass defect of the helium-4 nucleus

The mass defect is equal to the binding energy of the protons and neutrons in the nucleus. The energy required to remove all the nucleons from the nucleus is the binding energy of that nucleon in the nucleus. It is equal to energy that is required to remove all the nucleons from the nucleus without giving it any kinetic (movement) energy.

The binding energy of a nucleus is defined as the amount of work that must be done in order to break up the nucleus into its constituent nucleons. From the law of conservation of energy when a nucleus is formed, the same amount of energy must be released as is put in to break it up.

Mass and energy are related by Einstein's mass–energy equivalence relationship:

$E = mc^2$

where

energy transferred = mass difference × (speed of light)^2

in SI units.

Worked example

A nuclear reaction involves a mass change of 7.47×10^{-31} kg. Calculate the energy released in joules. $E = mc^2$; $E = 7.47 \times 10^{-31}\,\text{kg} \times (3 \times 10^8\,\text{m s}^{-1})^2 = 6.72 \times 10^{-14}\,\text{J}$.

These numbers are very small and awkward to work with, so nuclear chemists often measure mass in terms of the atomic mass unit (amu) (1 amu = 1.661×10^{-27} kg). An energy unit that is more appropriate for this scale is often used. The electron volt is the amount of energy gained by an electron as it accelerates through a potential difference of 1 V. 1 J = 6.25×10^{18} eV.

Expert tip

The mega electronvolt (MeV) is a convenient energy unit, as many energy changes that take place in the nucleus are in the order of several MeV. The MeV is the energy gained by one electron when it is accelerated through a potential difference of 10^6 V. The energy equivalent to the mass defect of 1 amu is 931 MeV which is equivalent to 1.503×10^{-10} J.

Expert tip

Einstein's relationship shows that energy and mass are interchangeable quantities. During a chemical reaction, it is assumed that energy is conserved, and that mass is conserved separately. However, during nuclear processes, we need only assume that the total quantity of mass and energy are conserved.

Binding energy

Revised ☐

Binding energy (Figure 24.17) is the energy required to separate (to infinity) of all the nucleons of a nucleus. Binding energy is equivalent to the mass defect of a nucleus. Energy, called the binding energy, must be supplied to break the nucleus apart into its constituent protons and neutrons. Each of the separated nucleons is at rest and out of the range of the forces of the other nucleons.

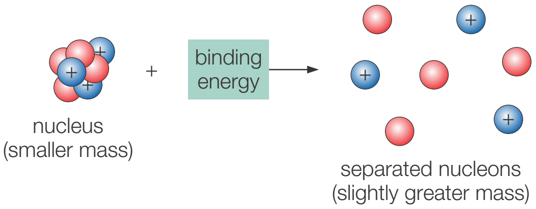


Figure 24.17 Concept of binding energy

QUICK CHECK QUESTIONS

17 Distinguish between mass defect and binding energy.

18 Calculate the binding energy (in joules) of the nucleus in vanadium-51. The mass of the proton is 1.672622×10^{-27} g and the mass of the neutron is 1.674927×10^{-27} g.

Nuclear stability is measured by binding energy of the nucleons in the nucleus. Binding energy per nucleon is defined as the binding energy divided by the number of nucleons in the nucleus. Figure 24.18 shows the variation with nucleon number of the binding energy per nucleon for different nuclides.

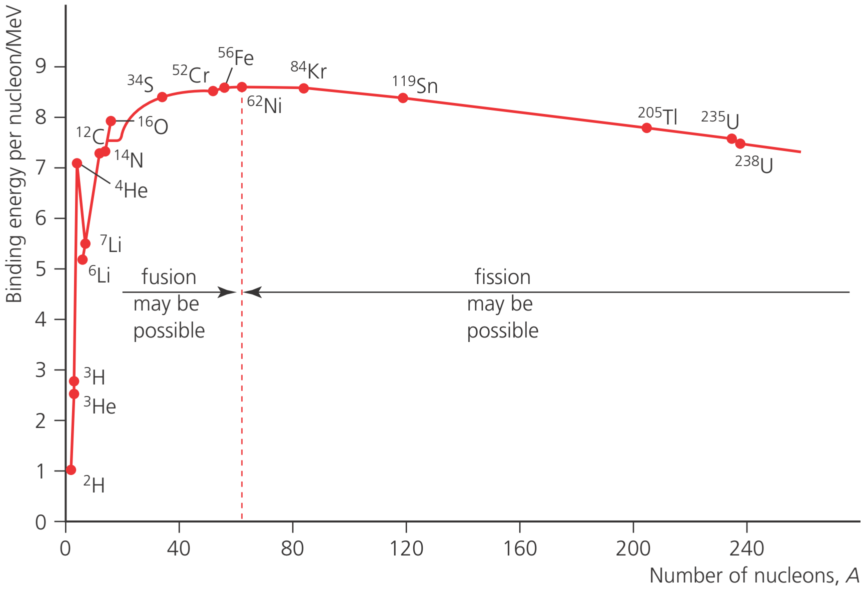


Figure 24.18 The variation of nuclear binding energy with nucleon number

Worked example

The binding energy for the carbon-12 nucleus is – 92.16 MeV. Calculate the binding energy per nucleon = – 92.16 MeV/12 = – 7.68 MeV. Since the mass of the nucleus is less than the mass of the protons and neutrons, the binding energy must be negative.

The general shape of the curve suggests the mechanisms by which nuclear energy is released. Nuclear energy can be released either by the fission of heavy nuclei or the fusion of light nuclei from lighter ones. Energy will be released in nuclear reactions for which the binding energy per nucleon in the end products exceeds the binding energy per nucleon in the original nuclei.

Nuclear fusion and fission

Revised ☐

Light nuclei may combine or fuse to form larger nuclei with larger binding energies per nucleon. This process is called nuclear fusion and requires extremely high temperatures and pressures.

The process of fusion in the Sun can be described by the following nuclear equation:

$$4\,{}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{-1}\mathrm{e} + \text{energy} + \text{neutrinos}$$

Heavy nuclei, when bombarded with slow moving neutrons, may form two (or more) smaller nuclei, again with larger binding energy values per nucleon values (Figure 24.19). This process is called nuclear fission.

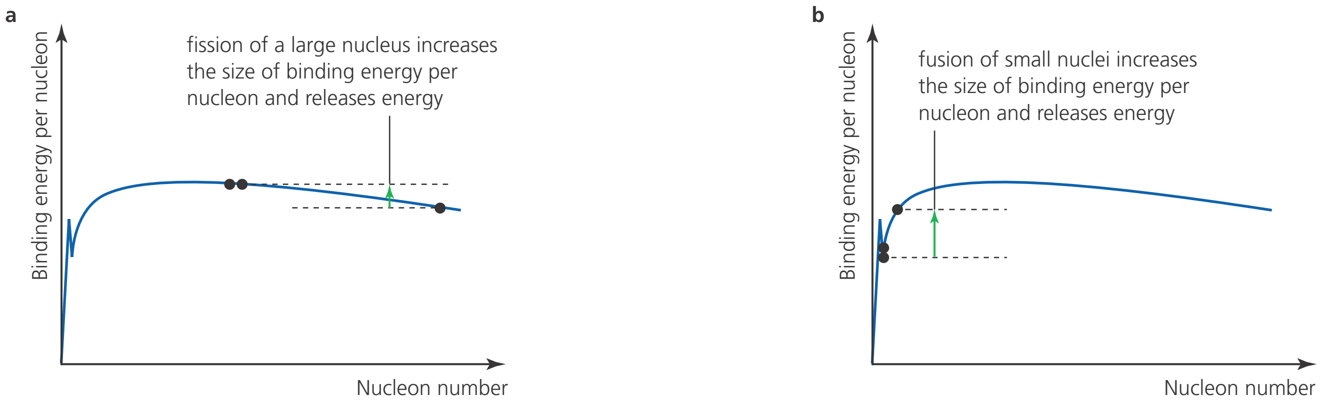


Figure 24.19 An increase in binding energy per nucleon occurs during fission and fusion

There are several possible fission reactions which may occur in a nuclear reactor and most can be represented by the following general equation:

$${}^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{236}_{92}\mathrm{U} \rightarrow 2 \text{ new nuclides} + 2 \text{ or } 3 \text{ neutrons} + \text{energy}$$

The nuclides formed are known as fission fragments and are highly radioactive.

Each fission reaction releases two or three neutrons. If these neutrons are absorbed by U-235 nuclei, they will undergo fission, thereby releasing even more neutrons. This is a chain reaction (Figure 24.20) and if it continues uncontrolled in a critical mass results in a nuclear explosion. The minimum quantity of nuclear fuel needed to sustain a chain reaction is called the 'critical mass'.

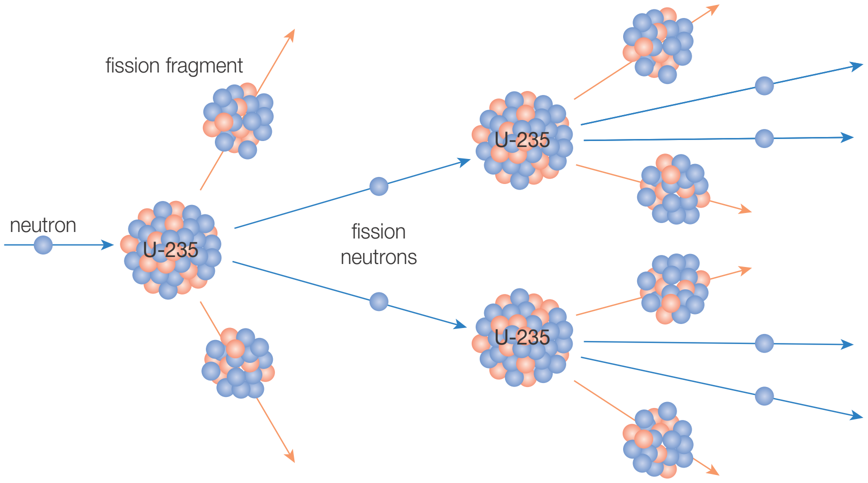


Figure 24.20 A nuclear chain reaction

■ QUICK CHECK QUESTION

19 Discuss the similarities and differences between nuclear fission and nuclear fusion, in terms of the masses and energies of the particles involved.

Nuclear fission and fusion are compared in Table 24.12.

Table 24.12 A comparison of nuclear fission and fusion

Similarities and differences	Nuclear fusion	Nuclear fission
Description	Lighter nuclei combine to form a heavier and larger nucleus	Heavy unstable nucleus splits into two or more lighter nuclei
Where process occurs	In the Sun and other stars	Artificially induced; does not normally occur naturally
Typical reactants	Isotopes of deuterium (${}^{2}_{1}H$) and tritium (${}^{3}_{1}H$)	Uranium-235 nuclides plus high-speed neutron that are slowed down
Conditions	Very high temperature and plasma (ionized gas)	Requires critical mass and high-speed neutrons
Reaction products	Few or no radioactive particles formed (unless a fission 'trigger' is used, radioactive particles will result from that)	Produces highly radioactive particles
Type of reaction	Fusion reaction (not a chain reaction)	Fission chain reaction
Energy released	Several times greater that energy from fission reaction per unit mass	About a million times greater than chemical energy per unit mass, but lower than energy released by nuclear fusion
Energy production	Fusion is an experimental technology for producing electrical power	Fission is used in nuclear power plants

■ Nuclear power

The principle of the nuclear reactor is controlled nuclear fission. A nuclear reactor consists of: a fissionable material as nuclear fuel, such as uranium-235; a moderator (graphite or heavy water) to slow down the neutrons; circulating coolant to remove heat from the reactor, used to boil water and drive turbine generators and control rods of boron steel or cadmium capable of absorbing neutrons.

■ QUICK CHECK QUESTION

20 In the neutron-induced fission reaction of ${}^{235}_{92}U$, one of the products is ${}^{95}_{37}Rb$, three neutrons and another nuclide are also produced. Identify the other nuclide.

Plutonium and breeder reactors

A breeder reactor is a nuclear reactor that produces more fissile material than it consumes. A naturally occurring sample of uranium contains a high proportion of uranium-238, which does not undergo fission. Breeder reactors can also use the waste from uranium processing plants and spent fuel from conventional fission reactors and depleted uranium from nuclear weapons. In a breeder reactor this can be converted (by bombardment with fast neutrons) to plutonium-239 which does undergo fission.

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{94}\mathrm{Pu} + 2\,{}^{0}_{-1}\mathrm{e}$$

$$^{1}_{0}\mathrm{n} + {}^{239}_{94}\mathrm{Pu} \rightarrow {}^{90}_{38}\mathrm{Sr} + {}^{147}_{56}\mathrm{Ba} + 3\,{}^{1}_{0}\mathrm{n} + \text{energy}$$

The problems associated with nuclear reactors and the methods of disposal of nuclear waste are enumerated in Tables 24.13 and 24.14.

Table 24.13 Problems associated with nuclear power (fission reactors)

Health issues	Exposure to high levels of radioactivity in the core can cause radiation poisoning, sterility and increased risks of cancer.
Thermal meltdown	If the chain reaction becomes uncontrollable or cooling systems malfunction, the core can overheat and fuel rods may melt, causing highly radioactive material to escape into the environment if the containment vessel is breached.
Nuclear weapons	Plutonium-239 from breeder reactors and uranium fuel could be enriched to 90% uranium-235 and used to construct nuclear weapons.

Table 24.14 Radioactive waste

Low-level waste	High-level waste
Lower activity – usually contains radioisotopes with shorter half-lives.	Higher activity – usually contains radioisotopes with longer half-lives.
Items that have been contaminated with radioactive material or have been exposed to radioactivity in a nuclear power stations, e.g. gloves, clothing and robot arms and from hospitals, medical instruments and diagnostic agents.	For example, spent fuel rods which no longer contain fissionable uranium-238.
May be stored on site until it has undergone significant decay, buried underground (near surface disposal) in individual concrete canisters or released in the sea and diluted.	Stored in cooling ponds before being buried deep underground in thick concrete containers. It may also be fused with additives such as silicon dioxide and aluminium oxide to form a glass (vitrification).

Nuclear fusion

Nuclear fusion occurs when a hydrogen bomb is detonated, but such a rapid energy release is unsuitable for a power station. Controlled nuclear fusion with hydrogen isotopes, when feasible and economic, would give clean and safe power.

One fusion reaction under investigation is:

$$^{2}_{1}\mathrm{H} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{3}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} + \text{energy}$$

The fusion reaction generates a larger and more stable helium-3 nucleus in which the binding energy is greater than hydrogen-2 (deuterium). The extra binding energy is released as heat and kinetic energy. The reaction between deuterium and tritium atoms to form helium-4 atoms and neutrons is also under investigation as the basis for commercial fusion power.

Three main engineering problems in the development of this energy source have been encountered.

- maintaining the very high temperature of 100 000 000 °C required for the reaction
- containing the plasma (highly ionized gas) at such high temperature – recent experiments have involved the use of extremely strong magnetic fields (often in the form of a torus (doughnut shape)
- the containment vessel needs to be able to sustain neutron bombardment and becomes heavily radioactive.

NATURE OF SCIENCE

Reducing global warming will mean using less fossil fuel and making more use of renewable energy sources. Unlike fossil fuels, no greenhouse gases are produced when transferring energy from nuclear fuel, although the mining of uranium does generate some greenhouse gases. A coal-fired power station releases more radioactivity into the environment than a nuclear power station.

Absorption spectra of stars

Revised ☐

Absorption spectra are generated when electrons in a sample of low-pressure gas are excited (thermally or electrically) and are promoted from lower energy levels to higher energy levels. Each electronic transition absorbs energy and, in the visible region, produces a sharp black line on the continuous spectrum of white light. This absorption spectrum is the exact converse of the emission spectrum for the same gas. You will be familiar with emission spectra from Topic 2. Each element has its own unique emission spectrum (Figure 24.21) or absorption spectrum, and these can be used to identify the element in our Sun or more distant star.

Hydrogen and helium atoms form approximately 99% of the Sun's mass and hydrogen is the most abundant element (75%) in the universe. When astronomers analyse light from distant stars which are surrounded by cooler gases (at low density), it results in the absorption spectrum of the gas consisting of sharp dark lines in a continuous spectrum.

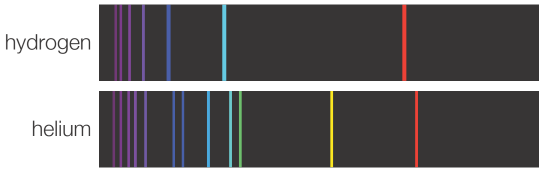


Figure 24.21 Emission spectra of hydrogen and helium atoms

For light, the relationship between the energy of the photons and the frequency and wavelength is given by the expression $E = h\nu = \frac{hc}{\lambda}$, where E is energy, λ is the wavelength, ν is the frequency, h is Planck's constant and c is the speed of light in a vacuum.

■ QUICK CHECK QUESTION

21 A strong absorption line in the helium absorption spectrum occurs at a wavelength of 587.562 nm. Convert the wavelength to a frequency (in Hz), the energy (in joules) of one photon of light of this frequency and the energy of the light in kilojoules per mole.

24.4 Solar energy

Revised ☐

Essential idea: Visible light can be absorbed by molecules that have a conjugated structure with an extended system of alternating single and multiple bonds. Solar energy can be converted to chemical energy in photosynthesis.

Solar energy

Revised ☐

- Light can be absorbed by chlorophyll and other pigments with a conjugated electronic structure.
- Photosynthesis converts light energy into chemical energy:
  $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$
- Fermentation of glucose produces ethanol which can be used as a biofuel:
  $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$
- The energy content of vegetable oils is similar to that of diesel fuel but they are not used in internal combustion engines as they are too viscous.
- Transesterification between an ester and an alcohol with a strong acid or base catalyst produces a different ester:
  $RCOOR^1 + R^2OH \rightarrow RCOOR^2 + R^1OH$
- In the transesterification process, involving a reaction with an alcohol in the presence of a strong acid or base, the triglyceride vegetable oils are converted to a mixture mainly comprising alkyl esters and glycerol, but with some fatty acids.
- Transesterification with ethanol or methanol produces oils with lower viscosity that can be used in diesel engines.

Photosynthesis

Revised ☐

Photosynthesis absorbs solar (light) energy from the Sun and, in plant leaves in the presence of chlorophyll (inside chloroplasts), converts water and carbon dioxide into carbohydrates and oxygen. The overall reaction occurs within chloroplasts inside plant cells and can be written as a molecular equation:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

Expert tip

The basic molecular equation is a simple summary of photosynthesis. It is a series of enzyme-controlled steps, many of which involve transfer of electrons (redox reactions). Some of these reactions take place in the inner membrane of the chloroplast.

Glucose is the monomer from which all carbohydrates, such as sugars, starch and cellulose, are made (via enzyme controlled condensation reactions) (Figure 24.22).

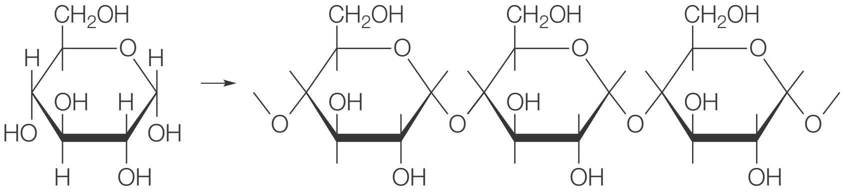


Figure 24.22 Polymerization of glucose to form starch

Figure 24.23 summarizes the main points of photosynthesis from a biological viewpoint.

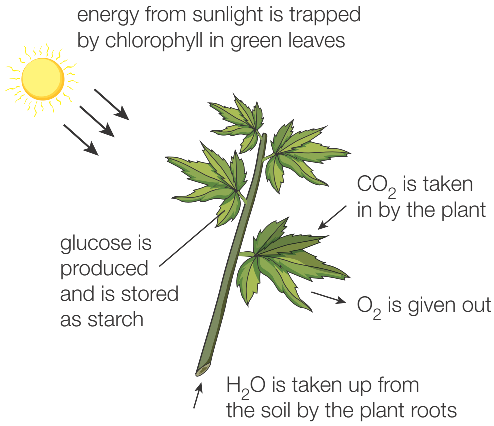


Figure 24.23 Summary of photosynthesis

■ **QUICK CHECK QUESTION**

22 Write a balanced molecular equation for photosynthesis. State the type of chemical reaction that occurs and state what is needed in leaves for it to occur.

The sunlight which reaches the Earth has a mixture of wavelengths, including those which we ‘see’ as colours. These are the visible radiations that are needed for photosynthesis. However, not all the colours of visible light are equally effective for photosynthesis. Chlorophyll appears green because it strongly absorbs both red and purple light (Figure 24.24).

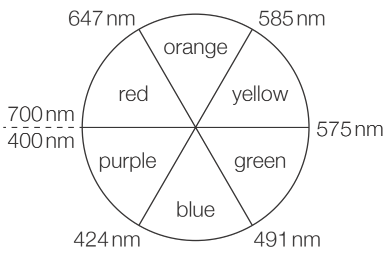


Figure 24.24 Colour wheel from the IB data booklet

The most abundant, and the most important, pigment for photosynthesis is chlorophyll a. Chlorophyll structures are shown in Figure 24.25. These chlorophylls are associated with proteins inside chloroplasts.

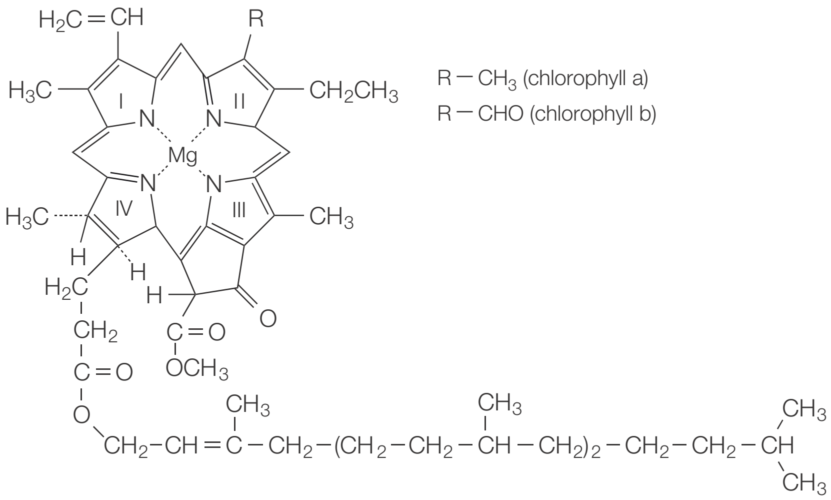


Figure 24.25 Structure of chlorophyll a (the shaded methyl group, $-CH_3$, is replaced by an aldehyde group, $-CHO$, in chlorophyll b)

Expert tip

The four nitrogen atoms in chlorophyll are part of a complex conjugated porphyrin ring, a flat heterocyclic structure. A heterocyclic compound or ring structure is a cyclic compound that has atoms with two or more different elements as members of its ring.

Chlorophyll is a complex molecule, but you will see that it contains a central magnesium ion bonded to four nitrogen atoms. The bonding is similar to that in a complex ion.

The structure of chlorophyll is related to its biological function:

- The long 'tail' of chlorophyll a is lipid soluble (non-polar) and is embedded within the inner chloroplast membrane.
- The 'head' is hydrophilic (polar) and may also lie within the surface of the membrane.
- The flat 'head' allows overlap of p orbitals to form a conjugated system responsible for the absorption of light.
- Changes in the energies of the delocalized π electrons in the flat 'head' section of the chlorophyll molecule enable it to absorb red and blue light very strongly, making it appear green in colour.

Photosynthesis can be divided into three stages:

1 absorption of light energy

2 using light energy to start photochemical redox reactions

3 reducing carbon dioxide to glucose (this does not require light).

Chlorophyll a is involved in the first two stages.

Photosynthesis is a redox reaction. Two half-equations can be written to summarize the reactions of water and carbon dioxide molecules:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \text{(oxidation)}$$

This reaction requires light and is known as photolysis.

$$4e^- + 4H^+ + CO_2 \rightarrow CH_2O + H_2O \qquad \text{(reduction)}$$

This reaction does not require light and requires a biological reducing agent, which acts as a source of hydrogen atoms.

Absorption of light by molecules

In order to absorb light in the visible region of the electromagnetic spectrum the molecule must contain a long, conjugated system. Pigments such as the chlorophylls, carotenoids, e.g. beta-carotene, and hemoglobin, contain an extensive conjugated system of delocalized π electrons and can absorb light throughout the visible region of the spectrum. The conjugated system of the beta-carotene molecule is highlighted in red in Figure 24.26.

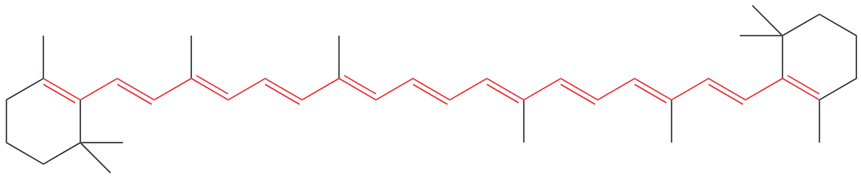


Figure 24.26 Structure of beta-carotene (the orange pigment in carrots)

The beta-carotene molecule has a large delocalized π molecular orbital located above and below the plane of the 'head' of the molecule formed from the sideways overlap of p orbitals on carbon atoms. It is this π system which is responsible for the intense orange colour of carrots. Similar delocalized π bond formation occurs in the 'head' of the chlorophyll molecule between alternating carbon and nitrogen atoms. A benzene ring is also a conjugated system.

When radiation is shone onto a sample of ethene molecules one of the π electrons in the π bonding molecular orbital may be excited to a higher energy level called a π* (anti-bonding π molecular orbital) (Figure 24.27).

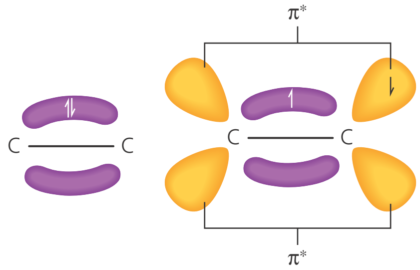


Figure 24.27 π → π* transition in a carbon–carbon double bond

The energy needed to promote the electron to this higher energy level corresponds to a photon of a specific frequency or energy. For most π bonded molecules, these photons are in the ultraviolet region, so there is no effect on the visible light region, and a sample of the molecules is colourless.

However, as more conjugated π bonds are added, the energy of the photons absorbs falls, as the π* energy levels decrease in energy (Figure 24.28). This means that the wavelengths absorbed increase until they appear in the visible region. Therefore, molecules with large conjugated systems absorb visible light, making them coloured.

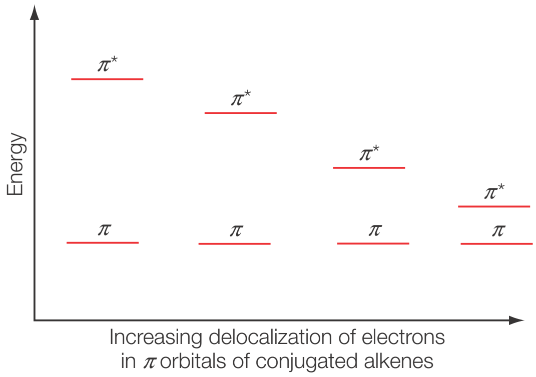


Figure 24.28 The effect of increasing conjugation on the pi energy gap between the π and π* molecular orbitals

Table 24.15 shows some examples of maximum absorption wavelengths (λ_{max}) for a series of organic molecules with increasing amounts of conjugation or pi delocalization.

Table 24.15 Showing λ_{max} for a series of organic molecules

Molecule	λ_{max}/nm	Colour
Ethene	175	Colourless (absorbs in ultraviolet region)
Buta-1,3-diene (2 conjugated C=C bonds or 4 p orbitals in conjugation).	217	Colourless (absorbs in ultraviolet region)
Hexa-1,3,5-triene (3 conjugated C=C bonds or 6 p orbitals in conjugation).	258	Colourless (absorbs in ultraviolet region)
β-Carotene (11 conjugated C=C bonds or 22 p orbitals in conjugation)	approximately 450	Orange (absorbs blue-violet light)
Chlorophyll a (24 p orbitals in conjugation)	approximately 650	Blue-green (absorbs red light)

Figure 24.29 shows the molecular orbital description of the buta-1,3-diene molecule. There is a delocalized pi bond (molecular orbital) extending over four carbon atoms.

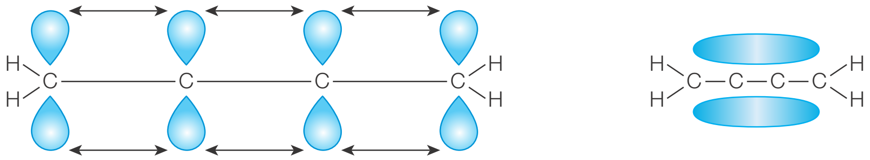
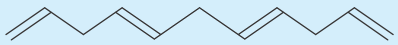


Figure 24.29 The overlap of four separate p orbitals on four adjacent carbon atoms leads to a delocalized pi orbital

Expert tip

Conjugation is completely broken by the introduction of a saturated or sp^3 hybridized carbon atom. The molecule below contains four carbon–carbon double bonds, but it is not conjugated.



A spectrometer can be used to measure the quantity of light absorbed by the pigment at each wavelength. The recorder plots out the intensity of absorption against the wavelength (Figure 24.30).

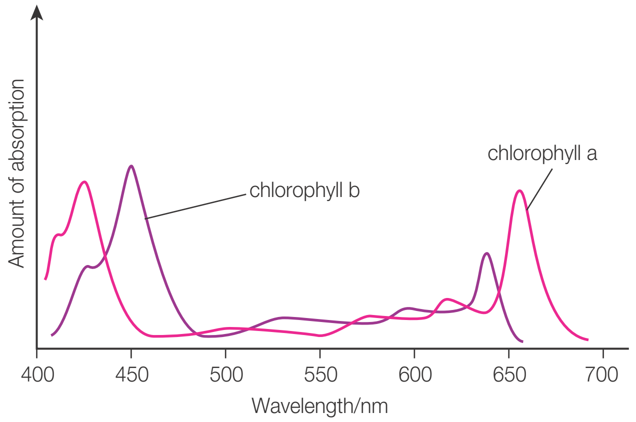


Figure 24.30 Absorption spectra of chlorophyll a and chlorophyll b

Biofuels

Revised ☐

A biofuel is defined as any fuel whose energy is obtained through a process of biological carbon fixation. A biofuel is derived from organic material. Biofuels are typically made using oils extracted from energy crops such as palm oil, sugar cane, corn and rape seed.

Common mistake

Biofuels are not fossil fuels. Fossil fuels are produced by geological processes from prehistoric biological remains.

Bioethanol

Bioethanol is ethanol produced by the fermentation of starchy or sugar-rich crops, including sugar cane, wheat, sorghum and corn. Modern car engines are able to run on a 10% bioethanol/petrol blend without modification or damage.

The production of bioethanol is a multi-step process, involving both physical and chemical conversions. It starts with grinding of the plant material, to produce a fine powder. The powder is mixed with water to form a mash to which an enzyme (amylase) is added which hydrolyses the liquefied starch into glucose.

Yeast (a single-celled fungus) is able to ferment (via a mixture of enzymes known as zymase) the glucose, forming ethanol and carbon dioxide gas. This process forms the basis of beer and wine making. The process can be simplified as:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

100% ethanol can be produced by fractional distillation. Bioethanol production is relatively inefficient since only about 30% of sugar cane is available for fermentation.

QUICK CHECK QUESTION

23 In Brazil, ethanol is mixed with petrol and the mixture used as fuel. Explain why ethanol and petrol mix. Suggest a reason why ethanol is not used on its own as a fuel.

Biodiesel

Biodiesel refers to alkyl ester fuels made by processing feed stocks such as vegetable oils including: soybean oil, canola oil and palm oil, animal fats (tallow) and even waste cooking oils.

These oils cannot usually be used as a fuel in diesel engines without processing. The energy content of vegetable oils is similar to that of diesel fuel, but they are not used in internal combustion engines as they are too viscous (too thick).

Common mistake

Such use (or when vegetable oils are mixed directly with diesel produced from crude oil without processing) is not normally regarded as being biodiesel.

The production of biodiesel involves three stages: purification, neutralisation and transesterification.

The purification process involves filtering especially if the oil has come from a food production source, such as waste oil. Any non-oil material and water must also be removed at this stage, so as not to interfere with following stages of the process.

The feedstock is then analysed to determine the level of free fatty acids present. Free fatty acids are long chain carboxylic acids used to synthesize triglycerides (fats and oils) in plants and animals.

The analysis allows the quantities required to complete the transesterification reaction to be calculated. If the levels of free fatty acids exceed 4%, they then undergo a pre-treatment in which they are converted to esters via an acid catalysed reaction with an alcohol. For example:

$$\underset{\text{free fatty acid}}{R_1COOH} + \underset{\text{alcohol}}{R_2OH} \xrightarrow{H_2SO_4} \underset{\text{ester}}{R_1COOR_2} + \underset{\text{glycerol}}{C_3H_8O_3}$$

R_1 and R_2 refer to alkyl groups and glycerol is propane-1,2,3-triol.

The transesterification reaction forms the alkyl esters derived from the original triglyceride (Figure 24.31).

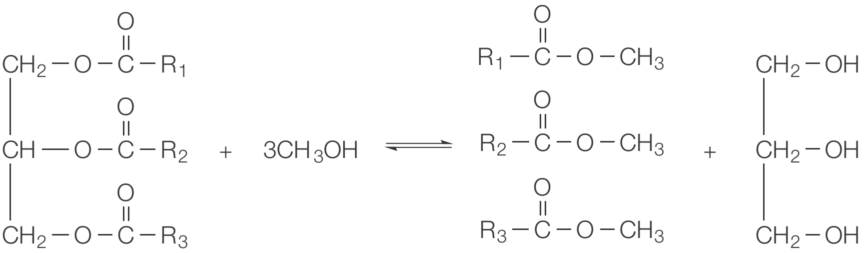


Figure 24.31 Transesterification of a triglyceride with methanol, producing methyl esters and glycerol

Transesterification with ethanol or methanol produces oils with lower viscosity that can be used in diesel engines. The reaction is an equilibrium system, so conditions have to be controlled to ensure maximum yield of alkyl esters. A temperature of 50 °C, a strong base catalyst and the addition of excess alcohol all combine to shift the reaction in favour of the products. The result is a yield of over 90%.

Expert tip

Transesterification is the process of exchanging the alkyl group R´´ of an ester with the alkyl group R´ of an alcohol.

Advantages and disadvantages of biodiesel and diesel

The advantages and disadvantages of biodiesel compared with diesel are summarised in Table 24.16.

QUICK CHECK QUESTIONS

24 A triglyceride is formed from the following three fatty acids (in condensation reaction):

capric acid, $CH_3(CH_2)_8COOH$, euric acid, $C_{22}H_{42}O_2$, linoleic acid, $C_{17}H_{31}CO_2H$

Deduce the number of carbon–carbon double bonds in each of the three fatty acids and state the level of saturation.

25 State the products of the following acid-catalysed transesterification reactions: $CH_3COOCH_2(CH_2)_8CH_3 + CH_3OH$ and $CH_3COOCH_2CH_2OCOCH_3 + 2CH_3OH$

26 Transesterification reactions allow waste cooking oils from kitchens to be converted to biofuels. Identify a reagent and catalyst needed for this conversion.

Table 24.16 Advantages and disadvantages of biodiesel compared with diesel

Advantages	Disadvantages
High flash point – less flammable than diesel; safer in a crash. (The flash point is the lowest temperature at which a liquid can form an ignitable mixture in air near the surface of the liquid.) Perform well as fuels, under most conditions. Higher octane rating.	More viscous (thicker) than diesel (due to presence of dipole–dipole forces), even when converted to methyl esters – requires pre-warming.
Lower carbon footprint – amount of carbon dioxide is the same, but carbon dioxide was absorbed by growing plants (via photosynthesis). The combustion of diesel introduces carbon dioxide into the atmosphere, that was not present before.	Slightly lower energy content than diesel. Uses agricultural resources and farming land resulting in increased food prices and monoculture.
More easily biodegradable (by bacteria) in the event of a spill. Free of sulfur, so no emission of sulfur dioxide and hence no contribution to acid rain. Also extends the life of catalytic converters.	The production of biodiesel from raw materials is more expensive than the production of diesel from crude oil (via fractional distillation).
Sustainable/'green'/environmentally friendly/renewable – the raw materials can be grown using solar (light) energy from the Sun as the source.	Biofuels may contain a higher percentage of nitrogen than diesel and other fossil fuels and hence release larger amounts of oxides of nitrogen (NO and NO_2), when burned. This will contribute to acid rain.
A good solvent – cleans the engine and reduces the need for maintenance except for filter replacement.	Dirt cleaned from engines tends to clog fuel filters and causes cars to stall. It can also dissolve paint and protective coatings.

Expert tip

Biofuels are described as carbon neutral, meaning the carbon atoms in the molecule of the biofuel originally were present in the atmosphere in the form of carbon dioxide molecules. These carbon atoms re-enter the atmosphere as carbon dioxide molecules when the fuel is combusted. There is no overall change in the amount of carbon dioxide in the atmosphere. However, this is a simplistic view and fails to take account of the carbon dioxide production involved in the transport of feedstock, biofuel production and distribution.

24.5 Environmental impact – global warming

Revised ☐

Essential idea: Gases in the atmosphere that are produced by human activities are changing the climate as they are upsetting the balance between radiation entering and leaving the atmosphere.

Environmental impact – global warming

Revised ☐

- Greenhouse gases allow the passage of incoming solar short wavelength radiation but absorb the longer wavelength radiation from the Earth. Some of the absorbed radiation is re-radiated back to Earth.
- There is a heterogeneous equilibrium between concentration of atmospheric carbon dioxide and aqueous carbon dioxide in the oceans.
- Greenhouse gases absorb IR radiation as there is a change in dipole moment as the bonds in the molecule stretch and bend.
- Particulates such as smoke and dust cause global dimming as they reflect sunlight, as do clouds.

Introduction – the greenhouse effect

Revised ☐

The temperature of the Earth depends on the amount of solar energy received, the proportions absorbed by the Earth or reflected back into space, and the extent to which the atmosphere retains the thermal energy.

There is a natural steady state ‘greenhouse effect’ due to the presence of molecules of water vapour, methane and carbon dioxide as greenhouse gases found naturally in the atmosphere.

The greenhouse effect (Figure 24.32) is the trapping of heat in the atmosphere. Short wavelength ultraviolet and visible radiation passes through the atmosphere to warm the Earth’s surface which absorbs some of the energy and re-radiates it as infrared radiation of longer wavelength.

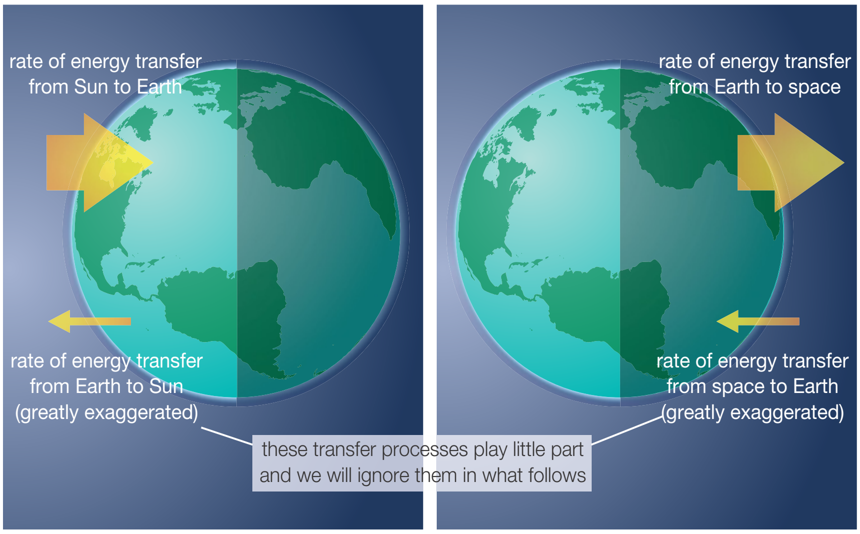


Figure 24.32 The greenhouse effect of the Earth’s atmosphere

This infrared radiation from the Earth is absorbed by the greenhouse gases, water vapour, methane and carbon dioxide and re-radiated back to Earth. Thus, greenhouse gases allow incoming solar radiation to reach the Earth, but absorb some of the heat radiated from the Earth, thus maintaining the global temperature (Figure 24.33).

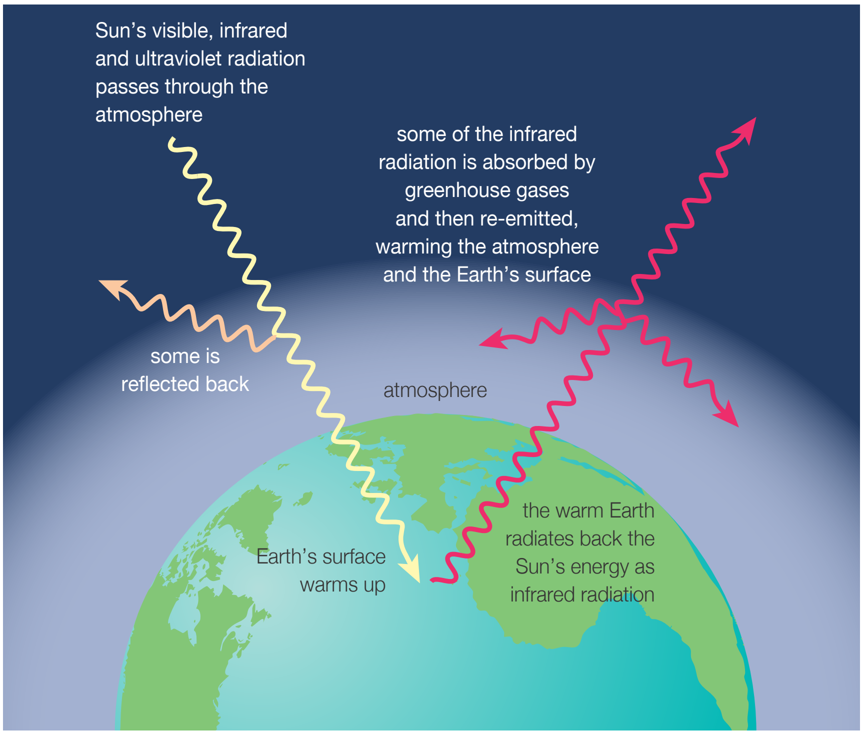


Figure 24.33 The different types of radiation involved in the greenhouse effect

Expert tip

Water vapour makes the largest contribution to the greenhouse effect and plays an important role in maintaining the atmospheric temperature at night when the surface is emitting radiation into space and not receiving energy from the Sun.

Global warming is the gradual increase in the average global surface temperature. There is strong evidence to suggest that global warming is taking place and has increased rapidly since the Industrial Revolution. Surface land and ocean temperature records exist for more than a century and analysis of ice cores, tree rings and lake sediment allow temperatures over many thousands of years to be estimated (Figure 24.34).

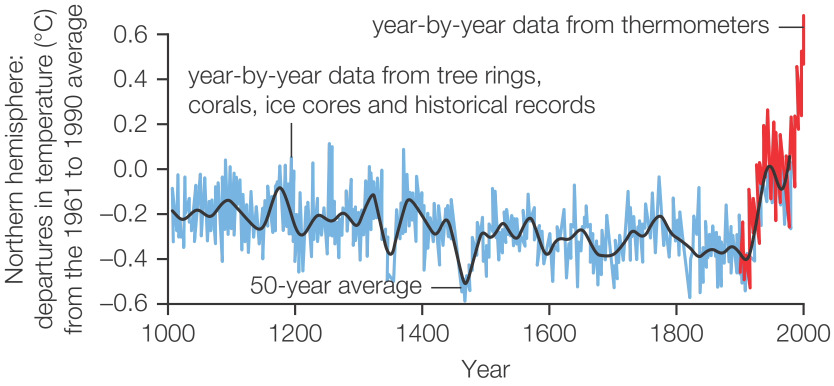


Figure 24.34 Variations in the Earth's surface temperature

Expert tip

Without the greenhouse effect, the surface temperature of Earth would be approximately −18 °C. The greenhouse effect keeps the average temperature of the Earth at about 15 °C.

The major greenhouse gases introduced into the environment are methane and carbon dioxide (Table 24.17). Their effect on global warming depends on their concentration in the atmosphere, their lifetime in the atmosphere and their ability to absorb infrared radiation. The global warming potential is a measure of the global warming caused by the gas in 100 years, relative to the same amount of carbon dioxide which is given a value of 1.

Table 24.17 Two major greenhouses gases compared

Gas	$CH_4(g)$	$CO_2(g)$
Main sources	Anaerobic decomposition of organic matter; from ruminant animals (cows and sheep by bacterial breakdown of cellulose), rice paddies, crude oil and gas fields	Combustion of fossil fuels; forest fire, volcanoes and decay of animals and plants
Concentration in air/ppm	1.75	380
% increase in concentration each year	12	50–200
Global warming potential	23	1
Atmospheric life time/years	12	50–200

Expert tip

It is important to differentiate between the natural greenhouse effect, which is essential for life to exist, and the enhanced greenhouse effect. This is the additional effect caused by the anthropogenic (man-made) emissions and believed by many scientists to be making a significant contribution towards causing global warming and climate change.

Atmospheric concentrations of greenhouse gases have increased significantly since the Industrial Revolution in the 18th century. Carbon dioxide concentrations have increased by 25% and methane concentrations have increased by 145%. The atmospheric concentration of methane is relatively low, but it is 30 times more effective than carbon dioxide (on a molecular level) at absorbing infrared radiation. However, methane has a short average atmospheric life time.

Greenhouse gases and global warming

Revised ☐

Many of the greenhouses gases (except the CFCs and SF_6) have natural sources in addition to man-made (anthropogenic) sources. The concentration of carbon dioxide in unpolluted air has risen steadily on an annual basis over the past 50 years (Figure 24.35). The peaks correspond to the winter months and the troughs to the summer months.

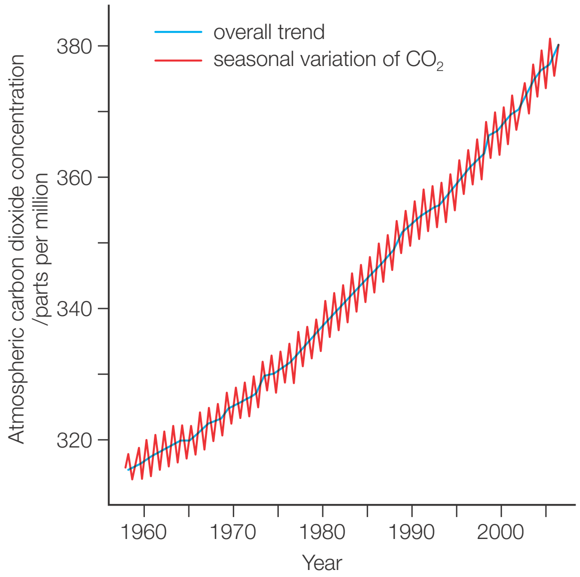
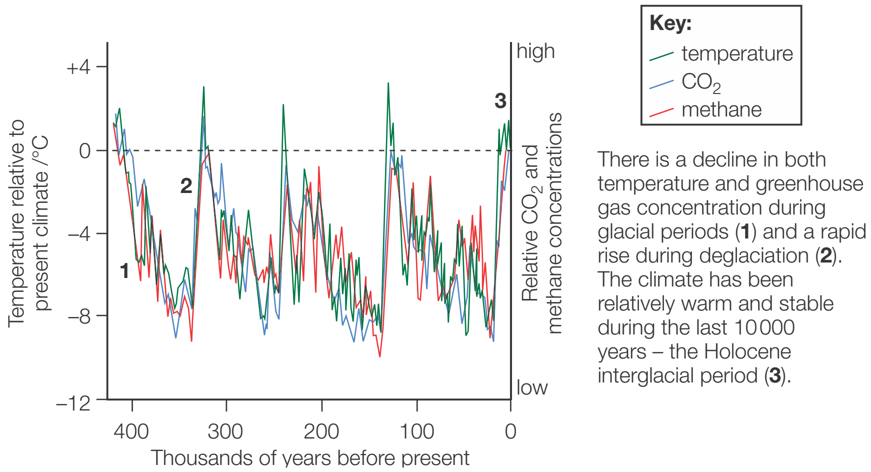


Figure 24.35 Atmospheric carbon dioxide levels recorded at Mauna Loa, Hawaii, 1957–2005

During this same recent time period average global temperatures have generally increased (except during periods of intense volcanic activity). Past measurements of carbon dioxide and temperature (Figure 24.36) suggest that the link between temperature and carbon dioxide is complicated. Methane and other greenhouses gases, such as N_2O, O_3, CFCs and SF_6, also contributes to global warming and small particles in the atmosphere called aerosols can cause cooling. Variations in solar energy and hence global temperatures are caused by the orientation of the Earth as it moves around the Sun.



There is a decline in both temperature and greenhouse gas concentration during glacial periods (**1**) and a rapid rise during deglaciation (**2**). The climate has been relatively warm and stable during the last 10 000 years – the Holocene interglacial period (**3**).

Figure 24.36 The three types of data recovered from the Vostok ice cores over 400 000 years of Earth history

Water vapour

The source of water vapour is largely a natural one. It comes from the evaporation of water from oceans, lakes and plants.

It does not trap as much heat as carbon dioxide as it is a poorer absorber of infrared radiation. However, owing to the sheer quantity of water vapour in the atmosphere, huge amounts of heat are trapped and it is the most important greenhouse gas.

Human activity does not contribute to water vapour levels in the atmosphere to any significant extent due to the activity of the water cycle. It is naturally occurring and it exists in huge quantities. Water vapour has the largest natural effect but is of less concern than carbon dioxide since its concentration is not increasing with time.

However, the effect of water vapour in contributing to the greenhouse effect is difficult to predict. As greater amounts of other greenhouse gases accumulate, increased heating will cause an increase in the amount of water vapour due to evaporation, resulting in a larger quantity of water vapour, hence an increased greenhouse effect. This is an example of a potential positive feedback loop.

However, the increased evaporation results in cooling on the surface of the Earth as water absorbs energy to evaporate. The larger amount of water vapour in the atmosphere also causes more clouds to form. The clouds will reflect mores sunlight back into space, resulting in cooling.

NATURE OF SCIENCE

In 2007, the Intergovernmental Panel on Climate Change (IPCC) stated that 'Most of the observed increase in global average temperatures since the mid-20th century is *very likely* due to the observed increase in anthropogenic (man-made) greenhouse gas concentrations. It is *likely* that there has been significant anthropogenic warming over the past 50 years averaged over each continent (except Antarctica)'.

Carbon dioxide

There are essentially three approaches to reducing emissions of carbon dioxide ('carbon emissions'): replacing fossil fuels with carbon-neutral biofuels (see 24.4 solar energy); the use of renewable energy sources, such as photovoltaic technology, or the use of carbon capture and storage, which prevents the carbon dioxide formed from entering the atmosphere.

Examples of carbon capture and storage techniques are:

- injecting carbon dioxide as a supercritical liquid deep into oceans
- storing carbon dioxide in deep geological formations
- reacting carbon dioxide with metal oxides to form metal carbonates.

Carbon dioxide dissolves and reacts with water by the following series of successive reactions:

$$CO_2(g) \rightleftharpoons CO_2(aq) \text{ (heterogeneous equilibrium)}$$

$$CO_2(l) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

Adding these equations gives an overall equation:

$$CO_2(g) + H_2O(l) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq)$$

Application of Le Châtelier's principle predicts that an increase in atmospheric carbon dioxide will lead to a greater amount of carbon dioxide dissolving in the oceans. This results in a decrease in pH (increase in $H^+(aq)$ concentrations) which reacts with the calcium carbonate present in the limestone of coral reefs:

$$CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(l)$$

The excess carbonate ions precipitate out as limestone (mainly calcium carbonate). The reverse reaction would occur if atmospheric levels of carbon dioxide fell.

QUICK CHECK QUESTION

27 Explain the effect of decreasing concentrations of atmospheric carbon dioxide on the pH of the oceans, including equations in your answer.

Effects of global warming

Revised ☐

Global warming causes the temperature of the sea to rise, which causes polar ice caps and glaciers to melt. This physical expansion of ocean water causes flooding of low-lying areas. Global warming also leads to unpredictable changes in weather patterns around the world, which is termed 'climate change'.

The mechanism of absorption of infrared radiation by greenhouse gases

Revised ☐

Different covalent bonds have different strengths due to the masses of different atoms at end of the covalent bond (which behaves like a spring). As a result they vibrate at different frequencies. The frequency of vibration can be found by detecting when the molecules absorb infrared radiation.

Molecules (at temperatures above absolute zero) have atoms that are constantly vibrating relative to one another – the covalent bonds may be lengthening or shortening (stretching), or the bonds may be bending and the bond angle changing.

Each of these molecular vibrations has a resonance frequency, called the vibration frequency, associated with it. The energies of molecular vibrations known as vibrational energies, are quantized, that is, they have certain allowed values.

When these molecules at lower vibrational energy level V_1 absorb radiation of a certain frequency the molecules will be promoted (Figure 24.37) to a higher or excited vibrational energy level V_2. The energies absorbed by covalent bonds correspond to the energies in photons of the infrared region of the electromagnetic radiation.

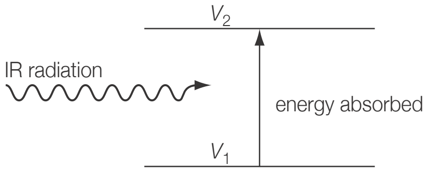


Figure 24.37 Vibrational excitation

However, the molecules in the higher vibrational energy level V_2 will undergo a transition and return to the lower vibrational energy level V_1 (Figure 24.38). The extra energy is released back to the surroundings and part of the energy will be radiated back towards Earth, which heats it.

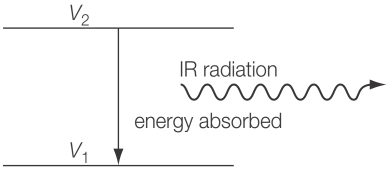


Figure 24.38 Vibrational de-excitation

Greenhouse gases

Not all gas molecules absorb infrared radiation. Gas molecules, polar and non-polar, are constantly vibrating (and their bonds behave like elastic springs). When the molecules vibrate, the bonds can stretch and bend (if the molecule has three or more atoms). The stretching and bending bonds may or may not result in a change in the dipole moment of the molecules.

If there is a change in dipole moment, the molecule in that vibrational mode will absorb infrared radiation and is described as IR-active. If the same molecule undergoes a different vibrational mode that does not result in a change in dipole moment, then the molecule in that vibrational mode is not IR-active.

Some molecules are not always IR-active, for example, N_2 and O_2, while others are always IR-active, for example, HCl. There are some other molecules which exhibit some vibration modes that are IR-active while other vibrational modes are IR-inactive.

Water

The water molecule has two O–H bonds that behave independently. Both bonds can stretch symmetrically or asymmetrically, resulting in a change in bond length, but not bond angle (Figure 24.39). The water molecule can also bend, resulting in a change in bond angle, but with bond lengths unchanged (Figure 24.40). All three vibrational modes are IR active.

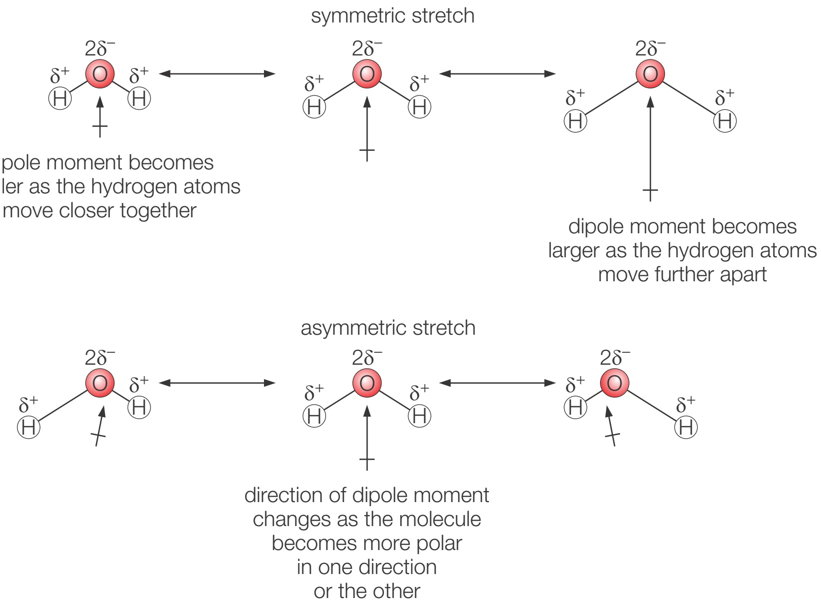


Figure 24.39 Stretching modes of water

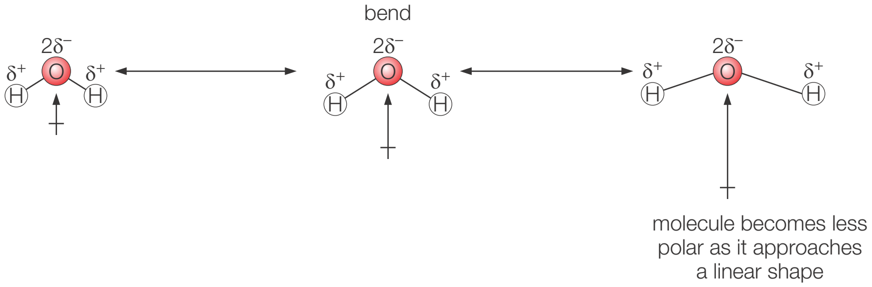


Figure 24.40 Bending modes of water

Carbon dioxide

Its vibrational modes are symmetric stretch, asymmetric stretch and bending and of these three vibrational modes, only the symmetric stretch is IR-inactive. The dipole moment remains zero.

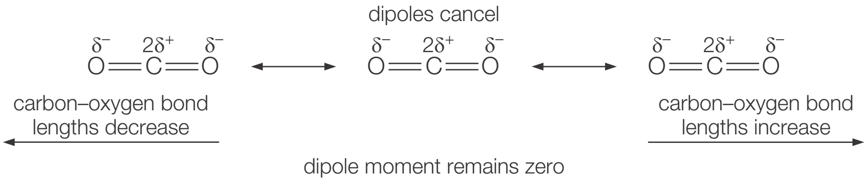


Figure 24.41 Symmetric stretching of carbon dioxide

The asymmetric stretch and bending modes result in a change in the molecular dipole moments and those vibrational modes of the carbon dioxide molecule are IR-active.

QUICK CHECK QUESTION

28 Sketch diagrams to show the IR-active modes of CO_2.

Methane

The vibrational modes of methane are more complex than carbon dioxide's due to it tetrahedral shape, resulting in more IR radiation absorbed, hence trapping more heat.

Unlike carbon dioxide, methane has two bending vibrational modes. One is IR-active while the other is not. Here are the two IR-active vibrational modes.

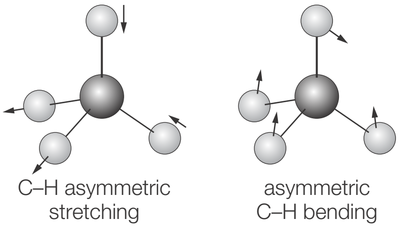


Figure 24.42 Two IR active vibrational modes of methane

Particulates

Revised ☐

Particulates (solid particles) suspended in the air can have the opposite effect to greenhouse gases: global 'dimming'. They cool the Earth's surface by scattering the short wave infrared radiation from the Sun and reflecting it back into space. The droplets and ice particles in low-level clouds are also involved during the day time in reducing ground temperatures.

Atmospheric particles originate from soil dust, spray from oceans forming salt particle, biological debris and volcanic dust. The release of sulfur dioxide from volcanic eruptions can lead to the generation of particles containing sulfate ions. Some airborne particles originate from fuel combustion, cars and industrial processes. The lowering of average global temperatures during the 1940s and 1960s has been attributed to increased volcanic activity during these periods.

QUICK CHECK QUESTION

29 Explain how greenhouse gases are thought to cause global warming.

24.6 Electrochemistry, rechargeable batteries and fuel cells

Revised ☐

Essential idea: Chemical energy from redox reactions can be used as a portable source of electrical energy.

Electrochemistry, rechargeable batteries and fuel cells

Revised ☐

- An electrochemical cell has internal resistance due to the finite time it takes for ions to diffuse. The maximum current of a cell is limited by its internal resistance.
- The voltage of a battery depends primarily on the nature of the materials used while the total work that can be obtained from it depends on their quantity.
- In a primary cell the electrochemical reaction is not reversible. Rechargeable cells involve redox reactions that can be reversed using electricity.
- A fuel cell can be used to convert chemical energy, contained in a fuel that is consumed, directly to electrical energy.
- Microbial fuel cells (MFCs) are a possible sustainable energy source using different carbohydrates or substrates present in waste waters as the fuel.
- The Nernst equation, $E = E^{\ominus} - \frac{RT}{nF} \ln Q$, can be used to calculate the potential of a half-cell in an electrochemical cell, under non-standard conditions.
- The electrodes in a concentration cell are the same but the concentration of the electrolyte solutions at the cathode and anode are different.

Introduction

Revised ☐

A voltaic (galvanic) cell acts as a simple battery. The free energy of an exothermic chemical reaction is converted into electrical energy. Such a cell, usually, consists of two electrodes immersed into one or more suitable electrolytes. When the electrodes are connected externally (via wires), a spontaneous chemical reaction occurs in the cell. The electrode at which oxidation occurs is the anode; the electrode at which reduction occurs is called the cathode.

A (galvanic) cell (Figure 24.43) consists of two electrodes, one of which acts as the cathode and one of which acts as the anode. Each electrode along with the electrolyte is known as a half-cell and the reactions that occur at the half-cell are termed the half-cell reactions.

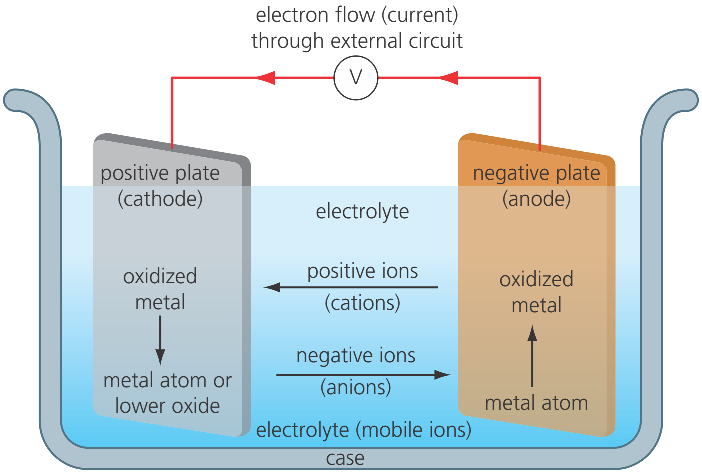


Figure 24.43 Structure of a generalized voltaic (galvanic) cell

Expert tip

The mass of the active material in the electrode of a cell is important since the number of electrons moved around the external circuit is a measure of how much work can be done before the reaction reaches equilibrium and the cell is discharged. Substances of low molar mass have an advantage.

Expert tip

A battery consists of two or more voltaic (galvanic) cells connected in series to make up a battery of cells. This is the correct meaning of the term 'battery'. However, the term 'simple battery' may refer to a single voltaic (galvanic) cell.

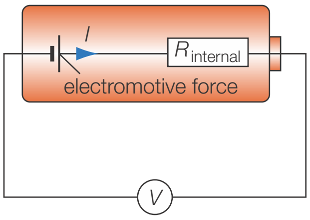


Figure 24.44 Internal resistance of a cell (*I* represents an electric current)

The maximum voltage provided by a voltaic (galvanic) or fuel cell is known as its electromotive force. The migration of the ions within the electrolyte of the battery takes a finite amount of time. There are other factors which also affect how fast the ions migrate through the battery, such as temperature. This results in internal resistance (Figure 24.44) and the voltage (cell potential) delivered by a battery is smaller than the electromotive force. Consequently, the maximum work that a battery can do is dependent on the design and construction of the battery.

Types of cells

Revised ☐

Primary cells produce electricity via a redox reaction which is not readily reversible. After they are discharged or 'flat', the cells are no longer useful as they cannot be recharged.

Also known as secondary cells, rechargeable cells produce electricity through a redox reaction which is readily reversible. The reversible reaction is not spontaneous and requires an external power source for the battery to be charged.

Power, voltage and current

Revised ☐

The power, P, generated by a battery is measured in watts (W) and is calculated as the product of the voltage V and the current I in amps:

$$P = V \times I$$

However, since $V = I \times R$ (Ohm's law), where R represents the electrical resistance:

$$P = I^2 \times R \text{ and } P = \frac{V^2}{R}$$

Larger batteries (of the same type) deliver more power because, although their voltage is unchanged, the maximum current they can deliver increases proportionally. The total energy E (in joules) generated by a battery is calculated as the product of the power, P, in watts and time, t, in seconds:

$$E = P \times t = V \times I \times t$$

A larger battery, containing more chemicals, will be capable of generating power for a longer period of time. Many commercial batteries express their total energy content using non-SI units, most commonly kilowatt-hours (kW h).

By combining two cells in series the voltage can be doubled (but the current unchanged). A lead–acid car battery consists of six cells connected in series.

QUICK CHECK QUESTION

30 Describe the difference between voltage and power for a battery and identify the factors that affect the voltage and the power of a cell.

Primary cells

Revised ☐

Carbon–zinc dry cell

The common dry cell (Figure 24.45) contains an aqueous paste of ammonium chloride and powdered manganese(IV) oxide as the electrolyte. The positive electrode (cathode) is made of a graphite rod (often with a brass cap) and the zinc casing is the negative electrode (anode). A porous separator acts as a salt bridge to allow ions to migrate. It also prevents the two electrodes touching and causing a short circuit.

When the cell is discharging, electrons flow from the zinc anode to the graphite cathode. Oxidation occurs at the anode (negative electrode):

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

Reduction occurs at the cathode (positive):

$$MnO_2(s) + NH_4^+(aq) + e^- \rightarrow MnO(OH)(s) + NH_3(aq)$$

where MnO(OH) is manganese(III) oxyhydroxide.

The ammonia molecules then react with the zinc ions to form the soluble complex ion $[Zn(NH_3)_4]^{2+}(aq)$, which prevents a build-up of ammonia gas within the sealed battery. In addition to having to replace the battery when it is 'flat', it has a poor shelf-life and the acidic ammonium ions can corrode the zinc casing. The voltage is 1.5 V.

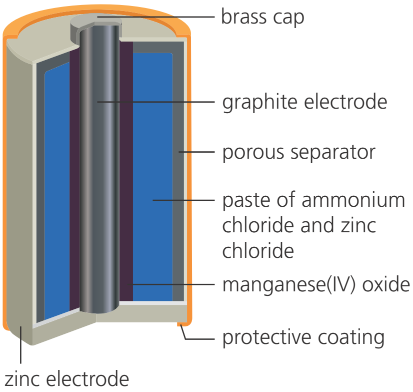


Figure 24.45 Carbon–zinc dry cell (in cross section)

Rechargeable batteries

Revised ☐

Lead–acid storage battery

The commonest storage or secondary cells are lead–acid cells used in car batteries and back-up lighting systems. These electrochemical cells are rechargeable because the chemical changes at the electrodes are reversible. The electrochemistry of lead–acid cells involves lead in three oxidation states: 0, +2 and +4.

In a fully charged lead–acid cell, the negative electrode (anode) consists of lead metal. The positive electrode (cathode) consists of lead coated with lead(IV) oxide. The electrodes dip into a solution of moderately concentrated sulfuric acid ($6\,mol\,dm^{-3}$) and these are the electrode processes as current flows and the battery discharges:

At the negative electrode:

$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-; E^\ominus = +1.69\,V$

At the positive electrode.

$PbO_2(s) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l); E^\ominus = -0.36\,V$

The overall reaction is:

$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l); E^\ominus_{cell} = 2.05\,V$

The equation helps to explain why the cell is rechargeable. As a current flows from the cell lead(II) sulfate, a solid with a low solubility is produced at the surface of both electrodes. This traps the lead(II) ions on the electrode surface instead of their dissolving in the sulfuric acid electrolyte. When the current is reversed to charge up the cell the two reaction can be reversed, turning lead(II) ions back to lead metal (lead atoms) at one electrode and back to lead(IV) oxide, PbO_2, at the other (Figure 24.46).

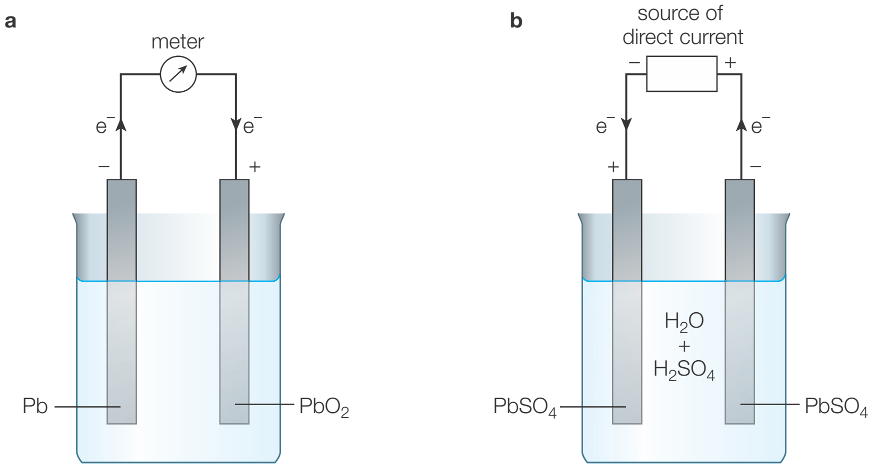


Figure 24.46 A lead-acid cell **a** discharging and **b** charging

As sulfuric acid is consumed during the discharge reaction, the density of the electrolyte can be measured using a hydrometer to indicate the state of the battery. The charging process can lead to a side reaction involving electrolysis of water molecules to release hydrogen and oxygen gases. Hence, non-sealed car batteries need occasional topping up with distilled water.

A lead–acid car battery consists of six lead–acid cells joined in series producing 12 V and able to supply large currents. The disadvantages of lead–acid batteries are their low energy density (60–110 KWh) due to the presence of lead and environmental concerns related to sulfuric acid and lead, a heavy metal.

QUICK CHECK QUESTION

31 One reaction that occurs in a lead–acid battery involves the conversion of lead(IV) oxide into lead(II) sulfate.

- **a** Write a half-equation for the reaction that occurs on the surface of the electrode.
- **b** State and explain whether this reaction occurs at the negative or positive electrode.

Nickel–cadmium (NiCad) battery

Rechargeable nickel–cadmium (NiCad) batteries are used in portable electronic and electrical devices. They have a cell potential of 1.2 V. The positive electrode is made of nickel oxyhydroxide which is separated from the negative electrode made of calcium hydroxide. The electrolyte is aqueous potassium hydroxide and during discharge the following reactions occur:

Cathode: $2Ni\,(OH)_2(s) + 2H_2O(l) + 2e^- \rightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$

Anode: $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$

The overall reaction during discharge is:

$2NiO(OH)(s) + Cd(s) + 2H_2O(l) \rightarrow 2Ni(OH)_2(s) + Cd(OH)_2(s)$

This process is reversed during charging. One of the disadvantages of NiCad batteries is that cadmium is an extremely toxic heavy metal and needs to be recycled.

QUICK CHECK QUESTION

32 The nickel–cadmium cell is a common rechargeable cell. The two electrodes are nickel and cadmium. The chemical reaction that takes place in the nickel–cadmium cell can be represented as:

$2NiO(OH)(s) + Cd(s) + 2H_2O(l) \Rightarrow 2Ni(OH)_2(aq) + Cd(OH)_2(aq)$

a Write down the half-equation for the reaction at the cathode and anode respectively.

b Explain why the Ni-Cad cell can be recharged.

Lithium ion battery

Handheld devices and laptop computers often use lithium ion batteries (Figure 24.47). The negative electrode is made of graphite and lithium atoms are intercalated between the layers. They release electrons to the circuit and migrate to the graphite electrode through a gel polymer electrolyte. The lithium ions accept electrons within a cobalt(IV) oxide lattice to form cobalt(III) oxide and lithium oxide.

Lithium ion batteries have a higher energy density (amount of energy per unit mass) than Ni-Cad batteries and produce a higher voltage, 3.6–4.2 V, but they do not have such a long lifespan.

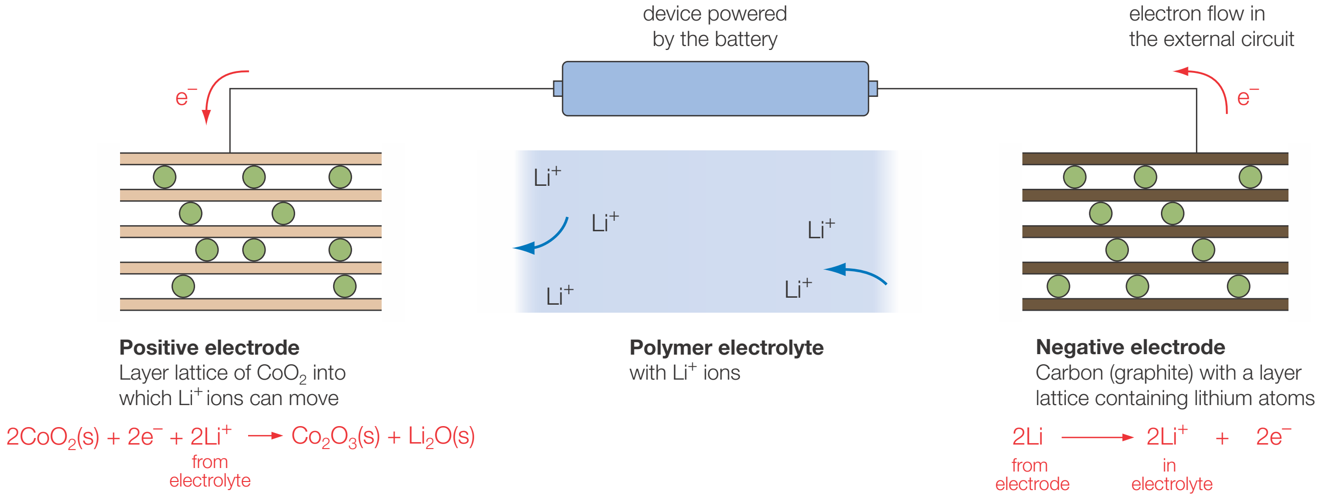


Figure 24.47 Schematic diagram of a lithium-ion polymer battery showing the battery discharging. The electrode processes are reversible so that the battery can be recharged

The advantages of different types of secondary cells

Revised ☐

When selecting a cell or battery for a particular use the following issues (see Table 24.18) may need to be considered:

- whether or not the cell can be recharged
- the dimensions and mass of the cell
- the voltage of the cell
- the chemical and physical nature of the electrolyte
- how long the cell can deliver current at its maximum voltage, and
- the cost of the cell.

Table 24.18 The advantages and disadvantages of different types of cell

	Advantages	**Disadvantages**
Lead–acid battery	Very well-established technology. Ability to deliver high current essential for vehicle applications (starter motor, ignition system). Battery can be recycled and lead re-used. Low internal resistance.	Low power-to-mass ratio. Suitable for small, slow electric vehicles such as golf carts, but not higher-performance vehicles. Not suitable for fast recharging, because it leads to electrolysis of water or break-up of the lead(II) sulfate layer, which shortens the battery life. Possibility of damage if left 'flat' for too long, owing to crystallization of lead(II) sulfate.
Nickel–cadmium battery	High number of charge–discharge cycles possible (thousands). Long storage time – can retain a charge 'on the shelf' for months.	Cadmium is a heavy metal highly toxic so batteries must be disposed of carefully. Memory effect – if the battery is not discharged fully it 'remembers' the lower-charge state and will not fully charge on subsequent cycles.
Lithium ion battery	High energy density – lithium ion batteries are light and powerful. Minimal memory effect – lithium ion batteries are more tolerant of incomplete charge–discharge cycles.	Manufacturing flaws or battery damage can lead to thermal runaway and the battery catching fire. Sensitive to higher temperatures

Fuel cells

Revised ☐

Fuel cells are different from batteries and the lead–acid battery because the substances from which they obtain electrical energy are continually fed into the system (as gases or liquids). As long the fuel and oxygen continue to be supplied the cell will continue to generate a voltage.

The first fuel cell to be developed used hydrogen and oxygen as reactants (Figure 24.48). The negative electrode is porous graphite coated with nickel and nickel(II) oxide. The function of the nickel and its oxide is to act as act as catalysts for the reactions that occur on the surface of the electrodes. The electrolyte that is in contact with both electrodes is aqueous potassium hydroxide (if an alkaline fuel cell) or phosphoric(V) acid (if an acidic fuel cell).

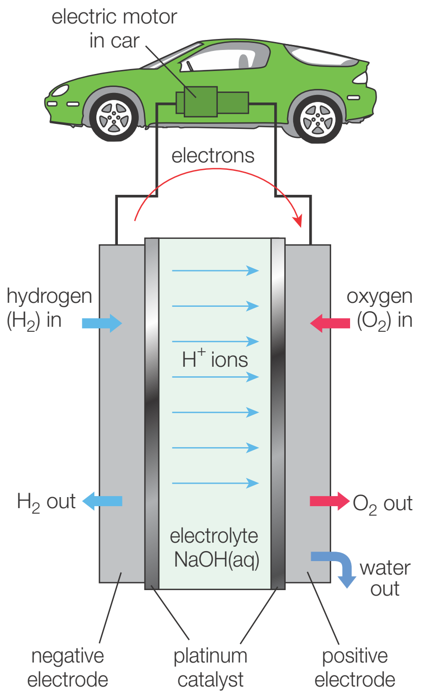


Figure 24.48 An alkaline hydrogen–oxygen fuel cell providing power to drive a car

Hydrogen gas is supplied to the negative electrode. Its molecules diffuse through the graphite and react with hydroxide ions to form water molecules:

$$2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$$

Oxygen gas is supplied to the positive electrode. Its molecules diffuse through the graphite and react to form hydroxide ion:

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

Adding the two electrode reactions together (and cancelling electrons and hydroxide ions) the overall reaction can be generated:

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

■ QUICK CHECK QUESTION

33 Suggest the advantages and disadvantages of a hybrid power system car versus an all-electric hydrogen fuel cell car.

Methanol fuel cells

Revised ☐

Hydrogen is a flammable gas that must be stored under pressure. Methanol, which is a liquid at room temperature and pressure, is easily stored and transported. Methanol can be stored in sealed cartridges which have an energy density far higher than hydrogen or even lithium ion batteries.

Methanol fuel cells use the catalytic oxidation of methanol to form carbon dioxide. The electrode reactions are:

Anode:

$$CH_3OH(l) + H_2O(l) \rightarrow 6H^+(aq) + 6e^- + CO_2(g) \text{ (oxidation)}$$

Cathode:

$$3/2O_2(g) + 6H^+(aq) + 6e^- \rightarrow 3H_2O(l) \text{ (reduction)}$$

Overall reaction:

$$CH_3OH(l) + 3/2O_2(g) \rightarrow CO_2(g) + 3H_2O(l) \text{ (redox)}$$

Methanol fuel cells use platinum as a catalyst at both electrodes, which contributes to the high cost of these cells. Although convenient, methanol fuel cells produce carbon dioxide (greenhouse gas) and methanol vapour is flammable.

Proton-exchange membrane fuel cells

Revised ☐

Proton-exchange membrane (PEM) fuel cells are currently in development. They replace the platinum electrodes with a very thin polymer membrane (i.e. a plastic film) into which much smaller amounts of platinum or other catalysts are embedded. The membrane needs to allow protons to flow through it with minimal resistance, while preventing electrons from passing through. It must also be impermeable to the gases entering the cell.

Thermodynamic efficiency of fuel cells

Revised ☐

This is given by the expression, thermodynamic efficiency = $\frac{\Delta G}{\Delta H}$, which is the ratio of the Gibbs free energy change to the enthalpy change.

The Gibbs free energy change, ΔG, may be calculated by using $\Delta G = -nFE^{\ominus}_{cell}$ and ΔH measured or calculated from enthalpies of formation.

Fuel cells have relatively high values of thermodynamic efficiency in the order of 80%.

Microbial fuel cells

Revised ☐

A microbial fuel cell typically uses waste water containing organic compounds, which are acted upon by bacteria to generate electricity. Instead of using inorganic catalysts such as platinum to enable the redox reactions, instead the cell taps into the electron transfer chains within the microorganism, using the microbe's biochemical pathways to catalyse the reaction.

Design of a microbial fuel cell

Like a hydrogen–oxygen fuel cell, the microbial fuel cell consists of two compartments separated by a membrane. At the anode, bacteria oxidize the organic substrate, generating carbon dioxide molecules, hydrogen ions (protons) and electrons. These enter the external circuit whilst the protons pass through the membrane (Figure 24.49). At the cathode, the protons combine with electrons and oxygen molecules, forming water molecules.

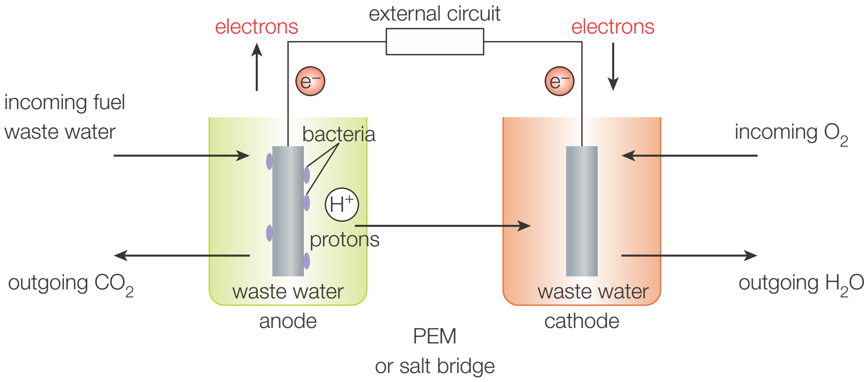


Figure 24.49 Microbial fuel cell

One particular reaction that shows promise is the use of the bacterium strain *Geobacter sulfurreducens* to oxidize ethanoate ions completely.

Anode:

$$CH_3COO^- + H_2O \rightarrow 2CO_2 + 5H^+ + 6e^- \text{ (oxidation)}$$

Cathode:

$$3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \text{ (reduction)}$$

Overall reaction:

$$CH_3COO^- + H^+ + 3/2\ O_2 \rightarrow 2CO_2 + 2H_2O$$

Microbial fuel cells offer a number of advantages: they produce useful energy from an organic waste product; they also help to clean up waste water by removing organic pollutants, and they decrease the demand for expensive metal catalysts such as platinum (see Table 24.19).

Table 24.19 Comparison of chemical and microbial (biological) fuel cells

	Chemical fuel cell	Microbial (biological) fuel cell
Catalyst	Noble (unreactive) metals	Bacteria/enzymes
pH	Acidic solution, pH <1	Neutral solution, pH 7.0–9.0
Temperature	> 200 °C	Room temperature, 25 °C
Electrolyte	Often phosphoric(V) acid	Phosphate solution
Capacity	High	Very low
Efficiency	40–60%	Over 40%
Fuel type	Methane, methanol, etc.	Any carbohydrates and hydrocarbons

Nernst equation

Revised ☐

Generalized

Consider a copper/silver voltaic (galvanic) cell made up from a silver electrode in contact with silver(I) ions and a copper electrode in contact with copper(II) ions.

The ionic reaction occurring is:

$$\mathrm{Cu(s) + 2Ag^{+}(aq) \leftrightharpoons Cu^{2+}(aq) + 2Ag(s)};\ E^\ominus \text{ cell} = +0.46\,\mathrm{V}$$

If the concentration of silver(I) ions is increased the equilibrium shifts to the right and the voltage of the cell increases. However, if the silver(I) ion concentration is decreased the equilibrium shifts to the left and the voltage of the cell decreases. Application of Le Châtelier's principle gives a qualitative explanation.

Figure 24.50 shows a linear relationship between the cell voltage and the logarithm of the silver(I) ion concentration (at a constant temperature of 298 K).

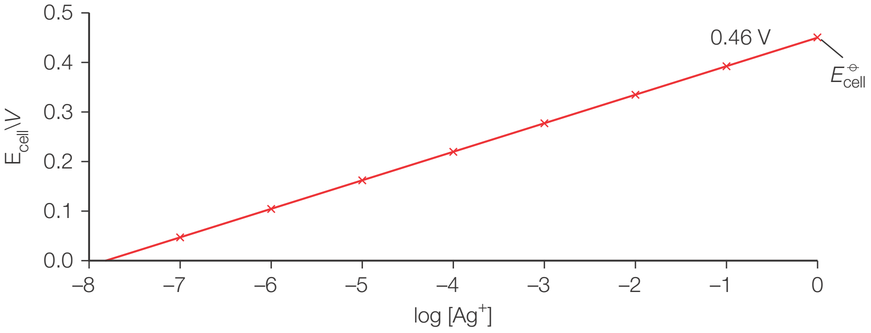


Figure 24.50 The effect of concentration and temperature on the value of the cell potential can be deduced using the Nernst equation

For the generalized case of a redox system:

$$\mathrm{Ox} + ne^{-} \leftrightharpoons \mathrm{Red}$$

where Ox is oxidized form and Red is the reduced form.

$$E = E^\ominus + \frac{RT}{nF}\ln\frac{\mathrm{Ox}}{\mathrm{Red}}$$

or

$$E = E^\ominus + \frac{RT}{nF}Q$$

where Q is the reaction quotient, E represents the cell voltage under non-standard conditions, R represents the gas constant (8.31 J mol^{-1} K^{-1}), F the Faraday constant (96500 C mol^{-1}), T the absolute temperature (in kelvin, often 298 K) and n represents the number of electrons transferred.

For a metal/metal ion system

$$\mathrm{M}^{n+}(\mathrm{aq}) + ne^{-} \leftrightharpoons \mathrm{M(s)}$$

$$E = E^\ominus + \frac{RT}{nF}\ln\frac{\mathrm{M}^{n+}(\mathrm{aq})}{\mathrm{M(s)}}$$

In these circumstances, the concentration of a pure solid, [M(s)], is taken as 1.

QUICK CHECK QUESTION

34 Calculate the cell voltage (emf) at 298 K for the reaction:

$\mathrm{Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)}$

if $[\mathrm{Cu^{2+}(aq)}] = 5.00\,\mathrm{mol\,dm^{-3}}$ and $[\mathrm{Zn^{2+}(aq)}] = 0.050\,\mathrm{mol\,dm^{-3}}$.

Concentration cells

Revised ☐

As the concentration affects the electrode potential of a half-cell, this means that it is possible to generate a cell voltage using two electrodes of the same material, and the same electrolyte, but at different concentrations (Figure 24.51).

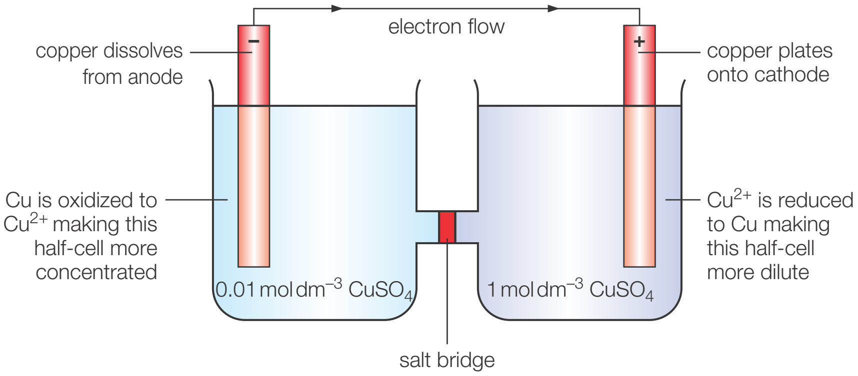


Figure 24.51 A copper concentration cell

In such cases, the standard electrode potential $E^{\ominus}_{\text{cell}}$ equates to zero, as this would have both electrolytes at 1 mol dm^{-3}. However, when the two concentrations are changed, a measurable voltage is produced.

For concentration cells at 298 K, the Nernst equation takes the form:

$$E = \frac{0\ 0257}{n} \ln \frac{C_2}{C_1}$$

where C_2 and C_1 represent the concentrations of electrolyte in the half-cells containing the anode and cathode.

■ QUICK CHECK QUESTION

35 a State the difference between a concentration cell and a standard voltaic cell.

b A galvanic cell has two half-cells each with nickel electrodes. One cell has a $[Ni^{2+}(aq)]$ = 1.00 mol dm^{-3} and the other has $[Ni^{2+}(aq)]$ = 0.001 mol dm^{-3}. Calculate the cell potential (emf) for this cell at 298 K.

24.7 Nuclear fusion and nuclear fission

Revised ☐

Essential idea: Large quantities of energy can be obtained from small quantities of matter.

Nuclear fusion and fission

Revised ☐

Nuclear fusion

- The mass defect (Δm) is the difference between the mass of the nucleus and the sum of the masses of its individual nucleons.
- The nuclear binding energy (ΔE) is the energy required to separate a nucleus into protons and neutrons.

Nuclear fission

- The energy produced in a fission reaction can be calculated from the mass difference between the products and reactants using the Einstein mass–energy equivalence relationship $E = mc^2$.
- The different isotopes of uranium in uranium hexafluoride can be separated, using diffusion or centrifugation causing fuel enrichment.
- The effusion rate of a gas is inversely proportional to the square root of the molar mass (Graham's law).
- Radioactive decay is kinetically a first order process with the half-life related to the decay constant by the equation $\lambda = \ln \frac{2}{t_{1/2}}$.
- The dangers of nuclear energy are due to the ionizing nature of the radiation it produces which leads to the production of oxygen free radicals such as superoxide ($O_2^{\bullet}$), and hydroxyl ($HO^{\bullet}$). These free radicals can initiate chain reactions that can damage DNA and enzymes in living cells.

Introduction

Revised ☐

Nuclear energy allows the transfer of large amounts of energy from small quantities of matter (see Section 24.1). This makes it a very important part of global energy sources, now and in the future.

Review of concepts from Section 24.3

The mass defect (Δm) is the difference between the mass of the nucleus and the sum of the masses of its individual nucleons (protons and neutrons). The energy produced in a fission reaction can be calculated from the mass difference between the products and reactants using the Einstein mass–energy equivalence relationship $E = mc^2$. The nuclear binding energy (ΔE) is the energy required to separate a nucleus into its individual protons and neutrons. The binding energy per nucleon is the nuclear binding energy divided by the number of nucleons. The higher the value, the more stable the nucleus. The unified atomic mass unit (amu) is equivalent to exactly $\frac{1}{12}$ of the mass of a carbon-12 atom.

Calculating the energy released during fusion and fission reactions

The difference in the mass of nuclei of the parent nuclides ('reactants') and daughter nuclides ('products'). The small amount of 'lost mass' is converted to energy according to the Einstein mass–energy equivalence relationship, $E = mc^2$.

Graham's law

Given a specific temperature and pressure, gases will move (diffuse or effuse) faster if their molar mass is low and slower if their molar mass is high. This is true because their kinetic energy is the same but lighter gases need to travel at greater velocities.

Graham's law states that the rate of effusion of an ideal gas is inversely proportional to the square root of the mass (or density) of its gaseous particles (atoms or molecules). Effusion is the process in which a gas escapes through a small hole.

Mathematically, the relationship can be written as:

$$\frac{\text{rate of diffusion of gas A}}{\text{rate of diffusion of gas B}} = \frac{\sqrt{\text{molar mass of B}}}{\sqrt{\text{molar mass of A}}}$$

or

$$\frac{\text{rate of diffusion of gas A}}{\text{rate of diffusion of gas B}} = \frac{\sqrt{\text{density mass of B}}}{\sqrt{\text{density mass of A}}}$$

Graham's law can also be used to find the approximate molar mass of a gas if one gas is a known species, and if there is a specific ratio between the rates of two gases. Graham's law is the basis for separating ^{235}U from ^{238}U found in uranium ore by diffusion.

Worked example

If equal amounts of helium and argon were placed in a porous container and allowed to escape (through the pores), deduce which gas will effuse faster, and how much faster.

$r1$ = rate of effusion of helium, let it be set as x

$r2$ = rate of effusion of argon, let it be set as 1

$$\frac{r1}{r2} = \frac{\sqrt{M_{r2}}}{\sqrt{M_{r1}}};\ \frac{x}{1} = \frac{\sqrt{39.95}}{\sqrt{4.00}};\ x = 3.16 \times \text{faster}$$

Worked example

If the density of hydrogen is 0.090 g dm^{-3} and its initial rate of diffusion is 5.93 times greater than chlorine, then deduce the density of chlorine at STP.

$r1$ = rate of diffusion of hydrogen, this is 5.93 times greater than that of chlorine

$r2$ = rate of diffusion of chlorine, let molar mass of chlorine = x

$$\frac{r1}{r2} = \frac{5.93}{1} = \sqrt{\left(\frac{x}{2.02}\right)};\ x = 71.03\,\text{g mol}^{-1};\ \frac{71.03\,\text{g}}{22.7\,\text{dm}^{-3}\,\text{mol}} = 3.13\,\text{g dm}^{-3}$$

Expert tip

Often the rate of effusion of one gas is given relative to the rate of effusion of the other gas. That allows you to set the rate of effusion for one of the gases to a numerical value of 1.

■ QUICK CHECK QUESTION

36 An unknown gas diffuses four times as quickly as oxygen. Calculate the molar mass of the gas and suggest the identity of the gas.

Extraction and enrichment of uranium

Revised ☐

Uranium is mined as an ore (and contains uranium(IV) oxide). The ore is crushed, processed and purified to uranium(IV) oxide (uranium dioxide). To allow an enrichment process the uranium(IV) oxide is converted to gaseous uranium(VI) fluoride by the following reactions:

$$UO_2(s) + 4HF(g) \rightarrow UF_4(s) + 2H_2O(l)$$

and

$$UF_4(s) + F_2(g) \rightarrow UF_6(g)$$

In mined uranium ore, 99.3% of nuclei are U-238 and 0.7% are U-235. Only U-235 is an effective fuel for nuclear fission, hence a process of enrichment must be carried out separating the two isotopes. Since U-235 atoms are lighter than U-238 atoms, in gaseous uranium compound the molecules containing U-235 atoms will diffuse slightly faster.

Diffusion of gaseous compounds (Table 24.20) can therefore be used to separate the isotopes of uranium. Because molecules that are less dense tend to move towards the inside when spun in a circle at very high speed, use of a high-speed centrifuge (Table 24.20) is another way that uranium enrichment can be carried out.

Table 24.20 Gas diffusion versus gas centrifugation

Gas diffusion	Gas centrifugation
UF_6 gas is forced at high pressure through a container with walls made of a porous membrane (Figure 24.52)	UF_6 is pumped into a large centrifuge spinning at high speed (Figure 24.53).
$^{235}UF_6$ effuses through the pores slightly faster (1.004 times) than $^{238}UF_6$ due to having a lower molar mass	The slightly heavier $^{238}UF_6$ molecules move towards the outside more than $^{235}UF_6$
Effused gas is slightly richer in $^{235}UF_6$ than before enrichment	Gas slightly richer in $^{235}UF_6$ found in the centre of the centrifuge and pumped out into a second centrifuge
Process is repeated hundreds of times with effused gas to achieve enrichment of a few percent	The process is repeated many times more to produce gas enriched in ^{235}U by a few percent

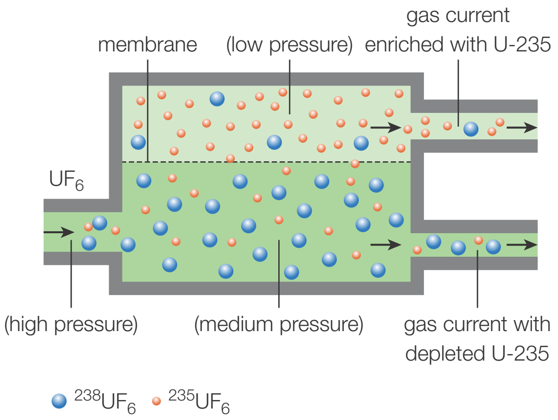


Figure 24.52 Separation of uranium isotopes by diffusion

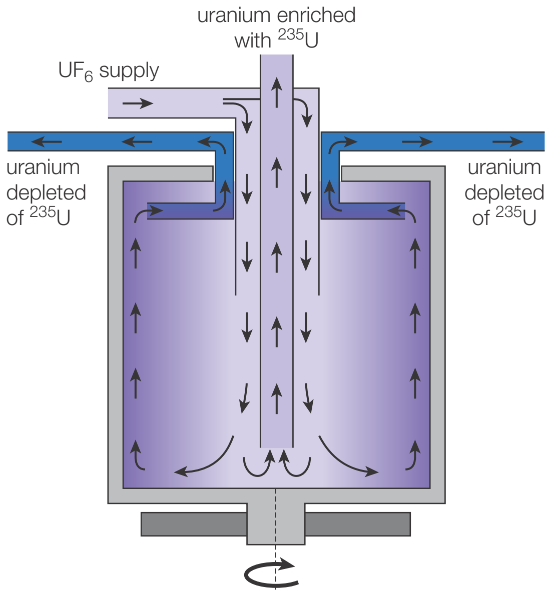


Figure 24.53 Gas centrifuge used for isotopic separation of uranium

The properties of uranium hexafluoride, a molecular compound, and uranium(IV) oxide, an ionic compound, are shown in Table 24.21.

Table 24.21 Comparing the physical properties of uranium hexafluoride and uranium(IV) oxide

Uranium hexafluoride, UF_6	**Uranium(IV) oxide, UO_2 [U^{4+} O^{2-}]**
White crystalline solid	Dark brown/black crystalline solid
Molecular solid	Ionic solid
Sublimes at 56 °C	Very high melting point (>2800 °C)
Strong polar covalent bonds between uranium and fluorine atoms	Strong electrostatic forces of attraction between highly charged ions (some covalent character)
Weak London (dispersion) forces operating between octahedral non-polar molecules in solid and liquid states	
Small amount of thermal energy required to release molecules from the molecular lattice in the solid state	A large amount of thermal energy required to release ions from the ionic lattice in solid state

NATURE OF SCIENCE

Fully fluorinated compounds tend to have relatively weak intermolecular forces. The weak London (dispersion) forces in solid UF_6 could be thought of as being 'anomalous' relative to compounds of similar molar mass that are not fully fluorinated, or relative to other U(VI) compounds.

Radioactive decay

Revised ☐

Radioactive decay is kinetically a first order process, meaning half-life and activity constant are related by the following equation:

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

If the decay constant, k, has unit of s^{-1}, the expression will give the half-life in seconds. Note that if the activity (decay rate) is large, the half-life is small, and vice versa.

This expression is obtained by integrating the following expression: $-\frac{d[N]}{dt} = \lambda[N]$

Dangers of nuclear energy

Revised ☐

Spent nuclear fuel rods and high-level nuclear waste will remain highly radioactive for long periods of time. They will contain a mixture of radioisotopes that release alpha particles, beta particles and gamma rays. Collectively, they are termed ionizing radiation since they cause the formation of ions in air, water and living organisms.

Ionizing radiation, especially alpha particles (slow moving and heavy), have sufficient kinetic energy to remove electrons and ionize molecules. The species formed initially by radiation give rise to other products by secondary reactions.

Ionizing radiation can kill living cells by breaking DNA strands and damaging enzymes or via the production of species, such as the hydroxyl radical, $^\bullet OH$, and the superoxide ion radical, $^\bullet O_2^-$.

These are both reactive oxygen species that can initiate chain reactions that can damage the bases of DNA (especially guanine), phospholipids (in cell membranes), unsaturated fatty acids and enzymes (in the cytoplasm) in living cells.

QUICK CHECK QUESTION

37 a Draw the Lewis (electron dot) structures of the superoxide ion, hydroxyl radical and the hydroxide ion.

b Explain why the first two species are classified as radicals.

24.8 Photovoltaic and dye-sensitized solar cells

Revised ☐

Essential idea: When solar energy is converted to electrical energy the light must be absorbed and charges must be separated. In a photovoltaic cell both of these processes occur in the silicon semiconductor, whereas these processes occur in separate locations in a dye-sensitized solar cell (DSSC).

Photovoltaic and dye-sensitized solar cells

Revised ☐

- Molecules with longer conjugated systems absorb light of longer wavelength.
- The electrical conductivity of a semiconductor increases with an increase in temperature whereas the conductivity of metals decreases.
- The conductivity of silicon can be increased by doping to produce n-type and p-type semiconductors.
- Solar energy can be converted to electricity in a photovoltaic cell.
- DSSCs imitate the way in which plants harness solar energy. Electrons are 'injected' from an excited molecule directly into the TiO_2 semiconductor.
- The use of nanoparticles coated with light-absorbing dye increases the effective surface area and allows more light over a wider range of the visible spectrum to be absorbed.

Conductivity in metals and semiconductors

Revised ☐

Metals

Metals contain cations (positively charged ions) arranged in a giant metallic lattice. The valence electrons are delocalized and are free to move carrying charge. Metallic bonding is the strong electrostatic attraction between closely packed positive metal ions and a 'sea' of delocalized electrons (the electron-sea model).

Metals are excellent electrical conductors because their delocalized valence electrons are free to move (as an electric current: an ordered flow of electric charge) through the lattice when a voltage (potential difference) is applied. The electrons will flow from the negative electrode to the positive electrode (in the external circuit). The electrical resistance of metals is due to collisions between the electrons and the cations in the lattice.

As the temperature increases, metal ions vibrate more vigorously and there is a larger cross-sectional for the electrons to collide with and the electrical conductivity decreases and resistance increases.

A more detailed and accurate model of describing metallic bonding is band theory. Atomic orbitals from each metal atom interact to create a very large number of orbitals delocalized over every metal atom (Figure 24.54). The energy levels of these delocalized orbitals cover a range of energies called a band, so that there is an orbital for any energy, as long as that energy is within the band.

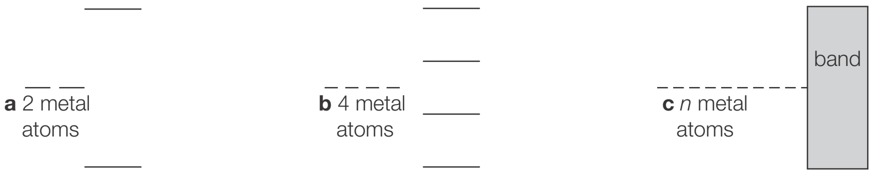


Figure 24.54 The interaction of two atomic orbitals leads to two well-separated molecular orbitals. The interaction of a large number (*n*) atomic orbitals in the metal lattice leads to a band of *n* energy levels

For a solid to be able to conduct electricity and behave like a metal, a band must be partially filled with electrons. If the band is empty, there are no electrons to carry the current; if the band is full, there are no empty energy levels for the electrons to move into.

Semiconductors

A semiconductor is a solid with intermediate electrical conductivity between that of a metal and an insulator (though closer to an insulator). Semiconductors are able to conduct electricity better under particular conditions, such as higher temperatures or in the presence of increased light intensity. Silicon is the most well-known semiconductor and the main element in the electronics and semiconductor industries. It has the same tetrahedral structure as diamond (Figure 24.55), but the bonds are longer and weaker (due to the greater atomic radius of silicon).

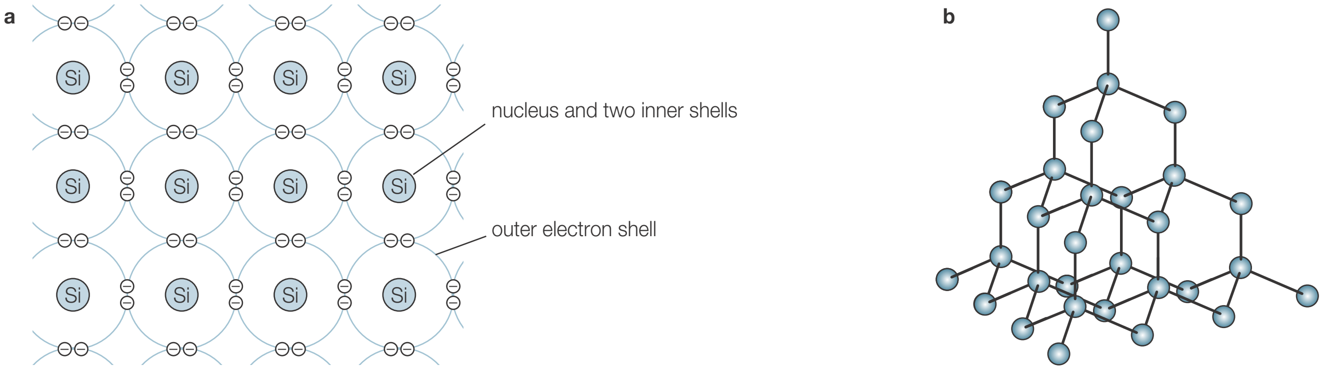


Figure 24.55 Structure of silicon

Semiconductor resistance decreases as temperature increases. This is the opposite behaviour to a metal. At higher temperatures more electrons are promoted to the conduction band and are free to move (Figure 24.56).

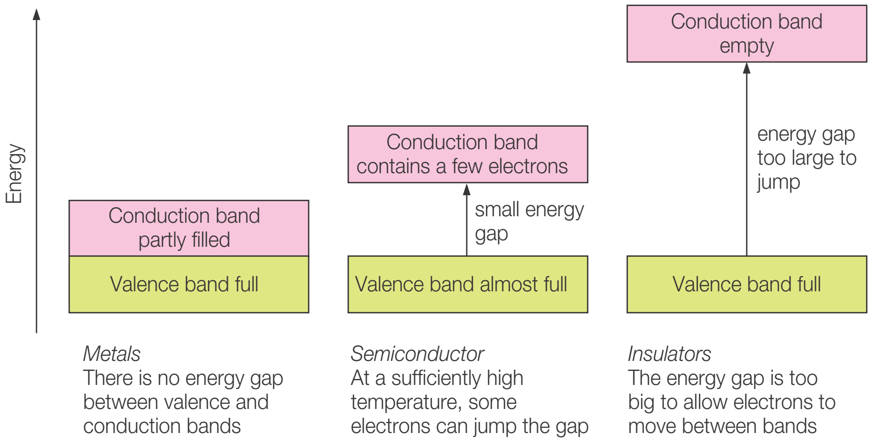


Figure 24.56 Bands in an insulator, semiconductor and conductor

Metals tend to have lower ionization energies than semiconductors (metalloids) in the same period (due to their large atomic radii). This means it takes less energy to remove electrons from metal atoms to generate delocalized electrons. The atoms of semiconductors require more energy to be absorbed to ionize and free the electrons.

QUICK CHECK QUESTION

38 Write equations showing the first ionization energies of aluminium and silicon atoms and state which atom has the lower value.

Silicon doping

The semiconductor silicon can be modified by doping in order to greatly increase its electrical conductivity. This involves adding a small amount of another element.

Adding a group 13 element, for example boron or indium; only three valence electrons are supplied instead of four, creating positive holes (Figure 24.57) in the valence band. Electrons are able to move into these holes and so electrical conductivity increases. As the charge carriers are the positive holes, these materials are called p-type semiconductors.

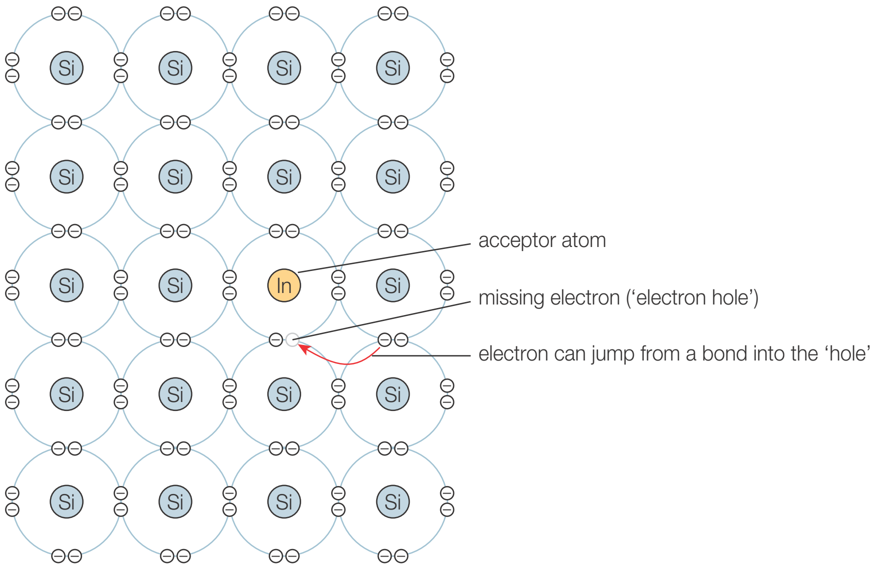


Figure 24.57 Doping of silicon with indium atoms (p-type semiconductor)

Adding a group 15 element, for example, phosphorus, antimony or arsenic: five valence electrons are supplied. Four are used in bonding and the fifth is promoted into the conduction band increasing the electrical conductivity. As the charge carriers are negative electrons, these materials are called n-type semiconductors (Figure 24.58).

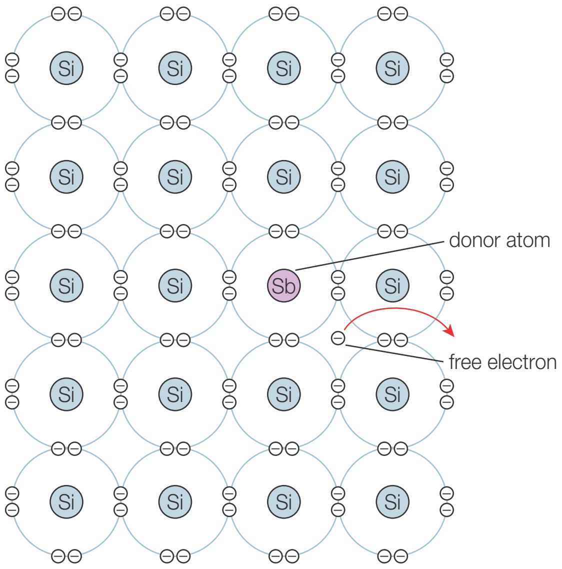


Figure 24.58 Doping of silicon with antimony atoms (n-type semiconductor)

■ QUICK CHECK QUESTION

39 a Discuss the doping of silicon to produce different types of semiconductors.

b Describe how sunlight interacts with semiconductors.

Photovoltaic cells

Revised ☐

When an n-type and a p-type semiconductor are joined together a potential difference is built up at the junction (between the two. A depletion layer is formed from a conducting region by removal of all free charge carriers, leaving none to carry a current.

When light (photons) hits the n-type semiconductor electrons are promoted to the conduction band. These electrons are not able to move directly from the n-type to the p-type, because the voltage across the p–n junction prevents this. They must travel from the n-type to the p-type through an external circuit, and this flow of electrons can be used to power an electronic device (Figure 24.59).

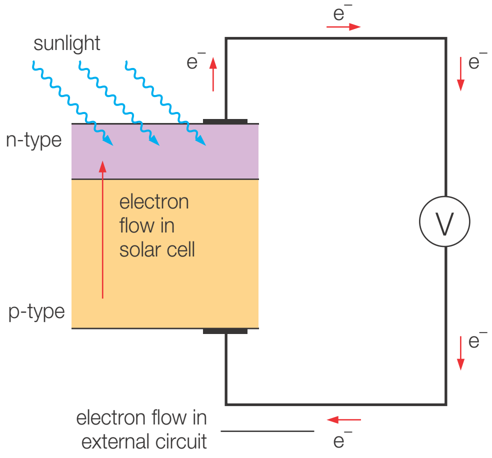


Figure 24.59 A silicon-based photovoltaic cell producing electric current in an external circuit

Dye-sensitized solar cells (DSSCs)

Revised ☐

The dye-sensitized solar cell (DSSC) is an electrochemical solar cell where light absorption occurs within dye molecules attached to a nanostructured titanium(IV) oxide, TiO_2 electrode.

Some DSSCs use plant organic dyes containing chromophores to mimic the natural process of photosynthesis (although the plant's system is a complex enzyme-controlled system). The sunlight is absorbed by the dye like chlorophyll molecules within chloroplasts do in green plants.

The dye molecule absorbs sunlight and in the process excites an electron, generating an excited state species. This excited state species of the dye can then inject this excited electron into the conduction band of the TiO_2 semiconductor and in the process the dye molecule becomes oxidized.

This results in the conversion of sunlight into electricity. Electrons are then transported to the current collector of the anode via diffusion. An electrical load can be powered if connected. The complete circuit of the DSSC involves the regeneration (by electron donation) of the oxidized dye.

An example of a dye used in a Grätzel DSSC is shown in Figure 24.60. It can be seen that it has a series of delocalized pyridine ring systems. The nitrogen atoms of the pyridine rings and thiocyanate ions, $[SCN]^-$ act as ligands (electron pair donors). The ring system is complexed with a central ruthenium(II) ion. This dye is able to absorb photons over a wide range of frequencies in the visible region, all the way down to the red end of the spectrum.

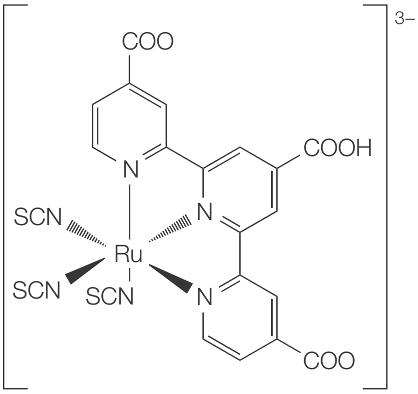


Figure 24.60 Ruthenium-based organic dye (Black Dye)

A DSSC typically uses a mesoporous layer (pores of diameter between 2 and 50 nm) of the titanium(IV) oxide (TiO_2) nanoparticles coated with a light-absorbing dye. Very small nanoparticles (a large number per unit volume) are used as this increases the effective surface area-to-volume ratio the dye can be adsorbed on and allows light over a wider range of the visible spectrum to be more efficiently absorbed. DSSCs have the potential to be highly economical in comparison to commercial silicon photovoltaic solar cells.

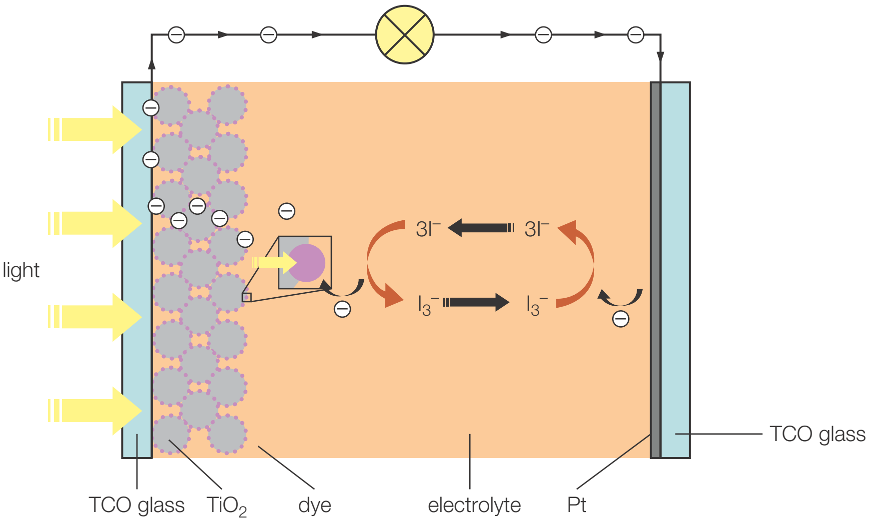


Figure 24.61 Energy flow in a DSSC

In a Grätzel cell (Figure 24.61), the anode is a transparent conductive oxide (TCO) glass surface made of TiO_2. The (negative electrode) anode attached to the dye allows sunlight through the TCO and absorbed by the dye.

The electrons transferred ('injected') from an excited dye molecule enter directly into the titanium(IV) oxide semiconductor and diffuse to the TCO anode. The anode transfers the excited electrons through the external circuit to the (positive electrode) cathode which is made of platinum (or graphite film). The dye is surrounded by an electrolyte solution, usually iodide (I^-) and tri-iodide (I_3^-) ions.

The process in the DSSC can be summarized (in a simplified form) as follows:

1. Excitation of the sensitized dye molecule (SD) by sunlight (photons): $SD + h\nu \rightarrow SD^*$ (dye molecule in the excited state). This is known as photo-excitation.
2. Oxidation reaction at the (negative electrode) anode and electron injection into the anode:
   $SD^* \rightarrow SD^+ + e^-$; SD^+ is the oxidized form of the dye (on the TiO_2 layer).
3. Reduction half reaction at the (negative electrode) platinum or graphite cathode: $I_3^- + 2e^- \rightarrow 3I^-$

Dye regeneration

The interconversion between iodide ions, I^-/tri-iodide ions, I_3^-, allows iodide ions to lose electrons to form tri-iodide ions; the oxidized dye accepts an electron to regenerate the dye (Figure 24.62).

$$3I^- \rightarrow I_3^- + 2e^-$$

$$SD^+ + e^- \rightarrow SD$$

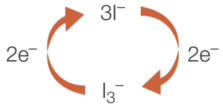


Figure 24.62 Summary of the reaction involving iodine species in a DSSC

It is the platinum counter electrode that promotes electron injection and results in the first reduction of I_3^-.

The overall reaction is obtained by summing the half-equations at the anode and cathode:

$$2SD + I_3^- \rightarrow 2SD^+ + 3I^-$$

In a photovoltaic cell the absorption of light (photons) causes the movement of electrons directly; in a DSSC the processes of absorption and movement of electrons are separated (as they are in photosynthesis, see Section 24.4).

Advantages and disadvantages of photovoltaic cells and dye-sensitized solar cells

Revised ☐

Table 24.22 Advantages and disadvantages of photovoltaic cells and dye-sensitized solar cells

Cell type	Advantages	Disadvantages
Silicon photovoltaic cell	Well-established technology is manufactured widely. Efficiency of silicon photovoltaics is usually still higher – typically around 23% (and tandem cells up to 48%).	Efficiencies did not improve initially (until development of tandem cells, where the spectrum is split and passed through several solar cells each optimized to a different region). Although economies of scale apply as they are widely made, they are still relatively expensive owing to the cost of processing silicon (but this is decreasing). At high temperatures the silicon cells' efficiency decreases. For this reason they are often protected by a glass cover, which adds cost and mass.
Dye-sensitized solar cell	The early stage of development means that significant advances are still being made to address the disadvantages of these cells. For example, gel or solid electrolytes are under development, which will remove the problem of the electrolyte solution. DSSCs do not require any complicated manufacturing steps, and the dyes are cheap to synthesize. The dyes are more effective at capturing sunlight even at low light levels, whereas silicon cells need a minimum light intensity to work effectively.	The electrolyte contains potentially harmful volatile organic compounds. The electrolyte solution also makes the cell less resistant to temperature changes. At low temperatures it can freeze, which shuts the cell down. At high temperatures it can expand, causing sealing problems. (Newer cells have moved away from this and now use solid state electrolytes or organic electrolytes and not iodide/triiodide.) DSSCs are typically less efficient than silicon-based cells, at around 11%, although 20 % efficiency has been achieved (with perovskite DSSCs). They are more useful for 'low-density' applications such as rooftop solar panels, where physical size can be slightly larger with no real disadvantage.

QUICK CHECK QUESTION

40 **a** Explain the operation of a Grätzel DSSC that contains an organic dye molecule on the surface of a titanium(IV) oxide semiconductor that is in contact with an electrolyte containing iodide ions.

b Explain the importance of nanotechnology in its construction and its advantage over silicon-based PV cells.

25 Option D Medicinal chemistry

25.1 Pharmaceutical products and drug action

Revised ☐

Essential idea: Medicines and drugs have a variety of different effects on the functioning of the body.

Pharmaceutical products and drug action

Revised ☐

- In animal studies, the therapeutic index is the lethal dose of a drug for 50% of the population (LD_{50}) divided by the minimum effective dose for 50% of the population (ED_{50}).
- In humans, the therapeutic index is the toxic dose of a drug for 50% of the population (TD_{50}) divided by the minimum effective dose for 50% of the population (ED_{50}).
- The therapeutic window is the range of dosages between the minimum amounts of the drug that produce the desired effect and a medically unacceptable adverse effect.
- Dosage, tolerance, addiction and side effects are considerations of drug administration.
- Bioavailability is the fraction of the administered dosage that reaches the target part of the human body.
- The main steps in the development of synthetic drugs include identifying the need and structure, synthesis, yield and extraction.
- Drug–receptor interactions are based on the structure of the drug and the site of activity.

Drugs

Revised ☐

The effects of drugs and medicines

A drug is a natural, synthetic or semi-synthetic substance that results in one or more of the following changes within the body: alters incoming sensory sensations (from eyes, ears and other sense organs); alters mood or emotions or alters the physiological state, including consciousness, metabolic activity level or coordination.

Medicinal drugs (medicines or pharmaceuticals) are taken to improve the physical and mental health. They have a therapeutic or healing action that benefits the body.

Expert tip

OTC refers to 'over the counter', drugs that can be bought at a pharmacy and not requiring a prescription from a medical doctor. Examples include mild analgesics (painkillers) and antacids.

Administration of drugs

The majority of drugs need to be absorbed into the bloodstream to reach their target cells. The method of drug administration determines the biological route taken by the drug and the rate at which it enters the plasma of the blood.

The five main methods of drug delivery are: oral (by mouth), inhalation (into the lungs), rectal (through the blood vessels of the anus) and by injection (parenteral) using a hypodermic needle (Figure 25.1) which is the fastest absorption method for drugs to enter the bloodstream. Drugs can also be applied topically in the form of creams onto the skin (transdermal).

QUICK CHECK QUESTION

1 There are various ways to administer drugs to a patient. One of the common methods, parenteral, is also known as injection. State and describe **two** other methods of administering drugs.

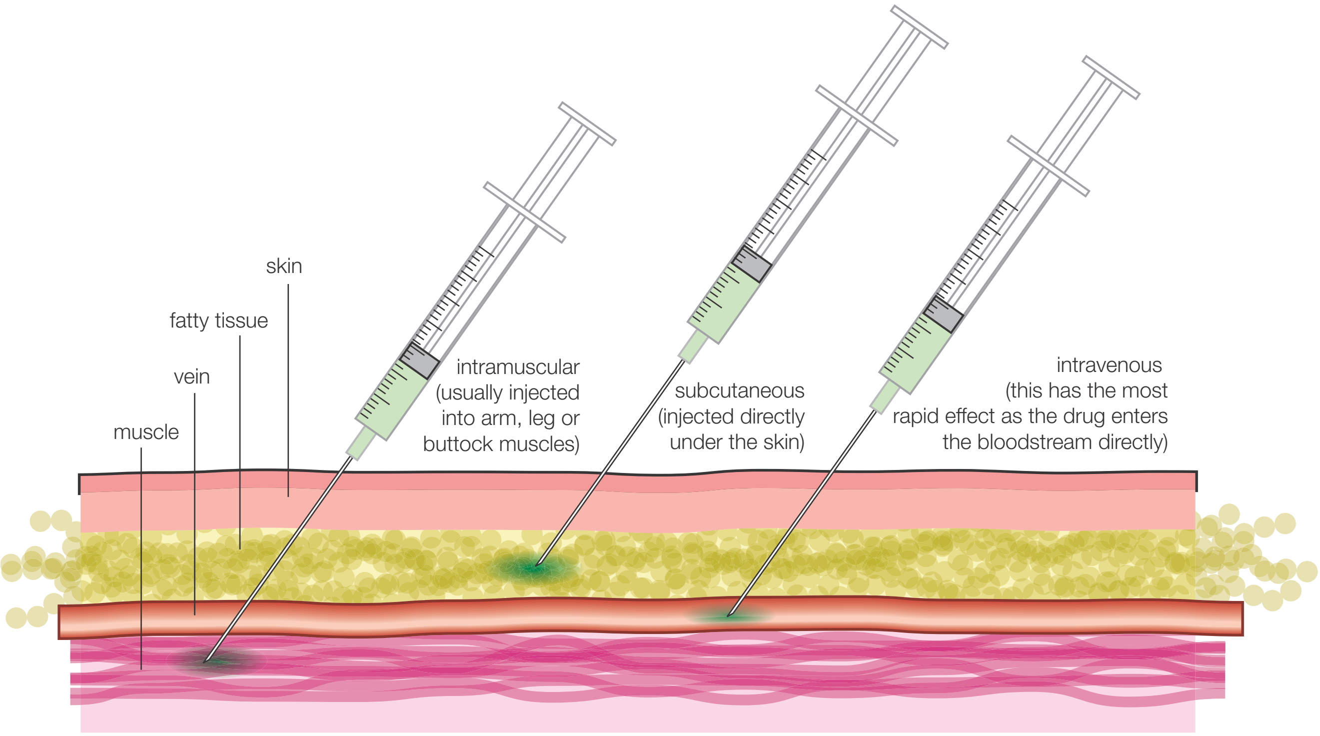


Figure 25.1 Summary of common methods of drug delivery by injection

Development and testing of new medicinal drugs

Revised ☐

The research and development of new drugs is a long and expensive process. A new lead compound (with biological activity) may be isolated and purified from an existing species, often a plant, fungus or marine organism. However, medicinal drug development often starts by finding an active compound from 'chemical libraries' containing thousands of synthetic molecules.

A lead compound is often chemically modified to improve its physical properties and biological effects. Some new medicinal drugs are developed by a process of rational design. They are designed (often via computer modelling) and synthesized knowing the structure and shape of the protein receptor the drug molecule interacts with.

Computer-aided drug design

Computers are an important part of the process of the design of synthetic drugs and have a large number of uses, which include structure analysis, structure comparisons, lead compound design, identification of active conformations (interconvertible three-dimensional shapes) and pharmacophores (a set of features common to a group of active molecules), protein and binding site structure and ligand binding. A ligand is a small molecule (that can be a drug) that binds to a receptor.

A potential drug candidate needs to undergo extensive testing *in vitro* testing with bacteria, cells or biological molecules and later with animals and humans (*in vivo* testing). Anti-cancer drugs are tested with cancer cells grown in culture. The results of large-scale animal testing will establish the lethal dose required to kill 50% of the animal test population. This is known as the LD_{50} value (Figure 25.2), but it is also important to carry out tests that identify chronic, long-term toxicity that is non-lethal.

QUICK CHECK QUESTION

2 Creating a new pharmaceutical compound is a long, expensive and complex process. Outline the main stages of this process in the correct order.

Expert tip

Medicinal chemists aim to have the minimum number of synthetic steps, to increase the overall yield.

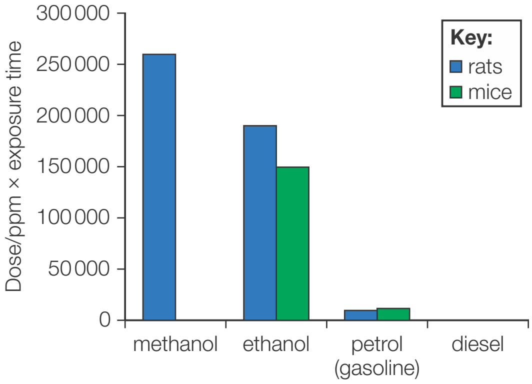


Figure 25.2 Inhalation LD_{50} values of common fuels

Expert tip

A large LD_{50} value means that the substance is relatively non-toxic and that a large quantity of the substance is required to cause a toxic response. A small LD_{50} value means that the substance is relatively toxic and that only a small quantity of the substance is needed to cause a toxic response.

The effective dose required to bring about a measurable effect in 50% of the test animal population will also be determined. This is known as the ED_{50} value. The therapeutic index can be calculated: LD_{50}/ED_{50}.

Drugs will then be subjected to a variety of clinical testing phases with volunteers (first phase) and at later stages with human patients subject to approval by a drug regulatory authority (Figure 25.3). In humans the therapeutic index is defined as TD_{50}/ED_{50}, where TD_{50} represent the toxic dose for 50% of the human test population.

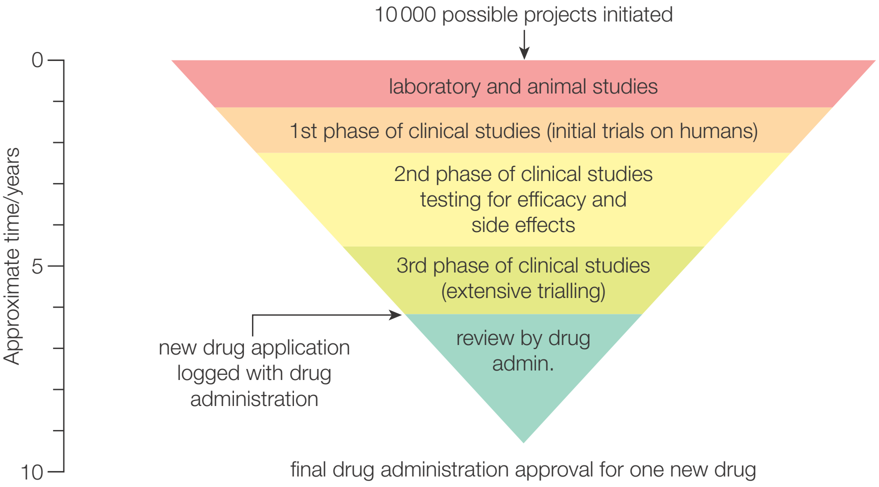


Figure 25.3 Summary of the steps in the development of a new drug

Expert tip

All substances are potentially poisonous: it is only the dose that determines whether a substance is poisonous. The concepts of toxicology imply that no drug is 100 per cent safe.

Human clinical trials will indicate whether there are any short-term side effects and allow the therapeutic window (Figure 25.4) to be established. This is the range of dosages between the minimal dose required to produce a therapeutic effect and a harmful effect due to toxicity at high dosage.

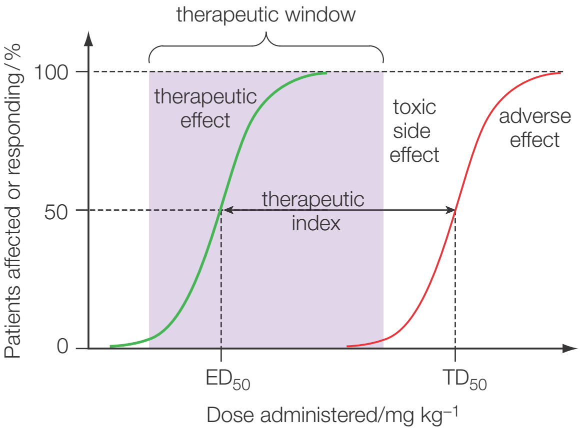


Figure 25.4 The therapeutic index and therapeutic window

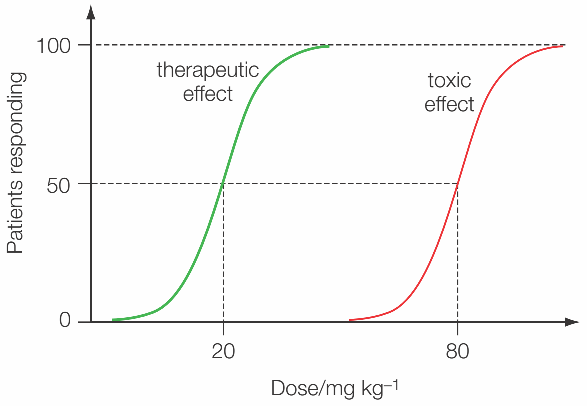
Side effects of a drug are unwanted, or unintended and sometimes harmful or unpleasant effects that appear with a dose within the therapeutic window. A risk to benefit ratio will determine whether the drug's side effects are critical. For example, side effects may be considered less of an issue if the drug is shown to be highly effective at treating a particular condition or infectious disease. They usually increase with dosage.

Expert tip

One side effect of aspirin is irritation of the stomach lining.

QUICK CHECK QUESTION

3 **a** The results for the therapeutic and adverse effects of a new potential drug for treating high cholesterol levels are shown below.



Calculate the therapeutic index of the drug. Label on the graph the therapeutic window of the drug.

b Another drug that has the same effect was also studied and the therapeutic index of the second drug is 110. State and explain which of the two drugs is more likely to be approved for over the counter (OTC) sales.

NATURE OF SCIENCE

Abuse potential refers to a drug that is used in non-medical situations for the positive psychoactive effects it produces. These drugs are characterized by their central nervous system (CNS) activity. Examples of the psychoactive effects they produced include sedation, euphoria, distortions of perception, hallucinations, and mood changes. Drugs with abuse potential often produce psychic or physical dependence and may lead to the disorder of addiction.

Drug testing on human patients is usually carried out using a double blind approach with a placebo. Half of the clinical patients are administered with the drug and the other half are given an inert chemical placebo, which resembles the drug in appearance and taste, but has no bioactive chemicals. The term double blind (Figure 25.5) means that neither the patients nor the medical staff administering the drug know which patients are receiving the drug.

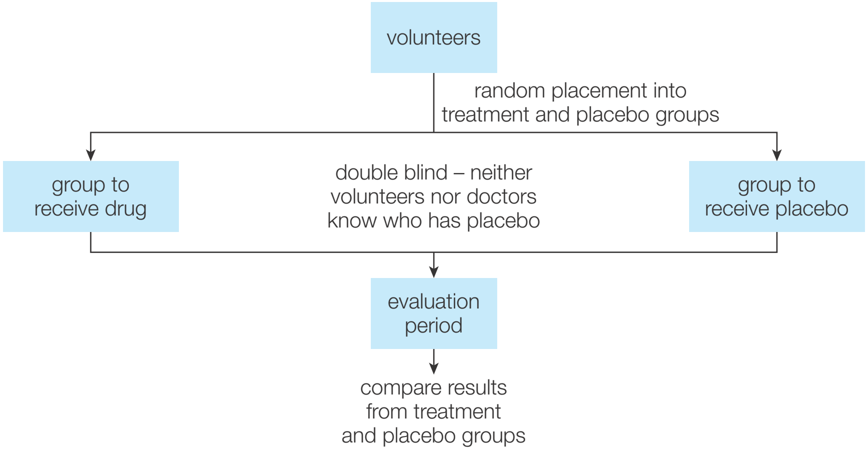


Figure 25.5 Double blind testing

Expert tip

The placebo effect occurs when a placebo promotes the 'natural healing' effects of the human immune and endocrine system. Any medicinal drug needs to be more effective than a placebo during clinical trials. It is not clear why the placebo works, but a person's hope about a treatment can trigger a biochemical effect presumably via the immune system and endocrine (hormone) system.

■ QUICK CHECK QUESTION

4 The properties of three medicinal drugs are summarized below.

Drug	Physiological effect	Side effects	Therapeutic window
X	Very high	Very severe	Medium
Y	Moderate	Moderate	Narrow
Z	Low	Minimal	Wide

a Suggest which drug (X, Y or Z) could be considered safe enough to be taken by patients without medical supervision; administered only by qualified medical staff; or used only in a medical emergency.

b Explain the terms therapeutic window and placebo.

Tolerance and addiction

Revised ☐

Tolerance towards a drug often occurs as the body's immune system and target cells adapts to the continued presence of a drug. A person who develops tolerance will require larger doses of the drug to achieve the same biological effect (Figure 25.6). Tolerance raises the risk of dependence and reaching a toxic or lethal dose. Some drugs, especially opiates (see Section 25.3), can also cause addiction, where withdrawal symptoms are likely to occur when the drug is not taken or the dose decreased.

Common mistake

Tolerance and addiction are different and unrelated medicinal chemistry concepts.

Drug action

Revised ☐

Drugs bring about their effects by reversibly binding to receptors. These receptors are usually proteins located within the cell membrane, cytoplasm or cell nucleus. The drug molecule and receptor (often an enzyme) have an induced fit relationship. Their interaction is reversible and involves the formation of a variety of weak intermolecular interactions (Figure 25.7).

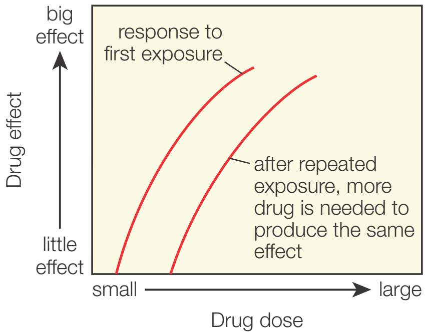


Figure 25.6 The concept of drug tolerance

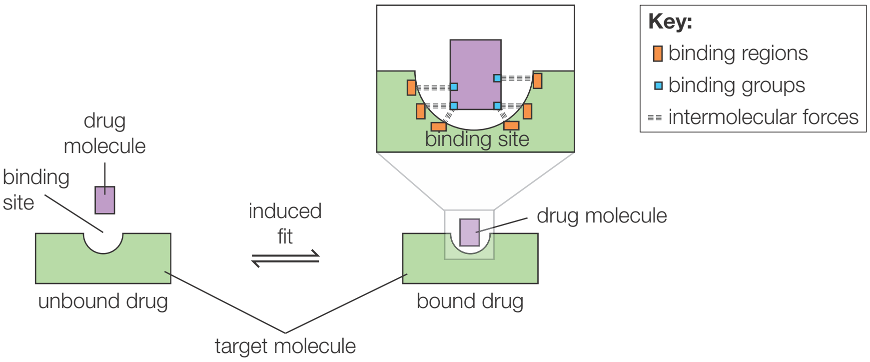
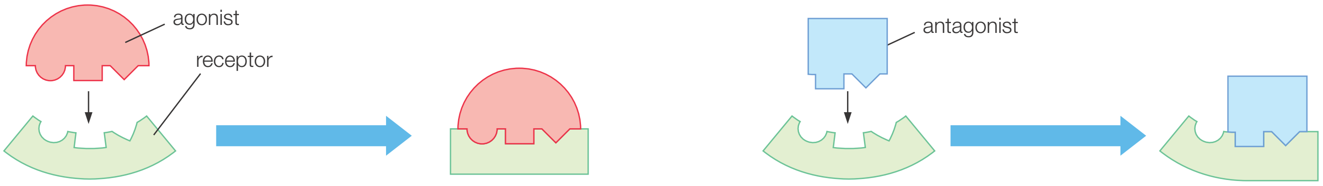


Figure 25.7 The equilibrium of a drug being bound and unbound to its target molecule

Drugs can have different biochemical effects on their target receptor (protein):

- *Agonistic*: the drug molecule acts in a very similar way to the normal ligand, activating the receptor upon binding and producing a similar biological response.
- *Antagonistic*: the drug molecule blocks the ligand-binding site and stops the natural ligand from binding and activating the receptor (Figure 25.8).



The agonist binds to the receptor and induces changes in it that lead to the appropriate response

The antagonist binds to the receptor but it does not induce the correct change in it, so it does not produce a response

Figure 25.8 An illustration of an agonist and an antagonist binding to a receptor site on a protein molecule

- *Allosteric*: the drug molecule binds to a site on the surface of the protein other than the substrate binding site. This action changes the three-dimensional shape of the protein which may increase or decrease (Figure 25.9) the receptor's response to the natural substrate (ligand).

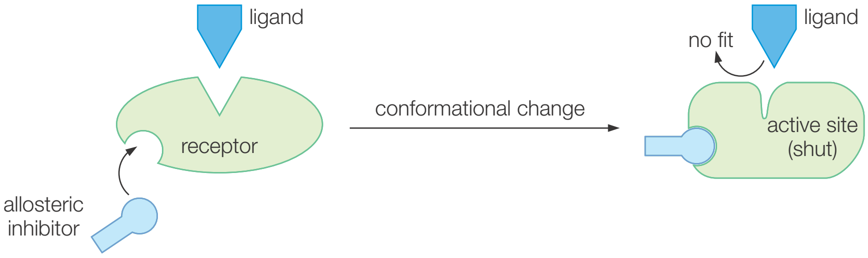


Figure 25.9 Allosteric inhibition of a drug

Bioavailability

Revised ☐

The bioavailability of a drug is the fraction of an administered dose of drug that reaches the bloodstream.

Except for intravenous injections, a drug must be transported across the blood vessels, which contain a fatty or lipid layer (the cell membrane). Drugs which dissolve readily in fats (lipophilic) are therefore more easily absorbed. Drugs can be absorbed into the bloodstream from a region of high to low drug concentration, by simple diffusion.

The structure of the molecule determines its shape, chemical reactivity, solubility and its polarity, in aqueous solution (a polar medium) and cell membranes (a non-polar medium) and hence its bioavailability. The presence or absence of functional groups are often critical to drug interactions and hence activity.

Hydrophilic functional groups (e.g. $–NH_2$, $–COOH$ and $–OH$) increase water solubility and lipophilic functional groups (e.g. $–C_6H_5$) increase lipid solubility and both affect drug absorption into the blood.

Drugs with acidic groups (e.g. $–COOH$) are more likely to be absorbed in the stomach (e.g. aspirin) whereas drugs with basic groups (e.g. $–NH_2$) (e.g. quinine) are more likely to be absorbed from the intestines.

Bioavailability is also affected by dissolution of solids (drugs may be molecular or ionic), absorption into the blood (if not administered intravenously), distribution to tissues, by the circulatory system, metabolism (under enzyme control) in the liver to inactive compounds and excretion is mostly through urine via the kidneys.

Except for intravenous injections, a drug must usually be transported across the blood vessels (especially those supplying the brain), which contain a lipid bilayer (the cell membrane. Most drugs can escape blood vessels through pores or gaps between the cells lining the blood vessel walls.

Drugs which dissolve readily in fats (lipophilic) are therefore more easily absorbed. Drugs can be absorbed into the bloodstream from a region of high to low drug concentration, by simple diffusion.

Expert tip

Aspirin can be taken in a molecular form and a water-soluble ionic form (salt).

QUICK CHECK QUESTION

5 **a** State the bioavailability of a drug that is given by intravenous injections.

b When a drug is given orally, not all of the dose will reach the general blood circulation. State **two** factors that will affect the fraction of a drug dose that survives to reach the general blood circulation.

25.2 Aspirin and penicillin

Revised ☐

Essential idea: Natural products with useful medicinal properties can be chemically altered to produce more potent or safer medicines.

Aspirin and penicillin

Revised ☐

Aspirin

- Mild analgesics function by intercepting the pain stimulus at the source, often by interfering with the production of substances that cause pain, swelling or fever.

- Aspirin is prepared from salicylic acid.
- Aspirin can be used as an anticoagulant, in prevention of the recurrence of heart attacks and strokes and as a prophylactic.

Penicillin

- Penicillins are antibiotics produced by fungi.
- A beta-lactam ring is a part of the core structure of penicillins.
- Some antibiotics work by preventing cross-linking of the bacterial cell walls.
- Modifying the side-chain results in penicillins that are more resistant to the penicillinase enzyme.

Aspirin

Revised ☐

Aspirin is a mild analgesic (painkiller) and can be prepared in the laboratory by reacting 2-hydroxybenzoic acid (salicylic acid) with ethanoic anhydride (in the presence of concentrated sulfuric acid, which acts as a catalyst) (Figure 25.10). Aspirin (2-ethanoyl-2-hydroxybenzoic acid)) is the ethanoate ester of 2-hydroxybenzoic acid. (Ethanoyl chloride can also be used as an acetylating agent.)

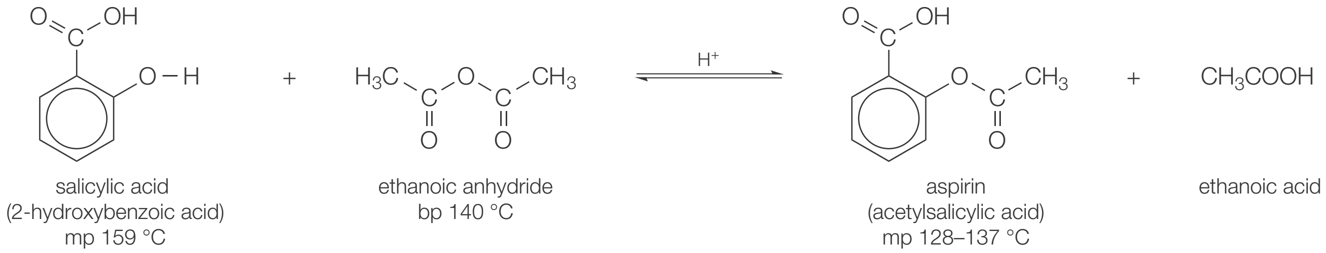


Figure 25.10 Reaction between salicylic acid and ethanoic anhydride to form aspirin (acetylsalicylic acid)

The crude (impure aspirin) crystals can be removed by suction filtration, washed with cold water and then purified by recrystallization. The product can be recrystallized from hot water to obtain pure aspirin. Soluble impurities are left in solution.

The process of recrystallization involves dissolution of the solid in an appropriate solvent at an elevated temperature and the subsequent re-formation of the crystals upon cooling, so that any impurities remain in solution.

The experimental yield can be measured from the mass of pure aspirin obtained and the percentage yield can be calculated using the stoichiometric equation and molar masses of reactant and products.

The purity of the aspirin can be determined from the melting point of the crystals. The presence of impurities will lower the melting point and cause it to melt over a wider range of temperatures.

Infrared spectrum of aspirin

The purity of aspirin can also be investigated by recording the infrared spectrum (Figure 25.11). It shows two peaks at 1750 cm^{-1} and 1680 cm^{-1} due to the presence of two carbonyl groups, >C=O and a very broad absorption peak between wavenumbers 2500 and 3500 cm^{-1}. This is due to the carboxylic acid group, –COOH (which engages in hydrogen bonding).

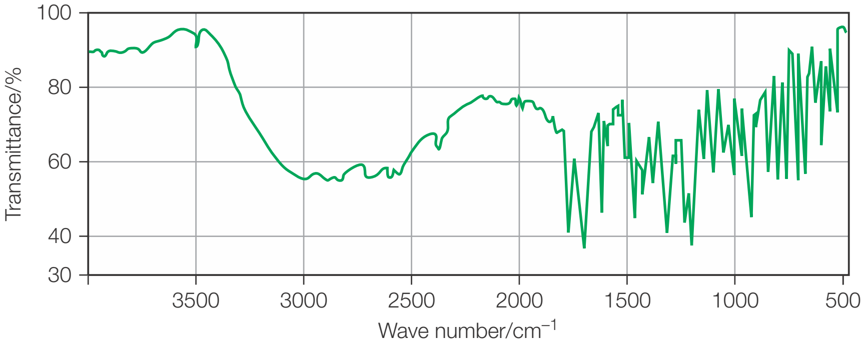


Figure 25.11 The infrared spectrum of aspirin

QUICK CHECK QUESTION

6 Identify the type of reaction used to convert 2-hydroxybenzoic acid to aspirin.

Expert tip

There is often a smell of 'vinegar' in old aspirin bottles because aspirin tends to hydrolyse spontaneously to some extent.

Expert tip

The melting point is lowered by impurities because the regular packing in the lattice is disrupted and the intermolecular forces weakened.

Therapeutic properties of aspirin

Aspirin can be used as an antipyretic (to reduce fever) and an anti-inflammatory. It blocks the function of platelets (to make the blood thinner and be more easily pumped), to help prevent the recurrence of heart attacks and strokes and is also used as a prophylactic.

Salicylic acid (2-hydoxybenzoic acid) is also an analgesic but irritates and damages the mouth, oesophagus and stomach lining, so has been replaced by aspirin. It can be extracted from the bark of a willow tree.

Expert tip

A prophylactic is a medicine used to treat or prevent the occurrence of a disease or condition.

Mode of action

The mechanism of aspirin's analgesic properties involves inhibiting the enzyme cyclooxygenase at the site of an injury. The enzyme is involved in catalysing the formation of substances known as prostaglandins. They accumulate at the site of injury and are involved in the transmission of nerve impulses to the brain (which are interpreted as pain).

The most common side effect of aspirin is that it can cause bleeding in the lining of the stomach. This effect is increased when taking aspirin tablets with alcohol (ethanol) which has a synergistic effect.

Young children are not advised to take large dosages of aspirin during a viral infection since it is linked to Reye's syndrome, a potentially fatal liver and brain disorder. Aspirin causes convulsions if injected into the brain. This is a toxic effect caused by the release of 2-hydroxybenzoic acid by hydrolysis. Very large dosages of aspirin orally can be fatal due to acidosis, a lowering of the pH of the blood.

Expert tip

A synergistic effect occurs when the combination of the two drugs is greater than either individual effect. This can be beneficial but can also be very harmful.

QUICK CHECK QUESTIONS

7 Outline how aspirin functions as an analgesic.

8 State **one** important use for aspirin other than the relief of pain and fever.

Soluble aspirin

The molecular or free acid form of aspirin has limited solubility in water due to the presence of a non-polar benzene ring. It is in reversible equilibrium with its carboxylate anion (Figure 25.12) and its bioavailability in blood is limited.

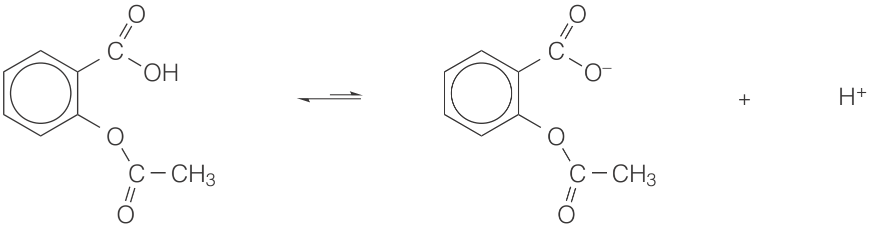


Figure 25.12 Partial dissociation of aspirin in water

The carboxylic acid group of aspirin can be ionized via a neutralization reaction with a strong base or calcium hydroxide to convert onto a more soluble ionic form. This is known as 'soluble aspirin' (Figure 25.13).

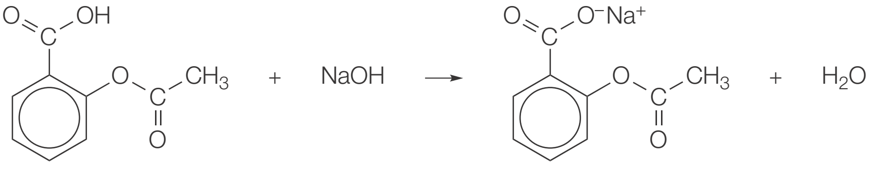


Figure 25.13 Formation of the soluble sodium salt of aspirin

However, once the aspirin anion reaches the acidic gastric juice of the stomach it is converted back to its molecular (free acid) or un-ionized form.

QUICK CHECK QUESTION

9 A soluble ionic version of aspirin can be made by reacting it with a strong base, such as sodium hydroxide. Explain why this process increases the bioavailability of the drug.

Penicillin

Revised ☐

General structure

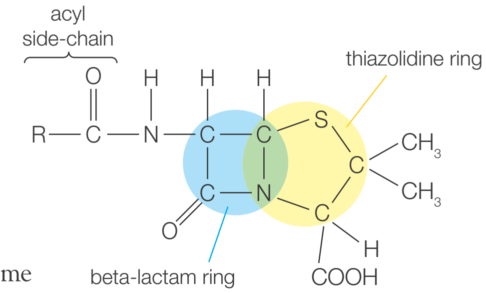


Figure 25.14 Generalized structure of the penicillins

Penicillins are a group of antibiotics originally isolated from a mould named *Penicillium notatum*. Antibiotics are substances that kill bacteria or inhibit the growth of bacteria.

Penicillins are known as beta-lactam antibiotics and their general structure is shown in Figure 25.14. The penicillins differ in the chemical nature of the acyl side-chain. The beta-lactam ring is a strained four-membered cyclic amide.

Bacteria are single-celled microorganisms; many are harmless or beneficial but some cause infectious diseases. Their cell membrane is surrounded by a protective cell wall (Figure 25.15) that is formed from covalently linked amino acids and sugars (*N*-acetylmuramic acid, NAM, and *N*-acetylglucosamine, NAG.

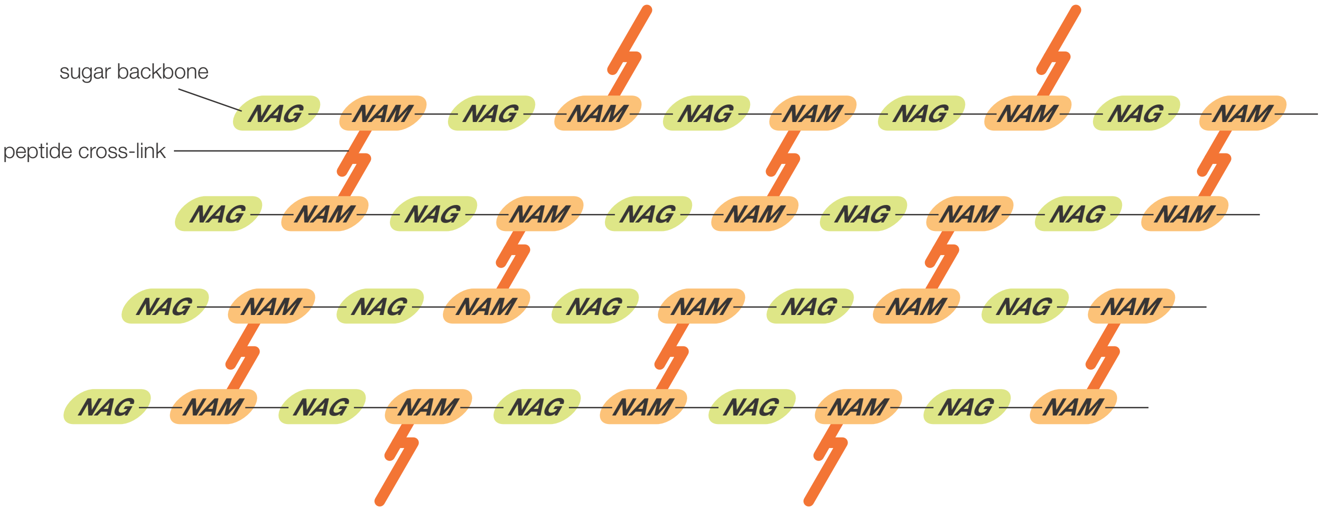


Figure 25.15 Simplified structure of the bacterial cell wall

Penicillin inhibits the action of an enzyme involved in catalysing the formation of cross-links that give the bacterial cell wall its strength and protective ability. The absence of cross-links makes the bacterial cell permeable to water which enters via osmosis. The bacterial cell swells and bursts (lyses).

All penicillins contain a reactive functional group known as the beta-lactam ring. This is a cyclic amide with bond angles of 90°. This part of the molecule is under strain (high energy) which makes the amide group within the ring system highly reactive and prone to hydrolysis.

Penicillins inhibit the final step in the synthesis of bacterial cell walls. The final step involves the enzyme-controlled cross-linking and penicillin resembles the dipeptide (alanine–alanine) that is part of the substrate by the transpeptidase enzyme for the cross-linking reaction (Figure 25.16).

Expert tip

A broad-spectrum antibiotic is active against a wide range of bacterial diseases or bacterial strains. A narrow-spectrum antibiotic is active against only a small range of bacterial diseases or bacterial strains.

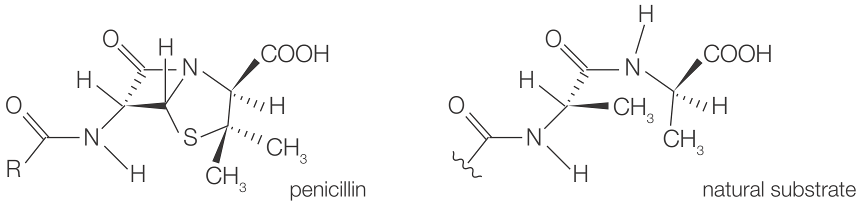
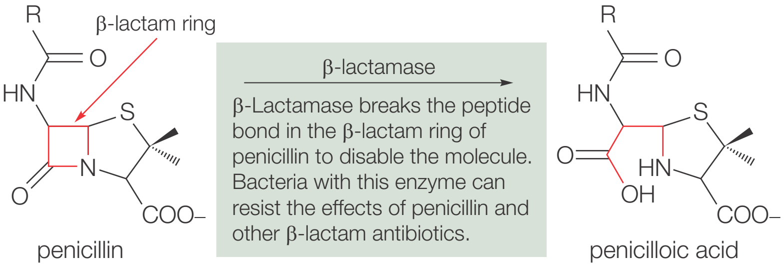


Figure 25.16 Structures of penicillin and alanine–alanine, the substrate for transpeptidase

The penicillin mimics the shape of the enzyme's normal substrate and hence enters the active site. The enzyme becomes covalently attached to the penicillin molecule and is then not capable of catalysing any further reactions.

Antibiotic resistance

Some bacteria in a population of a strain of bacteria may be naturally resistant to the effect of an antibiotic. For example, some strains of bacteria secrete an enzyme known as penicillinase (β-lactamase) (Figure 25.17) which hydrolyses penicillin G (where R is the benzyl group, $–CH_2–C_6H_5$). Penicillin G was the first penicillin to be developed but had to be injected intravenously because it was hydrolysed by the acid in the stomach. The activity of penicillinase can be potentiated by the co-administration of β-lactase inhibitors such as clavulanic acid.



β-Lactamase breaks the peptide bond in the β-lactam ring of penicillin to disable the molecule. Bacteria with this enzyme can resist the effects of penicillin and other β-lactam antibiotics.

Figure 25.17 Action of pencillinase (beta-lactamase)

Medicinal chemists have synthesized a large number of other penicillins which have a chemically modified side-chain, for example, penicillin V where R = $C_6H_5OCH_2$–). This molecule has a different structure and shape from penicillin G and does not act as a substrate for pencillinase. It is resistant to gastric juice.

Patients not completing the full prescribed course of antibiotics and the use of antibiotics in animal feeds have contributed to the development of antibiotic resistance.

Bacteria either have pre-existing resistance to drugs, or they develop resistance. Often resistance to a certain drug from a particular class leads to resistance to all other drugs in that class. Mechanisms involve enzymes that break down antibiotics or pump them out from the cytoplasm. Over-prescription of antibiotics also increases the chance of antibiotic-resistant strains developing or being selected for. The antibiotics can also enter humans via eating meat and dairy products.

NATURE OF SCIENCE

Scientific creativity takes various forms. One of these is serendipity – discovering phenomena while diverting from intended research. In 1928 Alexander Fleming returned to his laboratory in a London hospital, he picked up a culture plate of the *Staphylococcus* bacteria that he had left on the bench for some weeks. A contaminating mould had grown on the dish and around it for some distance the bacterial colonies were absent or dead. Subsequent research by Fleming revealed that the 'mould juice' was effective against a wide range of bacterial strains including many that are highly pathogenic to humans.

Expert tip

Compliance with a course of antibiotics means that the full course of antibiotics is taken and administered at the correct times.

QUICK CHECK QUESTIONS

10 Identify the functional group present in the β-lactam ring and explain why the ring is important in the functioning of penicillin as an antibacterial.

11 Modern penicillins have a similar structure to penicillin G but a different side-chain. State **two** advantages of modifying the side-chain.

12 The efficiency of certain drugs is strongly dependent on the frequency and regularity of their administration.
Explain the importance of patient compliance when the patient is treated with antibacterials.

25.3 Opiates

Revised ☐

Essential idea: Potent medical drugs prepared by chemical modification of natural products can be addictive and become substances of abuse.

Opiates

Revised ☐

- The ability of a drug to cross the blood–brain barrier depends on its chemical structure and solubility in water and lipids.
- Opiates are natural narcotic analgesics that are derived from the opium poppy.

- Morphine and codeine are used as strong analgesics. Strong analgesics work by temporarily bonding to receptor sites in the brain, preventing the transmission of pain impulses without depressing the central nervous system.
- Medical use and addictive properties of opiate compounds are related to the presence of opioid receptors in the brain.

Opiates

Revised ☐

Opiates are natural narcotic analgesics that are derived from the opium poppy (*Papaver somniferum*). The unripe seed pods contain opium and are the source of morphine and codeine. Opiates are natural alkaloids found in opium. Alkaloids are nitrogen-containing bases extracted from plants (Figure 25.18).

Morphine is a powerful painkiller (strong analgesic) with sleep-inducing properties (narcotic). Morphine is available only on prescription and is given to relieve the pain caused by severe injury, surgery and cancer, although patients often develop tolerance and dependence. It can be taken orally or injected. Codeine is used in cough mixtures and is a less powerful analgesic. Codeine is a pro-drug and in the body about 10% of codeine is converted to morphine.

Diamorphine (heroin) is easily synthesized from morphine via a simple single-step synthesis. Morphine can also be converted to codeine, by replacing an alcohol group, –OH, by an ether group, –OCH_3 (methoxy). This can be achieved by reacting morphine with CH_3I in KOH(aq).

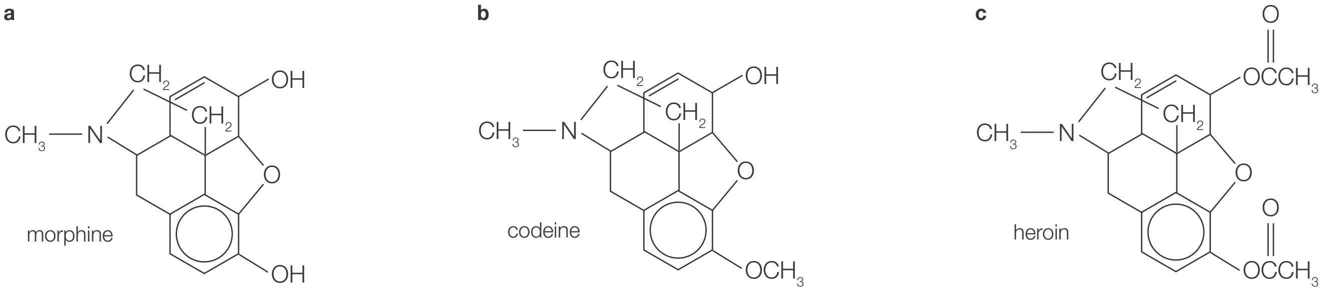


Figure 25.18 Structures of morphine, codeine and heroin (diamorphine)

The structure of morphine consists of five rings forming a T-shaped molecule. The important binding groups on morphine are the phenol, the benzene ring, and the ionized amine. All the opiates have a common structural feature known as the phenylamine chemical moiety which gives the molecule rigidity and allows it to interact strongly with the opioid receptors.

The opiates work as powerful analgesics by binding and interacting with opioid protein receptors (Figure 25.19) on the surfaces of brain cells (neurons). They prevent nerve impulses (pain signals) from causing changes inside brain cells without depressing the central nervous system (brain and spinal cord).

Opioids is a more general term used to describe all compounds with structures similar to morphine. The term narcotic originally referred medically to any compound with any sleep-inducing properties. It has since become associated with opiates and opioids.

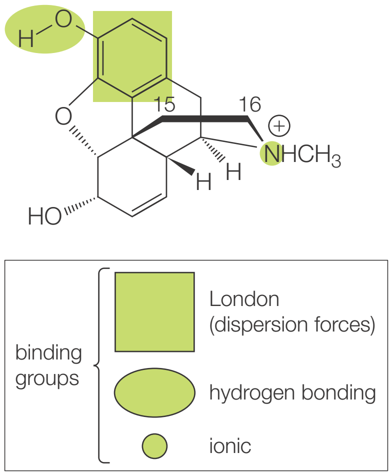


Figure 25.19 Important functional groups for analgesic activity in protonated morphine

Diamorphine (heroin)

Diamorphine (heroin) is a semi-synthetic opiate. It can be prepared from morphine by reaction with ethanoic anhydride in an acetylation reaction (–O–CO–R is an acetyl group) (Figure 25.20).

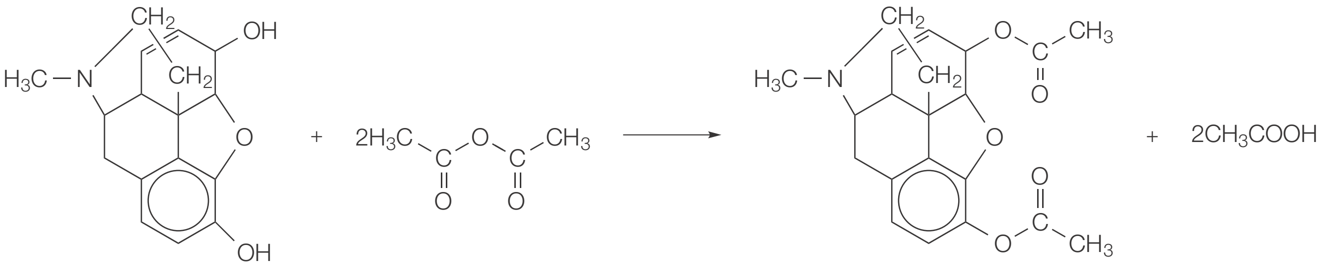


Figure 25.20 The formation of diamorphine (heroin)

During the acetylation of morphine both hydroxyl groups are substituted with ester groups which significantly reduces the polarity of the molecule. This increases its lipophilicity (ability to dissolve in lipids) and hence its ability to cross the blood–brain barrier (Figure 25.21).

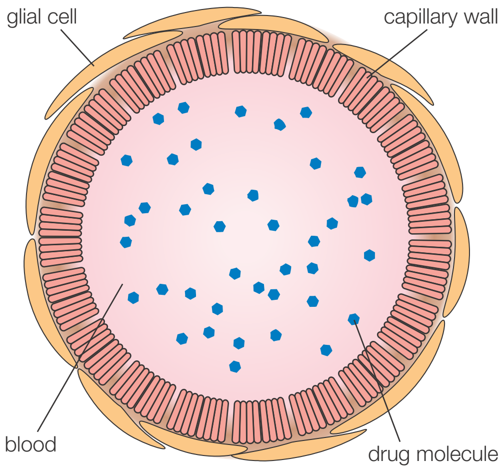


Figure 25.21 The blood–brain barrier: many large drug molecules cannot pass through the capillary wall and glial cells

In the brain, diamorphine is rapidly metabolized into morphine, which binds to the opioid receptor. This makes diamorphine about five times more effective an analgesic than morphine when injected into the blood because it crosses the blood–brain barrier in greater quantities. The morphine and diamorphine molecules both contain a tertiary amine group and can both be converted into ionic salts by reacting with hydrochloric acid to form a soluble tertiary ammonium salt. Morphine is often injected in the form of morphine hydrochloride to increase its bioavailability. It reverts back to the undissociated or free base form to cross the blood–brain barrier.

■ QUICK CHECK QUESTIONS

13 Identify the reagent and by-product when diamorphine (heroin) is synthesized from morphine.

14 Discuss how the differences in structure between morphine and diamorphine (heroin) affect their absorption across the brain–blood barrier.

Effects of opiates

Revised ☐

All of the classical opiates can cause addiction and lead to the development of tolerance to dependence. Withdrawal symptoms occur within one day for addicts if the drug usage is stopped. These include hot and cold sweats, diarrhoea, anxiety, weakness and muscle cramps that can last for months.

The short-term and long-term effects of strong opiates are summarized in Table 25.1.

Table 25.1 Short-term and long-term effect of opiates

Short-term effects	Long-term effects
Induces a sense of euphoria (great happiness)	Constipation (anti-diarrhoeal)
Dulling of pain (analgesic)	Loss of sex drive
Depress nervous system (sedation); vasodilation (blood vessels widen)	Disrupts the menstrual cycle
Slow breathing rate and heart rate	Reduced appetite
Cough reflex inhibited (antitussive)	Risk of HIV, hepatitis infection, etc. through the use of shared needles
High dosages can lead to coma or death via suffocation	Social problems, such as theft and prostitution

Some side effects can be advantageous. For example, the observation that morphine causes constipation has led to the design of opioids which are used in the treatment of diarrhoea. Euphoria can be a useful side effect when treating pain in terminally ill patients. However, the effect is not observed in patients suffering severe pain.

Methadone (Figure 25.22) is a synthetic opioid which is frequently used to treat heroin addicts. Although chemically different from morphine and heroin, it acts on the same opioid receptors in the brain and produces many of the same effects, with the exception of the euphoria.

■ QUICK CHECK QUESTIONS

15 Explain what is meant by developing tolerance towards codeine (present in cough mixtures) and state why this is dangerous.

16 Compare and contrast the functional groups present in methadone and diamorphine (heroin).

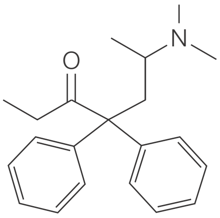


Figure 25.22 Structure of methadone

Methadone’s usefulness in treating heroin addicts is due to its long duration of effect and its ability to block the heroin withdrawal symptoms. At high concentrations it can block the euphoric effects of heroin and morphine.

25.4 pH regulation of the stomach

Revised ☐

Essential idea: Excess stomach acid is a common problem that can be alleviated by compounds that increase the stomach pH by neutralizing or reducing its secretion.

pH regulation of the stomach

Revised ☐

- Non-specific reactions, such as the use of antacids, are those that work to reduce the excess stomach acid.
- Active metabolites are the active forms of a drug after it has been processed by the body.

Gastric acid release

Revised ☐

Gastric juices consist of a protease and hydrochloric acid designed to break down protein. Hydrochloric acid is secreted from parietal cells, and the stomach secretes a layer of mucus to protect itself from its own gastric juices. Hydrogencarbonate ions (a buffer) are also released and are trapped in the mucus to create a pH gradient within the mucus layer.

When the nervous system is stimulated, a signal is sent to the parietal cells, resulting in the release of the neurotransmitter acetylcholine at the nerve endings. Acetylcholine activates receptors of the parietal cells, leading to the release of gastric acid into the stomach. The trigger for this process is provided by the sight, smell or thought of food.

Nerve signals also stimulate a region of the stomach called the antrum (Figure 25.23), which contains cells that release a hormone known as gastrin, which is also released when food enters the stomach. Gastrin enters the blood supply and travels to the parietal cells, stimulating the release of gastric acid. Release of gastric acid is therefore inhibited by antagonists blocking either the receptor for acetylcholine (M_3) or the receptor for gastrin (Cck_2).

The local hormone histamine (Figure 25.24) also stimulates the release of gastric acid by interacting with a specific type of histamine receptor called the H_2 receptor.

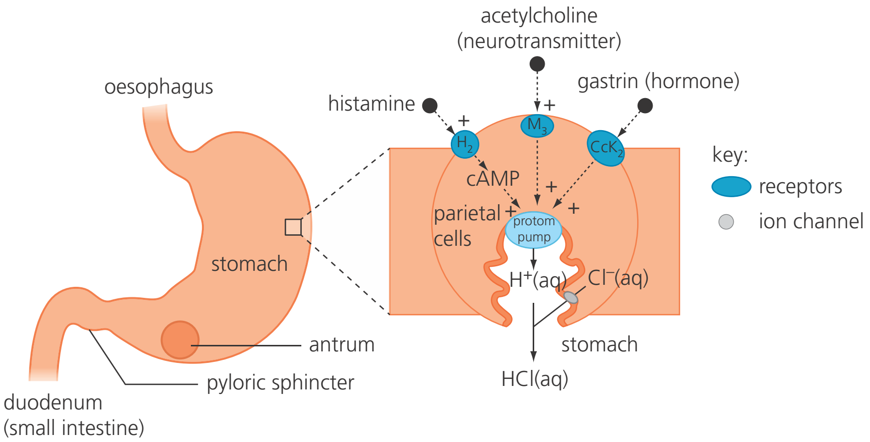


Figure 25.23 Factors influencing the release of gastric acid

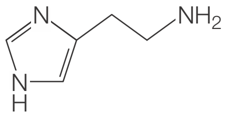


Figure 25.24 Structure of histamine

Antacids

Revised ☐

Dyspesia, or indigestion, occurs when excess gastric juice (hydrochloric acid) is secreted by the stomach and there is reflux into the oesphagus. Antacids are medicines to reduce excess hydrochloric acid in the stomach. They are weak bases and remove the excess hydrogen ions via neutralization. Suitable compounds to act as antacids are metal hydroxides (unless alkalis), metal carbonates, metal hydrogencarbonates and some metal oxides.

Expert tip

Alkalis are not suitable for use as antacids. They are highly corrosive and their neutralization is more exothermic than an insoluble weak base. Typical neutralization reactions are:

$$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$$

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

$$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$$

$$Al(OH)_3(s) + 3HCl(aq) \rightarrow AlCl_3(aq) + 3H_2O(l)$$

$$Ca(OH)_2(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + 2H_2O(l)$$

Expert tip

Note that aluminium hydroxide neutralizes three moles of acid (H^+) per mole of base compared to two moles of acid (H^+) neutralized per mole of calcium hydroxide.

A calculation based on the mole concept and a balanced equation allows the most effective antacid by mass to be determined.

Worked example

Rolaids is a commercial antacid used to treat dyspepsia caused by excess acidity in the stomach. Its active ingredients are calcium carbonate (500 mg) and magnesium hydroxide (100 mg).

Write balanced equations for the reactions of magnesium hydroxide and calcium carbonate with the acid present in gastric juice

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$$

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

State one reason why potassium hydroxide is not used in antacids.

It is an alkali/strong base; corrosive with a high enthalpy of neutralization.

State one problem when using large amounts of calcium carbonate compared with magnesium hydroxide in Rolaids.

Bloating/flatulence/production of carbon dioxide gas, CO_2.

■ QUICK CHECK QUESTION

17 A 1.20 g antacid tablet contains 80.0% by mass of magnesium hydroxide as the active ingredient. Deduce what volume of 0.1500 mol dm^{-3} HCl the antacid tablet can neutralize.

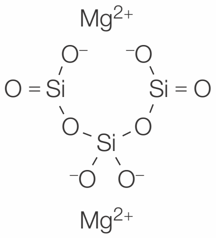
Table 25.2 is a comparison of compounds used in antacid preparations.

Table 25.2 A comparison of compounds used in antacid preparation.

Antacid compound	Action	Side effect
Calcium hydroxide, $Ca(OH)_2$	Although is a strong base, $Ca(OH)_2$ is only slightly soluble in water, and the solution is thus weakly basic. A saturated solution of calcium hydroxide (limewater) rapidly neutralizes stomach acid.	A strong base is rarely used as an antacid as extended use can lead to tissue damage.
Magnesium hydroxide, $Mg(OH)_2$	$Mg(OH)_2$ also rapidly neutralizes stomach acid but has a laxative effect and can cause diarrhoea.	Laxative properties; excess quantities can lead to toxicity; effects include severe allergic reactions, nausea and black faeces.
Aluminium hydroxide, $Al(OH)_3$	Aluminium hydroxide has a very low solubility in water and dissolves slowly in the stomach to relieve indigestion. It may cause constipation.	The aluminium ion, Al^{3+}, has a high charge density due to its high charge to size ratio and can effectively bind drugs, calcium or phosphate ions thus inhibiting its absorption; depletion of calcium ions, Ca^{2+}, leads to a risk of weaker bones.
Calcium carbonate, $CaCO_3$	Calcium carbonate, $CaCO_3$, is a strong fast-acting antacid and the same mass works longer than that of sodium hydrogencarbonate, $NaHCO_3$.	Repeated use as an antacid may lead to excessive amounts of calcium ions being absorbed into the body and may result in kidney stones; calcium carbonate, $CaCO_3$, can produce the acid rebound effect resulting in the stomach quickly having excess gastric juice within a short time.
Sodium hydrogencarbonate, $NaHCO_3$, as a solid mixture with citric acid	Reacts in water to release carbon dioxide, CO_2 gas; induces belching and flatulence, thus relieving discomfort. $NaHCO_3$ is soluble in water, works quickly and provides short-term relief.	Fluid retention (bloating) and alkalosis (low pH) due to high HCO_3^-(aq) concentration. High Na^+(aq) concentration leads to high blood pressure, heart failure or kidney problems and may lead to hypertension (high blood pressure).

■ QUICK CHECK QUESTIONS

18 An antacid called magnesium trisilicate may be recommended for recurring heart burn or indigestion. Its use may lead to high a magnesium level and muscle weakness.



- **a** State the types of bonding present in magnesium silicate.
- **b** State **one** function of the hydrochloric acid present in gastric juice.
- **c** Magnesium trisilicate reacts with hydrochloric acid to form silicon dioxide, water and magnesium chloride. Write a balanced equation for this reaction. State a possible effect of the silicon dioxide.

19 A laboratory test to determine how much hydrochloric acid is neutralized by a brand of antacid does not give a complete picture of its effectiveness in the stomach. State and explain what other factors might be important when assessing antacids.

20 Some antacids fizz when dissolved in a glass of water. They contain sodium hydrogen carbonate and citric acid. Write an ionic equation for the reaction.

21 Explain how heartburn is caused.

Specific inhibition of hydrochloric acid production in the stomach

Revised ☐

Excessive production of hydrochloric acid can be inhibited using drugs, such as ranitidine (Zantac) (Figure 25.25), which act as an antagonist of the histamine-H_2 protein receptor on parietal cells, which is responsible for promoting hydrochloric acid production.

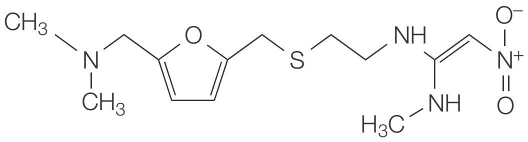


Figure 25.25 Structure of ranitidine (Zantac)

Ranitidine is an example of rational drug design: the design of drugs to specifically work for their respective targets. Previously the emphasis was on synthesizing as many analogues of the lead compound as possible. Rational drug design is based on an understanding of the drug's mechanism of action and its target structure. The design of H_2 antagonists was based on the natural agonist histamine as a lead compound.

Ranitidine (and related H_2 antagonists) have largely replaced drugs known as proton pump inhibitors. These work by irreversibly inhibiting an enzyme complex called the proton pump present in parietal cells.

All the proton pump inhibitors act as pro-drugs, since they are activated when they reach the parietal cells. Once activated, they bind irreversibly to exposed cysteine residues of the proton pump and 'block' the pump, preventing further release of hydrochloric acid.

Omeprazole (Prilosec) (Figure 25.26) and esomeprazole (Nexium) (Figure 25.27) are the R and S enantiomers of a synthetic proton pump inhibitor. Esomeprazole is an example of chiral switching where a racemic drug is replaced with a single enantiomer. There is no difference between the mechanism of action of the two enantiomers of omeprazole, but it is possible to use double the dose levels of esomeprazole, resulting in greater activity.

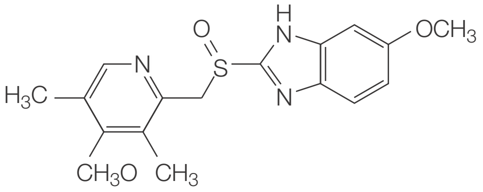


Figure 25.26 Structure of omeprazole (Prilosec)

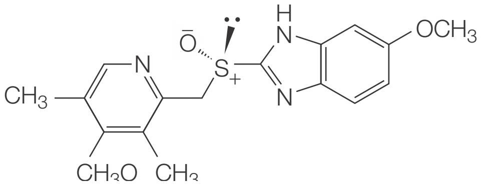


Figure 25.27 Structure of esomeprazole (Nexium)

Owing to their low polarity, omeprazole and esomeprazole readily cross the lipid bilayer of cell membranes and enter the cytoplasm of parietal cells containing hydrochloric acid. In this acidic environment near the parietal cell surface both enantiomers undergo a series of acid-catalysed chemical changes and produce the same active metabolites, which bind to the proton pump of the parietal cell (via a sulfur–sulfur bridge) and inhibit the hydrochloric acid.

Omeprazole becomes ionized when the weak base molecule is protonated and hence unable to cross back into the cell through the cell membrane. This mechanism of action increases the efficiency and bioavailability of both drugs and allows a reduced frequency of administration. Omeprazole and proton pump inhibitors have very few side effects because of their selectivity and mechanism of action. The drugs are effective for an extended period of time until the cell is able to synthesize new proton pumps.

■ QUICK CHECK QUESTIONS

22 Compare and contrast the use and omeprazole (Prilosec) and metal hydroxide antacids.

23 Outline why the development of the drug ranitidine (Zantac) was based on the structure of histamine.

Buffer calculations

Revised ☐

Buffers are solutions of weak acids with their salt or weak base with their salt. They resist changes in pH when small amounts of acid or base are added to them. Their behaviour can be explained via the action of reversible equilibria (Figure 25.28).

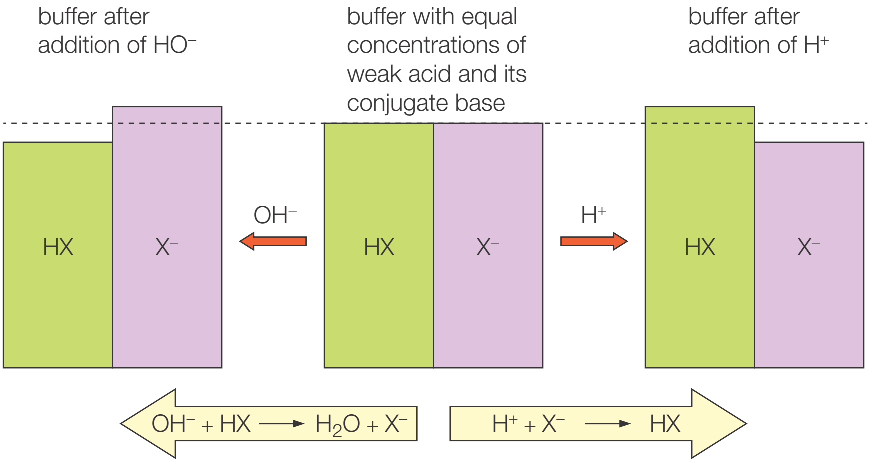


Figure 25.28 Action of an acidic buffer

A buffer consists of a mixture of a weak conjugate acid–base pair, here represented as HX and X^-. When a small portion of OH^- is added to the buffer (left), it reacts with HX, decreasing [HX] and increasing $[X^-]$ in the buffer. When a small portion of H^+ is added to the buffer (right), it reacts with X^-, decreasing $[X^-]$ and increasing [HX] in the buffer.

The pH of a buffer solution can be calculated with the logarithmic form of the equilibrium law applied to the dissociation of a weak acid:

$$\mathrm{pH} = \mathrm{p}K_a + \log_{10}([\text{salt}]/[\text{acid}])$$

This expression is known as the Henderson–Hasselbalch equation. The buffer will be most effective when the concentration of the weak acid is equal to the concentration of the salt of the weak acid.

Worked example

Calculate the pH of a buffer containing 0.100 mol dm^{-3} phenylamine, $C_6H_5NH_2$, and 0.250 mol dm^{-3} phenylammonium chloride, $C_6H_5NH_3^+$. K_a of $C_6H_5NH_3^+$ = 2.63×10^{-5}.

$$\mathrm{pH} = \mathrm{p}K_a + \log_{10}([A^-(aq)]/[HA(aq)])$$

$$\mathrm{pH} = 4.58 + \log_{10}(0.1/0.25) = 4.58 + (-0.398) = 4.18$$

Expert tip

Diluting a buffer solution with water does not change the ratio of the concentrations of the salt and acid so the pH does not change (unless the dilution is so great that the assumptions made when deriving the equation no longer apply).

Calculations with the Henderson–Hasselbalch equation may require conversions involving H^+ and pH; K_a and pK_a and calculations of concentrations from masses of pure substances and volumes of solutions.

How buffer solutions limit changes in pH

Revised ☐

It is possible to show quantitatively the ability of buffer solutions to limit changes in pH. For example, a buffer made from 0.60 mol dm^{-3} HClO ($K_a = 3.7 \times 10^{-8}$) and 0.20 mol dm^{-3} NaClO has a pH of 7.0.

If 0.01 moles of HCl are added to 100 cm^3 of the buffer:

	$ClO^-(aq)$ +	$H_3O^+(aq)$ →	$HClO(aq)$ + $H_2O(l)$
Initial amounts:	0.02	0.01	0.06
Final amounts:	0.01	–	0.07

So the [base]/[acid] ratio is 0.01/0.07; pH = pK_a + $\log_{10}$([base]/[acid]) = 6.58 (a change of 0.4 units). If 0.01 moles of HCl were added to 100 cm^3 of pure water, the pH of the resulting solution would be 1.0 (a change of 6 pH units).

If 0.01 moles of NaOH are added to the buffer:

	$HClO(aq)$ +	$OH^-(aq)$ →	$ClO^-(aq)$ + $H_2O(l)$
Initial amounts:	0.06	0.01	0.02
Final amounts:	0.05	–	0.03

So the [base]/[acid] ratio is 0.03/0.05; pH = pK_a + $\log_{10}$([base]/[acid]) = 7.21 (a change of 0.2 pH units). If 0.01 moles of NaOH were added to 100 cm^3 of pure water, the pH of the resulting solution would be 13.0.

Hence buffer solutions do not significantly change their pH on adding small quantities of acid or alkali.

However, it is possible to exceed the buffering capacity of a buffer solution by adding too much acid or alkali; in such cases the buffer will be unable to maintain the pH and the pH will change dramatically. This would be the case of more than 0.02 moles of HCl or more than 0.06 moles of NaOH were added to the above mixture.

Worked example

Determine the pH of a buffer solution formed by adding 50.00 cm^3 of 0.0100 mol dm^{-3} sulfuric acid to 50.00 cm^3 of 0.0400 mol dm^{-3} methylamine.

$n(H_2SO_4)$ = (50.00/1000) dm^{-3} × 0.0100 mol dm^{-3} = 0.5$n(CH_3NH_2)_{reacted}$ = 0.5$n(CH_3NH_3^+)_{buffer}$; $n(CH_3NH_2)_{buffer}$ = (50.00/1000) dm^3 × 0.0400 mol dm^{-3} – 2 × (50.00/1000) dm^3 × 0.0100 mol dm^{-3}; $n(CH_3NH_2)$ = $n(CH_3NH_3^+)$; $[CH_3NH_2]$ = $[CH_3NH_3^+]$ in buffer; pOH = pK_b = 3.34, pH = 10.66.

Worked example

Calculate the ratio of methanoate ions/methanoic acid to give a buffer of pH 4.00. The pK of methanoic acid is 3.75.

pH = pK_a + $\log_{10}$[base]/[acid]; 4.00 = 3.75 + $\log_{10}$ $[HCO_2^-]/[HCOOH]$; so $[HCO_2^-]/[HCOOH]$ = 100.25 = 1.78

Worked example

Calculate the amount (in mol) of sodium hydroxide that must be added to 100.0 cm^3 of 0.20 mol dm^{-3} HCOOH to prepare a solution buffered at pH 4.00.

If the concentration of OH^- which is added is x mol dm^{-3} then this will react with HCOOH to produce $HCOO^-$ so that: [HCOOH] = (0.20 – x) mol dm^{-3} and $[HCOO^-$ = x mol dm^{-3}. If the pH = 4.00, then $[HCOO^-]/[HCOOH]$ = 1.78. Hence: $x/(0.20 - x)$ = 1.78, x = 0.13. To achieve $[OH^-(aq)]$ = 1.13 mol dm^{-3} in 100 cm^3, the amount of NaOH that must be added is 0.13 mol dm^{-3} × 0.1000 dm^3 = 0.013 mol.

QUICK CHECK QUESTIONS

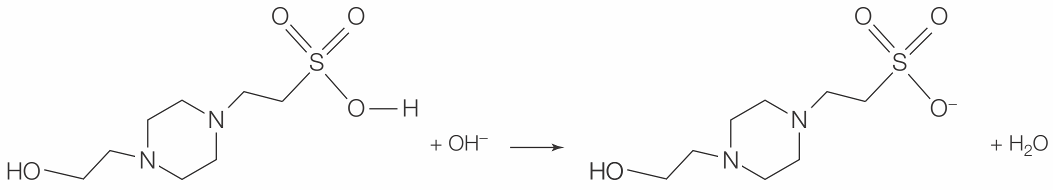
24 The pH of blood is 7.4 and is regulated by the bicarbonate buffering system composed of carbonic acid, H_2CO_3, and hydrogencarbonate ion, HCO_3^-.

a Using relevant chemical equations, show how this buffering system keeps the pH of blood constant when a small amount of acid or alkali is added.

b The pK_a of carbonic acid is 6.1. Calculate the ratio of the concentrations of carbonic acid and hydrogencarbonate in blood and comment on the buffering capacity of blood.

25 HEPES is a zwitterionic buffer that can be made by dissolving solid sodium hydroxide in a HEPES solution.

Calculate the pH of the buffer solution formed when 20.00 g of sodium hydroxide is added to 1.00 dm^3 of a 1.00 mol dm^{-3} solution of HEPES (pK_a = 7.50). Assume that there is no change in volume when the sodium hydroxide is added.



HEPES

25.5 Anti-viral medications

Revised ☐

Essential idea: Anti-viral medications have recently been developed for some viral infections while others are still being researched.

Anti-viral medications

Revised ☐

- Viruses lack a cell structure and so are more difficult to target with drugs than bacteria.
- Anti-viral drugs may work by altering the cell's genetic material so that the virus cannot use it to multiply. Alternatively, they may prevent the viruses from multiplying by blocking enzyme activity within the host cell.

Bacteria

Revised ☐

Bacteria (Figure 25.29) are single-celled (unicellular) microorganisms that reproduce outside cells by binary division (a form of asexual reproduction). Bacterial cells are too large to enter human cells.

Bacteria can exchange genetic material and acquire genes for antibiotic resistance by a process known as conjugation (involving the pili). There is no nuclear membrane surrounding their DNA and no membrane bound structures within their cytoplasm. They have a protective cell wall and some species have a rotating flagellum for movement.

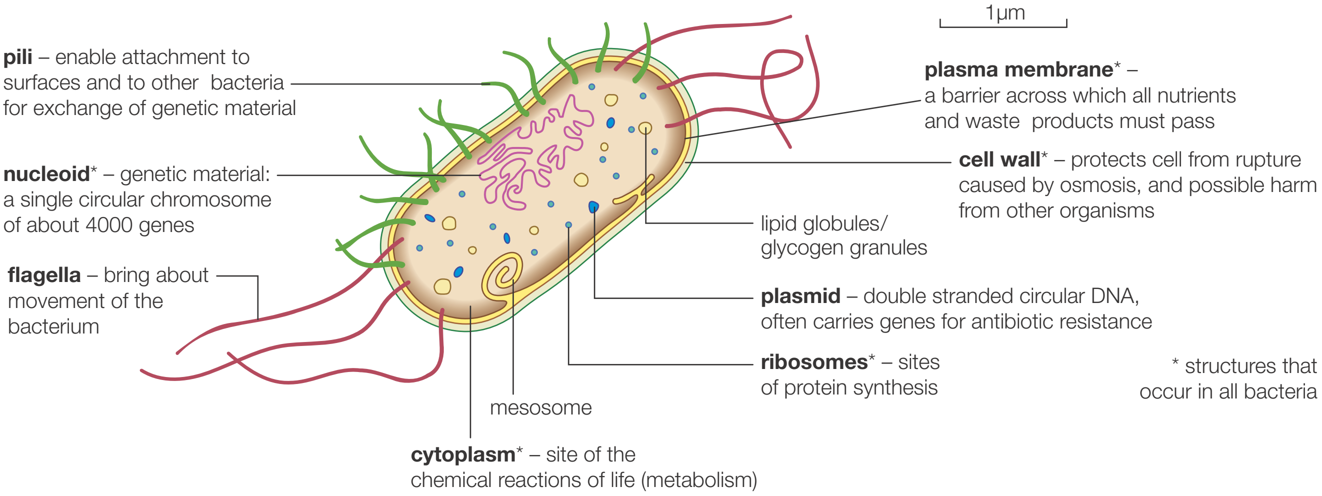


Figure 25.29 The structure of *Escherichia coli* – a 'typical' bacterium

Viruses

Revised ☐

Viruses are much smaller and simpler in structure than bacteria. Viruses (Figure 25.30) contain DNA or RNA surrounded by a capsid composed of regularly packed capsomeres, each containing a number of protein molecules. Some viruses, such as HIV, have a cell membrane formed from their host cell. Viruses are non-cellular (acellular): there is no nucleus or cytoplasm. They cannot self-multiply and can only replicate inside a living cell (host cell). Viruses are typically 100× smaller than bacteria.

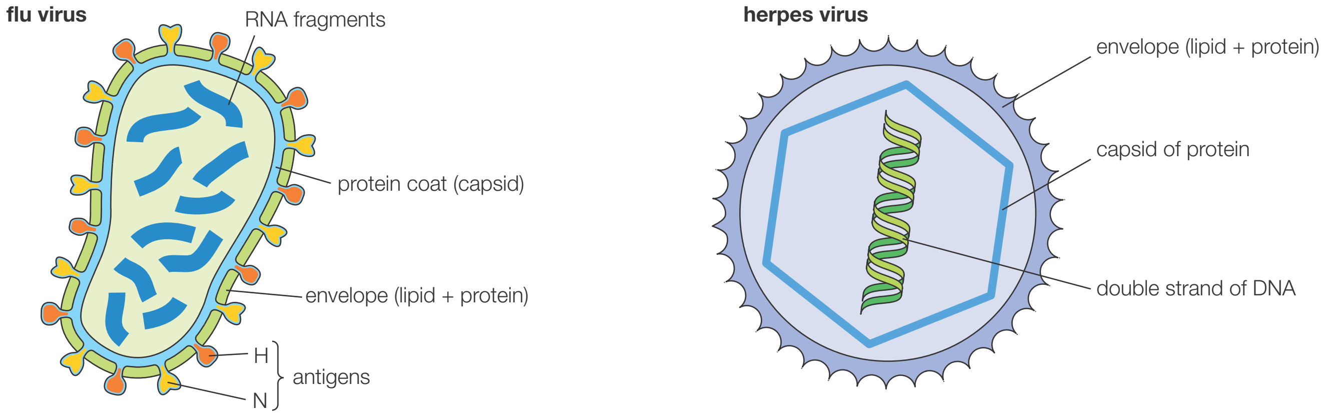


Figure 25.30 The structures of the influenza and herpes viruses: antigens are 'foreign' proteins recognized by the immune system

Once a virus or its nucleic acid enters a cell the host cell's enzymes and ribosomes are used to make new viral proteins and enzymes that self-assemble into viruses. The viruses will then exit from the cell through the cell membrane (lysis), leaving behind a dead or damaged cell.

Retroviruses

In many RNA and DNA viruses, such as flu and herpes, nucleic acid replication occurs entirely in the cytoplasm.

However, in retroviruses, such as HIV, their RNA is used as a template for making viral DNA, using a viral enzyme called reverse transcriptase. In viral infections involving retroviruses, the viral DNA becomes integrated into the host's DNA (via the action of viral integrase) and may not kill the host or cause any obvious illness (Figure 25.31) until years later.

Expert tip

Ribosomes are structures found in all cells and are involved in protein synthesis. They may be free in the cytoplasm or associated with internal membranes (except in bacteria). Some antibiotics, such as erythromycin, function by inhibiting bacterial ribosomes. Viruses do not contain ribosomes.

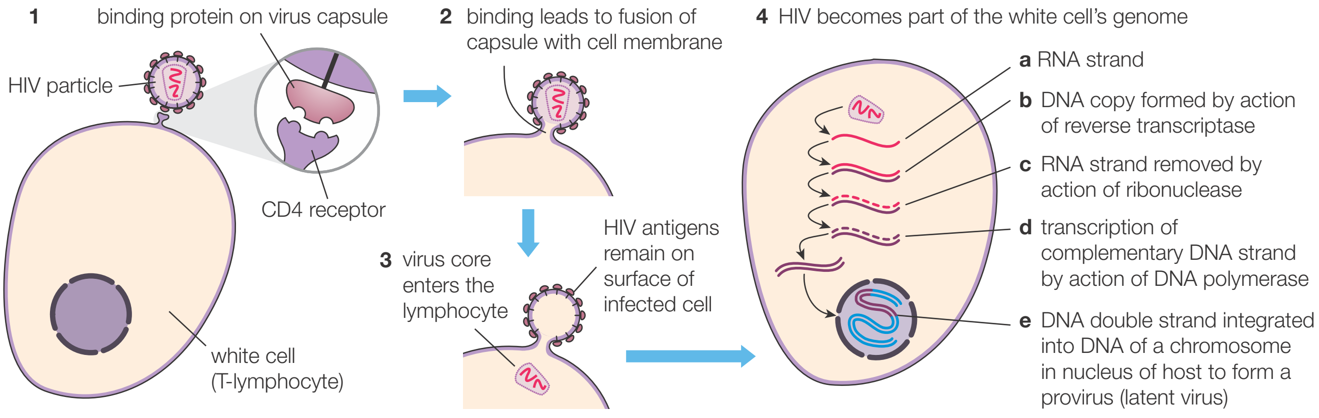


Figure 25.31 HIV infection of a T-lymphocyte: a type of white blood cell

The human immunodeficiency virus (HIV) infects T-lymphocyte cells, which are crucial to the control of the immune system, which provides protection against viruses and microorganisms. With a weakened immune system people infected with HIV are prone to a range of opportunistic secondary infections. This condition is known as AIDS.

Expert tip

All viruses contain one or more molecules of either RNA or DNA, but not both. They can, therefore, be defined as RNA or DNA viruses.

Differences between viruses and bacteria

Viruses are different in many ways from bacteria. Table 25.3 shows some of the main differences between bacteria and viruses.

Expert tip

Reverse transcriptase catalyses the conversion of single-stranded RNA to double-stranded DNA. This process does not occur in normal cells.

Table 25.3 The main differences between bacteria and viruses

	Bacteria	Viruses
Ribosomes	Present	Absent
Number of cells	Unicellular; one cell (but can form cooperating colonies)	No cells (acellular)
Internal structure	DNA floating freely in cytoplasm; has cell wall and cell membrane	DNA or RNA enclosed inside a coat (capsid) of protein or glycoproteins
Cell wall composition	Peptidoglycan/lipopolysaccharide	No cell wall; protein coat (capsid) present instead
Treatment	Antibiotics	Vaccines prevent the spread of infection and anti-viral drugs help to slow replication but cannot stop it completely
Enzymes	Yes	Yes in some, for example reverse transcriptase in retroviruses
Nucleus	No – the nuclear material (nucleoid) is not surrounded by a nuclear membrane	No
Virulence	Yes	Yes
Infection	Localized	Systemic
Reproduction	Binary fission – a form of asexual reproduction	Invades a host cell and takes over the cell, causing it to make copies of the viral genome (DNA or RNA); destroys or damages the host cell, releasing new viruses
Size	Larger (1000 nm	Smaller (20–400 nm)

Anti-viral drugs

Revised ☐

Anti-virals are medicinal drugs (medications) useful in treating or controlling viral infections. Viruses are a serious health threat and there is a need for new anti-viral drugs. Vaccination is effective against many viruses, but is less effective against viruses that readily mutate. Anti-viral drug research has been helped by advantages in molecular biology, genetic engineering, computer modelling and X-ray crystallography.

In general, there are four types of actions for anti-viral drugs:

- Preventing the genetic material from being injected through the cell membrane (Figure 25.32); viruses have to interact and bind with specific receptors (proteins or glycoproteins) on the cell membrane of a cell and release its genetic material.
- To block entry, anti-viral molecules can be synthesized that are structurally similar to the virus-associated protein so they bind strongly to the receptor or even bind to the viral capsid (protein coat). They can also inhibit the uncoating process: the release of viral nucleic acids from the capsid that covers them.
- Inhibiting the replication of the virus: the drug may mimic nucleotides, the monomers of DNA or RNA, so that they are incorporated into the enzyme-controlled synthesis of DNA or RNA, which is then terminated (Figure 25.33). These anti-viral agents are known as nucleoside analogues.
- Inhibiting the action of reverse transcriptase present in retroviruses, for example HIV (Figure 25.34).

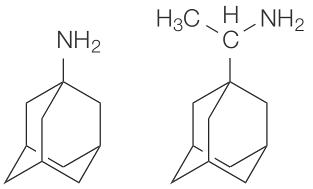


Figure 25.32 Structures of amantadine and rimantadine: uncoating inhibitors

QUICK CHECK QUESTIONS

26 State the function of reverse transcriptase in the HIV virus and other retroviruses.

27 Outline why viruses are often more difficult to target with drugs than bacteria.

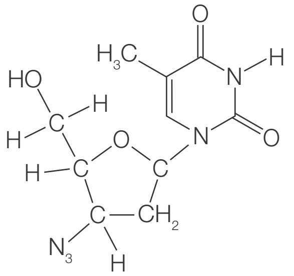


Figure 25.33 Structure of azidothymidine (AZT) or Zidovudine, used in the clinical treatment of AIDS

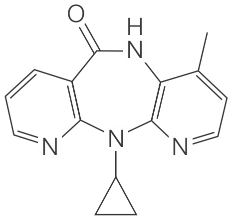


Figure 25.34 Nevirapine, a non-nucleotide reverse transcriptase inhibitor for the treatment of HIV infection

Preventing new viruses from leaving the cell: new DNA and viral proteins self-assemble into new viruses (viral particles). Following rupture of host cell membranes (or budding), these viruses leave the host cell; this then results in new infections in other cells of the body. Drugs may be developed that prevent the exit of the mature viruses.

Designing safe and effective anti-viral drugs is difficult, because viruses use the host's cells to replicate. This makes it difficult to find targets for the drug that would interfere with the virus without also harming the host organism's cells. The major problem in developing vaccines and anti-viral drugs is due to viral variation and rapid evolutionary change leading to drug resistance. Many anti-virals can only slow down or sometimes stop the replication of the virus.

HIV infection

HIV is spread from contact with infected blood, semen or vaginal fluids. Most people get the virus by having unprotected sex with someone who has HIV. Another common way is through sharing drug needles with someone who is infected with HIV. The virus can also be passed from a mother to her baby during pregnancy (via the placenta), birth or breast-feeding.

HIV therapy

There is no effective vaccine; current anti-viral drugs for treating HIV just slow down the replication rate of the HIV virus. A mixture ('cocktail') of anti-virals is most effective in managing HIV infection. Retroviruses, such as HIV, have a higher mutation rate than DNA viruses, which leads to drug resistance and the need for new anti-virals. Preventing infection by the use of condoms is the most effective method for reducing HIV infection rates. However, HIV is also transmitted by blood and can pass from an infected mother to her baby.

Social and economic issues related to HIV

There are also social and economic issues related to the issue of AIDS and HIV infection. Countries with the highest rates of infection including new infections are often poor developing countries and unable to afford retroviral medication. Education related to the treatment and prevention of HIV infection may not be present in certain areas. The use of condoms may not be acceptable to certain cultures or religious groups.

HIV/AIDS affects economic growth by reducing the availability of human capital (workers). Without proper prevention programmes, nutrition, health care and medicine that is available in developing countries, large numbers of people are dying of HIV in some developing countries, especially Africa (where the virus originated). People with HIV/AIDS ('HIV positive') will not only be unable to work, but will also require significant medical care. In some heavily infected areas, the epidemic has left behind many orphans.

Oseltamivir and zanamivir

Oseltamivir (Tamiflu) and zanamivir (Relenza) are two anti-viral drugs specifically designed to treat influenza (flu), caused by the influenza A and B viruses. Oseltamivir is taken orally and zanamivir is inhaled as a dry powder. The prodrug oseltamivir is itself not virally effective; however, once in the liver it is hydrolysed to its active metabolite – the free oseltamivir carboxylate.

Oseltamivir and zanamivir are neuraminidase inhibitors (Figure 25.35), acting as a competitive inhibitor (by reversibly binding to the active site) of the activity of the viral neuraminidase enzyme upon sialic acid, found on glycoproteins on the surface of the host cells. By blocking the activity of the enzyme, oseltamivir and zanamivir prevent new virus particles from departing the host cell.

QUICK CHECK QUESTIONS

28 Anti-viral drugs work in a number of ways to inhibit viral activity. State **two** general ways by which an anti-viral drug may work.

29 Describe the differences in the ways that bacteria and viruses multiply.

30 Explain why effective treatment of AIDS with anti-viral drugs is difficult.

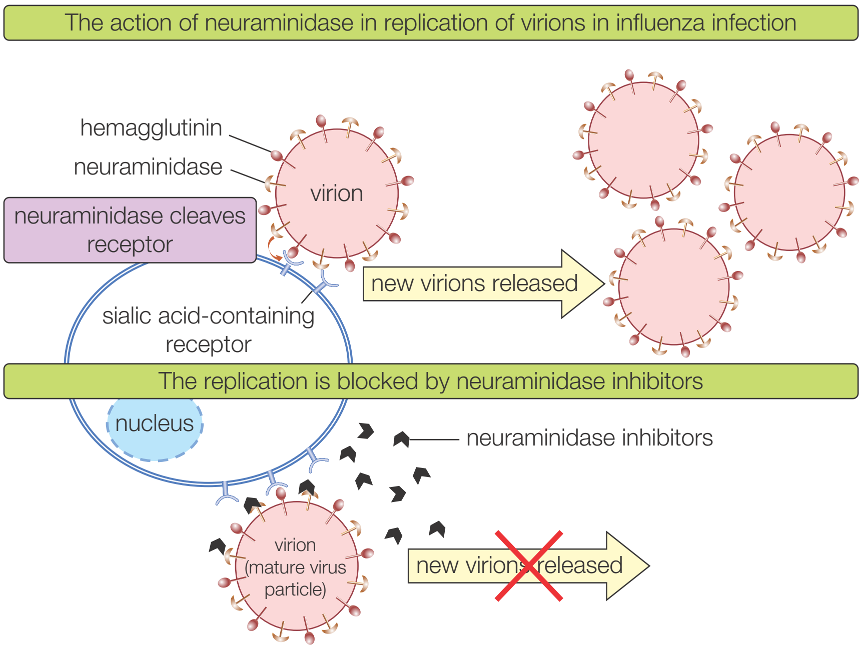


Figure 25.35 Oseltamivir and zanamivir are neuraminidase inhibitors

Both molecules contain a six-membered ring with three chiral carbon atoms (marked with asterisks in Figure 25.36). Both drugs engage in a variety of favourable interactions, including hydrogen bonding and ionic interactions with the active sites of neuraminidases.

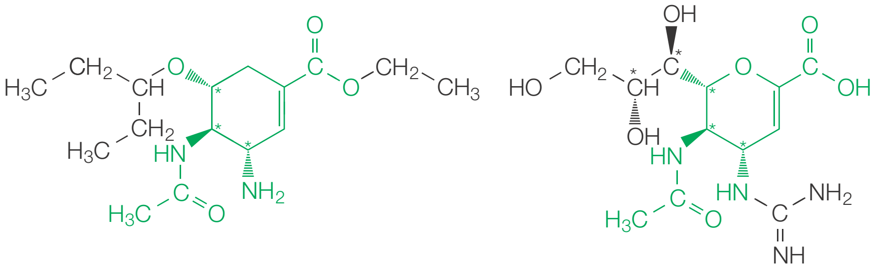


Figure 25.36 The structures of oseltamivir and zanamivir (the chiral carbon atoms are marked with *; common structural features are shown in green)

Zanamivir contains a number of polar hydroxyl and amine groups together with an ionizable carboxylic acid group which make it more soluble in water.

25.6 Environmental impact of some medications

Revised ☐

Essential idea: The synthesis, isolation and administration of medications can have an effect on the environment.

Environmental impact of some medications

Revised ☐

- High-level waste (HLW) is waste that gives off large amounts of ionizing radiation for a long time.
- Low-level waste (LLW) is waste that gives off small amounts of ionizing radiation for a short time.
- Antibiotic resistance occurs when microorganisms become resistant to antibacterials.

Antibiotic waste

Revised ☐

Bacteria in fresh water or in the water within soil can absorb antibiotics that enter the sewage from the urine or being disposed of in water. The bacterial population will be subjected to natural evolution for antibiotic resistance (Figure 25.37). This often occurs via production of enzymes that degrade the antibiotic or catalyse the formation of modifications to the cell wall.

If these bacteria enter drinking water they can cause an infectious disease that will be resistant to one more antibiotics. Antibiotics also enter fresh water from farms where animals have been given antibiotics. The antibiotic enters the water from the faeces and urine.

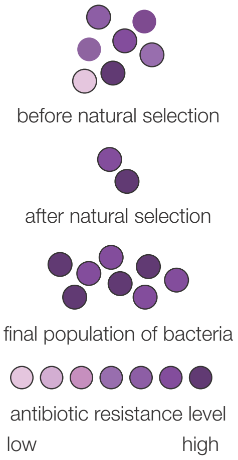


Figure 25.37 Outline of process of antibiotic resistance

Solvent waste

Revised ☐

Many different solvents may be used in the synthesis of medicinal drugs (pharmaceuticals). Solvents are usually organic liquids that are used to extract or dissolve substances. Most industrial solvents used in industry are organic and, due to their weak intermolecular forces, have low boiling points and hence high volatility.

Many organic solvents are flammable and their vapours may contribute to the greenhouse effect and hence global warming. Chlorinated solvents contribute to ozone depletion. The carbon–chlorine bonds are broken in the presence of ultraviolet radiation (of the appropriate energy), releasing reactive chlorine atoms. They are also involved in the formation of hydrogen chloride in photochemical smog.

Chlorinated waste cannot be incinerated with common organic waste because their incomplete combustion could produce highly toxic phosgene ($COCl_2$) and dioxins. To minimize the formation of such by-products, chlorinated solvents must be incinerated separately at very high temperatures or recycled by distillation.

Some of the organic solvents, such as benzene, carbon tetrachloride and chloroform (trichloromethane) are carcinogenic; others are toxic. Health issues from exposure to organic solvents include damage to the skin, eye injury, damage to the kidneys, the liver and reproductive organs, and cancer, including leukemia.

Environmental problems include pollution of the air, soil and water leading to harmful effects to plants, animals and aquatic organisms. Chlorinated compounds tend to be non-biodegradable and become concentrated as they move up food chains.

■ QUICK CHECK QUESTIONS

31 State **two** problems with the overuse and over-prescription of antibiotics.

32 Dichloromethane can undergo combustion to form carbon dioxide, water and chlorine, or carbon dioxide and hydrogen chloride.

  a Write balanced equations.

  b State **two** environmental problems associated with chlorinated solvents.

Radioactive waste

Revised ☐

Radioactive waste can be divided into high-level waste (HLW) and low-level waste (LLW). Low-level waste include items such as rubber gloves, syringes, vials, paper towels and protective clothing, such as gloves, that have been used in areas where radioactive materials are handled.

Sources of radiation that expose patients to radiation in hospitals include radiotherapy using gamma radiation (from cobalt-60), diagnostic medical nuclear procedures, X-rays, PET (positron emission tomography) scans, bone scans, thyroid scans and radioisotope therapy where a radioisotope is attached to another molecule or antibody, which then guides it to the target tissue after being injected or taken orally. The level of activity is low and the half-lives of the radioactive isotopes (radioisotopes) are generally short – minutes or a few days.

HLW has high activity and generally the isotopes have long half-lives so the waste will remain active (and often hot) for many years. It is generated in nuclear power stations.

Any type of radioactive waste needs to be kept separate from other types of waste. LLW is usually disposed of in a landfill or diluted in the sea; HLW is vitrified (turned into an inert glass-like material) and stored underground in concrete bunkers.

LLW will have low-energy alpha and low-energy beta particles from radioisotopes of short half-lives, whereas HLW will release radiation from high-energy beta and gamma emitters.

Nuclear waste can be present in the solid, liquid or gaseous form. If present in fresh water it can enter into food chains and radioactive substances can then be passed up the food chain (and sometimes concentrated) via plants to animals and humans.

■ QUICK CHECK QUESTION

33 High-level nuclear waste is generated by nuclear fission power stations. An example of low-level nuclear waste is a smoke detector. Compare the activities and half-lives of low-level and high-level nuclear waste.

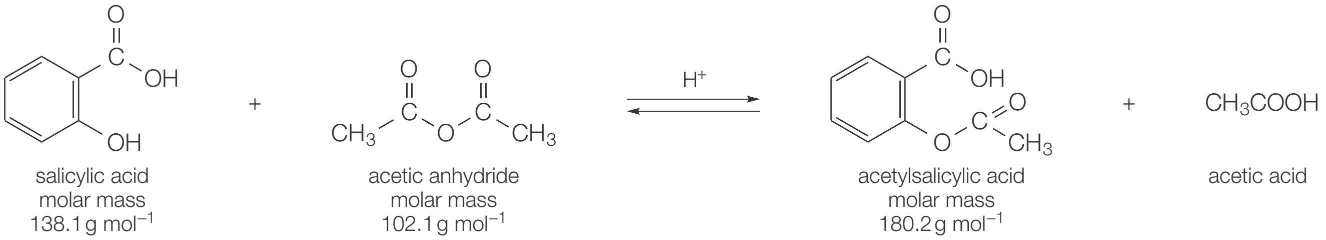
Green chemistry

Revised ☐

Green chemistry (also known as sustainable chemistry) aims to minimize the production and use of hazardous chemical substances. This reduces the pollution at its source and conserves natural (chemical and biological) resources including energy. This is especially important in the pharmaceutical industry where often the research and development of a new drug involves many steps, each involving many potentially polluting substances, including organic solvents, acids and alkalis.

Important factors when designing and producing new pharmaceuticals include:

- Aiming for a high atom economy and low environmental factor. The atom economy (Figure 25.38) is the ratio of the total mass of the desired product(s) to the total mass of all the products. Essentially this is a measure of how much of the reactants remain in the final product.



$$\%\ \text{atom economy} = \frac{180.2}{138.1 + 102.1} \times 100\% = 75.0\%$$

Figure 25.38 Atom economy for the synthesis of aspirin

- The environment factor (E-factor) is defined as the mass of the total waste product divided by the mass of the desired product.

$$\text{E-factor} = \frac{\text{total waste (kg)}}{\text{mass of desired product (kg)}}$$

- Pharmaceutical chemistry, where almost all the products contain carbon, also considers the concept of carbon efficiency.

$$\text{Carbon efficiency} = \frac{\text{amount of carbon in product}}{\text{total amount of carbon present in reactants}}$$

The number of steps in a multi-step synthesis should be kept to a minimum. Generally the more separate steps required to reach the desired product the lower the percentage yield and the higher the amount of waste reactant and products and the more energy used.

Medicinal chemists, where possible, will use greener and safer solvents, such as liquid (supercritical) carbon dioxide, and reactants. Solvents, especially organic solvents, play an important role in many of the separate steps in an organic synthesis. The energy and materials needed to manufacture the solvent as well as the problems caused by the disposal of the solvents (if they cannot be recycled) all need to be considered.

In addition, green synthetic chemists will also consider using renewable feedstocks, using suitable catalysts to reduce energy demands by lowering operating temperatures and to consider the potential drug regarding its breakdown product and disposal after use.

One example of the use of green chemistry in practice is the development of the influenza drug Tamiflu (oseltamivir). It acts as an enzyme inhibitor and is an example of rational drug design – meaning its structure was designed by computer modelling to fit the active site of a specific enzyme neuraminidase.

Tamiflu was first synthesized in very small amounts using lithium nitride, LiN_3 [$Li^+N_3^-$], which acts as a strong reducing agent. The first commercial scale production was developed by the pharmaceutical company GlaxoSmithKline. Chemists here avoided the use of lithium nitride but still used other azides (containing the unstable nitride (azide) ion, N_3^-) and ion exchange chromatography as a purification technique rather than the greener recrystallization.

Since then a number of synthetic approaches to Tamiflu have been developed, each with a more sustainable route. One of the problems is that one of the naturally occurring starting materials is a compound called shikimic acid (Figure 25.39) which is currently uneconomical to synthesize and is isolated from the Chinese star anise plant (Figure 25.40) (*Illicium anisatum*). One green approach is its production by bioengineering using fermenting *E. coli* bacteria.

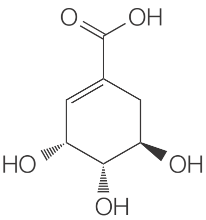


Figure 25.39 Shikimic acid (3,4,5-trihydroxycyclohex-1-ene-1-carboxylic acid)

Figure 25.40 Chinese star anise fruits and seeds

Expert tip

The atom economy calculation is a very simple representation of the 'greenness' of a reaction as it can be carried out without the need for experimental results. However, it is useful as a low atom economy at the design stage of a reaction prior to entering the laboratory can lead to the design of a cleaner synthetic strategy (Figure 25.41). However, it does ignore solvents and any inorganic reagents, such as acids and bases.

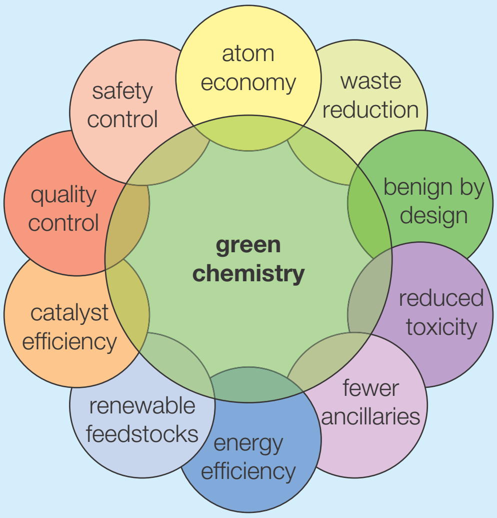


Figure 25.41 Principles of green chemistry

■ QUICK CHECK QUESTIONS

34 The ester 2-methylpropyl methanoate can be formed by reacting 2-methylpropan-1-ol with methanoic acid in the presence of an acid catalyst. Write an equation for this reaction and calculate an approximate value for the atom economy. (A_r: O = 16, C = 12 and H = 1)

35 Other than atom economy, state **three** factors that are considered in determining the sustainability and environmental friendliness ('greenness') of an industrial chemical process.

36 State **one** advantage of using genetically modified (GM) bacteria to act as source of shikimic acid compared with harvesting the Chinese star anise plant.

37 Explain why it better to prevent pollution and the production of hazardous materials than to produce them and then clean them up.

38 Suggest why using a catalyst (or a more efficient catalyst) might make a chemical process 'greener'.

25.7 Taxol – a chiral auxiliary case study

Revised ☐

Essential idea: Chiral auxiliaries allow the production of individual enantiomers of chiral molecules.

Taxol – a chiral auxiliary case study

Revised ☐

- Taxol is a drug that is commonly used to treat several different forms of cancer.
- Taxol naturally occurs in yew trees but is now commonly synthetically produced.
- A chiral auxiliary is an optically active substance that is temporarily incorporated into an organic synthesis so that it can be carried out asymmetrically with the selective formation of a single enantiomer.

Taxol

Revised ☐

Taxol (paclitaxel) (Figure 25.42) is a chemotherapeutic agent used to treat cancers of the ovary, brain, breasts and lungs. It is administered intravenously as an emulsion in water. It works by preventing cancer cells from undergoing cell division. It binds to and stops microtubules extending during cell division (mitosis) and so does not allow the chromosomes to separate.

Taxol was originally isolated from the bark of the Pacific yew tree (*Taxus brevifolia*) but the yield by repeated liquid–liquid solvent extraction was extremely low. The removal of the bark kills the trees. Several multi-step total syntheses of Taxol have been developed, but the overall yield is low and not commercially viable for Taxol production. A semi-synthetic and renewable route was developed from the compound 10-deactylbaccatin III (Figure 25.43) found in the needles of the European yew tree, *Taxus baccata*. As the needles regrow, this is a renewable source of a useful precursor to Taxol.

Expert tip

Natural products, often from plants, are a rich source of biologically active compounds. Many of today's medicines are either obtained directly from a natural source, or were developed from a lead compound originally obtained from a natural source.

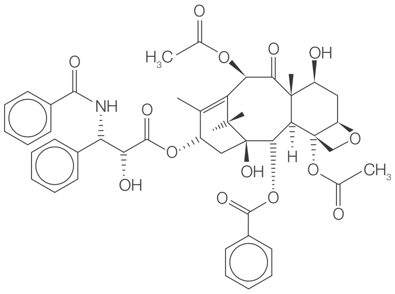
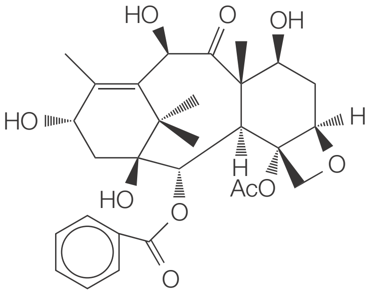


Figure 25.42 Structure of Taxol (paclitaxel)



10-Deacetylbaccatin III

Figure 25.43 Structure of 10-deacetylbaccatin III (Ac = ethanoyl ('acetyl'))

QUICK CHECK QUESTIONS

39 a State what cancers Taxol is used to treat.

b Outline what is meant by the term 'semi-synthetic' drug.

40 The intraperitoneal LD_{50} for Taxol (rat): 32.53 $mg\,kg^{-1}$. Explain the meaning of this term.

Chiral auxiliaries

Revised ☐

Taxol has 11 chiral carbon atoms (Figure 25.44) and hence a large number (2^{11}) of stereoisomers, only one of which is Taxol. The stereochemistries of the intermediates have to be carefully controlled during the total synthesis of Taxol.

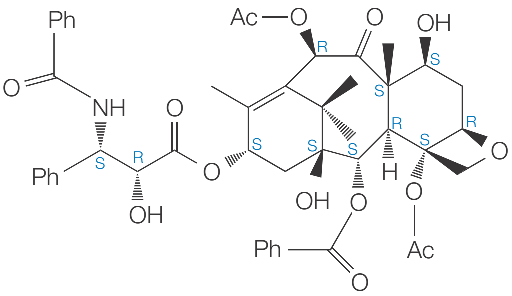


Figure 25.44 The structure of Taxol showing the absolute stereochemistry at each chiral carbon

The ability to synthesize single enantiomers of chiral molecules is important as different enantiomers can interact with biological receptors very differently (Figure 25.45).

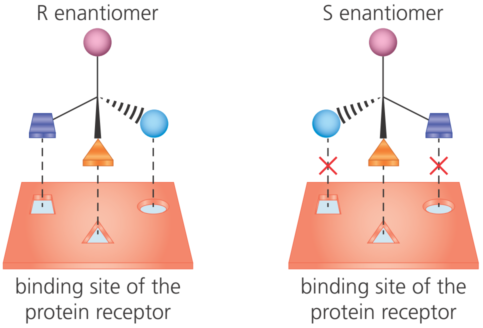


Figure 25.45 The importance of chirality in drug action – only one enantiomer can bind to the receptor strongly

A chiral auxiliary (Figure 25.46) is a chiral control element temporarily incorporated into the structure of the substrate in order to direct the stereochemistry at new stereogenic centre(s) formed in a reaction. The chiral auxiliary is removed (either immediately during work-up or in a separate subsequent step) and may be recovered for re-use. Prochiral molecules are those that can be converted from achiral to chiral in a single step. A diastereoselective reaction is one in which one diastereomer is formed in preference to another.

Expert tip

A molecule is chiral if it is non-superimposable on its mirror image. Any molecule that has a single stereogenic centre can exist as two enantiomers.

QUICK CHECK QUESTIONS

41 State the importance of chirality in drug action.

42 The semi-synthesis of Taxol often uses a chiral auxiliary. Describe the use of chiral auxiliaries in asymmetric synthesis.

43 Suggest the properties of a good chiral auxiliary.

44 Suggest **two** disadvantages of the use of a chiral auxiliary.

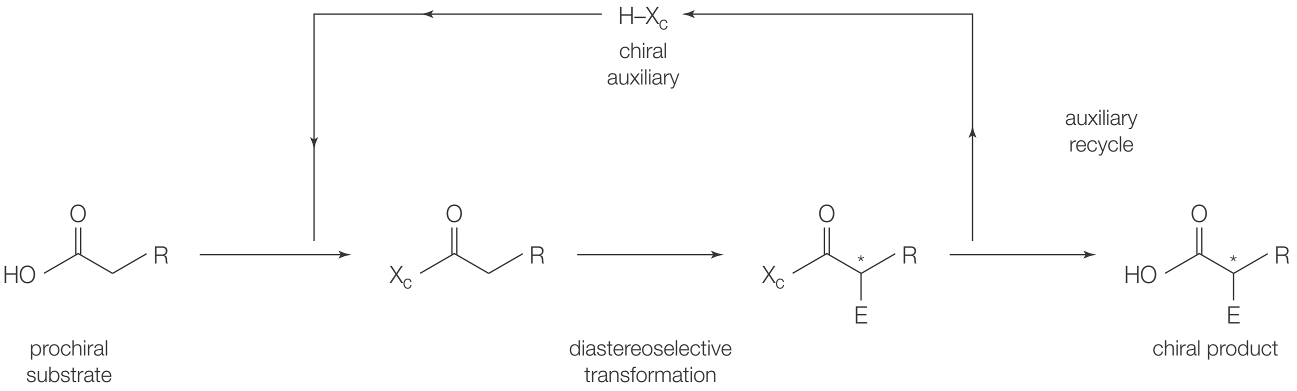


Figure 25.46 The use of a chiral auxiliary

The chiral auxiliary used in one synthesis of Taxol is a single enantiomer of *trans*-2-phenylcyclohexanol (Figure 25.47) that has two stereogenic centres. These favour the formation of specific diasteroisomers in the subsequent steps of the synthesis.

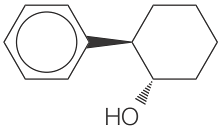


Figure 25.47 The structure of the chiral auxiliary *trans*-2-phenylcyclohexanol

Polarimetry

Revised ☐

Two enantiomers have the same properties (NMR, solubility, melting point, etc.), except in the presence of other chiral molecules or in their interaction with plane polarized light (Table 25.4).

Pure enantiomers can be distinguished by the use of a polarimeter because they rotate the plane of plane polarized light by the same angle but in opposite directions to each other (clockwise versus anti-clockwise).

The direction of rotation allows the identification of which enantiomer is present. The angle of rotation can be used to provide an indication of the composition of a mixture of two enantiomers.

If the sample does not rotate the plane polarized light then it either contains achiral (optically inactive) compounds or a pair of enantiomers in equimolar quantities – a racemic mixture, or racemate. The effect of equal amounts of each enantiomer on the plane polarized light cancels each other out.

Table 25.4 The physical properties of enantiomers A and B compared

Property	A alone	B alone	Racemic A and B
Melting point	Identical to B	Identical to A	May be different from A and B
Boiling point	Identical to B	Identical to A	May be different from A and B
Optical rotation	Equal in magnitude but opposite in sign to B	Equal in magnitude but opposite in sign to B	Zero degrees

The optical purity of a mixture of enantiomers can be calculated from the following expression:

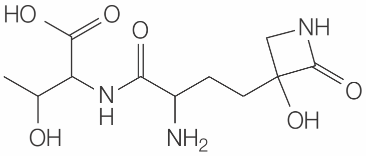
$$\frac{\text{observed specific rotation}}{\text{specific rotation of pure enantiomer}} \times 100$$

For example, a sample of (+) limonene contaminated with (–) limonene has a specific rotation of +106° but the literature value is +123°. Hence the optical purity = (+106/+123) × 100 = 86%.

QUICK CHECK QUESTIONS

45 Describe the composition of a racemic mixture.

46 Tabtoxin is a natural toxin produced by bacteria found in lilac trees. Its skeletal structure is shown below.



a State **two** techniques that could be used to extract impure tabtoxin from the tree.

b Identify the chiral centres present in a molecule of tabtoxin and state the number of diastereoisomers.

c Identify an apparatus that can be used to distinguish between a pair of enantiomers of tabtoxin.

d Explain how the differentiation between the pair of enantiomers is obtained using this apparatus.

25.8 Nuclear medicine

Revised ☐

Essential idea: Nuclear radiation, while dangerous owing to its ability to damage cells and cause mutations, can also be used to both diagnose and cure diseases.

Nuclear medicine

Revised ☐

- Alpha, beta, gamma, proton, neutron and positron emissions are all used for medical treatment.
- Magnetic resonance imaging (MRI) is an application of NMR technology.
- Radiotherapy can be internal and/or external.
- Targeted alpha therapy (TAT) and boron neutron capture therapy (BNCT) are two methods which are used in cancer treatment.

Nuclear medicine and radiotherapy

Revised ☐

Nuclear medicine is the use of radioactive materials (usually in the form of soluble complexes or salts) in medicine for diagnostic imaging and therapy (usually cancer treatment). Diagnostic imaging is mainly performed using two different types of equipment; a gamma camera and a positron emission tomography (PET) scanner.

In radiotherapy, the aim is to localize the radioactive material in cancerous (malignant) cells so they are killed by the ionizing radiation. Targeted radionuclide therapy involves introducing a radioisotope by injection or ingestion. For example, radioactive compounds containing iodine-131 are used in the treatment of thyroid tumours. External beam radiotherapy involves the use of a beam of ionizing radiation directed at the tumour (most commonly gamma radiation). For example, gamma radiation from a linear accelerator or traditionally cobalt-60 (Figure 25.48).

Alpha, beta, gamma, proton, neutron and positron emissions are all used for medical treatment and/or diagnosis. The properties of alpha particles and beta particles are summarized below in Table 25.5.

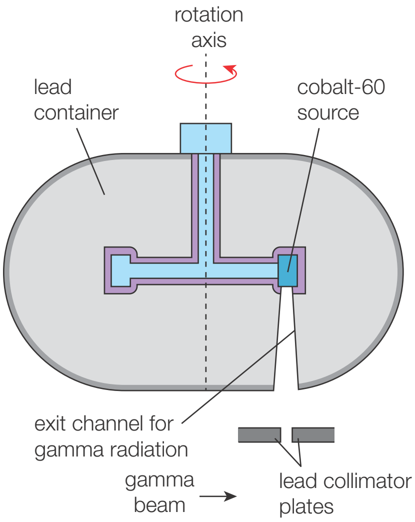


Figure 25.48 Gamma therapy

Table 25.5 The properties of alpha, beta (minus) and gamma radiations

	Alpha particle	Beta (minus) particle	Gamma ray
Relative charge and relative mass	+2 and 4	–1 and 0	0 and 0
Nature	Helium nucleus or helium ion	High-speed electron	Electromagnetic wave with very short wavelength <10^{-10} m
Representation	$^{4}_{2}He$	$^{0}_{-1}e$	$^{0}_{0}\gamma$
Action of magnetic field	Deflected towards cathode (negative)	Deflected towards anode (positive)	Not deflected
Velocity	1/10 speed of light	Up to 9/10 speed of light	Speed of light ($3.00 \times 10^{9}\,m\,s^{-1}$)
Ionizing power	Very high; nearly 100× that of beta particles	100× times less than that of gamma rays	Low
Penetrating power	Low; easily stopped by air	100× that of alpha particles	10× that of beta particles
Kinetic energy	High	Considerably less than alpha particles	Zero
Nature of product	Product obtained by the loss of one alpha particle has an atomic number less 2 units and a mass number less 4 units	Product obtained by the loss of one beta particle has an atomic number greater by 1 unit, without any change in mass number	There is no change in atomic number or mass number

Table 25.6 summarizes the nuclear symbols for the particles (emissions) used in medicine. An unstable nucleus emits radiation (alpha or beta particles or gamma rays) which carry energy away from the nucleus, thus making the nucleus more stable.

A positron is a particle that has the same mass as an electron, but an opposite charge. It is the anti-particle of the electron and produced during beta (positive) decay. The positron is represented as $^{0}_{1}e$. The isotope carbon-11 undergoes decay by positron emission: $^{11}_{6}C \rightarrow\, ^{11}_{5}B +\, ^{0}_{1}e$. The positron has a very short life because it is annihilated and converted to energy (gamma rays): $^{0}_{1}e +\, ^{0}_{-1}e \rightarrow 2\,^{0}_{0}\gamma$.

Table 25.6 Nuclear symbols

Particle	Symbol
Neutron	$^{1}_{0}n$
Proton	$^{1}_{1}H$ or $^{1}_{1}p$
Electron	$^{0}_{-1}e$
Alpha particle	$^{4}_{2}He$ or $^{4}_{2}\alpha$
Beta particle	$^{0}_{-1}e$, $^{0}_{-1}\beta$ or β^{-}
Positron	$^{0}_{+1}e$, $^{0}_{1}\beta$ or β^{+}

Nuclear equations and radioactive decay calculations

Revised ☐

In nuclear equations, reactant and product nuclides are represented by their atomic numbers, mass numbers and chemical symbols. The totals of the mass numbers and atomic numbers on both sides are equal.

Radioactive decay (Figure 25.49) is governed by an exponential decay of the numbers of radioactive nuclei N, $N_t = N_0e^{-kt}$, where N_0 is the number of such nuclei at time zero and k is the decay rate for the process. The half-life of the reaction is the time for half of the nuclei to decay and is related to the decay rate by $t_{\frac{1}{2}} = \ln\frac{2}{k}$ or $t_{\frac{1}{2}} = 0.693/k$.

Worked example

Iron-59 is used to study iron metabolism and has a half-life of 45.1 days. Determine how many days it would take for 32 mg to decay to 1 mg.

32 → 16 → 8 → 4 → 2 → 1, 5 half-life, 5 × 45.1 days = 225.5 days.

Worked example

${}^{49}_{21}$Sc produces a beta (minus) particle and a neutron. Write a nuclear equation describing this process.

${}^{49}_{21}Sc \rightarrow {}^{48}_{22}Ti + {}^{0}_{-1}e + {}^{1}_{0}n$: (mass (nucleon) number: 49 = (48) + (0) + (1); atomic number (proton number): 21 = 22 → Ti + (–1) + (0).

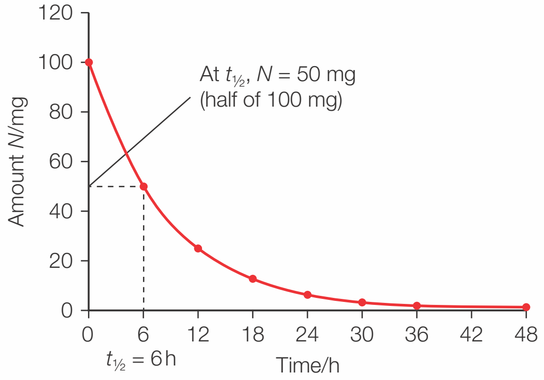
Worked example

Technetium-99m has a half-life of 6 hours. Draw a graph showing how 100 mg of ${}^{99}_{43}$Tc decays over time.

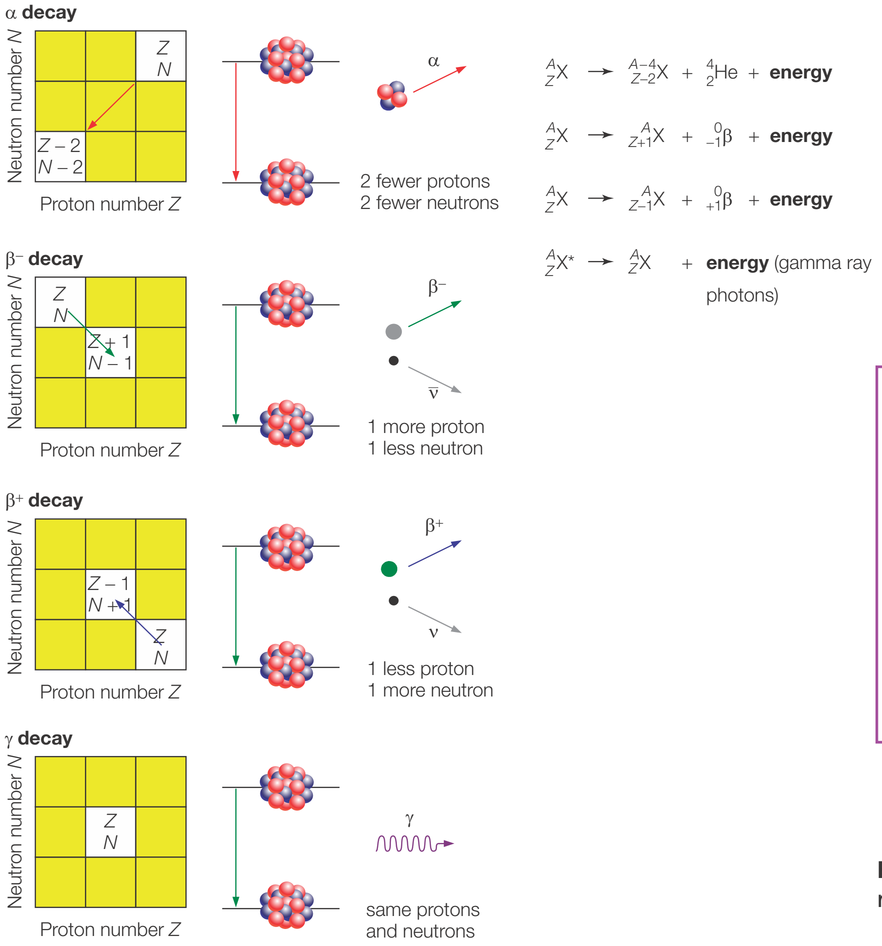
Calculate the mass of ${}^{99}_{43}$Tc remaining after 2.00 days.

$k = \frac{\ln 2}{t_{½}}$; $k = 0.693 / 6 = 0.1155$ hours

$N = N_0\ e^{-kt}$; $N = 100e^{(0.1155 \times 48)} = 0.391$ mg.



Radioactive decay processes



$${}^{A}_{Z}X \rightarrow {}^{A-4}_{Z-2}X + {}^{4}_{2}He + \textbf{energy}$$

$${}^{A}_{Z}X \rightarrow {}^{A}_{Z+1}X + {}^{0}_{-1}\beta + \textbf{energy}$$

$${}^{A}_{Z}X \rightarrow {}^{A}_{Z-1}X + {}^{0}_{+1}\beta + \textbf{energy}$$

$${}^{A}_{Z}X^{*} \rightarrow {}^{A}_{Z}X + \textbf{energy}\text{ (gamma ray photons)}$$

Figure 25.49 A summary of radioactive decay processes

■ QUICK CHECK QUESTION

47 The radionuclide cobalt-60 ($t_{\frac{1}{2}}$ = 5.3 years) is used in external radiotherapy. It emits a beta particle and a gamma ray, producing a stable isotope of another element.

a Deduce the nuclear equation for the decay of cobalt-60.

b Outline the technique of external radiotherapy.

Magnetic resonance imaging (MRI)

Revised ☐

Proton nuclear magnetic resonance (NMR) detects the presence of hydrogen atoms (protons) by placing them in a very powerful magnetic field, then exciting the hydrogen atoms (protons) with a pulse of radio frequency radiation. This corresponding to the resonance energy required to cause the hydrogen atoms (protons) to move to the high energy state where the hydrogen atom's (proton's) internal magnetic field is aligned anti-parallel to the external magnetic field.

The NMR instrument then detects the weak radio frequency radiation from the protons as they 'relax' back to their original energy states. The frequency of this signal from the proton is proportional to the magnetic field to which they are subjected during this relaxation process.

In magnetic resonance imaging (MRI) (Figure 25.50), an image of a cross-section of a body can be made by producing a magnetic field gradient across the tissue so that a certain value of magnetic field can be associated with a given location in the tissue.

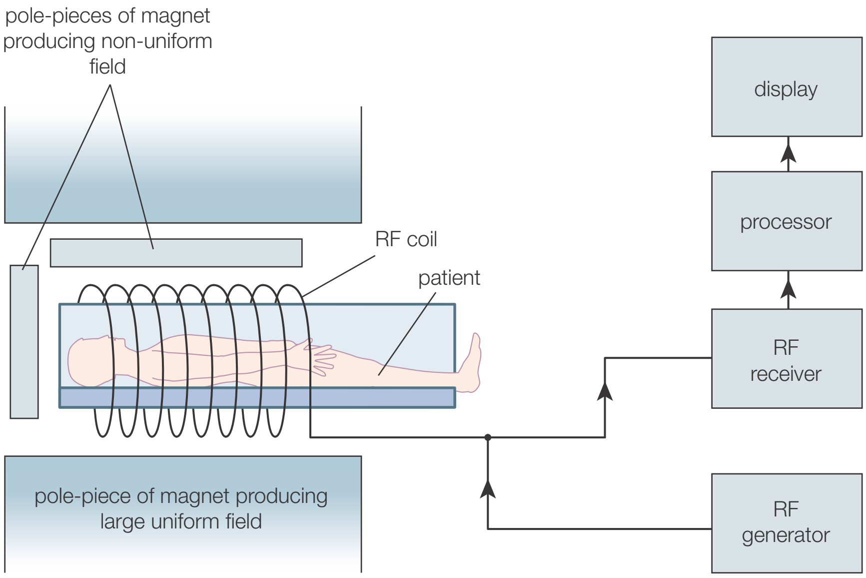


Figure 25.50 Schematic diagram of a magnetic resonance scanner. (The magnetic field is usually generated by a.c. currents in wires rather than using permanent magnets.)

Since the hydrogen atom (proton) signal frequency is proportional to that magnetic field, a given proton signal frequency is associated to a location in the tissue (Figure 25.51). This provides the information to map the tissue in terms of the protons present there. Since the proton density varies with the type of tissue, a contrast agent is present to image the organs and other tissue variations in the body. The three-dimensional information then comes from varying the gradient in three orthogonal directions (x, y and z) of the magnetic field.

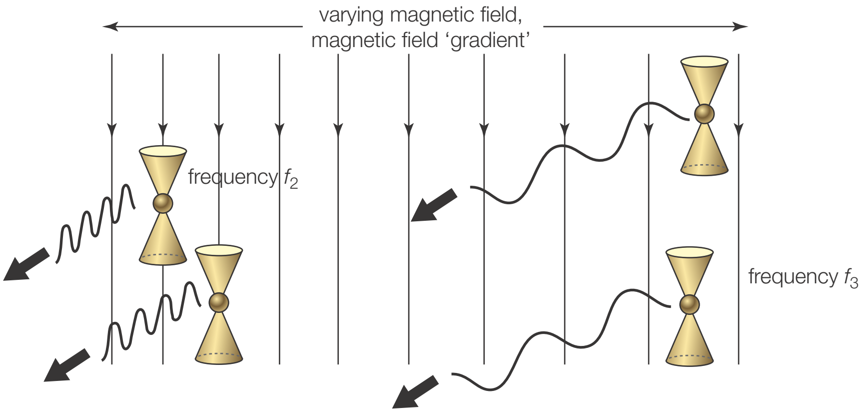


Figure 25.51 Protons undergoing relaxation and releasing radio waves of different energy (frequency) that depends on the position (strength of the magnetic field) in the magnetic field gradient

Expert tip

MRI is not an example of nuclear medicine: compared with nuclear medicine which uses ionizing radiation, MRI uses non-ionizing radiation in the form of radio frequency waves.

Positron emission tomography (PET)

Revised ☐

A beta-positive (i.e. positron) emitting radioactive substance (usually fluorine-18) is introduced into the body (through an intravenous injection). The positrons emerge into the surrounding tissues, meet electrons, and both electron and positron cease to exist. This is called mutual annihilation (Figure 25.52), and involves conversion of the masses of the particles into energy that is carried away by two gamma ray photons which can be detected from outside the body (by a PET scanner; Figure 25.53). Scintillators convert gamma photons into visible light; photomultipliers multiply the current produced by incident light.

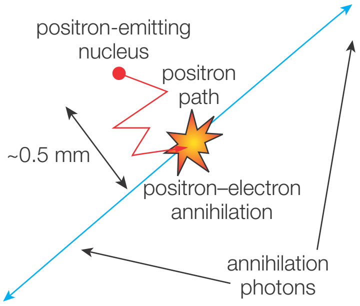


Figure 25.52 General principle of PET imaging

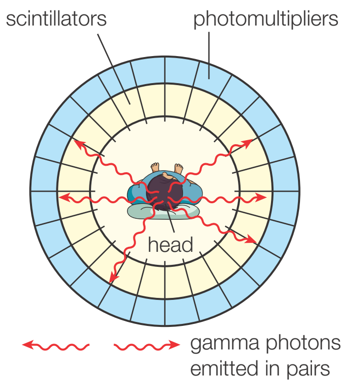


Figure 25.53 Arrangement of PET scanners for a PET scan

Worked example

A freshly prepared sample of the radioisotope fluorine-18 has a mass of 0.010 g. The decay constant of fluorine-18 is $1.05 \times 10^{-4}\,s^{-1}$. Determine the initial activity of the sample, the activity after 2 hours and the half-life of the isotope.

Initial number of ^{18}F nuclei in sample $= (\frac{0.01}{18}) \times 6.02 \times 10^{23} = 3.344 \times 10^{20}$

Initial activity, $A_0 = \lambda N_0 = 1.05 \times 10^{-4} \times 3.344 \times 10^{20} = 3.512 \times 10^{16} = 3.5 \times 10^{16}$ disintegrations per second

Activity after 2 hours, $A = A_0 e^{-\lambda t} = 3.512 \times 10^{16} \times e^{-1.05 \times 10^{-4}} \times 2 \times 360 = 1.6 \times 10^{16}$ disintegrations per second

Half-life $= \frac{\ln 2}{\lambda} = \frac{\ln 2}{(1.05 \times 10^{-4})} = 6.6 \times 10^{3}\,s = 110$ minutes

Targeted radionuclide therapy

Revised ☐

Targeted alpha therapy (TAT)

TAT is used to direct alpha radiation directly at cancerous cells. The range of alpha particles in human tissues is typically 50–100 µm, the diameter of about ten cells. The energy from the alpha radiation is largely contained within the tumour cells and there is little damage to the surrounding normal cells.

Lead-212 atoms are typically used in targeted alpha therapy:

$$^{212}_{82}Pb \rightarrow ^{208}_{80}Hg + ^{4}_{2}He$$

The specific ‘targeting’ of cancer cells is achieved by using tumour-selective carrier molecules, such as monoclonal antibodies (Figure 25.54) or peptides (small proteins). Often a chelating or complexing agent is used. TAT is used to treat cancers that have spread and formed secondary tumours within the body.

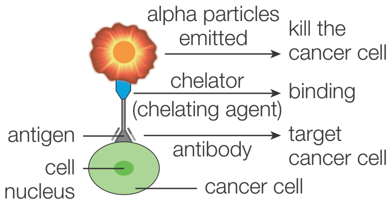


Figure 25.54 Target alpha therapy

QUICK CHECK QUESTIONS

48 Define targeted alpha therapy. Write a balanced nuclear equation showing the loss of an alpha particle from actinium-225.

49 Explain how targeted alpha therapy works well for cancers that have spread around the body.

Boron neutron capture therapy (BNCT)

High-intensity boron neutron beams are used in BNCT, which uses the ability of non-radioactive boron-10 nuclei to absorb neutrons and undergo a transmutation reaction.

After capturing a low-energy neutron a lithium-7 nuclide and a high-energy alpha particle are formed:

$$^{10}_{5}\text{B} + ^{1}_{0}\text{n} \rightarrow ^{7}_{3}\text{Li} + ^{4}_{2}\text{He}$$

The cancer patient is injected with a boron compound which is selectively absorbed by cancer cells. The patient is then irradiated with neutron radiation which causes production of high-energy alpha particles inside the tumour cells (Figure 25.55).

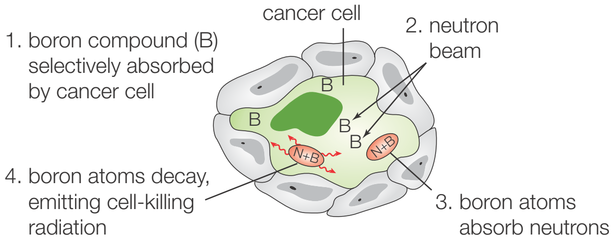


Figure 25.55 Boron neutron capture therapy

Expert tip

A transmutation is a nuclear reaction involving the formation of a new daughter nuclide.

Other targeted therapy

Other examples of radioisotopes used in targeted radionuclide therapy are lutetium-177 (beta and gamma emitter) and yttrium-90 (beta emitter). Lutetium-177 has a shorter penetration range than yttrium-90 making it suitable for treating smaller tumours.

Lutetium-177 is often used in conjunction with a peptide (small protein) to selectively target neuro-endocrine tumours. Yttrium-90 therapy is often used in the treatment of liver cancer. Large numbers of small plastic or glass beads containing yttrium-90 are injected directly into the arteries that supply blood to the liver.

QUICK CHECK QUESTIONS

50 Explain how boron neutron capture therapy can be used to kill cancerous cells.

51 **a** Write a nuclear equation for the beta decay of lutetium-177.

b A patient is given a 20.0 mg dose of a soluble lutetium-177 compound. Given that the half-life of lutetium-177 is 6.71 days, calculate how much of the lutetium-177 is present in the patient's body after 4 weeks.

52 ^{90}Sr is a radioisotope and is a long-term health problem because it substitutes for calcium in bones. Suggest why strontium can readily substitute for calcium.

Proton beam therapy

Revised ☐

Proton beam therapy (Figure 25.56) or proton therapy is a recent development of nuclear medicine which uses protons to irradiate cancerous tissue. A linear accelerator imparts high kinetic energies to protons in a narrow beam, which is then directed at a tumour. The protons damage the DNA of cells, causing them to die or be unable to divide. Cancer cells are particularly vulnerable to DNA damage because of their high rate of cell division.

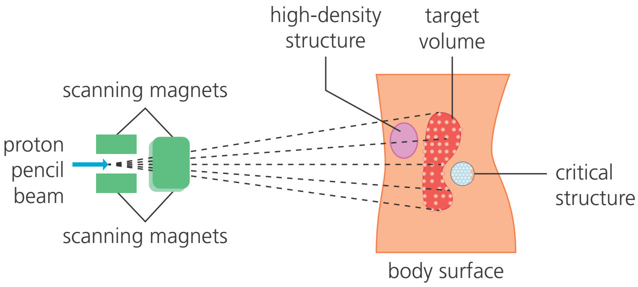


Figure 25.56 Proton beam therapy

In contrast to other types of nuclear or ionizing radiation the absorption of protons reaches a maximum within a narrow range, deep inside the patient's body. This phenomenon is known as the Bragg peak effect (Figure 25.57) and allows the proton beam to be focused on the tumour with minimal damage to surrounding healthy tissue. The Bragg peak effect occurs because all the protons in the beam have the same speed and hence the same kinetic energy.

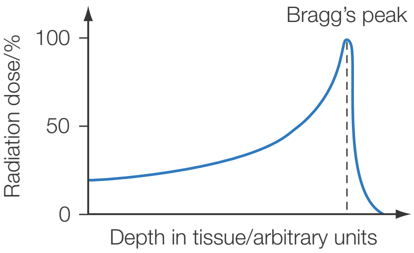


Figure 25.57 Absorption of protons (with high kinetic energy) by cells in body tissue

QUICK CHECK QUESTION

53 Explain why proton beam therapy is more effective in treating cancers than traditional methods of external radiotherapy, such as cobalt-60.

Use of technetium-99m

Revised ☐

Technetium-99m is used in nuclear medicine for gamma camera imaging and imaging and SPECT (single photon emission computed tomography). It is the most commonly used radioisotope in nuclear medicine. It decays to form a stable daughter product and emits gamma rays which readily pass out and through the body and can be easily detected. Its half-life of six hours minimizes the patient's exposure to gamma radiation. Technetium is a transition metal and exists in several stable oxidation states, e.g. technetate(VII), TcO_4^-, and forms complex ions with a variety of ligands.

■ QUICK CHECK QUESTION

54 Write a nuclear equation describing the formation of technetium-99m from molybdenum-99 by beta decay.

Diagnostic radiography

Revised ☐

Owing to its relatively short half-life, Tc-99 is generated in hospitals by the beta decay of molybdenum-99. It can be used diagnostically, for example, to determine the flow of blood through the brain's hemispheres. Its progress through the body can be followed by detecting the gamma radiation it emits.

The decay product, Tc-99 (in the ground state) is a beta emitter, but the energy released within the body is relatively low and the amount of Tc-99m in the body rapidly decreases over time.

$$^{99m}_{43}\text{Tc} \xrightarrow[6\,\text{h}]{\gamma} {}^{99}_{43}\text{Tc} \xrightarrow[21100\text{y}]{} {}^{99}_{44}\text{Ru} + {}^{0}_{-1}\text{e}^-$$

Side effects from radiotherapy

Revised ☐

The side effects of ionizing radiation depend upon the type of emission, the intensity and duration of the ionizing energy. External radiotherapy tends to cause more side effects than targeted therapy, as more healthy tissue and organs are irradiated in the process. Common side effects include hair loss, nausea, fatigue, loss of appetite and sterility.

The cells of the body may undergo physical and chemical changes because of exposure to ionizing radiation. Physical changes involve burning; chemical changes may involve damage to DNA molecules (mutation), which can lead to cancer.

■ QUICK CHECK QUESTIONS

55 State **two** reasons why Tc-99m is suitable for medical imaging.

56 State **two** common short-term side effects of radiotherapy.

57 Outline **one** ethical implication of using radioisotopes in nuclear medicine.

NATURE OF SCIENCE

Exposure to ionizing radiation can have many benefits for individuals and society. Medical imaging examinations that involve radiation determine whether organs are functioning properly or bones are broken and in treating cancer. Low levels of radiation exposure are used for most medical examinations involving radiation, although when we are using radiation to treat a disease (e.g. cancer), very high doses are needed to kill the cancer cells. Ionizing radiation has benefits, but there are also risks and these have to be evaluated. The small radiation doses used to conduct medical examinations carry little or no risk, while exposure to high levels may cause observable health effects.

25.9 Drug detection and analysis

Revised ☐

Essential idea: A variety of analytical techniques is used for detection, identification, isolation and analysis of medicines and drugs.

Drug detection and analysis

Revised ☐

- Organic structures can be analysed and identified through the use of infrared spectroscopy, mass spectroscopy and proton NMR.
- The presence of alcohol in a sample of breath can be detected through the use of either a redox reaction or a fuel cell type of breathalyser.

Identification of drugs using spectroscopic and spectrometric analysis

Revised ☐

Mass spectrometry can be used to determine the molecular mass of molecules and give insight into the structure of molecules from a consideration of fragment ions.

Infrared spectroscopy can identify specific functional groups as the bonds connecting different types of atom vibrate at different frequencies and so absorb in different regions of the infrared spectrum.

A ^{1}H NMR spectrum consists of a series of resonances that correspond to protons in different chemical environments. The position of each resonance (chemical shift) and area under each resonance gives information about the relative number of hydrogen atoms (protons) and the particular chemical environment in which each different hydrogen atom (proton) exists.

The shape of the resonance (multiplicity) gives information about how many protons are attached to the atoms adjacent to the proton causing the resonance. If there n adjacent protons, then the resonance will be split into $n + 1$ peaks.

These techniques are routinely applied to assigning structures of drugs or their precursors.

Infrared spectrum

GBL (γ-butyrolactone) (Figure 25.58) can be used as a recreational drug and has effects similar to alcohol. Figure 25.59 shows the infrared spectrum of GBL.

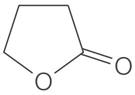


Figure 25.58 Structure of gamma-butyrolactone (dihydrofuran-2(3H)-one)

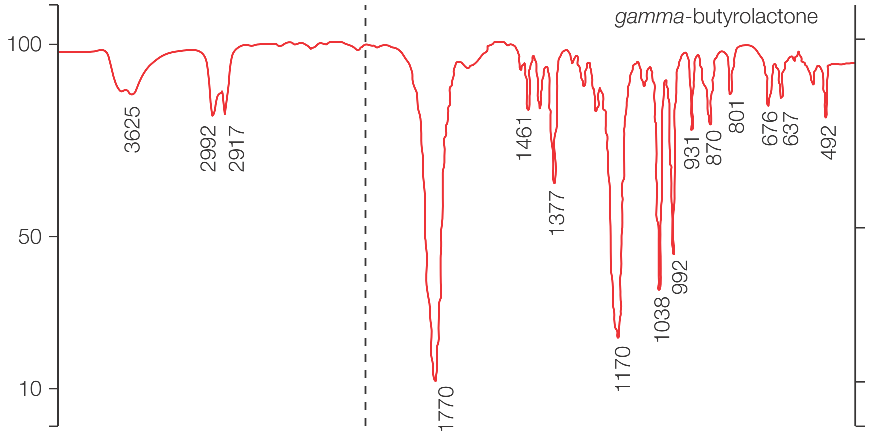


Figure 25.59 Infrared spectrum of GBL

Table 25.7 shows an analysis of the absorption bands in the infrared spectrum of GBL.

Table 25.7 An analysis of the absorption bands in the infrared spectrum of gamma-butyrolactone (GBL)

Vibrational mode	Wavenumber/ cm^{-1}	Strength of peak
Carbonyl stretching mode	1770	Very strong
C–H bond	2992	Relatively weak
In-plane deformation of the carboxyl hydrogen and stretching of the carbon–oxygen bond in the carboxyl group	1450–1150	Strong
Stretching C–O bond of the terminal hydroxyl group	1038	Strong

Expert tip

The weak –OH stretch observed in this spectrum is from contaminating water.

Nuclear magnetic resonance

Ethyl 3-oxobutanoate (Figure 25.60) is a chemical intermediate for the synthesis of antibiotics, analgesics and antimalarial agents.

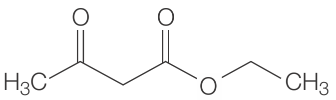


Figure 25.60 Structure of ethyl 3-oxobutanoate

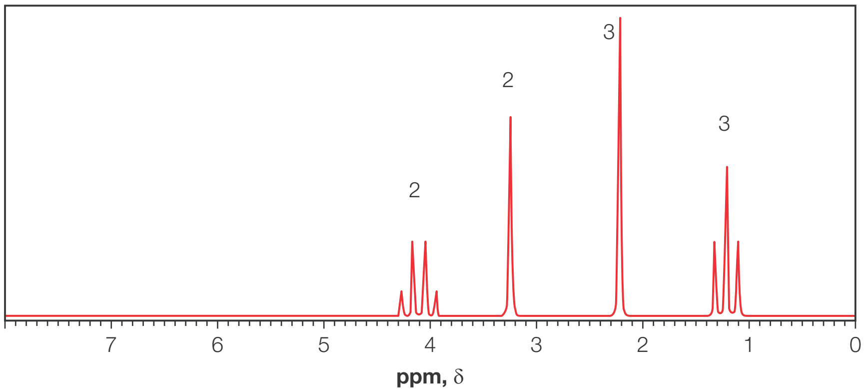
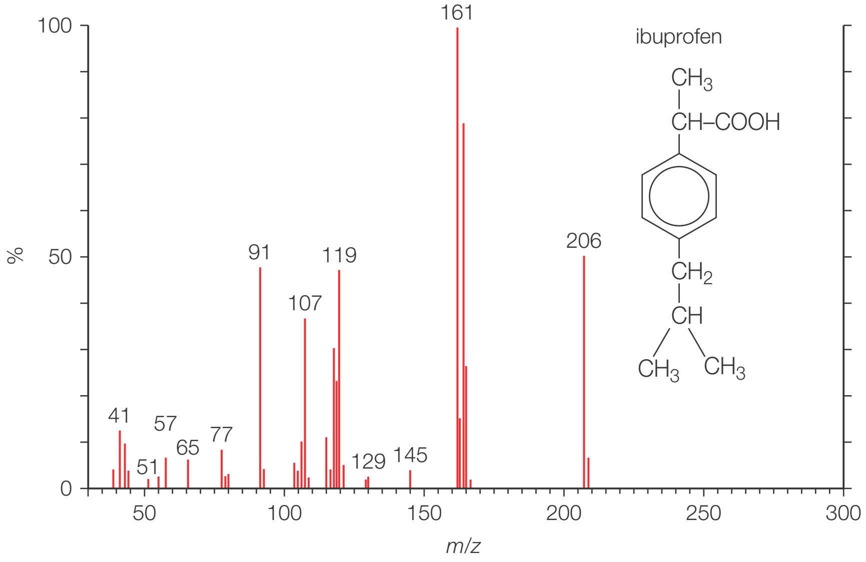


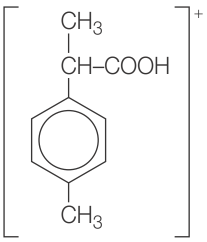
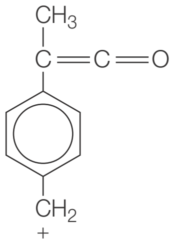
Figure 25.61 ^{1}H NMR spectrum of ethyl 3-oxobutanoate

The proton or ^{1}H NMR spectrum (Figure 25.61) has a quartet coupled to a triplet indicative of an ethyl group. The methylene group, –CH$_2$–, must be adjacent to an electron withdrawing group since it is shifted to 4.1δ. The two singlets at 2.2δ and 3.2δ suggest isolated –CH$_2$– and –CH$_3$ groups and the –CH$_2$– group must be adjacent to one or more electronegative groups.

Mass spectrometry

The molecular ion, M$^+$, of ibuprofen (a mild analgesic) is expected at 206 (Figure 25.62).



m/z	ion		
206	M$^+$		
164	$(M{-}C_3H_6)^+$	*i.e.*	
163	$(M{-}C_3H_7)^+$		
145	$(M{-}C_3H_7{-}H_2O)^+$	*i.e.*	
107	$C_7H_7O^+$		

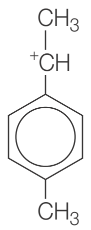
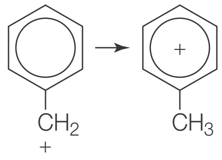
m/z	ion		
207	M$^+$		
161	$(M{-}COOH)^+$		
119	$(M{-}COOH{-}C_3H_6)^+$	*i.e.*	
91	$(M{-}COOH{-}C_3H_6{-}C_2H_4)^+$	*i.e.*	
65	$(M{-}COOH{-}C_3H_6{-}C_2H_4{-}C_2H_2)^+$		

Figure 25.62 The mass spectrum of ibuprofen

The fragment ions indicate that fragmentation occurs from both side-chains. Losing the carboxylic acid group is the most common first fragmentation.

Expert tip

The IB will assume that H_2O and CO_2 are not lost from the molecules (due to the low pressure) and knowledge of rearrangements will not be tested.

Purification of organic products

Revised ☐

Mass spectrometry and a variety of spectroscopic techniques are used to identify pure substances. There are a number of physical techniques that can be used to purify mixtures and prepare pure substances.

For small amounts, chromatography can be used to separate and identify mixtures, often containing a large number of components, both qualitatively and quantitatively. It can also be used to determine the purity of a substance.

In all forms of chromatography there is a solid stationary phase and a liquid mobile phase that flows across the stationary phase. Chromatographic techniques depend on the components in the mixture having different tendencies to adsorb onto a surface or partition (distribute) with a solvent.

Fractional distillation (Figure 25.63) is a method for separating mixtures of miscible liquids with different boiling points. On a laboratory scale, the process takes place using distillation apparatus with a glass fractionating column between the flask and the still-head. The column is hotter at the bottom and cooler at the top.

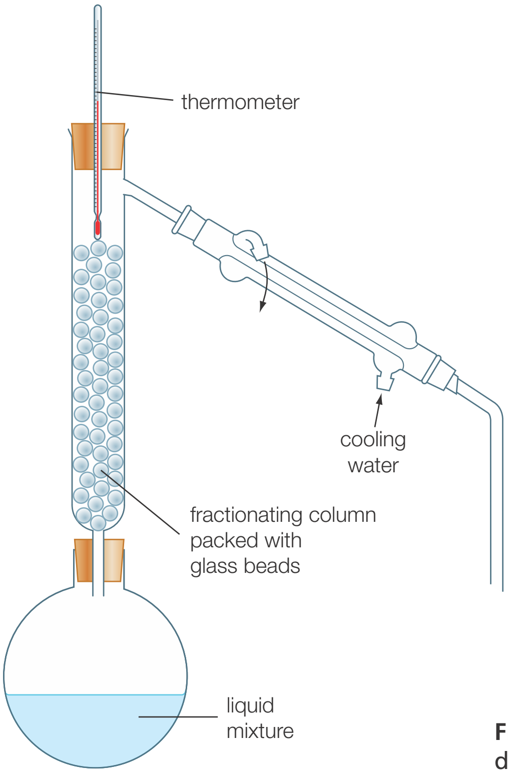
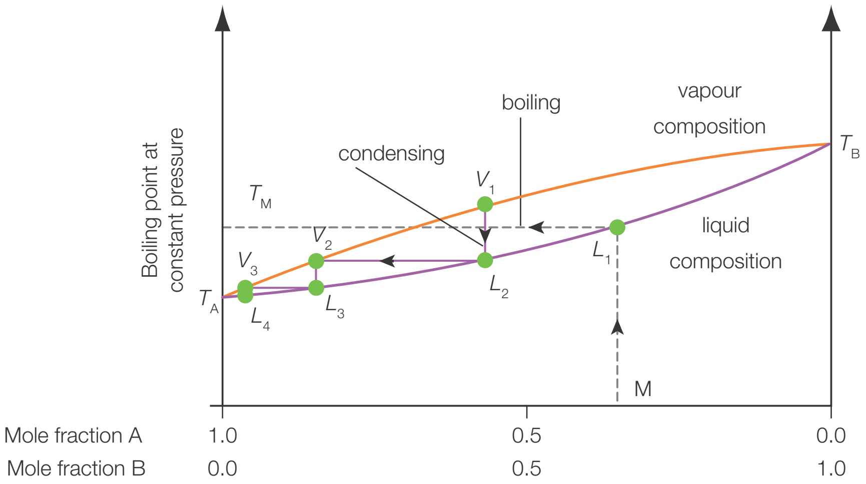


Figure 25.63 Fractional distillation

If the flask contains a mixture of two liquids, the boiling liquid produces a vapour that is richer in the more volatile of the two liquids (the liquid with the lower boiling point).

As the vapour condenses in the fractionating column it runs back into the flask. As it does, it meets more of the rising vapour, some of which condenses as it transfers its heat energy to the descending liquid. That, in turn, may vaporize again. In this way the mixture repeatedly boils and condenses as it rises up the fractionating column. It is in effect like carrying out a whole series of simple distillations. This can be represented as a series of steps in a boiling-point composition diagram (Figure 25.64).



where T_A is the boiling point of pure A

T_B is the boiling point of pure B

Figure 25.64 The boiling-point composition diagram for the a mixture of two ideal liquids with different boiling points

The 'mole fraction' is a way of expressing the concentration of a solution or mixture. It is equal to the amount (in mol) of one component divided by the total amount (in mol) in the solution or mixture.

Another form of distillation is steam distillation (Figure 25.65), which is useful for separating an organic material with a high boiling point and poor solubility in water. The technique is used when organic compounds decompose below their normal boiling point.

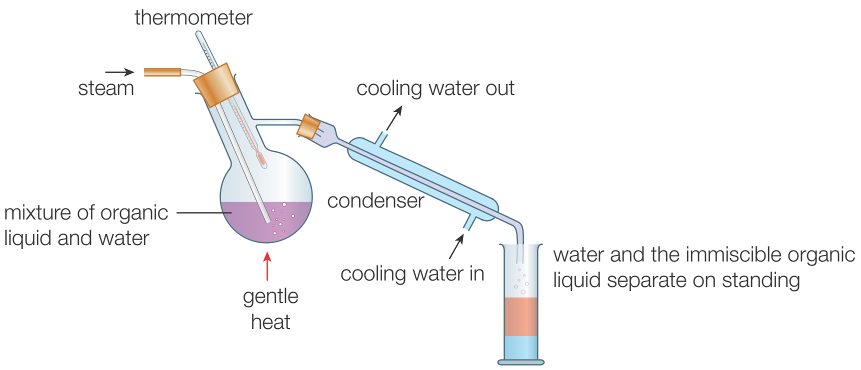


Figure 25.65 Steam distillation

Solvent extraction can be used for compounds that distribute between two solvents, one of which is usually aqueous. This depends upon the relative solubility of a substance in the two solvents. An organic substance is extracted into the layer in which it is more soluble and the layers separated using a separating funnel (Figure 25.66). A drying agent (usually an anhydrous salt) is added to remove traces of water in the organic layer and then filtered off. The solvent is then evaporated to leave the required compound.

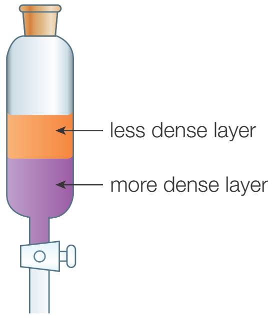


Figure 25.66 Use of a separating funnel

If the solute is in the same molecular state in both liquid phases, the following simple partition equilibrium expression will apply:

$$P_c = \frac{[X(organic)]}{[X(aq)]}$$

P_c is called the partition/distribution coefficient. It has no units and is temperature dependent.

If more of the substance X is added to the system, the solute will distribute itself between the immiscible liquids so that the ratio of the solute concentrations remains the same at constant temperature independently of the total quantity of X in the same molecular state (known as the partition equilibrium law).

Expert tip

Normally, the aqueous layer is the bottom layer as water usually has higher density than the organic solvent.

The hydrophobicity of a molecule of an organic molecule is measured by its log P_c value where P_c can be measured experimentally by measuring the relative solubility of a compound in an octano-1-ol/water mixture.

$$P_c = \frac{[\text{X(octan-1-ol)}]}{[\text{X(aq)}]}$$

The more hydrophobic the compound is, the greater the proportion of it will dissolve in the organic layer, and the higher the value of P_c or $\log_{10}P_c$.

Raoult's law

In a system consisting of a mixture of two miscible liquids at equilibrium, Raoult's law states that each component will exert a vapour pressure proportional to its mole fraction.

Expert tip

Raoult's law describes an ideal mixture of liquids in which the intermolecular forces in both liquids are almost identical (Figure 25.67). This occurs with similar compounds, such as isomers, with identical molar masses.

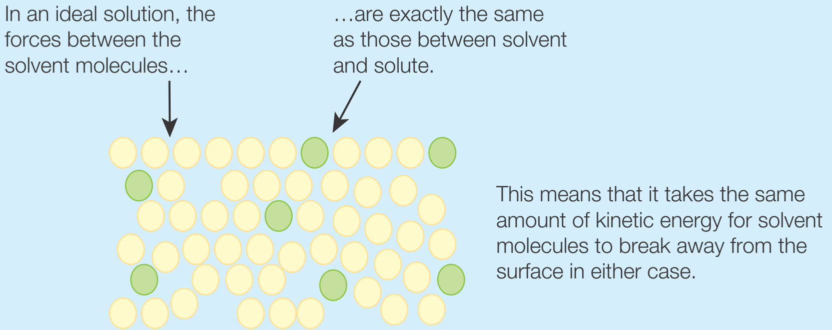


Figure 25.67 Concept of an ideal solution

Raoult's law can be expressed mathematically:

$$p(\text{A}) = p^\circ(\text{A}) \times x(\text{A})$$

where $p(\text{A})$ is the vapour pressure of A over the mixture of the two liquids (at a given temperature); $p^\circ(\text{A})$ is the vapour pressure over a pure sample of A at the same temperature and $x(\text{A})$ is the mole fraction of A, which is the ratio of the amount of A to the sum of all the amounts of the component liquids in the mixture.

This means that a graph of mole fraction against vapour pressure for each of the liquids will be of the type shown in Figure 25.68, that is, a straight line passing through the origin.

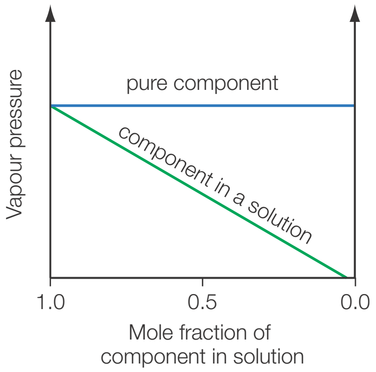
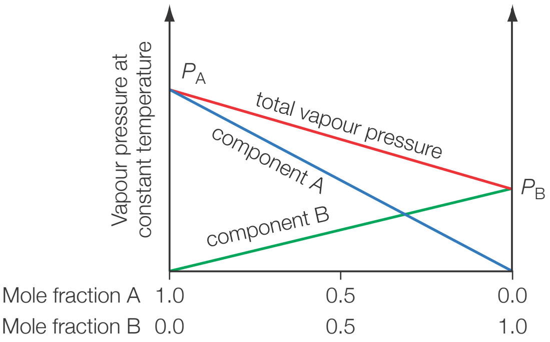


Figure 25.68 The relationship between vapour pressure and mole fraction for components in an ideal mixture of liquids

The total vapour pressure of the liquid mixture is found by adding the vapour pressures of the two components (two liquids) and it will vary with composition as shown in Figure 25.69.



where P_A is the vapour pressure of pure A
P_B is the vapour pressure of pure B

Figure 25.69 The relationship between mole fractions and partial and total vapour pressures for an ideal mixture of two liquids

Worked example

At 80 °C, the vapour pressure of benzene is 1.0×10^5 Pa and the vapour pressure of methylbenzene is 4.0×10^5 Pa. An ideal solution contains 7.812 g of benzene and 36.86 g of methylbenzene. These are two miscible liquids.

Calculate the amounts (mol) and mole fractions of benzene and methylbenzene. Apply Raoult's law to calculate the partial pressures of benzene and methylbenzene and the total vapour pressure.

Amount of benzene = 7.812 g/78.12 g mol^{-1} = 0.1 mol

Amount of methylbenzene = 36.86 g/92.15 g mol^{-1} = 0.4 mol

Mole fraction of benzene = 0.1/(04 + 0.1) = 0.2

Mole fraction of methylbenzene = 1.0 − 0.2 = 0.8 mol

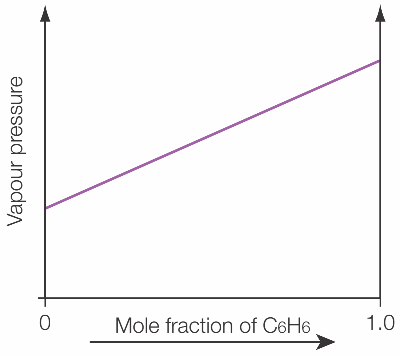
Partial pressure of benzene = 1.0×10^5 Pa × 0.2 = 2×10^4 Pa

Partial pressure of methylbenzene = 4.0×10^4 Pa × 0.8 = 3.2×10^4 Pa

Total pressure = 2×10^4 Pa + 3.2×10^4 Pa = 5.2×10^4 Pa

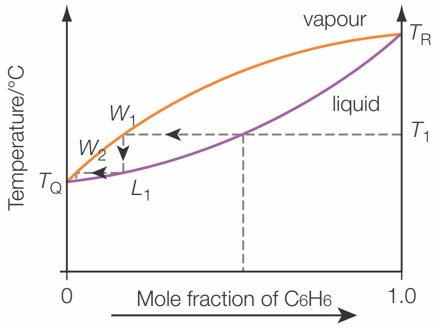
Worked example

The vapour pressure-composition diagram for a mixture of benzene and methylbenzene is shown below.



Sketch and explain the boiling-point composition diagram for the mixture.

Use your graph to explain what happens in the distillation column when a mixture containing 50% by mass of benzene is fractionally distilled.



When a mixture containing 50% by mass of benzene is fractionally distilled it boils at T_1 and gives a vapour (W_1) which is richer in benzene. When this vapour comes into contact with the cold surfaces of the glass beads in the fractionating column, it condenses into a liquid (L_1). The condensed liquid (L_1) boils again when it comes into contact with the ascending hot vapour to produce another vapour (W_2), which is even richer in benzene. The process of vaporization and condensation repeats in the fractionating column. Finally, pure benzene is distilled over at a constant temperature of T_Q.

■ QUICK CHECK QUESTIONS

58 **a** Define the term vapour pressure of a liquid.

b State **two** factors that affect the value of the vapour pressure of a liquid mixture.

59 Two liquids X and Y boil at 110 °C and 140 °C. Which of them has the higher vapour pressure at 50 °C?

60 The vapour pressure of a pure a liquid is 30 mmHg at 320 K. The vapour pressure of the liquid in the solution with liquid B is 28 mmHg at the same temperature. Deduce the mole fraction of B in the solution if it obeys Raoult's law.

61 State and explain which of the following pairs of liquids is/are expected to obey Raoult's law: hexane and heptane; chloromethane and propanone; cyclohexanol and water

Testing for drugs in athletes

Revised ☐

Steroids are molecules that contain four rings fused together in a cyclopentaphenanthracene system: three of the rings are six-membered, one is five-membered (Figure 25.70).

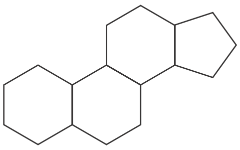


Figure 25.70 The fused four ring structure common to steroids

A course of anabolic steroids can increase muscle mass, strength and stamina in both male and female athletes. They have similar effects to testosterone, but without promoting the secondary male characteristics. Long-term use can lead to damage to the heart and liver.

The usual method of detecting steroids relies upon identifying their metabolites. While some steroids are excreted unchanged, most undergo processes such as hydroxylation, oxidation or reduction. These metabolites are excreted in the urine or faeces.

Analysis of urine samples from athletes by gas chromatography-mass spectrometry can identify metabolites from anabolic steroids (Figure 25.71) up to a week after their use.

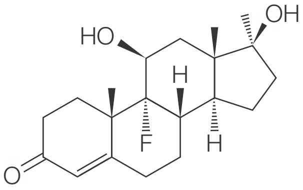


Figure 25.71 Fluoxymesterone (trade name Halotestin)

Gas-chromatography mass-spectrometry

Revised ☐

In gas chromatography a long capillary glass tube has its inside coated with an inert liquid (often a long chain alkane) adsorbed onto a solid and this coating acts as the stationary phase. An inert carrier gas such as helium, argon or nitrogen is the mobile phase used to separate the volatile components of a mixture of liquids at elevated temperature. At the end of the column a range of detectors can be used to identify each component and the retention time (inside the column) for each component can be recorded.

In gas-chromatography mass-spectrometry (GC-MS) (Figure 25.72) the separated components are ionized as they emerge from the column and both the molecular mass and structural composition can be analysed by mass spectrometry.

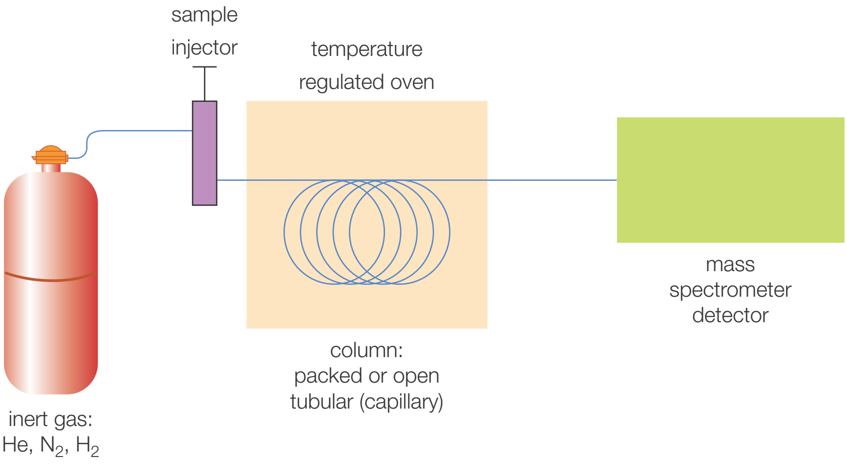
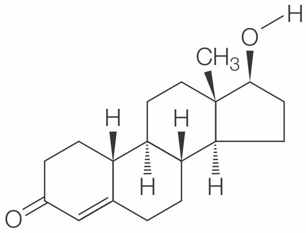


Figure 25.72 Schematic diagram of GC-MS

■ QUICK CHECK QUESTION

62 The structure of an anabolic steroid, nandrolone, is shown below.



a Identify the three functional groups of nandrolone and deduce its molecular formula.

b State the effect on athletes who take anabolic steroids.

c Outline how anabolic steroids can be detected in the urine.

Alcohol breathalyser

The earliest form of the breathalyser (Figure 25.73) involved blowing into a sealed tube that contains supported crystals of potassium (or sodium) dichromate(VI) crystals that turn green as they undergo reduction by oxidizing ethanol molecules in the breath. The police officer could determine the concentration of alcohol in the driver's breath by seeing what length of the crystals in the tube had changed colour.

Ethanol is oxidized to ethanol and then ethanoic acid.

$$\underset{\text{ethanol}}{CH_3CH_2OH} \rightarrow \underset{\text{ethanal}}{CH_3CHO} + 2H^+ + 2e^-$$

$$\underset{\text{ethanal}}{CH_3CHO} + H_2O \rightarrow \underset{\text{ethanoic acid}}{CH_3COOH} + 2H^+ + 2e^-$$

Green chromium(III) ions are formed as the ethanol molecules are oxidized.

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

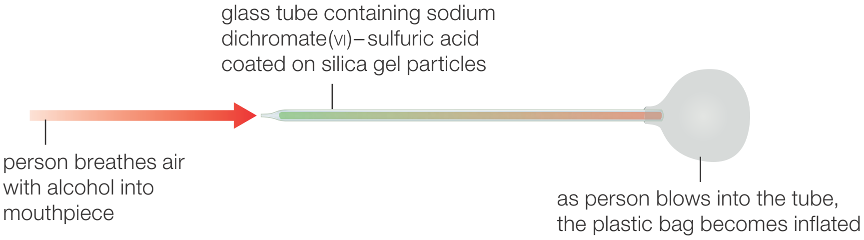


Figure 25.73 A simple breathalyser

Modern hand-intoximeters may be based on a redox reaction based on fuel cell technology. It takes the form of a porous disc with catalytic platinum, silver or gold electrodes saturated with an electrolyte of phosphorus(V) acid or sodium hydroxide.

When the driver breathes into the intoximeter the ethanol in the breath is catalytically oxidized to ethanoic acid at the metal electrode on one side of the membrane:

$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^-$

Oxygen is kept in contact with the metal on the other side to act as a reference electrode (cf. the standard hydrogen electrode). The oxygen is reduced to water:

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

The instrument is calibrated by passing air with known ethanol concentrations through and measuring the resulting cell voltage.

■ QUICK CHECK QUESTION

63 Ethanol is relatively volatile and at high concentrations can be detected in the breath using a breathalyser that contains potassium dichromate(VI). Deduce the oxidation and reduction half-equations that occur in the breathalyser.

Acknowledgements

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