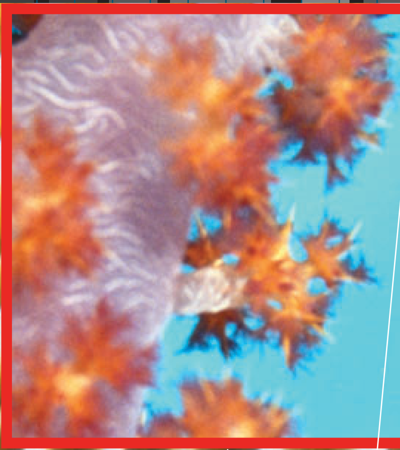
Contexts

Corrosion at a cost
Polymers
Soaps and detergents
Mining in the north
Chemicals from the sea
Electrochemistry
Food analysis

Chapters

6 Precipitation reactions
7 Redox reactions
8 Acid–base reactions
9 Organic chemistry
10 Polymerisation



area of Study 4

Chemical reactions

corrosion

at a cost

Have you ever considered living in paradise in a home by the beach? Many of us dream about it but the reality brings a new perspective. Have you ever considered just how many items around your home are made of metals?

When you live by the beach it becomes very obvious because anything made of metal soon shows signs of corrosion—light fittings, ceiling fans, steel door surrounds, door locks and window catches. Many electrical items only last a few years and are almost treated as disposable. Stereo systems and television sets often stop working after only a couple of years and there is little hope of repair. Backing up the data on your computer is essential since you may come home one day to find that it just won't start anymore. The family car is a similar story. You may have learned in the past of the wonders of aluminium and how a protective coating forms on its surface to stop corrosion. Beside the ocean even aluminium corrodes and you will see the affects of it as door frames and windows need replacing.

figure co.1 The joys of living beside the beach—sun, sand, saltwater and corrosion!

Metals are used for these types of items because they are strong, easily shaped and cost-effective compared to the alternatives. As we learn of the causes of corrosion and how it works we are better prepared to find ways of preventing it from happening.

The corrosion process

Corrosion is the degradation of a metal as it reacts with other elements, loses electrons and forms other compounds. The process of corrosion is a redox reaction. Oxidation has become known as a process in which one element loses electrons to another element, not just oxygen.

* Section 7.1 **Oxidation and reduction** (page 338) and Section 7.2 **Redox reactions** (page 341) describe the background knowledge needed to understand corrosion reactions.

Dry corrosion

Dry corrosion is a direct reaction between a metal and oxygen in the air. It involves a metal reacting with oxygen, resulting in a metal oxide. It is a relatively slow process for most metals at room temperature.

At times you will have used strips of magnesium in science experiments. Before performing the experiment it is normally necessary to use sandpaper or steel wool to remove the dull powdery coating and expose fresh metal.

On the laboratory shelf magnesium ribbon will react with oxygen in the air to form an oxide coating.

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

During this process magnesium loses two electrons according to the half reaction:

$$Mg(s) \rightarrow Mg^{2+}(s) + 2e^-$$

figure co.2 The magnesium oxide coating needs to be removed when performing experiments with magnesium ribbon.

figure co.3 Aluminium is used for window frames because it is strong, light and corrosion resistant.

These electrons are transferred to the oxygen atoms.

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

Magnesium has been oxidised and oxygen has been reduced, resulting in the production of magnesium oxide.

Aluminium undergoes a similar process to form a layer of aluminium oxide.

$$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$$

Aluminium oxide is a tough impenetrable coating that protects the metal underneath from further corrosion. If this coating is scratched, fresh aluminium oxide forms restoring the protection. However, if this process is continual under extreme conditions (for example near the ocean) aluminium will also eventually be completely oxidised.

Wet corrosion

As implied by the name, wet corrosion occurs in the presence of water whether that be moisture in the air or total immersion in water. In the presence of water, metals don't have to directly lose their electrons to another element. The most common experience of corrosion for many people is that of rust, the corrosion of iron. The formation of rust is outlined in table co.1.

The red-brown substance $Fe_2O_3.xH_2O$ is rust. Unlike the tough aluminium oxide coating that forms on aluminium, this iron(III) oxide (hydrated), flakes off the surface of iron exposing the metal underneath, which can then corrode.

A droplet of water on the surface of a piece of iron sets up a tiny electrochemical cell similar to those described in section 7.4 Ease of oxidation.

* Section 7.4 **Ease of oxidation** describes electrochemical cells (page 348).

table co.1 The formation of rust from iron.

Step	Description	Reactions
1	The first step in the formation of rust is the loss of electrons by iron atoms. Oxygen dissolved in the water gains the electrons lost by the iron.	Anodic reaction $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ Cathodic reaction $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ Overall reaction $2Fe(s) + O_2(g) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4OH^-(aq)$
2	Iron(II) ions react with hydroxide ions forming the green precipitate iron(II) hydroxide.	$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$
3	The iron(II) hydroxide in turn reacts with oxygen and water to produce iron(III) hydroxide, a red-brown precipitate.	$4Fe(OH)_2(s) + O_2(aq) + 2H_2O(l) \rightarrow 4Fe(OH)_3(s)$
4	The iron(III) hydroxide can lose water to form $Fe_2O_3.xH_2O$, a red-brown substance.	For example $2Fe(OH)_3(s) \rightarrow Fe_2O_3.2H_2O(s) + H_2O(l)$

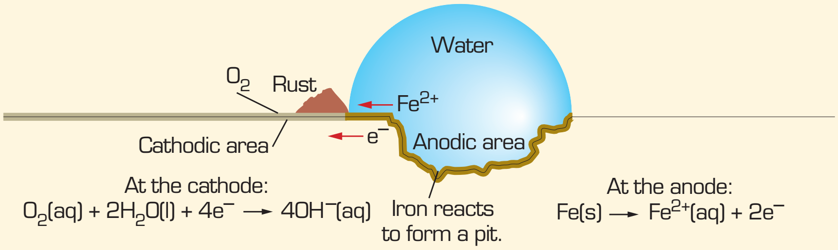


figure co.4 A drop of water on a piece of steel can create an electrochemical cell. Electrons flow from the site of oxidation to the site of reduction.

The edge of the droplet, where oxygen concentration is high, acts as the cathodic area of the electrochemical cell. The region beneath the water droplet, where the oxygen concentration is low, forms the anodic area. Electrons flow from the anodic area to the cathodic area as the initial redox reactions of the corrosion process takes place (figures co.4 and co.5).

Section 7.3 **Oxidation numbers and half equations** describes one method for writing balanced chemical reactions for corrosion (page 343).

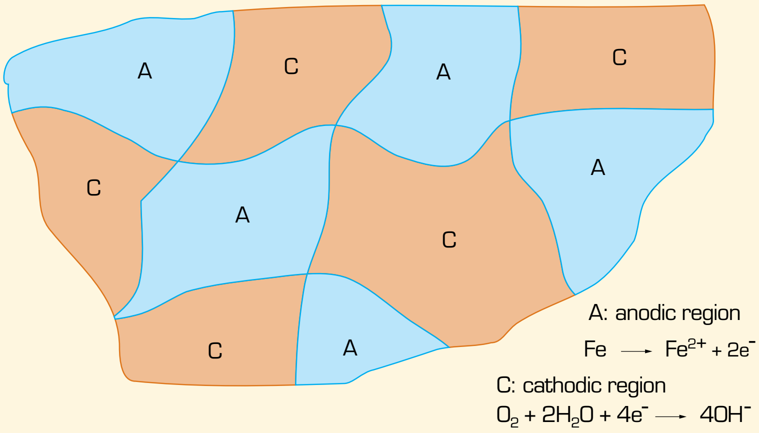


figure co.5 The surface of a piece of corroding steel develops anodic regions where oxidation occurs and cathodic regions where reduction occurs.

Experiment co.1

Observing corrosion

Purpose

To investigate how several different treatments affect the corrosion of iron.

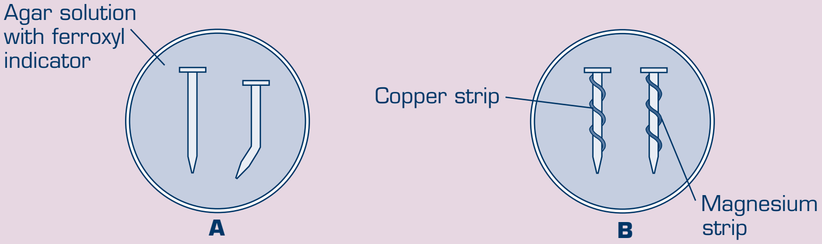


figure co.6

Method

1. Clean all nails with emery paper or steel wool.
2. Treat the nails as shown in figure co.6.
3. Place the nails in the Petri dishes.
4. Pour warm agar solution with ferroxyl indicator over the nails until they are covered.
5. Allow the agar to cool then cover with a lid, and label.
6. Draw diagrams of the nails and use labels and sketches to note any changes observed after:
   - a 20 to 30 minutes
   - b 24 hours
   - c 1 week.

Some information

Pink areas: Phenolphthalein indicates the presence of hydroxide ions. This is the region where reduction is taking place according to the equation

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

Blue areas: Iron is oxidised to Fe^{2+} and these ions react with the hexacyanoferrate(III) ions to produce the insoluble blue substance iron(II) hexacyanoferrate(III).

Discussion

1. a Describe the observable changes that have taken place to indicate that the iron nail has corroded.
   b Identify the ions present in these areas.
2. Observe Petri dish A. Which regions of the iron nail have corroded the most? Give an explanation.
3. Observe Petri dish B. Describe the effects of having the nails in contact with each metal. Include half equations to show what happens at the anode and cathode.
4. Describe how corrosion has been accelerated or prevented by the conditions in this experiment.

materials

(per group)

- 4 iron nails
- 2 Petri dishes with lids
- emery paper or steel wool
- 250 mL agar solution with ferroxyl indicator (10 g sodium chloride, 1 g potassium ferricyanide, 1 g phenolphthalein, 500 mL distilled water)
- 2 mm strips of copper and magnesium

safety

- Wear safety glasses and a laboratory coat for this experiment.
- Phenolphthalein is a powerful laxative. Do not ingest.
- Potassium ferricyanide is slightly toxic if ingested and a skin irritant.
- Take care when transferring hot agar.
- Wash hands thoroughly.

The rate of corrosion

The conditions in which a metal is placed determine the rate of corrosion. Wet corrosion is much faster than dry corrosion because the metal can lose its electrons to form ions in water and doesn't have to lose electrons directly to another element. Cars used in inland country areas tend to show fewer signs of corrosion than those in coastal areas. By the ocean, dissolved salt tends to accelerate the rate of corrosion but other impurities such as acidic pollutants from the air also cause corrosion to occur more rapidly.

In an effort to counteract the effects of sea water, pieces of zinc are attached below the water line of steel-hulled boats. This zinc acts as a sacrificial anode—the zinc is oxidised and the steel is protected. An electrochemical cell has been constructed with the zinc as the anode and the steel as the cathode. When a more reactive metal is attached to a less reactive metal the less reactive one is protected against corrosion. Boat builders need to be careful of the screws, bolts and other metal fittings they use. If a less reactive metal is attached to the steel, corrosion of the steel will be accelerated.

Some impurities in metals can cause them to corrode more rapidly. Other impurities, such as those added to produce various alloys, can make metals extremely resistant to corrosion. Stainless steel (iron combined with small amounts of molybdenum, manganese, nickel and chromium) is valued for its corrosion resistance.

figure co.7 This 1500-year-old pillar in Delhi shows little signs of rust due to the high purity of iron from which it is made.

figure co.8 Stainless steel sinks rarely show any signs of corrosion despite being in almost constant contact with water.

One way of preventing corrosion of a metal is to coat it in a layer that is impermeable to oxygen. The paint on a car is one example of this. If the paint on a car is chipped, a cell can be formed similar to the drop of water described earlier. The exposed area is the cathodic area and the corrosion actually occurs at an anodic area below a section of undamaged paint. Food cans are steel coated with a thin layer of tin. The tin protects the steel from oxygen in the air, but if the tin is scratched it actually accelerates corrosion as it is a less reactive metal than the steel.

If a metal has been stressed by bending, working or a collision it is more susceptible to corrosion. If cars have been left out in a hail storm, they are often sold cheaply by the dealers to panel beaters who repair them and resell them. Even though they may be competently repaired, these cars are susceptible to corrosion at the previously dented sites.

Table co.2 describes the main conditions under which corrosion is accelerated and inhibited.

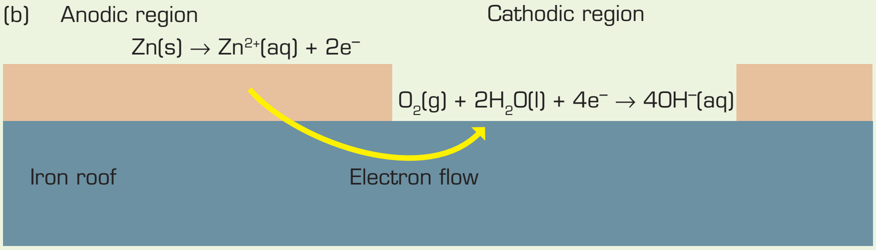
figure co.9 The zinc coating of galvanised steel house frames protects the steel in two ways: it forms a barrier that prevents oxygen from reaching the surface of the steel and also it is oxidised in preference to the steel due to its greater reactivity.

table co.2 Preventing and accelerating corrosion.

Corrosion acceleration	Corrosion prevention
The presence of moisture allows ions to form and react together.	The reactions of corrosion occur at a greater rate in solution. Removing moisture can slow or even stop corrosion.
Impurities in water such as salt and acidic pollutants accelerate corrosion.	A sacrificial anode can be used to minimise corrosion. A more reactive metal attached to a less reactive one protects the less reactive metal.
Some impurities within a metal can cause it to corrode faster.	Alloys contain beneficial impurities. Some alloys of steel are highly resistant to corrosion due to the metals with which they are combined.
When the surface protection on a metal (such as paint on a car) is chipped or damaged a cell is formed as in the water drop of figure co.4. Rust begins to form below the paint surface adjacent to the chip.	Paint and other protective coatings keep oxygen away from the metallic surface. The zinc surface of galvanised iron simultaneously protects the surface from oxygen and acts as a sacrificial anode.
The sites of stress on a metal such as those caused by bending or hammering are prone to corrosion.	Car panels after accidents and iron roofs after hail storms are often replaced as even after repair they are still susceptible to corrosion.

figure co.10 The Sydney Harbour Bridge is a 53 000-tonne steel structure protected from corrosion by paint. This is a continuous process that uses 90 000 litres of paint per coat.

figure co.11 (a) Galvanised iron roofs are common throughout Australia. (b) The iron is protected as the zinc coating gives up its electrons.



Experimental investigations

There are a variety of ways of approaching an investigation into corrosion. Experiment co.1 may give you a starting point. There are many variables that you can change to observe the extent of corrosion or the rate at which it occurs under different conditions. Some of these variables are listed below.

1. **The metal**—iron nails are easy to obtain and fairly uniform in size and shape but you may have access to other forms of iron such as lathe turnings from an engineering works. Samples of metals such as copper or aluminium may also be available.
2. **Atmospheric conditions**—samples of a metal could be observed in water, humid air and dry air. You may like to observe a sample that is partially immersed in water to see the effects.
3. **Impurities in water**—solutions containing different substances could be compared for their ability to accelerate corrosion, for example salt water, acids or bases. You could also compare the effects of different concentrations of these.
4. **Oxygen content of water**—dissolved oxygen can be removed from water by boiling and kept out with a layer of oil. A layer of oil will also maintain the amount of oxygen in water. The effects of different concentrations of oxygen on corrosion may be observed.
5. **Barrier protection**—you might like to test the ability of different substances to protect a metal. Different commercial paints could be compared with oils or greases.
6. **Metal combinations**—investigate the effects of combining metals on the rate of corrosion. You might like to extend the investigation of this context using other metals besides copper, iron and magnesium.
7. **Applied voltage**—this is another method sometimes used to protect metals from corrosion. You could test whether it is the positive or negative electrode of a power supply that protects the metal. A comparison of different voltages may also prove interesting.
8. **Physical treatment**—a variety of metals could be treated (or mistreated) by hammering, scratching, rolling or some other method that you devise. See how these treatments affect the ability of the metal to resist corrosion.
9. You may even decide to combine several of these treatments together; for example, you could physically treat samples of metals by hammering and then paint them with rustproof paint. Library and Internet research could also provide ideas for further investigation. There may be a local business that works in metals and consulting with their staff may prove fruitful.

polymers

Everyday most people unknowingly come into contact with many different types of polymers—though some are mistakenly referred to as plastics. Plastic is not a substance or a particular type of substance, it is a property that a substance can have. A plastic substance is able to be moulded into new shapes. Clay is a plastic substance, as is a sheet of copper, which is malleable and can be beaten into shape. Many of the products that are commonly referred to as plastic are formed from polymers that have been heated until soft and then moulded into shape by a variety of means.

figure po.1
Polymers, not plastics. The substances we often call plastics are actually polymers.

The development of polymers

From the mid-1800s improved scientific understanding allowed the development of a wide range of new materials to meet the changing needs of a modern society. Conducting and insulating materials were needed to allow the use of electricity in homes. Lightweight materials were developed for aircraft construction. Insulating materials allowed exploration and research in colder climates. The needs of military and space exploration accelerated development of a wide range of materials that have become commonly used in our homes. Many of these new substances were polymers.

Polymers are large molecules made up of many small repeating units. Each polymer molecule can contain thousands of atoms. By producing polymers with different structures they can be manufactured with the specific properties needed for particular purposes.

* Section 10.1 **The structure and properties of polymers** describes the general structure of polymer molecules and relates this to their characteristic properties (page 409).

table po.1 A timeline for the development of some early polymers.

1843	Vulcanisation of rubber discovered by Charles Goodyear in the USA.
1869	John Hyatt patented celluloid, a cellulose nitrate polymer. It was used to make combs, knife handles, dolls, etc. It is still used to make products such as table-tennis balls.
1888	Dunlop patented the pneumatic tyre in the USA.
1907	Bakelite was patented. This is a phenol formaldehyde thermosetting polymer. The dark-brown light-switches in houses more than 40 years old are usually made of Bakelite.
1927	Polyvinyl chloride was first used commercially.
1933	Polytetrafluoroethene or teflon was developed.
1933	Polyethene was developed.
1936	Polymethylmethacrytate or Perspex was manufactured by ICI in England. During World War II, Perspex was used extensively for the manufacture or aircraft windows and gun turret domes.
1938	Du Pont Company in the USA brought the first nylon plant into operation.
1943	Dow-Corning Company was formed in the USA. One of their first products was a silicone insulating grease. Other silicone products followed—oils, rubbers, resins and waterproofing agents.
1953	Ziegler in the USA showed that polyethene can be made at room temperature and pressure by using a special catalyst.
1960	Polypropene was first manufactured on a large scale in Britain.

* Section 10.2 **Addition polymerisation** (page 414) and Section 10.3 **Condensation polymerisation** (page 416) describe the production, structure and properties of specific polymers.

Many of these polymers are in common use today. The structure of polymers, their intermolecular forces and the lengths of their chains determines their properties. In the following section you will be guided through the sampling and testing of some common recyclable polymers to allow you to compare their properties and account for these from their structures.

Investigating polymers

There is a wide range of polymers available, each with a different chemical formula and molecular structure. It is not possible to distinguish one from the other by just looking at them. When performing a test on a substance it is important that you are able to identify the substance you are testing.

With the growing popularity in recycling materials as a way of protecting the environment, it became a requirement of manufacturers to identify the polymers from which products are made by using specific symbols. Some of these are shown in figure po.3.

Some types of recycling involve the mixing of any types of polymers together, heating the mixture and moulding it into products such as garden stakes and edging for flower beds. Better use of recycled polymers is made when items of the same type of polymer are recycled together. This gives a material of higher purity with known properties which is able to be moulded into items such as bottles and containers.

figure po.2 Plastic items need to be sorted into polymers of the same type for recycling.

Identifying polymers

The polymer numbering system shown in figure po.3 will enable you to collect samples of particular polymers for testing. By selecting recyclable polymers for testing you will be looking only at thermoplastics and ignoring the thermosetting plastics. You may decide to test and compare as many types as possible or you could test a limited range of polymers and look for similarities and differences in, for example, high density polyethene and low density polyethene.

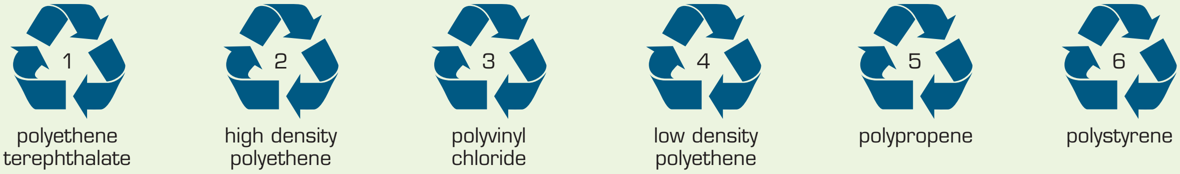


figure po.3 Recycling symbols enable items to be identified by the polymers from which they were made.

✱ Section 10.1 **The structure and properties of polymers** describes thermosetting and thermoplastic polymers, and their different properties (page 409).

Whatever types of tests you decide to perform, you will need to keep your samples as uniform as possible. Containers can be cut into sample pieces of similar size and shape. Try to use the flat sections of containers and avoid the curved sections. Depending on the tests you devise you may use square or rectangular samples or narrow strips. (Kitchen shears will be useful for this task. Avoid using normal scissors, knives or box-cutters with sharp blades as these can operate unpredictably when used on containers.) A valid test will need to make use of samples that are as close as possible to identical. The only variable in your samples should be the material from which they are made.

Experimental investigations

When it comes to devising experiments to perform on your polymer samples, consider the properties that can be compared. Some of these could include strength, flexibility, hardness, the effects of heat, compressibility and resistance to puncturing.

An Internet search using the keywords 'polymer testing' will result in the discovery of many websites. Most of these will be commercial sites offering services or supplying polymer testing equipment. These sites can provide you with ideas for ways that polymers are tested and you may be able to set up a simpler version in the school laboratory for tests such as the one shown in figure po.4.

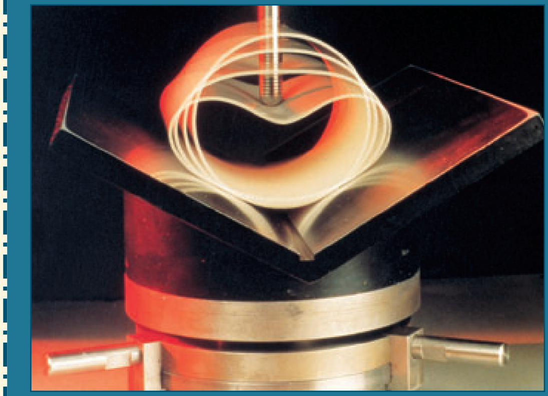


figure po.4 The commercial testing of polymers.

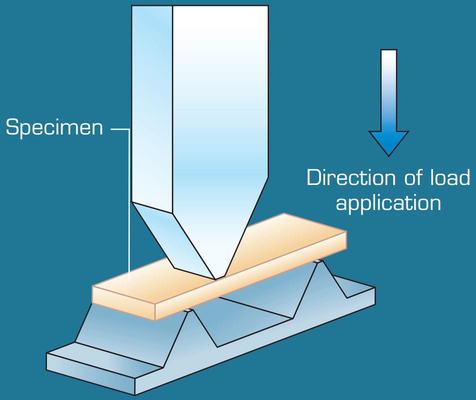


figure po.5 Simple tests like this can be used to measure the flexibility of polymer samples.

Testing the properties of polymers

Discuss your ideas with other students and your teacher to ensure that your tests are valid and safe. Remember to change only one variable at a time for each experiment (e.g. the type of sample) and keep all other factors the same.

You might like to try your own version of some of the following tests.

1. Scratch test—a harder sample will scratch a softer sample but not the other way around.
2. Hardness—an object like a large ball-bearing dropped on a sample will leave indentations that can be compared.
3. Shrink test—samples of polymers heated in an oven will shrink to varying degrees.
4. Water absorption—the water absorbed by samples left in water overnight will result in a higher mass.
5. Puncture test—a piece of PVC pipe can be used to direct a dart onto a sample. The depth of the puncture along the shaft of the dart can be measured.

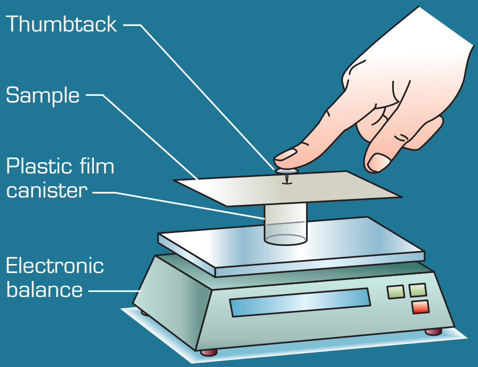


figure po.6 In this experiment the force applied to puncture the sample is indicated by the reading on the electronic balance.

When devising tests with heat, be aware that burning polymers tend to give off toxic fumes. Use an oven, electric hotplate or a nail heated in a Bunsen burner flame using tongs. Do not expose your samples directly to a flame.

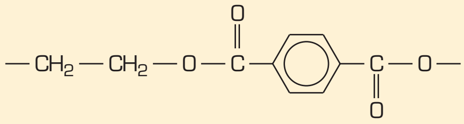
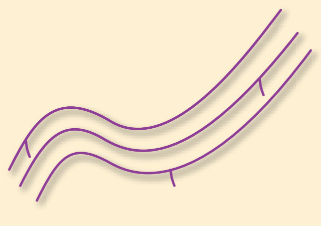
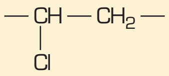
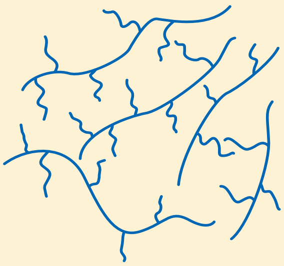
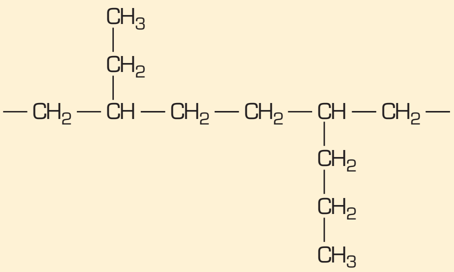
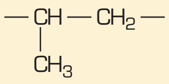
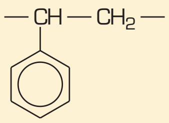
Repeat your tests several times to ensure that results are consistent. Measured results can be averaged.

Interpreting your results

A discussion of your results can be used to relate the properties that you observe in your experiments to the molecular structure of each polymer (table po.2).

* Section 2.3 **Covalent bonding** describes intermolecular forces (page 233).

table po.2 The structure of some recyclable thermoplastic polymers.

Polymer	Structure
polyethene terephthalate (PETE)	
high density polyethene (HDPE)	 $-CH_2-CH_2-CH_2-CH_2-$
polyvinyl chloride (PVC)	 $-\underset{\underset{Cl}{\vert}}{CH}-CH_2-$
low density polyethene (LDPE)	 
polypropene (PP)	 $-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-$
polystyrene (PS)	

Some of the properties you observe may be able to be explained in terms of molecular structure and intermolecular forces. The production methods for the type of polymer as well as those used in the actual item may also account for the observed properties. You may need to do some library research in order to explain the results of your tests.

In your final report you have the opportunity to relate the properties you have observed to the uses of individual polymers. For example, why is polypropene used for takeaway food containers but not for soft drink bottles? Why are there two types of polyethene (high and low density)? Why is bleach supplied in high density polyethene bottles but not in polyethene terephthalate ones?

figure po.7 A variety of polymers for a variety of uses.

Synthetic fibres and composites

Nylon and polyester are polymer materials that have been used to make synthetic fibres that can be woven into fabrics. They are used widely in clothing. These have been commonly in use since the mid-twentieth century.

* Section 10.3 **Condensation polmerisation** describes the production of polyester and nylon 66 (page 416).

The development of new polymers continued beyond those described in table po.2. More recently materials known as Kevlar and Nomex have gained wider use. They are produced by the large chemical manufacturer Dupont.

Kevlar

Kevlar is an extremely strong lightweight polymer fibre, first made in the late 1960s and marketed in the early 1970s. Kevlar has been found useful in items as diverse as bulletproof vests, trampoline mats, tennis racquets, skate shoes, windsurfing sails and to reinforce wooden skateboard decks. It has been used as cables for underwater structures as it is corrosion resistant and twenty times stronger than steel. Kevlar has also been used to build tornado shelters within houses. Puncture-resistant tyres have been developed using Kevlar. These tyres can be driven on when punctured without damage to the wheel of the car or bicycle.

The strength of Kevlar is a result of the ring structure and the amide structure of the molecule.

Kevlar is a fibre—a bundle of these polymer chains together. These polymer chains are strongly attracted to each other. The Kevlar fibres are highly ordered and held in place like atoms in a crystal. They have few structural flaws or weak spots, and this is what makes Kevlar exceptionally strong.

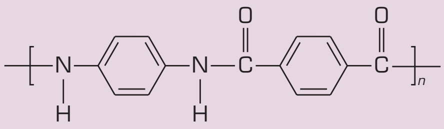


figure po.8 The structure of Kevlar.

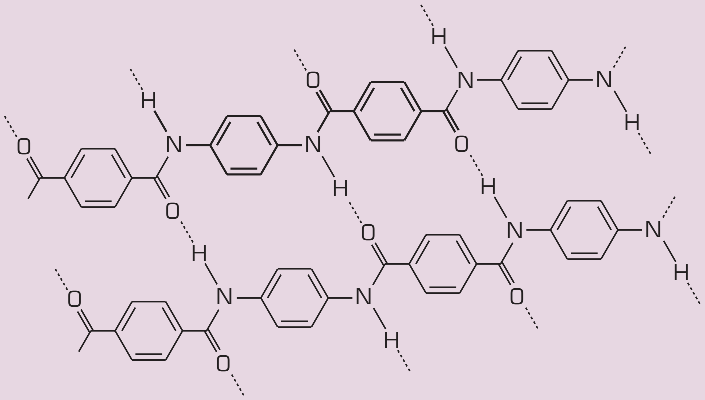


figure po.9 Kevlar polymer chain interactions.

Kevlar is one example. As research continues, expect the development of more synthetics like Kevlar with improved characteristics and new applications.

Nomex

Nomex was developed after Kevlar and has a slightly different structure. It is strong, light, a non-conductor of electricity and highly heat and flame resistant. Nomex also has good textile properties making it comortable to wear and suitable for clothing used by firefighters, jet pilots, racing car drivers and those working in power plants and factories. It is also used as an electrical insulating material and for filtration in high temperature situations. These properties have also meant that Nomex has been used extensively in the interiors of aircraft, railroad cars and as furnishings for commercial buildings (upholstery, floor coverings), where strong, light and fire-resistant materials are needed.

Some products are also made from blends of Kevlar and Nomex to give materials with the properties of both polymers. These types of materials are known as composites.

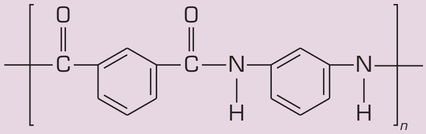


figure po.10 The structure of Nomex.

Buckyballs and nanotubes

The development of giant molecules has continued as an area of scientific research. Two of the better know examples are buckyballs and nanotubes.

Buckyballs …

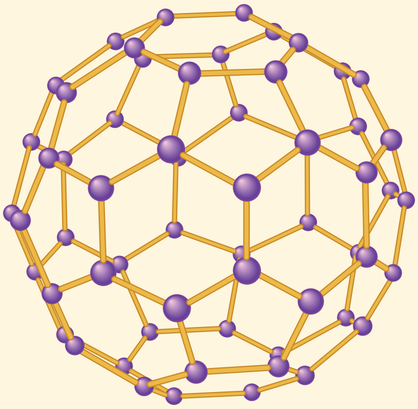


figure po.11 Buckminsterfullerene.

In the mid 1980s, two Texan chemists, Robert Curl and Richard Smalley, together with Harry Kroto, a British chemistry professor, used lasers to initiate chemical reactions at very high temperatures. Kroto was particularly interested in long-chain carbon molecules with multiple bonds because he thought these might be the type of compounds created in certain stars called red giants.

The three scientists discovered that in these experiments, carbon molecules of formula C_{60} were produced over and over again, for which they eventually suggested a structure familiar to all of us—a geodesic shape like a soccer ball. It took 5 years to prove the structure and they were almost beaten to it by two other scientists.

Kroto named C_{60} buckminsterfullerene in honour of the architect Buckminster Fuller who designed a striking geodesic dome made up of hexagons and pentagons for the 1967 Montreal World Exhibition. The technical name for this shape is a truncated icosahedron. Each ‘buckyball’ consists of twenty hexagons (the white patches of leather on a soccer ball) and twelve pentagons (black patches of leather on a soccer ball) connected to form a hollow sphere (Figure po.11). Other fullerene-related structures include ‘fuzzyballs’ ($C_{60}H_{60}$), ‘bunnyballs’ (a C_{60} molecule with two short organic side chains) and ‘buckybabies’, smaller deriviatives (C_{32}–C_{58}), and bigger molecules, C_{70}, shaped like a rugby or Australian Rules football.

Buckyballs form a very stable structure. They are elastic and initially feel soft but if compressed by more than 30% they will harden more than diamond. Each buckyball in a crystal rotates at approximately 20 billion revolutions per second.

The most common place to find buckyballs is in the soot from a candle flame. Various uses have been suggested, especially as superconductors—materials with very little resistance to electrical current.

… and nanotubes

Imagine one layer of a graphite lattice—an infinite array of carbon atoms bonded into hexagonal rings—rolled up to make a cylinder, the atoms matching so it appears as a seamless tube. This cylinder is 1 nm (10^{-9} m) in diameter and about 10–1000 μm (0.01–1 mm) long. This ‘nanotube’ was first discovered by Japanese scientist Sumio Iijima in Tsukuba in 1991, using a high-resolution electron microscope.

Nanotubes are the strongest fibres known. They are much stronger than carbon fibres. A single perfect nanotube is about 10–100 times stronger than steel per unit weight. Carbon fibres consist of individual layers of graphite wound together, whereas nanotubes consist of carbon atoms bonded into a perfect cylindrical structure. Nanotubes can be single-walled or nested inside each other, creating a multiwalled tube.

Nanotubes have unique electrical properties. They can be excellent conductors of electricity, behaving as a metal, because the electrons are confined to the tube and can move along the nanotube axis.

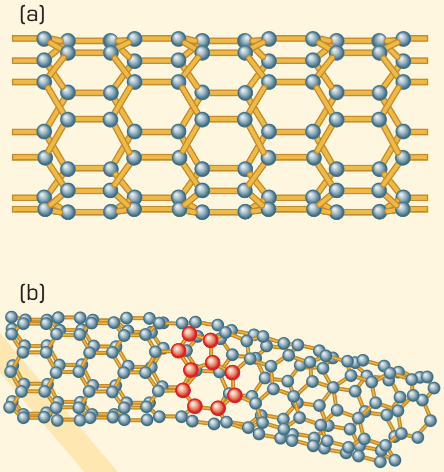


figure po.12 (a) A single-walled carbon nanotube; (b) a single-walled carbon nanotube with a twist.

Alternatively, nanotubes can behave as semiconductors. The exact electrical properties of a nanotube depend on how the graphite sheet has been ‘rolled’ to create the tube.

Single-walled nanotubes are very flexible. They can be twisted, flattened and bent into circles without breaking. They can also be compressed. Carbon fibres break easily when compressed.

After the discovery of buckyballs, it was expected that scientists would find many applications for these beautiful symmetrical structures but that did not happen. At present, nanotubes are used in various electrical devices. Their properties as fibres appear to have great potential if only they could be made slightly longer. Australia’s research organisation, CSIRO, is working with scientists in Dallas, Texas, to develop a process for ‘growing’ carbon nanotubes and using them as textiles with unique properties.

Consider this

Consider the sections on Kevlar and Nomex and use the following questions to guide you through an analysis of their structure and associated properties.

- **a** Outline the similarities and differences in the properties and uses of Kevlar and Nomex.
- **b** Would Kevlar and Nomex be useful as recyclable polymers? Explain your answer.
- **c** Explain the properties and differences in properties of these two polymers in terms of their molecular structure and intermolecular forces.
- **d** What type of polymerisation process would be used to form Kevlar and Nomex?
- **e** Propose the molecular starting materials from which each polymer is made.

Further investigations

1. Conduct some library research into other recent developments in polymer materials. These could include composite materials and polymer nanostructured materials. Relate the structures of these materials to their unique properties. Present your findings to other members of your class as a poster, brochure or multimedia demonstration.
2. Work on buckyballs and nanotubes continues. Find out about the most recent developments of these materials. Has the initial excitement of their discovery lived up to expectations? Select one of the discoveries and write a press release describing the development and possible applications.

Soaps

and detergents

Personal hygiene means keeping our bodies and clothes clean. To keep clean you need to regularly wash to remove sweat, excess oils and dirt from yourself and the clothes you wear. Cleaning is important for the long-term health of your skin. It reduces bacteria and associated odours, keeps pore ducts open and removes dried-up surface skin cells.

The practice of good personal hygiene includes:
- frequently washing your hands
- having a daily shower or bath
- regularly washing your hair
- daily brushing and flossing your teeth
- using a deodorant to reduce body odour
- wearing clean clothes, especially a daily change of socks and underwear
- keeping your fingernails and toenails trimmed.

Chemistry helps us to maximise the benefits of good personal hygiene, to look good and to feel good.

figure sd.1 Wash your hands often.

A major part of our body is the skin. In fact the skin is the largest organ in the body, forming a complete external cover.

Glands in our skin secrete oils and sweat. These materials are important. The oils keep our skin flexible, while sweat helps us to maintain a constant body temperature. Sweat is mainly water with about 1% sodium chloride (salt). Sweat glands concentrated in some areas of the body, for example the armpit, secrete oils as well as sweat. Bacteria attack these oils and can cause offensive body odour. To reduce bacterial action and body odour wash frequently. This cleans the sweat, excess oils and dirt from the skin.

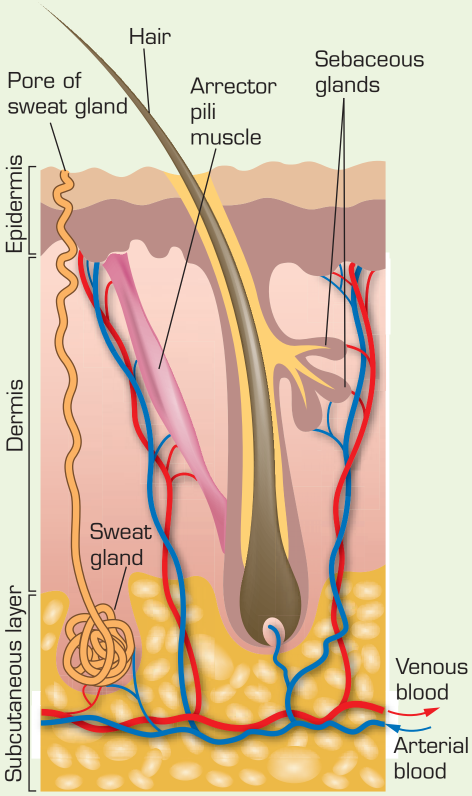


figure sd.2 To keep your skin healthy eat properly, keep clean and avoid getting too much sun.

When you spend too long in the swimming pool or bathtub your skin becomes wrinkled. Have you ever wondered why? The outer layer of your skin, the epidermis, produces an oily substance called sebum that keeps water out. If you spend too long in the water most of the sebum is washed off. The epidermis then starts to absorb water and swells, causing the skin to wrinkle.

Surfactants

Cleaning agents—soaps and synthetic substitutes—were collectively called detergents. After the 1950s the synthetic cleaning agents became more widely used and people referred to them as ‘detergents’ as distinct from ‘soap’. Cleaning agents in the bathroom include shampoos and soaps. In the kitchen and laundry you will find dishwashing liquid and washing powders.

Cleaning agents remove dirt, oils and grease by dissolving them. Their key ingredient is a surfactant—a surface active agent.

Surfactant molecules have both fat-soluble and water-soluble parts. This is shown in figure sd.3. The fat-soluble part of the molecule is referred to as hydrophobic (water-hating). This part is non-polar and can also be described as lipophilic (fat-loving). It sticks to oil and dirt. The water-soluble part of the molecule is hydrophilic (water-loving) and sticks to the water molecules. The molecule’s dual nature allows the almost water-insoluble dirt and grime to be pulled away from the surface being cleaned and carried away as small particles in the water (see figure sd.4). Even though washing-up detergents and shampoos work in the same way, it is not advisable to wash your hair with dishwashing liquid. The dishwashing liquid is formulated to remove thick grime from pots and pans, not to gently clean your hair.

A surfactant is a surface active agent and is the key ingredient in detergents.

*Section 2.3 **Covalent bonding** describes intermolecular forces and polar bonding (page 233).

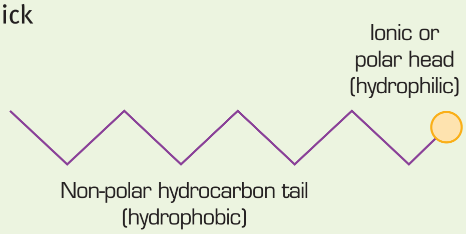


figure sd.3 $CH_3(CH_2)_{16}COO^-Na^+$, sodium stearate soap. Surfactant molecules have a hydrophilic head and a hydrophobic tail.

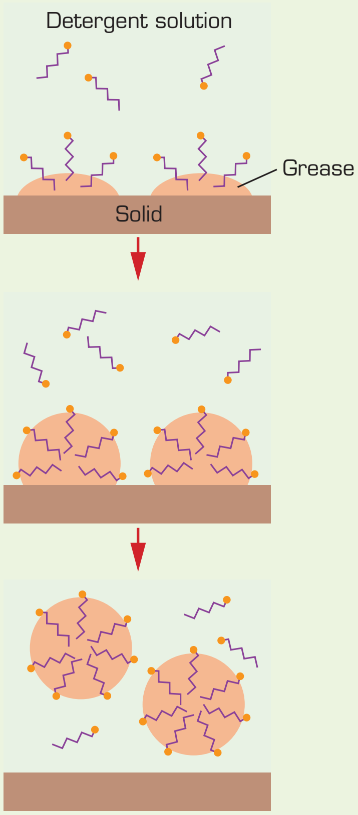


figure sd.4 Surfactants in action. The fat-soluble part of the molecule adheres to oil and dirt, while the water-soluble part of the molecule adheres to the water molecules. Agitation causes the grime to be cleaned from the surface and carried away in the water.

Soap making

Throughout history, soap has been valued for its ability to clean clothes and cooking utensils, and for bathing. It is no wonder that soap-making is one of the oldest chemical manufacturing processes. In the eighteenth century soap making was a profitable industry in Italy.

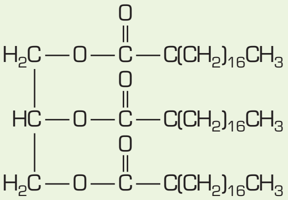
The cheapest and oldest way of making soap is by blending and boiling the basic ingredients of animal fat or a vegetable oil with water and sodium hydroxide. The chemical change is called saponification.

$$\text{a fat + a base} \rightarrow \underset{\text{soap}}{\text{salt of fatty acid}} + \text{glycerol}$$

figure sd.5 Soaps can be scented with herbs and fragrant oils to enhance their appeal.

Plants and animals use fats and oils as energy-storage compounds. Fats and oils are organic molecules called esters and most are triesters (see figure sd.6). They belong to the group of compounds call lipids. Lipids are soluble in organic solvents but insoluble in water. This means that they are difficult to wash from our clothing and our body without the aid of soaps and detergents. The marvels of chemistry allow the use of the material causing the problem to produce the product needed to solve the problem.

Soap is the end product of the saponification of a fat molecule. From figure sd.6 you can see that the structure of a fat is quite complex. The earlier equation for saponification showed no molecular formulae. To help you understand soap-making at the molecular level, examine the structures in the general reaction below and the sodium stearate example.



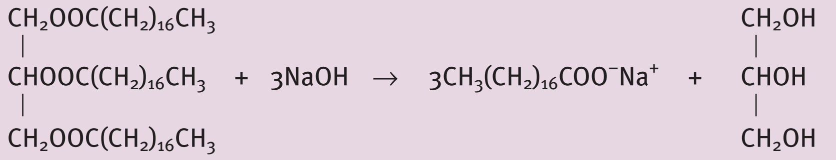
$$\begin{array}{l} H_2C-O-\overset{\overset{\displaystyle O}{\|}}{C}-C(CH_2)_{16}CH_3 \\ \;| \\ HC-O-\overset{\overset{\displaystyle O}{\|}}{C}-C(CH_2)_{16}CH_3 \\ \;| \\ H_2C-O-\overset{\overset{\displaystyle O}{\|}}{C}-C(CH_2)_{16}CH_3 \end{array}$$

figure sd.6 Beef tallow contains the fat **stearin**, triglyceride glyceryl tristearate (systematic name: propane-1,2,3-triyl trioctadecanoate) and makes the most common of soap, sodium stearate.

* Section 8.3 **Defining acids and bases** describes the chemical features of acids and bases (page 370).

General equation:

$$RCOOR' + NaOH \rightarrow RCOO^-Na^+ + R'OH$$



$$\begin{array}{l} CH_2OOC(CH_2)_{16}CH_3 \\ | \\ CHOOC(CH_2)_{16}CH_3 \\ | \\ CH_2OOC(CH_2)_{16}CH_3 \end{array} + 3NaOH \rightarrow 3CH_3(CH_2)_{16}COO^-Na^+ + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

stearin	sodium hydroxide	sodium stearate (soap)	glycerol

Sodium stearate soap is the sodium salt of stearic acid, found mainly in animal fat. A list of fatty acids and their sources is provided in table sd.1.

table sd.1 Some common fatty acids.

Found in	Common name	Structure
coconut oil	lauric acid	$CH_3(CH_2)_{10}COOH$
palm oil and most fats	palmitic acid	$CH_3(CH_2)_{14}COOH$
mainly in animal fat	stearic acid	$CH_3(CH_2)_{16}COOH$
olive oil and most fats	oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$

* Section 9.5 **Reactions of organic acids** describes the structure and properties of esters (page 401). Section 2.5 **Organic compounds** describes carboxylic acids (page 246).

figure sd.7 Soap will only lather up in soft water.

The decline of soaps

Soaps do not lather in all types of water. Differences between water sources are due mainly to the type and quantity of dissolved ions. Sea water, for example, contains a very large concentration of sodium and chloride ions and a relatively high concentration of calcium and magnesium ions. It is very difficult to get soap to lather and hence work properly in sea water. Water in which soap does not lather is called hard water. The calcium and magnesium ions in hard water combine with the long hydrocarbon part of soap to form an insoluble solid, or scum. This is a precipitation reaction.

$$2CH_3(CH_2)_{16}COO^-Na^+ + Ca^{2+} \rightarrow [CH_3(CH_2)_{16}COO^-]_2Ca^{2+} + 2Na^+$$

sodium stearate soap	calcium (or magnesium) ions in hard water	calcium stearate soap scum

Soap scum is an insoluble deposit that forms in hard water rendering a soap ineffective.

* Section 6.2 **Precipitation reactions** describes these types of reactions (page 331).

Experiment sd.1

The saponification reaction

Introduction

You will set up reflux apparatus and perform a saponification reaction using olive oil and solid sodium hydroxide, then test the prepared soap for its emulsifying properties.

On completion of this investigation, you will be able to:

- set up reflux apparatus
- identify processes occurring in the reaction flask
- demonstrate the emulsifying properties of produced soap.

Procedure

1 Set up the quick-fit reflux apparatus as shown in figure sd.8. To the reaction flask add 5 mL olive oil, 10 g sodium hydroxide pellets and 10 mL water.

2 Add a boiling chip to the mixture and reflux until the oil layer is no longer visible.

3 Remove the condenser and pour the mixture into a beaker containing 100 mL ice-cold brine.

4 Filter off the solid residue formed through the cheesecloth. (Filter paper is too slow.)

5 Wash the residue in a small amount of ice-cold distilled water.

6 Place 2 drops of olive oil into two separate test-tubes containing 10 mL water. To one of them add a piece of the soap produced in the reaction.

7 Set up a third test-tube containing 10 mL water and a small amount of soap.

8 Shake all three test-tubes vigorously and compare for lathering ability and emulsifying properties.

Discussion

1 To what group of substances does the solid product belong?

2 The principal acid derived from olive oil is oleic acid ($C_{17}H_{33}COOH$). Write a balanced equation for the saponification of olive oil (assuming this is the only acid present).

3 Briefly explain the function of the sodium chloride solution in this investigation.

4 What evidence was there to show that the soap has emulsifying properties?

Extension

Compare the conditions in the laboratory preparation of soap with an industrial soap-making process.

Disposal of waste

All water-soluble chemicals can be washed down the sink. Reuse olive oil or place on perlite, wrap up in paper and dispose of in the garbage bin.

materials

- 5 mL olive oil
- 10 g sodium hydroxide (NaOH)
- 50 mL ice-cold brine (saturated NaCl solution)
- quick-fit apparatus with 50 mL flask and condenser
- heating mantle
- cheesecloth or equivalent
- 400 mL beaker
- test-tubes
- boiling chips

safety

- Sodium hydroxide solid is highly corrosive to skin and eyes.
- Wear eye and skin protection.

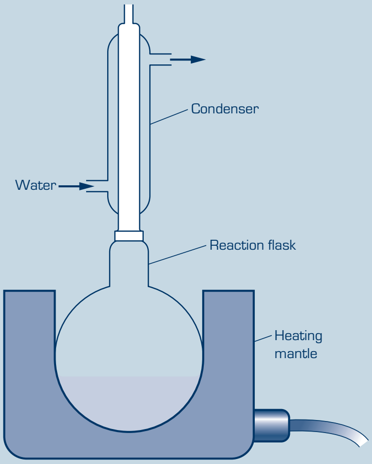


figure sd.8 Reflex apparatus set-up

The rise of synthetic detergents

Synthetic detergents are popular in areas with hard water. This is because synthetic detergents do not form a scum in hard water. Their calcium and magnesium salts are soluble. So how do synthetic detergents differ from soaps?

Synthetic detergents are made from petroleum products rather than the animal fats or vegetable oils from which soaps are made. They have to a large extent replaced soaps as the primary cleaning agent and outsell soaps by more than three to one.

figure sd.9 Synthetic detergents make up most of our cleaning products.

The oldest and still the most common detergents are the alkylbenzene sulfonates. A typical example is sodium dodecylbenzene sulfonate (figure sd.10). The alkylbenzene sulfonate detergents are more effective than soaps and are the major surfactants in laundry detergents and dishwashing liquids. They tend not to be used for personal hygiene as they remove too much oil from the skin and hair. The synthetic detergents work in the same way as soaps. They have a hydrophobic part and a hydrophilic part to their molecules. There are three main types of detergents: anionic (negatively charged), cationic (positively charge) and non-ionic (table sd.2).

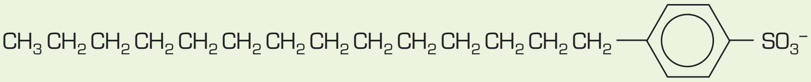


figure sd.10 Sodium dodecylbenzene sulfonate, a typical alkylbenzene sulfonate detergent.

figure sd.11 This OMO brand of detergent contains both anionic and non-ionic surfactants.

table sd.2 Structure and common uses of soap and the three different types of synthetic detergents.

Type	Non-polar portion	Polar portion	Common uses
soap			personal hygiene
anionic			laundry detergents and dishwashing liquids
cationic			hair conditioner, fabric softener
non-ionic			wetting agents (paint, pesticides), automatic dishwasher powders, cosmetics

Experimental investigations

1 Soaps from different oils

Using the method described in experiment sd.1 The saponification reaction, you could produce a range of soaps from different types of oil. For example, in place of olive oil you could try peanut, canola or sunflower oil. Test and compare the properties and effectiveness of each of the different soaps produced. The following investigations may assist you in devising these tests.

2 Action of a detergent on grease

The following procedure can be used to analyse the effectiveness of a detergent. You may like to collect a range of different brands and types of detergents and use this method to make a comparison.

Method

a Place 2 small lumps of margarine on opposite ends of a white tile. Sprinkle a small amount of red, oil-soluble dye on each and mix with a stirring rod until each lump of margarine turns red.

b Add 2 drops of water to one lump and mix. Add 2 drops of detergent solution to the other lump and mix. Record your observations.

c Wash the margarine from the surface of the tile and record your observations.

Discussion

a Account for the differences you observed in the behaviour of the water and the detergent solution when they were mixed with margarine.

b Use labelled diagrams to explain how the detergent removes the margarine from the surface of the tile.

3 Soap and synthetic detergent in hard and soft water

The following procedure could be used to compare the effectiveness of soaps and detergents in hard and soft water. You may decide to use this procedure to compare different brands of soaps and detergents or to compare the quality of water from different sources.

Method

a Pour 5 mL of deionised water into 2 test tubes and shake well. Record your observations.

b Add 0.5 mL of soap solution to the first test tube and shake well. Record your observations.

c Add 0.5 mL of synthetic detergent solution to the second test tube and shake well. Record your observations.

Discussion

a Explain why synthetic detergents are preferable to soap for washing clothes in regions that have hard water.

b When soap is used in hard water a scum may form. Write an equation for a reaction which may occur to produce this scum.

4 Water hardness

Water hardness can be classified using the equivalent quantity of calcium carbonate, as shown in table sd.3.

table sd.3 Classification of water hardness.

Concentration of $CaCO_3$ (ppm)	Classification
less than 70	soft
75–150	moderately hard
150–300	hard
more than 300	very hard

Method

a Plan and conduct an investigation to determine the hardness of a water sample.

b Write an article for a popular magazine that explains to the reader the differences between saturated and unsaturated fats, and between butter and margarine. Your article will also discuss these materials in terms of healthy eating.

c Examine the environmental impact of soaps and detergents and relate community concerns and scientific research to changes made in the production and use of detergents.

Consider **this**

Use the information presented in the context and related chapters to answer the following questions.

1 A soap contains the salt potassium palmitate, $CH_3(CH_2)_{10}COO^-K^+$.

   a Identify the reactants used to make this soap.

   b Identify the lipophilic end of the molecule.

   c Identify the hydrophilic end of the molecule.

   d Describe with the aid of an equation how the salt dissolves when placed in water.

   e Describe its cleaning actions using appropriate scientific language and diagrams.

2 Discuss similarities and differences between soaps and detergents. Present your information as a PowerPoint presentation or as a poster designed to inform the general public.

3 Sea water is a solution of salts and contains more than 70 dissolved elements. Salinity is the amount (in grams) of total dissolved salts present in 1 kilogram of water. Normal sea water has a salinity of 35 grams per kilogram (or litre) of water, which can also be expressed as 35 000 ppm (parts per million).

   a Table sd.4 lists the six most abundant ions in sea water. Complete the table by calculating (where required):

   - the percentage mass $\left(\dfrac{\text{mass of ion}}{\text{mass of solution}} \times 100\%\right)$
   - parts per million $\left(\dfrac{\text{mass of ion in mg}}{\text{mass of solution in kg}}\right)$

table sd.4 Concentrations of the six most abundant ions in sea water.

Ion		% mass in 1 kg of sea water	ppm
chloride	(Cl^-)	55.0	19 250
sodium	(Na^+)	30.6	
sulfate	(SO_4^{2-})	7.7	
magnesium	(Mg^{2+})		1291
calcium	(Ca^{2+})	1.2	
potassium	(K^+)		385

   b Calculate the mass of soap that would be precipitated as scum by 1 litre of normal sea water.

The international standard for seawater composition is determined using sea water from Wormly in southern England.

Further **investigations**

Research the types of hard water and methods of water softening. Present your findings as either a poster or a PowerPoint presentation.

mining in the north

figure mn.1 A geologist prospecting for minerals.

Mining is vital to the economy of Queensland and of Australia. The state is mineral-rich and huge increases in the amount of ore mined and processed are currently taking place. The sites of major Queensland mines are shown in figure mn.2.

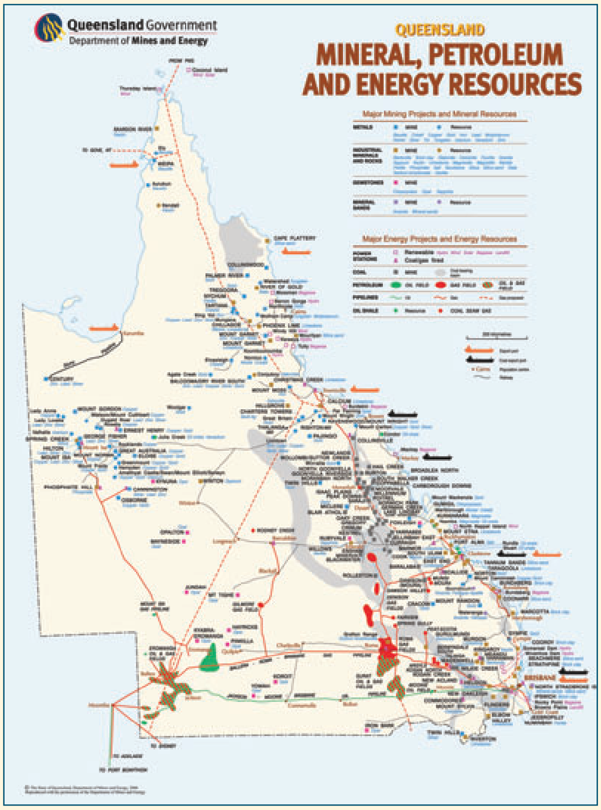


figure mn.2 Site of mines in Queensland.

The Queensland Department of Natural Resources and Mines has an interactive website showing the major mineral deposits and mines in the state. (See hi.com.au.) Queensland exports some minerals overseas for processing, but also has major processing plants and refineries that treat some ores and minerals from other states and countries.

Useful metals are nearly always found in the form of compounds called minerals. These minerals are found in ore bodies as heterogeneous mixtures with other minerals. After mining, the unwanted minerals, called gangue, must be separated from the desired minerals by various methods that depend on physical differences. The metal is then extracted from the mineral using chemical reduction. If the ore contains more than one useful mineral, these also need to be separated either before or after chemical extraction.

Sections 7.1 **Oxidation and reduction** (page 338) and 7.2 **Redox reactions** (page 341) describe the process of reduction, which is used to extract a metal from a mineral.

You may like to research the physical methods used to extract minerals from ores, and the chemical methods used to extract and refine metals from minerals. The chemical methods used for each metal differ and depend greatly on the ease of reduction of the metal ion in the mineral. For example, metals such as aluminium, magnesium and sodium must be extracted by electrolysis from molten liquids, rather than from aqueous solutions. This is because water will be reduced in preference to the metal ion in the solution.

Sections 7.4 **Ease of oxidation** describes the process of electrolysis (page 348).

Copper

Copper is a metal with a reddish lustre. It is an excellent conductor of electricity. Its major use is in electrical wiring and in components of electrical appliances. Alloys of copper and nickel are made into coins. Because it is less reactive than other metals such as iron, it is used in many other industrial and decorative situations.

Copper is a metal with low reactivity, so it can occasionally be found as native copper (in a chemically uncombined state), as in figure mn.3. It is more commonly found in various minerals such as chalcopyrite, $CuFeS_2$.

The city of Mt Isa has developed at the site of major copper ore bodies. The history of the mines at Mt Isa shows the interplay of factors that determine whether a mine will be economically viable or not. The grade (concentration) of the ore body and the value of the metal on world markets are important factors, but isolation, the depth of the ore body and distance from a major port are also important, and are factors that made life difficult for the mining company and miners in the early days. Silver, lead and zinc ores associated with the copper make the deposits more viable.

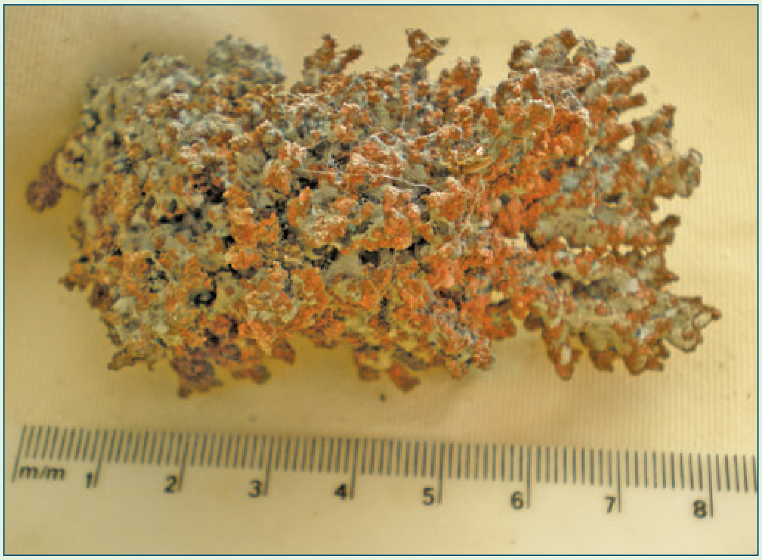


figure mn.3 A piece of native copper.

Ore from Mt Isa and another copper mine north of Cloncurry is crushed and concentrated. The concentrate contains 25%–33% copper that is chemically combined with sulfur and iron. Smelting supplies sufficient energy to decompose the copper minerals, and results in copper that is 99.7% pure. The following is a typical reaction for CuS:

$$CuS(s) + O_2(g) \rightarrow Cu(s) + SO_2(g)$$

The copper is cast into anodes, which are sent by rail to the copper refinery in Townsville.

Iron in the solid slag (iron waste) is used as underground fill, and 80% of the sulfur dioxide and sulfur trioxide is captured and used to make sulfuric acid.

Many of the ores around Mt Isa are refractory (difficult to process) and the mining company has developed other methods to extract the copper. Improved milling techniques allow the ore to be ground more finely, so that gangue and the copper minerals can be separated more effectively by methods such leaching. The Albion process is a method of leaching that has been developed at a mining research laboratory in Brisbane. Scientists developed it as a simpler, lower cost leaching method. A typical reaction in this process uses oxygen and sulfuric acid:

$$2CuS(s) + O_2(g) + 2H_2SO_4(aq) \rightarrow 2CuSO_4(aq) + 2S(s) + 2H_2O(l)$$

The copper extracted by the methods described is 99.7% pure, but this is not pure enough for most uses. At the refinery in Townsville, electrolytic refining results in 99.99% pure copper. At the anode, copper and any more easily oxidised contaminants are oxidised. Less easily oxidised contaminants fall to the bottom of the tank as anode 'mud'. This mud contains valuable metals such as silver, and is recovered. At the cathode, copper(II) ions are reduced to copper metal; other ions are left in solution. This can be summarised as:

Anode half-reaction: $Cu(s, impure) \rightarrow Cu^{2+} + 2e^-$
Cathode half-reaction: $Cu^{2+} + 2e^- \rightarrow Cu(s, pure)$

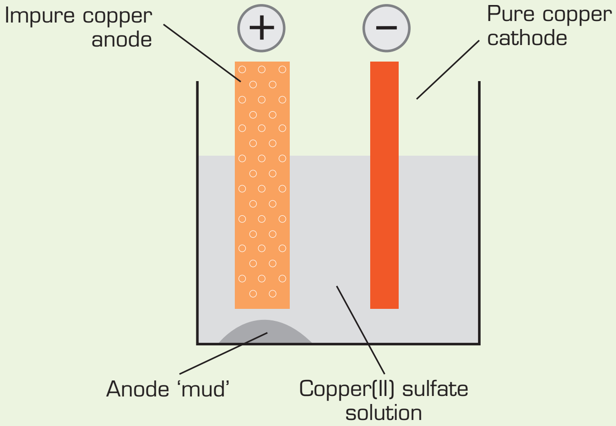


figure mn.4 Electrolytic refining of copper.

Huge advances in technology have led to the use of reusable stainless steel electrodes, improved efficiency and higher purity of product. This technology, developed for the Townsville refinery, is now used in other refineries worldwide.

Nickel

Nickel (Ni) is a grey metal that has a high melting point and magnetic properties, and is very strong. It was first isolated as a metal in the 1800s, but had no apparent use at the time. Today it is widely used in alloys, particularly stainless steel, due to its strength and resistance to corrosion. Australia is one of the world's major nickel producers. Queensland has a large nickel refinery at Yabulu, north of Townsville. This refinery is unique in that processing from the mined ore to the finished metal takes place at one site. Another valuable metal, cobalt, is frequently found in nickel ores, and the refinery is able to profit from extracting cobalt as well.

Nickel can be found in different forms. Until 1993 nickel ore, typically sulfide ores such as pentlandite [$(Ni,Fe)_9S_8$], was mined at Greenvale and railed to Yabulu. This ore was associated with volcanic rock and found well below the surface, with a grade of 1–4%. This mine has been closed as it is currently uneconomic to mine the very deep deposits that remain. A nickel mine has also operated near Marlborough in central Queensland.

figure mn.5 An open-cut nickel mine.

The Yabulu refinery now processes laterite nickel ore from New Caledonia and Indonesia, and refines processed mineral from Western Australia. Laterite ores are found closer to the surface, and have typically reacted by weathering. They consist of poorer quality nickel oxides, such as limonite [$(Fe,Ni)O(OH)$], from which it is more difficult to extract the nickel. They are cheaper to mine, as open-cut mines are usually used (figure mn.5). New research has resulted in chemical means that make processing these poorer quality ores economically viable, and the nickel refinery has undergone considerable modification, expansion and redevelopment. A solvent (ammonia) extraction plant was installed in 1989 to assist in the separation of higher quality nickel and cobalt products. High quality cobalt has been produced since 1997, when the cobalt plant was installed. The processing of this metal, found in the same ore, adds to the economic viability of the refinery. The refinery now produces about 2000 tonnes of cobalt per annum.

The rocks containing the nickel oxides or nickel sulfides are crushed into fine particles, then froth flotation is used to separate the mineral from the gangue. This process increases the concentration of nickel in the ore to about 20 times its initial concentration. The nickel ore is then dried, reduced and leached with ammonia. Nickel is precipitated as nickel carbonate, which is further treated to give a sinter (solid mass) of nickel and nickel oxide containing 85%, 88%, 98% or 99.5% nickel. Nickel oxide is reduced to nickel using hydrogen gas in furnaces:

$$NiO(s) + H_2(g) \rightarrow Ni(s) + H_2O(g)$$

Experiment mn.1

Froth flotation

materials

- copper oxide 'ore' (a prepared mix of copper oxide powder and sand)
- 20 mL washing detergent
- water bottle with nozzle
- filter paper
- glass stirring rod
- spatula
- 500 mL beaker
- 25 mL measuring cylinder
- electronic balance

Purpose

Froth flotation is a method of concentrating finely ground ores. The process involves chemical treatment of an ore pulp so that the desired mineral particles will attach themselves to air bubbles. The air bubbles carry the selected minerals to the surface of the pulp where they form a froth that can be skimmed off. One use of froth flotation is in nickel refining. In this experiment copper oxide will be used as the ore, but the principle is the same.

Method

1. Weigh 10 g of the copper oxide 'ore' into a 500 mL beaker.
2. Add 20 mL of detergent to the ore and stir thoroughly.
3. Squirt in 300 mL of water from a water bottle, stir vigorously to agitate the bubbles.
4. Scrape off the froth layer containing copper oxide with a spatula and wipe the froth onto a filter paper.
5. Examine the froth on the paper and the remains in the beaker.

Discussion

1. Discuss the efficiency of this type of physical separation of the copper oxide from the copper ore, with your group.
2. Chemists spend a great deal of time researching ways of optimising procedures. Try changing some of the variable in this experiment (e.g. the amount of detergent, method of adding water) to see if you can improve the efficiency of this process.

Zinc

Zinc has a typical silver, metallic lustre. It is more reactive than iron but develops a protective oxide layer, so it finds use in galvanising to provide anti-corrosion layers for iron and steel. Other uses are in brass and cosmetics (e.g. zinc cream). Figure mn.6 shows galvanised iron roofing.

Zinc is mined in various parts of north-west Queensland, which boasts some high-grade ores. The ore is finely crushed and then concentrated by froth flotation, before transport to a refinery in Townsville or overseas. In froth flotation the finely crushed ore is mixed with water and a flotation agent, which is a type of surfactant. The agent is attracted to the desired mineral fragments. Air bubbled through the mixture also attaches to the agent and the desired mineral floats to the surface and is skimmed off.

The concentrate contains zinc sulfide, ZnS, along with other minerals. At the refinery, roasting in air converts zinc sulfide to zinc oxide:

$$2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$$

The product of roasting contains 80% zinc oxide and is ready for leaching. When the zinc oxide is leached with a solution of sulfuric acid, the following reaction occurs:

$$ZnO(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + H_2O(l)$$

In the final stages of leaching, air is added, which oxidises Fe^{2+} to Fe^{3+} and causes $Fe(OH)_3$ to precipitate. This precipitate and solid silica (a waste mineral) settle out with the aid of a flocculant, leaving a solution that contains mostly zinc sulfate and a few other unwanted metal ions.

figure mn.6 Galvanising with zinc protects this roof from rusting.

Section 6.2 **Preciptation reactions** describes the formation of solid products from reactant solutions (page 331).

In the next process, purification, fine zinc powder causes ions of copper and cadmium to be reduced to solid metals. These solids are filtered out under pressure. Nickel and cobalt are reduced and removed by further addition of zinc. For example:

$Ni^{2+}(aq) + Zn(s) \rightarrow Ni(s) + Zn^{2+}(aq)$

Cooling the resulting solution allows calcium sulfate to crystallise and settle out:

$Ca^{2+}(aq) + SO_4{}^{2-}(aq) \rightarrow CaSO_4(s)$

The solution now contains zinc and sulfate ions. Electrolysis is used to reduce the zinc ions to zinc metal. This process, called electrowinning, may seem superficially similar to the electrorefining process used to purify copper. Can you identify the difference?

Like copper, but unlike aluminium (see next section), zinc is able to be reduced by electrolysis of an aqueous solution.

The half-reactions occurring are given.

Anode half-reaction: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode half-reaction: $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

The 99.995% pure zinc is cast into ingots and shipped worldwide. The spent solution from this process contains both hydrogen and sulfate ions, making it a solution of sulfuric acid, that can be reused during leaching.

Aluminium

Aluminium is the most common metal in the Earth's crust. Pure aluminium is a shiny, silvery-coloured metal. It is malleable and ductile and so can be used for a wide variety of purposes, including transport, packaging, electrical equipment and construction. Australia is a major world producer of bauxite (aluminium ore) with 22% of the world's reserves. Alumina and aluminium production are major industries and most of the mining and processing takes place in Queensland. Gladstone boasts the world's newest and most technologically advanced alumina plant and the world's largest aluminium refinery. More than 6% of the world's aluminium is produced here. This region was chosen because of its proximity to other natural resources and to energy supplies—it is close to coalfields and power stations. Another refinery may be built in the north of the state.

Aluminium is naturally found as bauxite, which contains the minerals gibbsite ($Al(OH)_3$), boehmite ($AlO(OH)$) and diaspore. Diaspore has the same composition as boehmite but is denser. Bauxite can be formed in different shapes and colours, but is often seen as small, hard, orange-red balls.

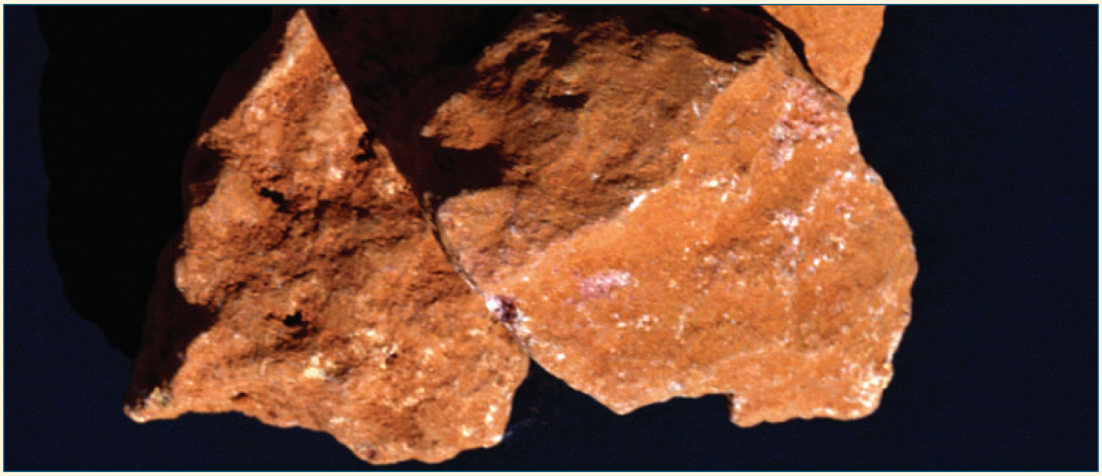


figure mn.7 Bauxite.

Bauxite is shipped to Gladstone from Gove (NT) and Weipa (Qld), which boasts the world's largest bauxite mine. In 1802, Matthew Flinders first noted the mineral potential at Weipa. Some alumina is also produced in Western Australia. The bauxite is mined in shallow, open-cut mines, and the area is revegetated after mining. The mined bauxite is washed and dried to remove mud and it is then processed in two stages. First bauxite is refined to produce alumina (aluminium oxide, Al_2O_3), then the alumina is processed to aluminium metal: 4 tonnes of bauxite produces about 2 tonnes of alumina and 1 tonne of aluminium.

Bauxite is refined into alumina, Al_2O_3, by the Bayer process. Extraction of aluminium from alumina is by the energy-intensive Hall-Héroult process, shown in figure mn.8. The alumina is mixed with molten cryolite, Na_3AlF_6 at 970°C. Electrolysis of the molten mixture reduces the aluminium ions to metallic aluminium, and oxidises the carbon anodes to carbon dioxide. Aluminium ions cannot be reduced from an aqueous solution because it is so difficult to reduce aluminium ions that water would be reduced instead.

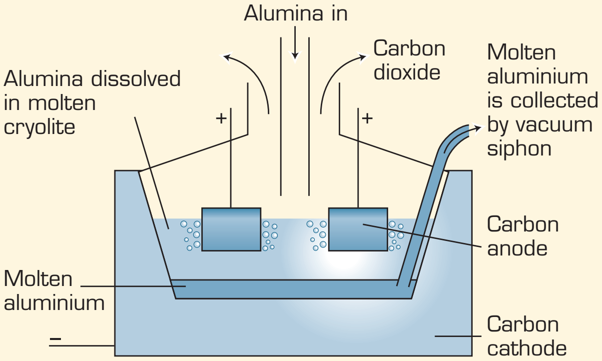


figure mn.8 In the Hall-Héroult process an electrolytic cell is used to produce the pure aluminium.

Consider this

1. One tonne of zinc concentrate contains 60% ZnS. Calculate the mass of ZnO formed during roasting. What volume of SO_2 measured at 30°C and 1 atm pressure would be produced? What is the total final mass of zinc metal formed, if the processes as a whole operate at 92% efficiency?
2. For the metals studied, use the reduction potentials in Table. 7.2 to arrange them in order. Discuss the relative difficulty of extracting each metal, in terms of the methods used, the energy consumed and the costs associated with the extraction, and relate it to the reduction potentials.
3. Western Australia produces 17% of the world's alumina, yet it is sent to Queensland for refining. Why is this?
4. Create a poster showing how aluminium can be recycled, and outline the advantages of recycling over producing aluminium from its ore.
5. Laterite nickel ores, which are oxides, are found much closer to the surface than nickel sulfide ores. Why is this? What happens to the sulfides when they are close to the Earth's surface?
6. In the pressure acid leach stage of nickel refining, the nickel ore is mixed with hot sulfuric acid in titanium-lined autoclaves. Why is it useful to have the containers lined with titanium?

Further investigations

Many other minerals are mined in Queensland, including corundum, ilmenite, rutile, salt and zircon. Find out more about one of these minerals, where it is mined and how it is processed. Share your knowledge with your class in an oral presentation.

chemicals from the sea

figure cs.1 Sea water—a subtle blend of compounds resulting in a distinct flavour.

Anyone who has had a swim in the ocean is aware of its salty taste. Sea water contains many salts besides the common sodium chloride. ‘Salt’ is a term used for an ionic substance usually made up of a metal cation and a non-metallic anion. The numerous substances dissolved in the world’s oceans result in a giant soup of ions.

* Section 2.2 **Ionic bonding** describes ionic substances and the ions of which they are made up (page 229).

What is in sea water?

From the amounts shown in figure cs.2, it can be seen that sodium chloride does make up a major portion of the dissolved salts in sea water but there are significant amounts of other ions present. The proportions of each ion shown are fairly constant worldwide although concentrations do vary.

In areas where a lot of fresh water enters the sea, the concentrations of dissolved salts are lower. These are areas near the mouths of rivers, places of high rainfall and polar regions with abundant icebergs. Areas that tend to have higher levels of dissolved salts include those where the rate of evaporation is high, i.e. regions of high temperatures, high winds and low rates of circulation of water.

Some of the salts in sea water are dissolved from soil as rain falls on the land and flows into rivers eventually arriving in the oceans. However chloride, bromide and sulfur ions found in sea water are not found in river water to any great extent. These must come from another source.

Volcanic activity on the ocean floor releases gaseous compounds of chlorine, bromine and sulfur into the water. Water also gushes into the cracks in the sea bed that open up during volcanic activity and dissolves soluble minerals. Molten material below the Earth's crust is a greater source of these elements than rocks and soil of the Earth's crust itself. Figure cs.3 shows the major sources of the various ions found in sea water.

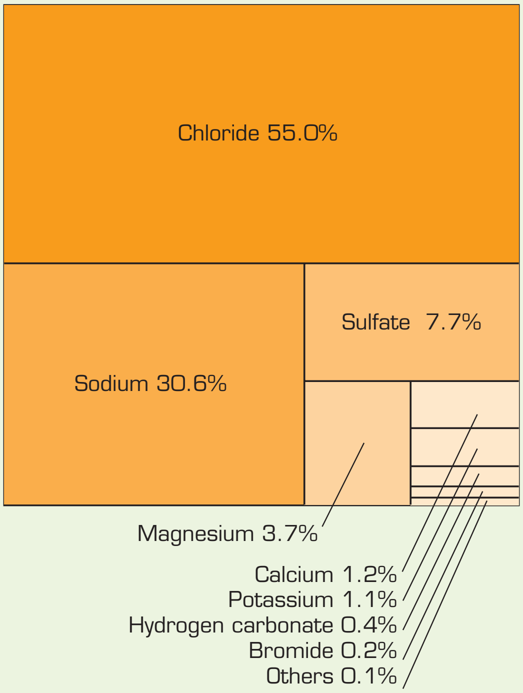


figure cs.2 The amounts of different ions in sea water as a percentage of the total mass of ions present.

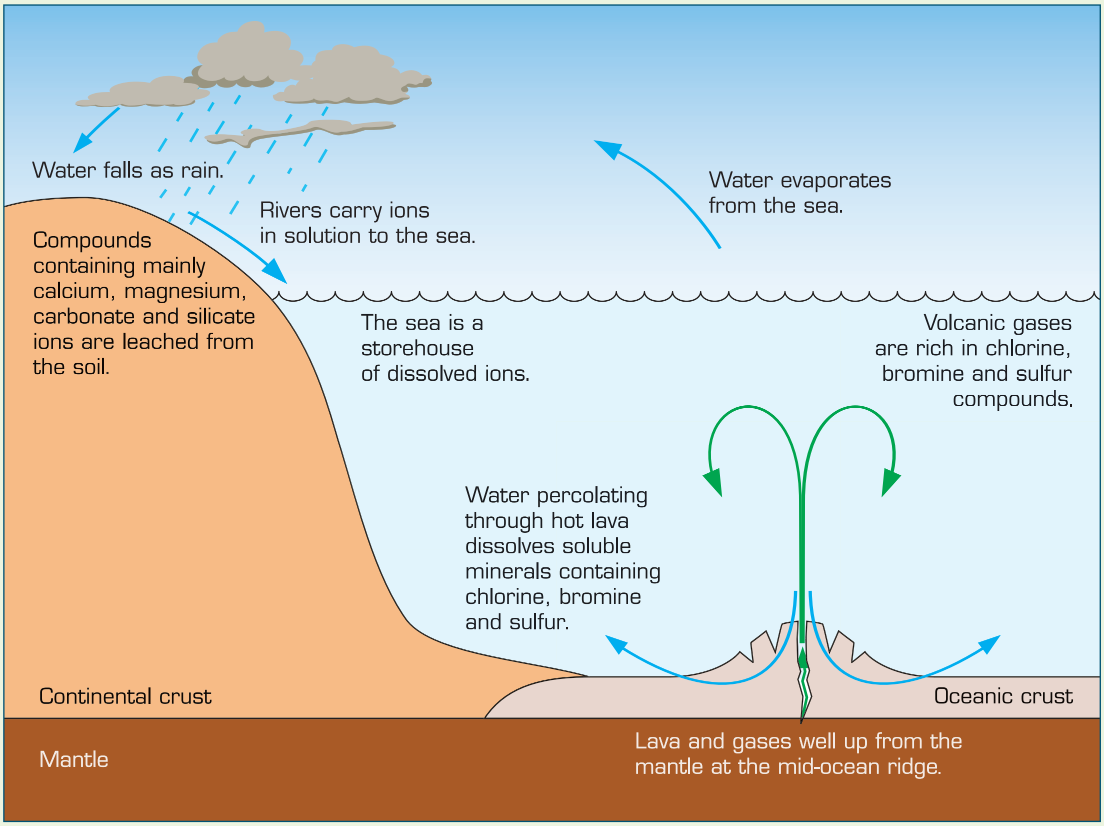


figure cs.3 The dissolved ions of sea water come from both the Earth's crust and the molten material below the Earth's crust.

Mining the sea

While the sea is likely to contain ions of most elements in vast quantities, the enormous volume of water means that they are present in tiny concentrations. Few are present in concentrations that make them economically viable to extract from the oceans' waters.

Common salt—sodium chloride

Sodium chloride is present in the body fluids of animals including humans and is essential for normal body function. Some is lost each day in urine and sweat, and needs to be replaced. Excess salt intake can be dangerous and result in poor health due to such ailments as high blood pressure. Long before the invention of refrigerators and freezers, salt was used as a substance to preserve food. The importance of salt and its value to society can be demonstrated by the way that it was used in ancient times as a means of paying Roman soldiers their salary.

Some countries, for example the UK, meet their demand for salt through the mining of large underground deposits of rock salt. In Australia, salt is obtained from salty inland lakes or by the evaporation of sea water by the heat of the sun at purpose-built facilities. In some countries where the climate does not allow the efficient evaporation of sea water by the sun, sea water is heated in factories to increase the rate of evaporation.

Since sea water contains more than just sodium and chloride ions the process involves more than just getting rid of water. As sea water comes to the boil some impurities (including biological impurities) form a scum on the surface which needs to be skimmed off. Calcium sulphate has one of the lowest solubilities of the substances present and forms a scum on the walls of the boiling vessel. As more water evaporates, sodium chloride crystals form and are removed before the magnesium compounds of higher solubility begin to crystallise. Magnesium compounds give the product a bitter taste if allowed to contaminate the collected salt.

* Section 4.1 **Dissolving** describes the different solubilities of ionic substances (page 286).

While sodium chloride solution can be a useful substance in itself, it can also be useful as a starting material from which to obtain other substances.

The electrolysis of a sodium chloride solution can be used to obtain chlorine and hydrogen gas.

At the anode $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

At the cathode $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$

figure cs.4 Salt is obtained from sea water by using evaporating lakes.

The sodium ions remaining in solution are able to combine with hydroxide ions to form sodium hydroxide.

If instead of an aqueous solution of sodium chloride, molten sodium chloride is used then the following reactions take place.

At the anode $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

At the cathode $2Na^+(aq) + 2e^- \rightarrow 2Na(l)$

* Section 7.4 **Ease of oxidation** describes the electrolysis of dissolved and molten sodium chloride (page 348).

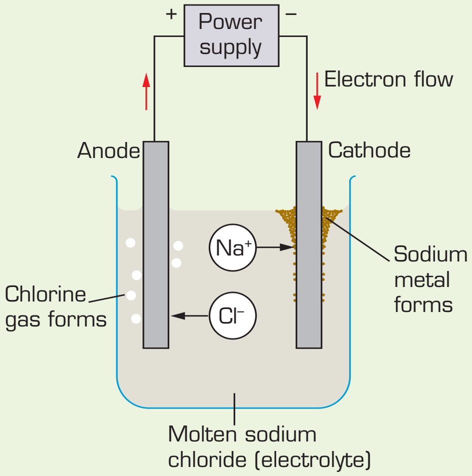


figure cs.5 The electrolysis of molten sodium chloride.

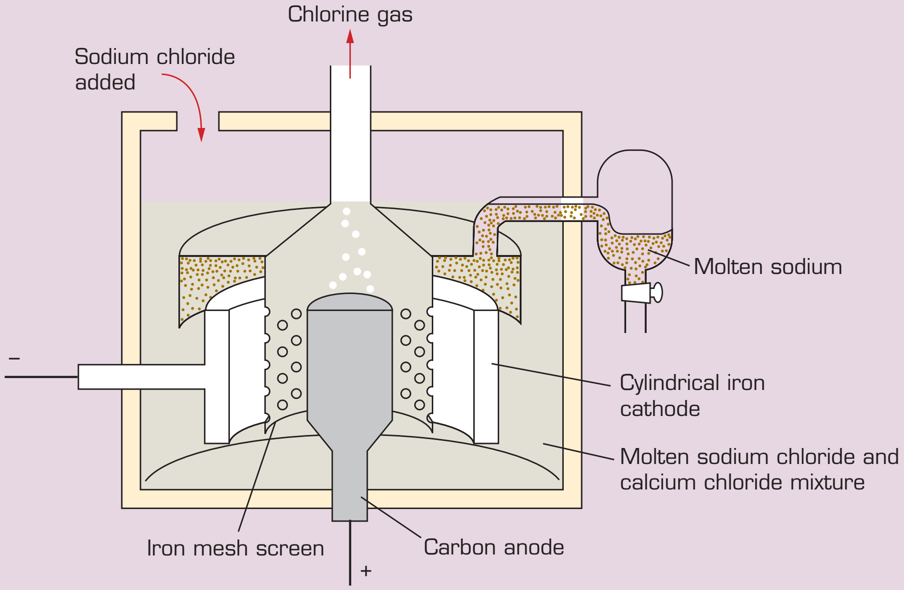


figure cs.6 The Downs cell for the commercial electrolysis of molten sodium chloride.

Gold

Fritz Haber, the German chemist famous for the process he developed to produce ammonia, designed a device to extract gold from the sea. After World War I, Germany had a massive war debt and Haber thought that this debt could be repaid by removing gold from gold compounds dissolved in sea water. His devices were attached to the German ships and as they travelled the world they were to collect gold along the way.

Haber had made his predictions based on an estimated concentration of gold in the sea. Unfortunately, the figure he used was unrealistically high and the vast amounts of gold he expected were never extracted. The estimates of gold concentration in the sea have been getting progressively smaller with time. Prior to 1988 the concentration was accepted as 4×10^{-9} g L^{-1} but a survey conducted from 1988 to 1990 came up with a maximum concentration of 1×10^{-11} g L^{-1} of gold in sea water. That means that 10^{11} L of water would have to be processed to obtain 1 g of gold.

Bromine

Bromide ions make up only 0.2% of total ions yet sea water is the main source of bromine. The highly corrosive liquid exists as a deep red liquid at room temperature but readily gives off a dense acrid vapour. It is manufactured on a large scale and used extensively in a range of important applications (figure cs.8).

Converting bromide ions into bromine can be done in the school laboratory by simply adding chlorine water to a solution containing the bromide ions. However, the low concentration of bromide ions in sea water means that industrially the four-step process outlined in table cs.1 is required.

figure cs.7 People have long tried to find easy ways to obtain gold. The oceans don't give up their gold easily.

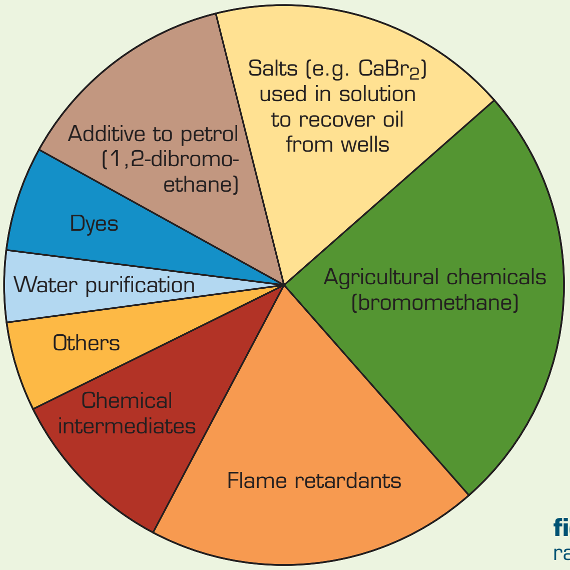


figure cs.8 The wide range of uses of bromine.

Chapter 7 **Redox reactions** describe oxidation and reduction processes (page 338).

table cs.1 The extraction of bromine from sea water.

Step	Process	Reactions
1 Bromide ions oxidised to bromine.	Sulfuric acid is added to sea water to lower the pH from about 8 to 3.5. This stops Br_2 and Cl_2 reacting with water. Excess chlorine is added to acidified sea water to produce bromine.	Reaction with water: $Br_2(aq) + H_2O(l) \rightarrow HBr(aq) + HBrO(aq)$ (Lowers the yield of Br_2 obtained.) $Cl_2(aq) + H_2O(l) \rightarrow HCl(aq) + HClO(aq)$ (This uses up chlorine that should be used in oxidising bromide ions.) $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$ (Bromide ions are oxidised.) $Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$ (Chlorine, the oxidising agent, is reduced.) $Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$
2 Bromine vapour removed.	In a blowing-out tower (figure cs.9) a current of air passes up as the treated water is sprinkled over a packing. The volatile bromine passes into the air ready for further concentration.	
3 Bromine reduced to hydrobromic acid.	Sulfur dioxide gas is injected into the blowing-out tower to reduce the bromine to hydrobromic acid (sulfuric acid also reforms). An injection of fresh water absorbs the acids which are condensed in absorber packing.	$Br_2(aq) + SO_2(g) + 2H_2O(l) \rightarrow 2HBr(aq) + H_2SO_4(aq)$
4 Hydrobromic acid oxidised to bromine.	In a steaming-out tower chlorine is used to oxidise the hydrobromic acid to bromine, which is then distilled using steam. As the hot vapour mixture cools it condenses into two liquid layers, an upper aqueous layer and a lower layer of bromine. Traces of water are removed using concentrated sulfuric acid.	$2HBr(aq) + Cl_2(g) \rightarrow Br_2(g) + 2HCl(aq)$

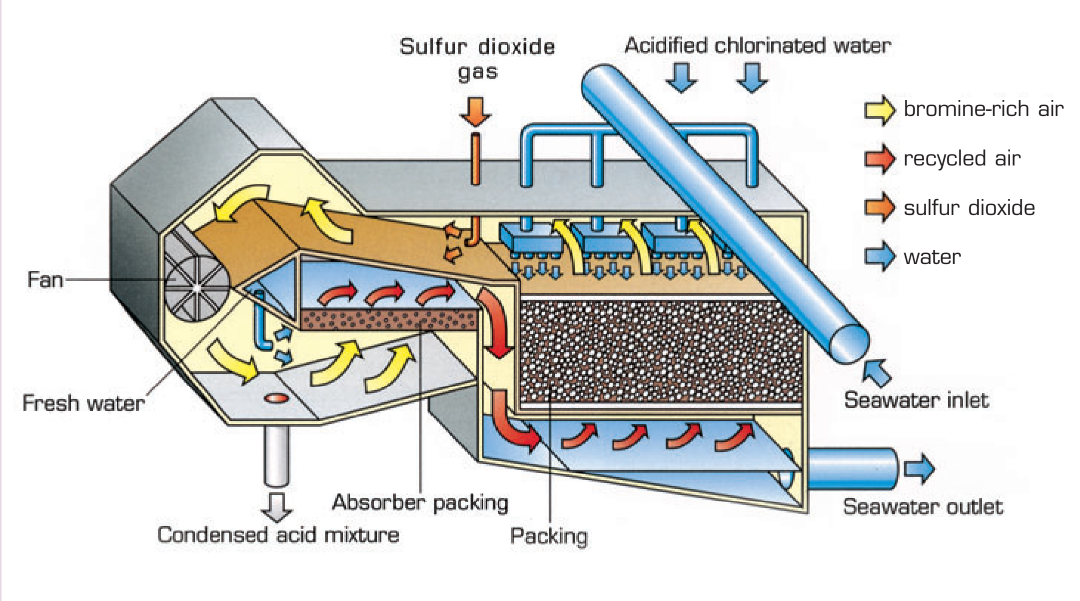


figure cs.9 A blowing-out tower used in the extraction of bromine from sea water.

figure cs.10 The liquid bromine produced after leaving the steaming-out tower.

The Dead Sea: a special case

The Dead Sea has the highest concentrations of dissolved ions of all the Earth's seas (table cs.2). It is a special case for several reasons.

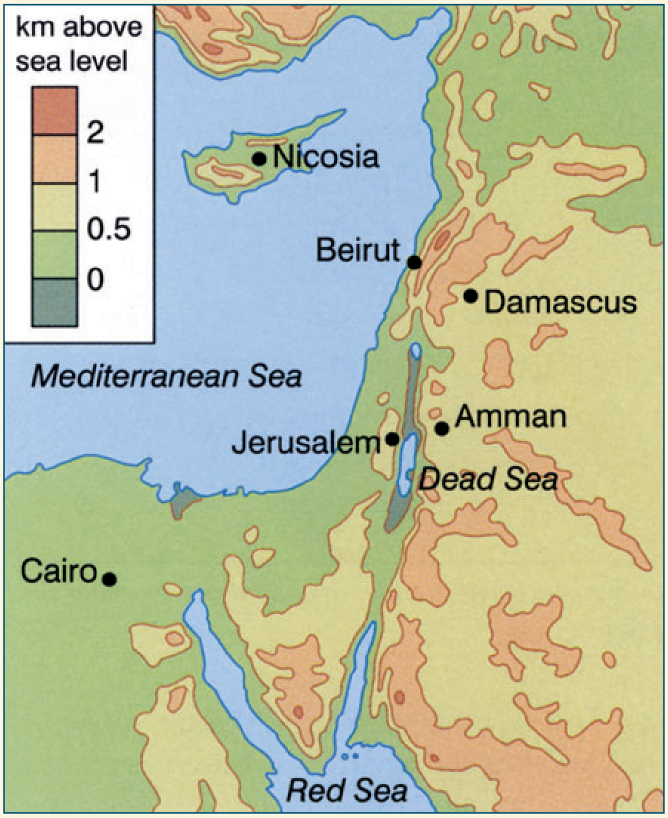
1. It is a dead end—the River Jordan flows into it but no water flows out.
2. It is in a deep valley and is actually 400 m below normal sea level. It is the lowest land surface on Earth.
3. It is surrounded by desert and the extreme heat steadily evaporates the water, resulting in a high concentration of ions.

A thriving chemical industry has developed around the Dead Sea. Just some of the chemicals produced from waters of the Dead Sea include:

- potassium chloride (potash) for use in the manufacture of fertilisers
- magnesium salts and metallic magnesium for use in alloys associated with the automobile and aerospace industries
- magnesium chloride flakes and pellets for de-icing roads in cold climates
- aluminium chloride for catalysis of organic reactions
- common table salt.

table cs.2 The typical analysis of ions in water from the Dead Sea compared to the Earth's oceans.

	Dead Sea water	Ocean water
Ion	Mass in g found in 1 L of water	Mass in g found in 1 L of water
Na^+	39	11
K^+	6.9	0.4
Mg^{2+}	39	1.3
Ca^{2+}	17	0.4
Cl^-	208	19
Br^-	5.2	0.07
HCO_3^-	Trace	0.1
SO_4^{2-}	0.6	2.5
Total	315.7	34.77



Companies associated with the Dead Sea chemical industries are among the largest providers of bromine and bromine compounds to the world markets. All of these products and many others are from an area which, prior to the 1980s, was regarded as being in short supply of natural resources.

figure cs.11 A map of the Dead Sea and surrounds.

Further investigations

1. Dissolved solids are continually being added to the Earth's oceans by rivers and volcanic activity and yet their concentrations have stayed pretty much the same for millions of years. Find out how this is possible by performing some research into the ways that ions are removed from the oceans by natural processes.
2. Find out the types of soluble gold compounds that could be present in sea water and devise a method for the extraction of gold. Conduct some research into the devices that Haber developed and find out how they worked.
3. Research industries that utilise sea water in Australia, the chemicals they extract and the methods they use.
4. Find out more about the chemical industries of the Dead Sea and the methods of extraction they use for products such as magnesium metal.
5. Are there any places in Australia that are geographically similar to the Dead Sea that would make a good site for a similar chemical industry? Do any such chemical industries already exist?
6. According to table cs.2 the concentration of most ions is higher in the Dead Sea than in ocean waters. However the concentration of sulfate ions is listed as lower in the Dead Sea. Find out about the sources of sulfate ions for both the Dead Sea and the oceans, and try to account for the difference.

electrochemistry

We are surrounded by objects made wholly from metal or that contain metal components. With only a few exceptions, metals are found in combination with other elements and undergo many processes to arrive at a stage that makes them useful. Many of the final processes involve the use of electrical energy to cause a chemical change that may purify a metal, to coat an object with a metal to protect it from corrosion or simply to make it look attractive. Electrochemistry involves using a chemical reaction to produce electrical energy or, in reverse, the use of electrical energy to produce a chemical change.

figure ec.1 To create this trophy, electrical energy has been used to cause a chemical change to create the final product.

Purifying metals

Electrorefining

Electrolytic cells are used in the electrorefining process to purify many metals such as copper, lead and silver. Figure ec.2 illustrates the electrorefining process of copper.

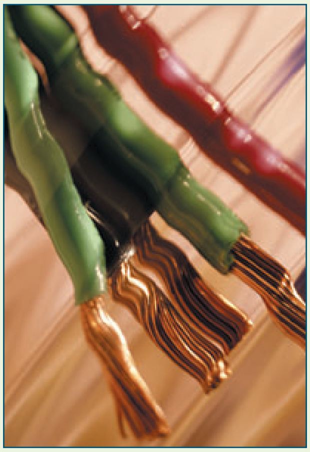


figure ec.3 Copper needs to be very pure to work effectively as an electrical conductor. Copper is refined to approximately 99.98% purity.

Electrorefining uses electrolysis to extract a metal from an impure anode. The pure metal is deposited at the cathode. Electrorefining is also referred to as electrolytic refining.

* Section 7.1 **Oxidation and reduction** describes the features of redox reactions of which electrochemical processes are examples (page 338).

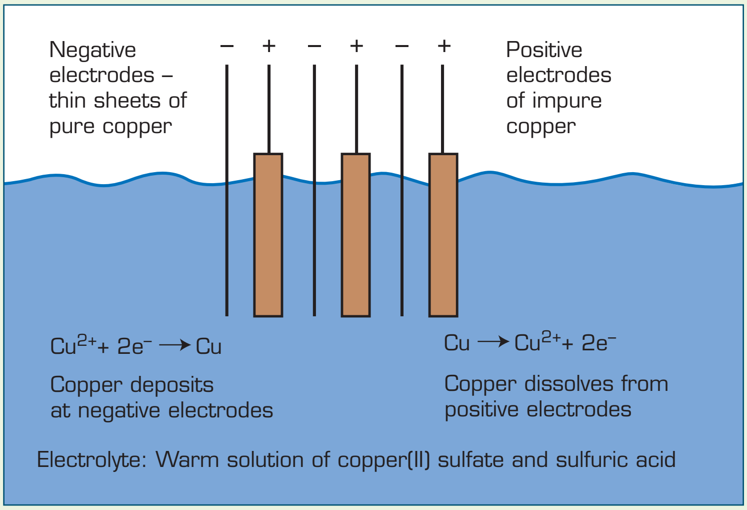


figure ec.2 The electrolytic cell set-up for the electrorefining of copper.

The anode half equation is

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

The cathode half equation is

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

The copper at the anode is impure. It loses electrons to form ions, which then accept electrons at the cathode made of pure copper. The copper that forms on the cathode during this process is pure. When the process is complete, which may take several weeks, the pure copper is literally peeled off in sheets from the cathode. Impurities in the original copper form a sludge at the bottom of the electrolytic cell and are removed to avoid any contamination. Some metals, particularly silver, platinum and gold, are removed from the sludge before disposal.

* Section 7.4 **Ease of oxidation** describes electrolytic cells (page 348).

figure ec.4 The electrowinning of zinc is an important industrial process. Zinc is alloyed with copper to make brass and form objects such as this brass key.

Electrowinning

Electrowinning uses electrolysis to extract metals from solution. As the metal to be purified is not solid, the anode is made from a material that is insoluble in the metal solution, such as lead. The pure metal is deposited on the insoluble cathode. Metals commonly purified by electrowinning include zinc, magnesium and aluminium.

In the electrowinning of zinc, an acidified solution of zinc sulfate is placed in an electrolytic cell. The lead anode becomes coated with an insoluble layer of lead(IV) oxide, PbO_2. Oxygen gas is liberated at the anode and zinc is deposited on an aluminium cathode. The zinc is removed from the cathode, melted and cast into ingots or slabs.

figure ec.5 Galvanising iron by electroplating protects the iron underneath from corrosion. Galvanised iron is commonly used as roofing.

Electroplating

Electroplating is an electrochemical process that involves coating a metal object with a thin layer of another metal. Galvanised iron is a sheet of iron that has been electroplated with zinc to protect the metal underneath from corrosion. Tin cans are made of steel with a thin coating of tin, again to prevent corrosion. Objects such as taps are coated with chrome to resist corrosion, as well as to look attractive. Solid silver or gold jewellery or cutlery would be expensive, so often they are made from a cheaper metal such as copper and then coated with a thin layer of a more expensive metal. The teapot in figure ec.7 has been electroplated with silver. It looks attractive and is inexpensive compared to a solid silver teapot.

Electroplating takes place in an electrolytic cell. Figure ec.8 shows how an electrolytic cell would be used to electroplate an object with silver. The object to be electroplated is used as a cathode and is immersed in a salt solution of the metal to be plated, in this case silver. The anode is a silver electrode from which electrons are drawn. Silver ions are formed and pass into the solution, replacing the silver ions being reduced. An electric current provided to the cell pushes electrons to the cathode. Silver ions in the solution accept electrons to form silver atoms, which adhere to the object being plated (used as the cathode).

The reaction at the anode is

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

The reaction at the cathode is

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

figure ec.6 Steel cans are electroplated with tin to prevent corrosion.

figure ec.7 This teapot looks as if it is made of solid silver. It is actually made from a cheaper metal with a thin layer of silver covering the outside.

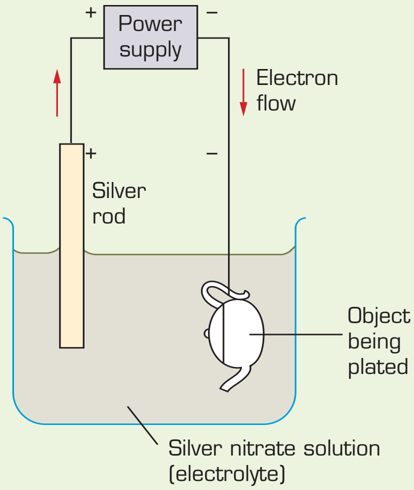


figure ec.8 An electrolytic cell for the electroplating of silver.

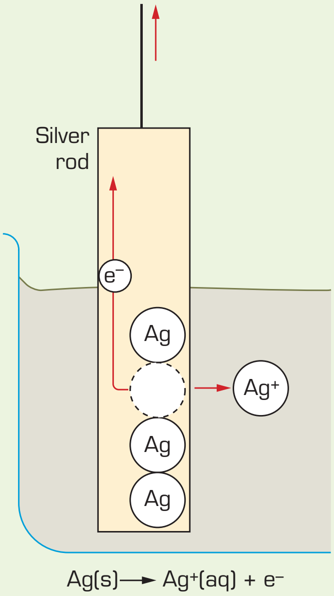


figure ec.9 The process occurring at the anode during electroplating.

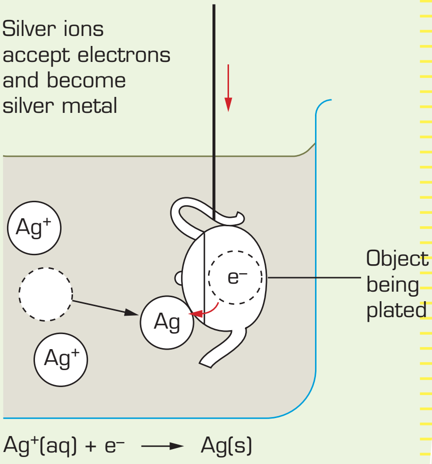


figure ec.10 The process occurring at the cathode during electroplating.

Experiment ec.1

Electroplating

Purpose

To construct and observe the operation of various electroplating cells and to investigate the changes in mass at the anode and the cathode.

Method

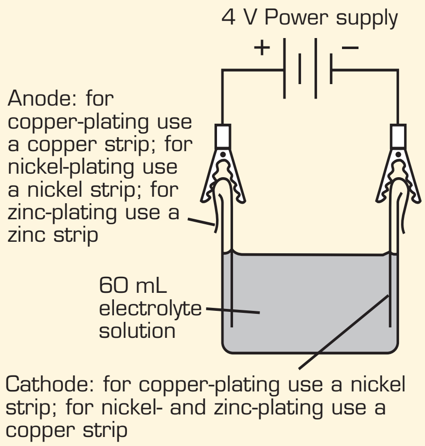


figure ec.11 Circuit for electroplating.

1. Your teacher will tell you which electroplating cell to construct first. Refer to figure ec.11 to determine which metal strips to use for the anode and cathode of the cell. (For nickel- and zinc-plating cells, use a copper strip as the cathode so that the metal deposit can be seen more clearly; use a nickel strip as the cathode in the copper-plating cell.) Before constructing your cell, clean the electrodes with a scourer.
2. Use a marking pen to label the electrode to be used as the cathode 'C'. Measure and record the mass of the anode and that of the cathode.
3. Construct the electroplating cell and electric circuit as shown in figure ec.11.
4. Adjust the voltage of the power supply to about 4 V. Operate the cell for 10 minutes, noting any changes that occur at the electrodes.
5. Carefully remove the electrodes from the electrolyte. Wash them by first dipping them into a 100 mL beaker half-filled with water and then into a 100 mL beaker half-filled with acetone. When the acetone dries, measure and record the mass of each electrode.
6. If directed to do so by your teacher, repeat steps 1–5 for another electroplating cell.

Discussion

1. Describe what happens at the electrodes of each cell. Write half equations for the electrode reactions.
2. Calculate the change of mass that occurs at the anode and at the cathode of each electroplating cell.
3. What can be said about the change in mass at the anode and at the cathode?
4. Predict what you would see if, after electroplating for several minutes, you reversed the connections of the wires to the electrodes.
5. Tin is electroplated onto steel cans to protect the iron in the steel from corroding. Sketch and label a cell that could be used for this purpose.

Alternative activity

A silver-plating cell could also be constructed. Prepare a suitable electrolyte by slowly adding saturated potassium iodide solution to 25 mL of 0.1 M silver nitrate solution in a 100 mL beaker. Continue adding the potassium iodide solution, stirring constantly, until the precipitate of silver iodide that forms just dissolves. A carbon rod may be used as the anode for the cell.

materials

- 60 mL electrolyte solutions for copper-, nickel- and/or zinc-plating cells
- copper, nickel and/or zinc strips (as appropriate), about 7 cm × 2 cm
- 50 mL acetone (propanone)
- 3 × 100 mL beakers
- scourer or sheet of emery paper
- marking pen
- 2 × wire leads with alligator clips
- DC power supply
- electronic balance

safety

- Wear safety glasses and a laboratory coat for this experiment.
- The electrolyte solutions are corrosive and toxic.
- Acetone is flammable. Do not use it near flames.
- Dispose of waste acetone by pouring it into an organic wastes container. Do this in a fume cupboard.

Anodising aluminium

Aluminium is a reactive metal, but when it reacts with oxygen in the air the oxide coating that forms is very resistant to corrosion. The reaction between aluminium and oxygen occurs spontaneously and forms a corrosion-resistant layer.

$$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$$

Anodising aluminium uses an electrolytic cell to increase the thickness of this oxide layer. This makes the anodised item hard and resistant to corrosion. During this process, the object can also be coloured and the result is an attractive appearance.

The reactivity of aluminium makes it difficult to extract from the alumina (Al_2O_3) found in the ore, bauxite. The solution was to use electrolysis and was discovered in the mid 1850s. Prior to this, aluminium was very expensive because of its rarity in its metallic form.

figure ec.12 Aluminium is used in objects such as cans, cooking foil, window frames and even aeroplanes.

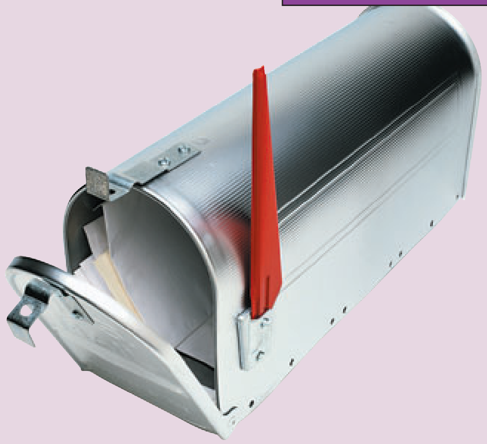


figure ec.13 Some objects are anodised so that they have an attractive appearance. Other objects, like letter boxes and window frames, are anodised so they will be corrosion resistant.

* Section 7.3 **Oxidation numbers and half equations** can be written for electrochemical processes (page 343).

Experiment ec.2
Anodising aluminium

Purpose

To anodise a sheet of aluminium using an electrolytic cell.

Method

A. Anodising aluminium

1 Bend the larger sheet of aluminium into a tubular shape and place it in a 250 mL beaker. This sheet will act as the cathode of an electrolytic cell. Fill the beaker to three-quarters of its volume with 2 M sulfuric acid and add two drops of detergent.

2 The smaller aluminium sheet is to be anodised. Handle it with tweezers, do not touch the aluminium surface. Clean this sheet by scrubbing it with a small piece of paper towelling that has been dipped in a mixture of water and detergent. Rinse the sheet under running water.

3 Use a drawing pin to attach the sheet to an icy-pole stick and suspend it in the centre of the beaker (as shown in figure ec.14). This sheet will act as the anode and must not be in contact with the

cathode. Connect the outer electrode (the larger sheet) to the negative terminal of a power supply and the inner electrode (the smaller sheet) to the positive terminal. Again check that the two electrodes are not in contact.

4 Adjust the voltage to 6 V and, if there is no evidence of a short circuit (e.g. sparking or operation of the circuit breaker in the power supply), increase the voltage to 12 V. Record your observations of the reaction at the cathode.

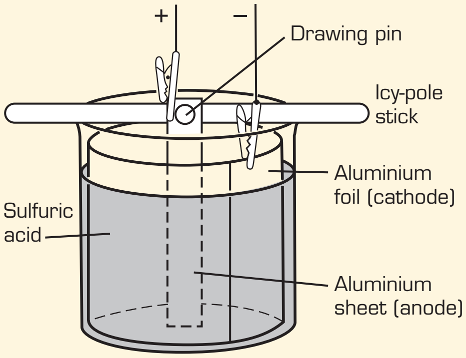


figure ec.14

5 Switch off the power supply after 10–15 minutes. Remove the anode using tweezers, wash it under running water, and record the appearance of the surface of the sheet.

B. Dyeing anodised aluminium

6 So that you will be able to identify it, use a marking pen to label your sheet with your initials and place the sheet in a hot dye bath for at least five minutes.

7 Remove the sheet from the hot dye bath. Seal the dye in the surface of the sheet by placing it in a boiling water bath for another five minutes. Record your observations.

C. Testing

8 Use a conductivity apparatus to test the conductivity of the anodised surface. Observe and record what happens when the probes of the apparatus touch the surface and when they are pushed hard into it. Compare this with what happens when the same tests are performed on the portion of the sheet that has not been anodised.

Theory

Aluminium metal is covered by a thin layer of aluminium oxide. The oxide layer becomes as much as 1000 times thicker as the aluminium metal is oxidised and tiny channels, or pores, are formed in the surface layer. These pores are usually sealed by immersing the anodised object in boiling water. The water penetrates the oxide to a limited extent, causing it to expand and the pores to close up.

Discussion

1 Why is the aluminium to be anodised cleaned and then handled using tweezers?

2 How does the appearance of the surface of the aluminium anode change during anodising?

3 Suggest the identity of the gas that forms at the cathode and write half equations for the electrode reactions.

4 Explain why the anodised aluminium sheet absorbs dye, and account for the results of the conductivity tests.

materials

- 200 mL of 2 M sulfuric acid
- aluminium sheet, 20 cm × 7 cm
- aluminium sheet, 2 cm × 10 cm
- detergent
- 250 mL beaker
- paper towelling
- tweezers
- 2 × wire leads with alligator clips
- DC power supply
- marking pen
- drawing pin
- icy-pole stick or pencil
- hot dye bath (shared by class)
- boiling water bath (shared by class)
- conductivity apparatus

safety

- Wear safety glasses and a laboratory coat for this experiment.
- Sulfuric acid is corrosive.
- Avoid breathing acidic spray produced during electrolysis.
- Ensure that the electrodes of the electrolytic cell do not touch as this forms a short circuit, causing sparks and possible damage to the power supply.

Experimental investigation

What are the optimum conditions for electroplating?

In Experiment ec.1 you set up various electroplating cells. You may have noticed that the electrode being electroplated didn't look that attractive and may not have coated evenly. In the school laboratory, it is difficult to obtain a bright shiny coating of the metal being electroplated. Industrial electroplating is carefully controlled to ensure a uniform coat of a desired thickness.

Find out how electroplating is performed in industry. Design and perform an experiment to determine the best conditions for electroplating. Below is a suggestion of how you could conduct the experiment. You may find that conditions vary depending on the metal being plated or the product being produced. Summarise the results of your investigation by writing a report.

Method

1 **a** Use figure ec.15 to construct an electroplating cell and circuit for electroplating copper metal. Before inserting the copper strip which is to act as the cathode in the cell, clean it using a scourer and measure and record its mass.

b Pass a current of 1.0 A through the cell for 10 minutes. (A voltage of about 8 V is required; adjust the current using the variable resistor.)

c Find the mass of the copper-plated cathode by carefully removing the cathode from the electrolyte, dipping it first into a 100 mL beaker half-filled with water and then into a 100 mL beaker half-filled with acetone. Allow the acetone to dry before measuring the mass of the electrode.

2 Modify the procedure in step 1 to investigate the significance of one or more of the following factors:

a concentration of the copper(II) sulfate solution

b temperature of the electrolyte

c current

d surface area of the cathode immersed in the electrolyte

e any other condition that you think may affect the quality of electroplating.

Be sure to only change one factor each time you perform an experiment.

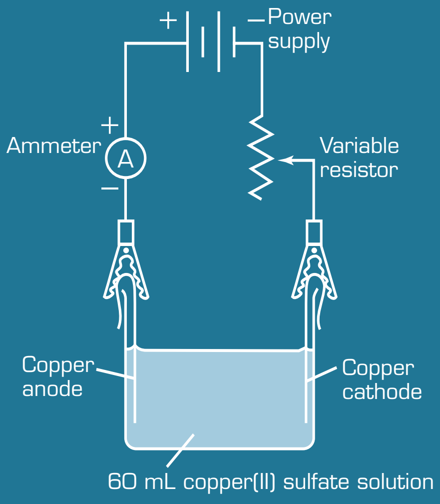


figure ec.15

materials

- 60 mL of 1 M copper(II) sulfate solution
- 2 × copper strips, approximately 7 cm × 3 cm
- 50 mL acetone (propanone)
- DC power supply
- ammeter
- variable resistor
- 3 × 100 mL beakers
- 4 × wire leads with alligator clips
- scourer or sheet of emery paper
- electronic balance
- other materials and equipment as required

safety

- Wear safety glasses and a laboratory coat for this experiment.
- Acetone is highly flammable. Do not use it near flames.
- Copper(II) sulfate solution is toxic and can damage the eyes.
- Dispose of waste acetone by pouring it into an organic wastes container. Do this in a fume cupboard.

Further investigations

1 Find out how electroplating is performed in industry. Find out if some metals are more suitable for electroplating than others.

2 Find out how other metals not discussed already are refined. You may want to present the information in a flowchart.

3 The principles of electrochemistry discussed in this context are used in many other electrolytic cells. Research other applications where electrolytic cells are used to make metals more useful. Look up terms such as electroforming, electroremediation, electropolishing, electroseparation and electrosynthesis. You may find an electrochemistry glossary a useful place to start.

4 Electrowinning is the last process in the extraction of zinc. Research the processes that occur prior to electrowinning. The information could be presented as a flowchart or PowerPoint presentation.

5 Find out how electrowinning is used in metal recovery and waste water reduction and treatment. Comment on its current and future applications.

6 Find out if there are any manufacturers in your area that use electrolytic cells to produce a product, and organise a visit.

food analysis

Consumers are becoming increasingly demanding of food manufacturers. They want to know exactly what is in the food they are eating. Some people need to be aware of the contents in food due to severe allergies, while others want to know so they can maintain a healthy diet. A combination of consumer demand, government regulation and the threat of legal action has resulted in the more specific labelling of food.

figure fa.1 Chemical analysis of food allows consumers to plan a healthy diet.

figure fa.2 Nutritional information on food packaging tells us what is in the food we are eating and in what quantities.

Testing for ions

Section 6.2 **Precipitation reactions** describes reactions with insoluble products (page 331).

Precipitation reactions are a useful way of analysing a substance for particular ions. They can be used to simply test for the presence of the ion or to make accurate measurements.

figure fa.3 Precipitation reactions provide simple means for testing for ions, both qualitatively and quantitatively.

The sample thought to contain an ion of interest is tested with a particular substance, or reagent, such that:

- the ions present in the sample and the reagent react to form a precipitate with a known formula
- the product has a low solubility and precipitates out of solution
- the precipitate is stable enough to withstand heating so it can be dried
- the reagent only precipitates with one ion that is likely to be present in the sample.

For example, silver nitrate is a suitable reagent for testing foods for salt since silver chloride has the properties described above. Silver ions will also form precipitates with bromide, iodide and sulfate ions, but these are unlikely to be present in foods in significant quantities.

table fa.1 The precipitates likely to be formed for this type of analysis.

Element to be analysed	Precipitate
chlorine	AgCl
bromine	AgBr
iodine	AgI
iron	Fe_2O_3
phosphorus	$Mg_2P_2O_7$
magnesium	$Mg_2P_2O_7$
sulfur	$BaSO_4$
barium	$BaSO_4$

Testing for salt

Scientists have found a link between elevated blood pressure and heart disease and excess consumption of sodium chloride (common salt). It is often recommended that people with these conditions reduce their salt intake. It is the sodium content of salty foods that is the main concern of health professionals. Snack foods like potato chips, nuts and fast foods, such as burgers and hot chips, are commonly high in salt.

figure fa.4 The salt added to many foods is a source of sodium. Excess consumption of these foods can lead to health problems.

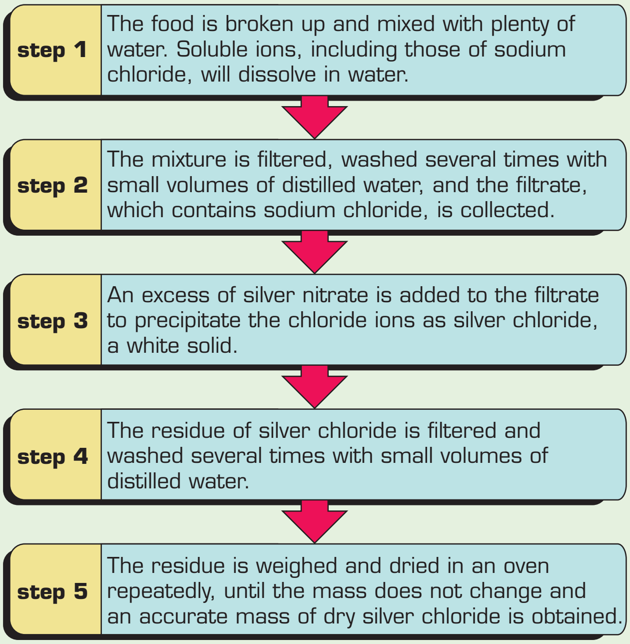
table fa.2 The sodium content of some processed foods.

Food	Sodium content* (g sodium/100 g food)
sausage	1.2
ham	1.1
cheddar cheese	0.7
meat pie	0.5
tomato sauce	1.2
soy sauce	7.0
bread	0.5
potato chips	1.0
olives (pickled)	2.3
salted nuts	4.0
doughnuts	0.5
ice-cream	0.08

*2.5 g of salt (sodium chloride) contains 1 g of sodium

Published nutritional information is often the result of testing by an independent analyst. The chemistry of testing food for salt is fairly simple.

Chapter 3 **Stoichiometry** describes the way amounts of various substances in a reaction can be calculated using a balanced equation (page 268).



step 1 The food is broken up and mixed with plenty of water. Soluble ions, including those of sodium chloride, will dissolve in water.

step 2 The mixture is filtered, washed several times with small volumes of distilled water, and the filtrate, which contains sodium chloride, is collected.

step 3 An excess of silver nitrate is added to the filtrate to precipitate the chloride ions as silver chloride, a white solid.

step 4 The residue of silver chloride is filtered and washed several times with small volumes of distilled water.

step 5 The residue is weighed and dried in an oven repeatedly, until the mass does not change and an accurate mass of dry silver chloride is obtained.

figure fa.5 The steps used for testing the levels of salt in food.

In this process the sodium chloride from the food reacts with the silver nitrate according to the equation

$NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

The net ionic equation is

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

From the mass of silver chloride, the number of moles of silver chloride can be calculated. From the number of moles of silver chloride, the amount (in mol) of sodium chloride can be found using the ratios in the reaction equation. The number of moles of sodium chloride can be used to find the mass of sodium chloride in the initial sample of food.

You can use this method to determine how much salt there is in a sample of chicken soup.

* Section 6.3 **Ionic equations** describes the use of chemical equations and ionic equations to explain precipitation reactions (page 333).

figure fa.6 Highly processed foods like tinned soups tend to have high levels of salt.

Worked example fa.1

A packet of powdered chicken soup was obtained from the supermarket. A 13.415 g sample was thoroughly mixed with approximately 100 mL of distilled water. The mixture was filtered and the residue washed several times with more distilled water from a wash bottle. The filtrate was diluted to 250 mL in a volumetric flask. A pipette was used to transfer 20.00 mL of this solution to a flask and excess silver nitrate added. The silver chloride precipitate was filtered, washed, dried and weighed giving a mass of 0.206 g.

To calculate the amount in moles of silver chloride precipitated:

$$n = \frac{m}{M}$$

$$= \frac{0.206}{143.4}$$

$$= 0.001\,44 \text{ mol AgCl}$$

From the equation

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

1 mol of NaCl yields 1 mol of AgCl.

$$\frac{n(\text{NaCl})}{n(\text{AgCl})} = \frac{1}{1}$$

$n(\text{NaCl}) = n(\text{AgCl}) = 0.001\,44$ mol in 20.00 mL sample

To calculate the amount in moles of NaCl in the whole sample:

$$0.001\,44 \times \frac{250}{20} = 0.0180 \text{ mol NaCl}$$

The mass of NaCl in the original sample is then:

$$\begin{aligned} m &= n \times M \\ &= 0.0180 \times 58.5 \\ &= 1.05 \text{ g NaCl} \end{aligned}$$

Therefore the 13.415 g sample contains 1.05 g of NaCl.
Percent composition (w/w) of NaCl:

$$\frac{1.05}{13.415} \times \frac{100}{1}\% = 7.83\%$$

The percent composition of sodium chloride in the chicken soup is 7.83% (w/w).

Testing for other substances

Some food ingredients cannot be tested directly as their elements are locked up in molecular compounds. These molecular compounds need to be converted into new ionic substances that can be tested by precipitation reactions.

Saccharine is an artificial sweetener sometimes used in diet foods as a replacement for sugar. It is a molecular substance ($C_7H_7NO_3S$) and will not react with ions to form insoluble compounds. If the sulfur in saccharine is first oxidised to sulfate it can be reacted with barium ions. Barium sulfate is low in solubility and will precipitate out of solution. Since each saccharine molecule has one sulfur atom, one sulfate ion will be formed. The amount of precipitated barium sulfate is a direct indication of the amount of saccharine in a sample of food.

Experimental investigations

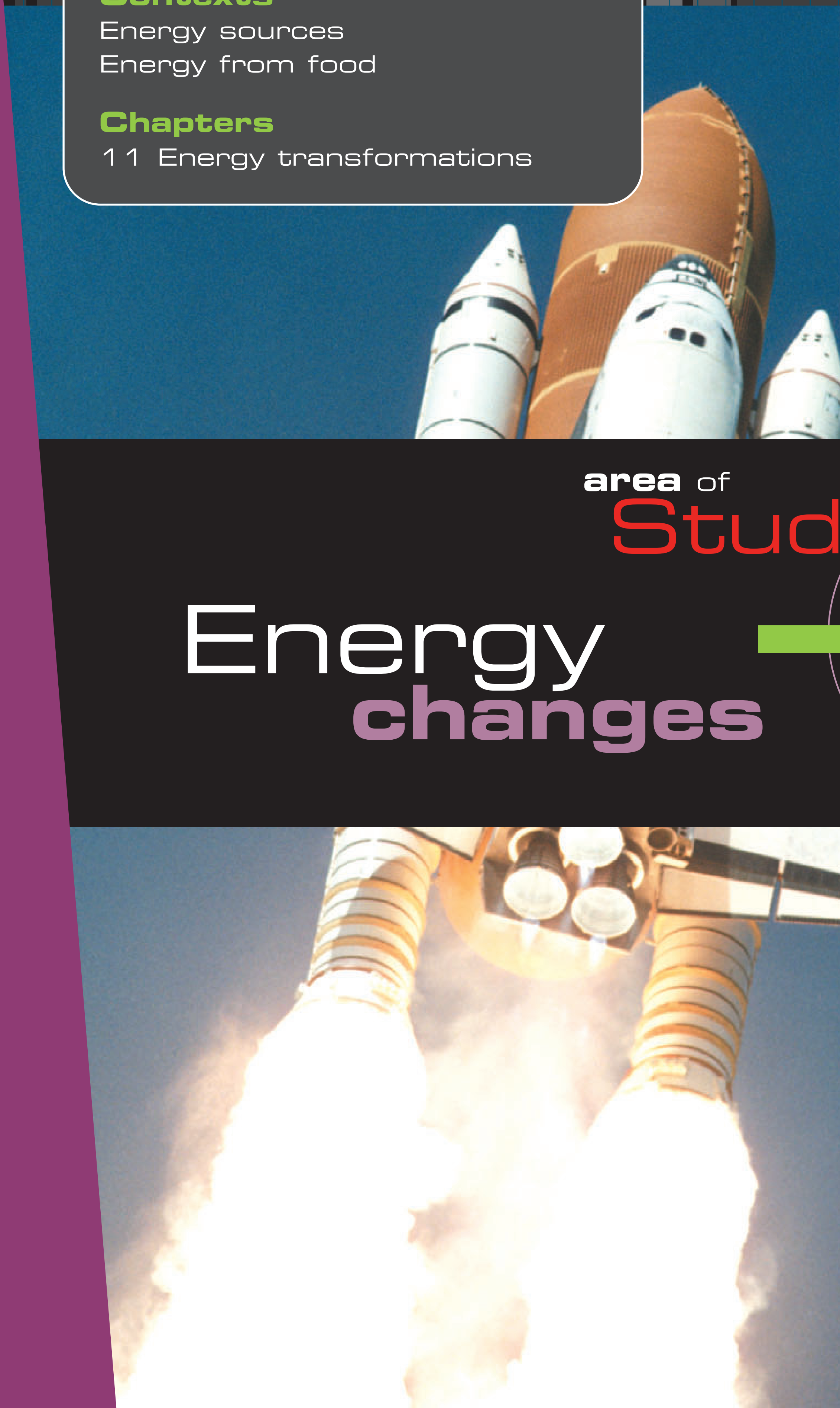
1. Select a range of foods to test for salt content. Compare your results with those advised by the manufacturer. You could check some of the foods of your school canteen for salt content.
2. From the table of solubilities in Chapter 4 (table 4.2), devise your own tests for ions and check these tests with selected foods.
3. When testing for salt, distilled (or deionised) water is used for dissolving and washing substances as tap water contains ions that will form precipitates with the reagents you are using. Try testing your local tap water for such reactions. Is the use of distilled or deionised water warranted? You could try testing various brands of mineral water to see if they contain the quantities of ions they claim. Are the levels high enough to be accurately tested by precipitation reactions? How does this compare to tap water?
4. There are tests for more complex molecules such as starches, sugars and proteins. Research these tests. The tests for starches, sugars and proteins involves colour changes and the formation of precipitates. Find out about the chemical reactions behind the changes observed in the presence of these food substances. Use these methods of testing for starches, sugar and protein, together with the tests for simples ions, for a more thorough understanding of a food sample.

Contexts
Energy sources
Energy from food

Chapters
11 Energy transformations

area of Study 5

Energy changes



energy sources

We all use energy. From the disposable cells in a wristwatch to the rechargeable batteries in our MP3 player or mobile phone, we depend on affordable, portable energy sources. For transport, we rely on the combustion of petrol in our cars. Electricity for our homes and businesses is generated in power stations. It is difficult to imagine life without such energy sources. A challenge for the future is to develop more sustainable ways of providing for our energy needs. All of our energy sources use chemical reactions that release energy. These are known as exothermic reactions.

figure es.1 Portable music players rely on the energy stored in the chemicals of the battery supply.

* Chapter 11 **Energy transformations** describes the energy involved in different reactions (page 423).

figure es.2 A power station. Most power stations in Australia use the combustion of coal as their power source.

figure es.3 Burning fossil fuels for energy.

Fuels

Fuels are materials that release chemically stored energy for use. The food we eat is the fuel used by the body during cellular respiration, providing the energy that allows cells to function. Burning wood in a campfire provides energy to heat water, cook food and keep campers warm. Petrol combusted in a car engine supplies the energy that ultimately allows acceleration and high speed travel, conveniently delivering passengers to their desired destination. Each of these examples illustrates the energy released as fuels undergo exothermic reactions. The energy released is that stored in the bonds of the fuel substances. New substances are also formed during these reactions.

* Section 11.1 **Enthalpy** describes how energy is released during exothermic reactions (page 424).

Combustion

From campfires providing warmth and heat for cooking to the gigantic coal-fired power stations of today, we have used combustion as a source of energy for a long time.

What occurs during combustion?

Notice what happens when a test tube is heated with the air holes of the Bunsen burner closed—the test tube becomes sooty. The soot is black, unburnt carbon. The fuel used in most laboratory Bunsen burners is LPG, or propane gas, which has the formula C_3H_8. In the presence of sufficient oxygen, the reaction for the combustion of propane is

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g);$$
$$\Delta H = -2220 \text{ kJ mol}^{-1}$$

This equation shows that one mole, or 44.0 g of propane releases 2220 kJ of energy when burnt in this reaction. If oxygen is limited, the products include carbon monoxide (CO), unburnt carbon (C) and fragments of other unburnt hydrocarbons. Low air to fuel ratios contribute many harmful pollutants such as unburnt hydrocarbons to the atmosphere. In situations in which the oxygen supply is limited, the amount of energy released during combustion is less than the maximum possible.

The complete combustion of hydrocarbons produces carbon dioxide and water vapour. Combustion of hydrogen as a fuel produces water vapour, and combustion of coal, which is mainly carbon, produces carbon dioxide.

The burning of fossil fuels increases the level of atmospheric carbon dioxide and other gases, which contribute to the greenhouse effect and global warming. At the high temperatures involved in combustion, nitrogen from the air reacts with oxygen, forming various oxides of nitrogen, NO_x. Fossil fuels, particularly coal, often contain sulfur. Burning them produces oxides of sulfur. Both nitrogen oxides and sulfur oxides can dissolve in, and react with, moisture in the air to form acids. Acid rain is another major pollution problem.

* Section 8.1 **Introducing acids and bases** describes properties of acids (page 366).

table es.1 Energy released by combustion of various fuels.

Heat released on combustion (kJ)	Hydrogen gas	Liquid hydrogen	Methane gas	LPG	Liquid octane	Ethanol
per mole	286	285	882	2 220	5 450	1 367
per gram	143	142	55	50	48	30
per litre	12	9970	36	25 600	34 000	23 485

The amount of energy that can be obtained from various fuels is shown in table es.1. In practical terms, the amount of energy released per gram and per litre is more important than the amount of energy released per mole. It is these values that affect decisions concerning the convenience and economy of transporting and using each fuel.

Fossil fuels

The energy requirements of developed countries come mainly from fossil fuels—coal and derivatives of crude oil. Crude oil can be separated into different fractions, mixtures of hydrocarbon molecules of similar mass and similar boiling point. Each of these fractions is used as fuels for specific purposes.

table es.2 Fractions of crude oil and their uses.

Name of fraction	Boiling range (°C)	Composition	% crude oil	Use
refinery gas	<25	C_1–C_4	1–2	• liquid petroleum gas (propane, butane) • blending in petrol feedstock for organic chemicals
gasoline	25–75	C_5–C_6	20–40	• petrol for cars
naphtha	75–190	C_6–C_{10}		• production of organic chemicals converted to petrol
kerosene	190–250	C_{10}–C_{14}	10–15	• jet fuel • heating fuel (paraffin)
gas oil	250–350	C_{14}–C_{20}	15–20	• diesel fuel • central heating fuel • converted to petrol
residue	>350	$>C_{20}$	40–50	• fuel oil (e.g. power stations, ships) • lubricating oils and waxes • bitumen or asphalt for roads and roofing

Crude oil enters the fractionating tower (figure es.4) as a mixture of vapour and liquid at 350°C. The temperature decreases up the fractionating tower. Each fraction has a boiling point range at which the vapour condenses and is collected. The lighter gaseous alkanes are collected at the top of the column while the heavier liquid alkanes are collected towards the bottom. The heaviest molecules (larger than C_{20}) remain at the very bottom of the fractionating tower.

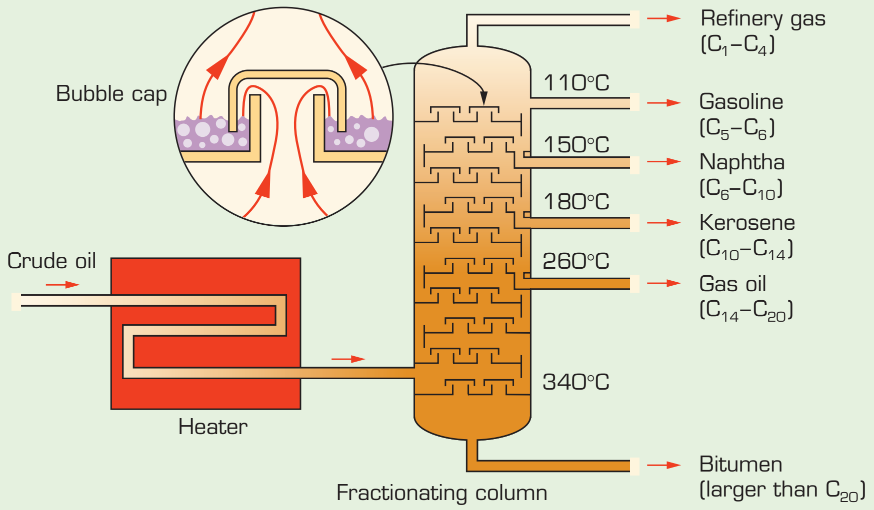


figure es.4 The separation of crude oil into fractions in a fractionating tower.

Section 2.5 **Organic compounds** describes the molecular structures of alkanes and alcohols (page 246).

Fuel alternatives

Ethanol

Ethanol mixed with petrol has been used as a fuel in Queensland and it may be used more widely in the future. Ethanol can be produced from crops such as sugar cane and wheat. The carbon dioxide produced during combustion will make no overall contribution to the greenhouse effect, as the plant uses it when more cane is grown.

Using ethanol as an alternative fuel has a number of advantages.

1. It is clean burning.
2. Mixtures of 10% ethanol in petrol can be burnt in car engines without modification.
3. Australia would be less dependent on fuel imports, particularly in times of political instability, and reducing costly imports has economic benefits.
4. Growers of sugar cane and other crops would have an alternative market for their product.
5. Ethanol could use the same infrastructure for supply and distribution as petrol, which is important in considering the viability of a potential fuel.

Alkanes and alcohols release energy by combustion. Both types of compounds undergo a similar process in which the molecules react with oxygen to produce water and carbon dioxide, releasing energy. Combustion reactions are redox reactions.

Combustion of hexane (gasoline fraction):

$$C_6H_{14}(g) + 9.5O_2(g) \rightarrow 6CO_2(g) + 7H_2O(g);$$
$$\Delta H = -5470 \text{ kJ mol}^{-1}$$

Combustion of ethanol:

$$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g);$$
$$\Delta H = -1367 \text{ kJ mol}^{-1}$$

Chapter 7 **Redox reactions** describes some combustion reactions as redox reactions (page 338).

Section 11.2 **Specific heat capacity** describes the type of calculations used in the following experiment (page 429).

figure es.5 Fuels can be made from renewable sources such as sugar cane.

Experiment es.1

Alcohols as fuels

Purpose

To measure the amount of heat produced when three different alcohols burn, and determine their molar heats of combustion.

Method

1. Set up the apparatus as shown in figure es.6.
2. Light the spirit burner.
3. Adjust the height of the can so that the tip of the flame just touches the can.
4. Replace the cap on the spirit burner to extinguish the flame. (Caution: Never blow out the flame.)
5. Using a measuring cylinder, add 200 mL of cold water to the can. Place a thermometer in the water and record its initial temperature.
6. Weigh the spirit burner with its liquid contents as accurately as possible, and record the mass.
7. Light the wick and stir the water gently with the thermometer. Monitor the temperature and observe the flame.
8. When the temperature has risen by about 10°C, record the temperature and extinguish the flame by replacing the cap.
9. Reweigh the burner immediately and record its final mass.
10. Examine the bottom of the can for soot accumulation. Remove the soot before repeating the procedure for the next alcohol.

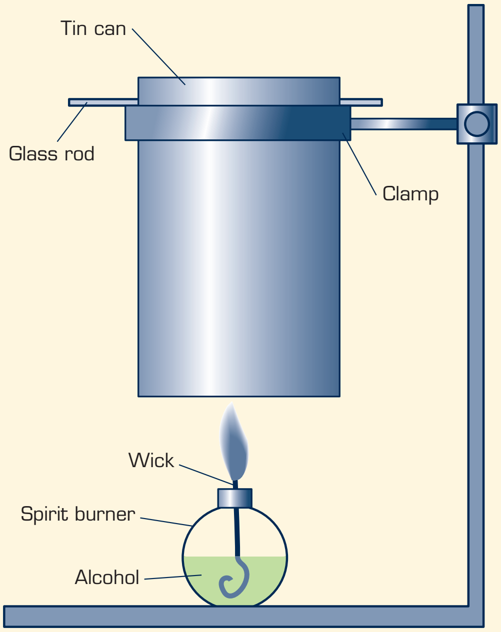


figure es.6

Calculations

1. Calculate the temperature rise of the water and the corresponding mass of each alcohol burned.
2. Using the relationship below, calculate the amount of heat energy supplied by each fuel.

$$\underset{\text{(joules)}}{\text{heat energy}} = \underset{\text{(g)}}{\text{mass of water}} \times \underset{(^\circ\text{C})}{\Delta T} \times \underset{(4.18\ \text{J g}^{-1}\ ^\circ\text{C}^{-1})}{\text{specific heat of water}}$$

3. Calculate the heat of combustion (J g^{-1}) for each alcohol tested.
4. Calculate the molar heat of combustion (kJ mol^{-1}).

materials (per group)

- tin can
- retort stand and ring clamp
- glass rod
- 3 spirit burners filled with methanol, ethanol and 1-propanol
- 250 mL measuring cylinder
- thermometer (0–100°C accurate to 0.1°C)
- electronic balance

safety

- Wear safety glasses and a laboratory coat for this experiment.
- Methanol: Toxic by all routes of exposure. It is also highly flammable.
- Ethanol: Highly flammable, slightly toxic if ingested.
- 1-propanol: Highly flammable, toxic if ingested or inhaled.

Discussion

1 Compare the wicks and tin can for soot (carbon) accumulation from each alcohol. Which alcohol produced the most soot? Explain why.
2 Which alcohol produced the most heat per gram of fuel?
3 Compare the molar heats of combustions for the three alcohols and summarise any trend evident from the calculated result.
4 The molar heats of combustion are methanol, −725 kJ mol^{-1}; ethanol, −1364 kJ mol^{-1}; 1-propanol, −2016 kJ mol^{-1}. Compare these with your calculated results and identify the sources of error in your measurements. How might this experiment be modified to minimise these errors?
5 Based on your experimental observations and safety and environmental considerations, which one of the tested alcohols would you recommend as the fuel of the future? Give detailed reasons.

Selecting the right fuel

Several factors need to be taken into account when comparing fuels. The efficiency of a fuel is a combination of these factors and cannot be measured by one characteristic. Some of the following factors may need to be considered.

1 The amount of heat released per unit mass or unit volume of the fuel (the heat of combustion). A higher amount of energy released doesn't necessarily indicate a better fuel. In some circumstances a fuel that releases less energy may be adequate. Table es.3 shows the heats of combustion for various fuels. For these fuels the volumes of gases are measured at SLC and the amounts of energy are for complete combustion, the products being carbon dioxide and water.

table es.3 The heats of combustion of various fuels.

Substance	kJ g^{-1}	Substance	kJ L^{-1}	Substance	kJ mol^{-1}
wood, dried	≈ 18	petrol, standard	≈ 33 800	natural gas (methane)	880
peat, dried	≈ 20	petrol, super	≈ 34 200	ethane	1560
brown coal, dried	≈ 30	kerosene	≈ 36 500	propane	2220
black coal, dried	≈ 33	diesel fuel	≈ 38 000	butane	2886
carbon (graphite)	33	heating oil	≈ 38 500	octane	5450
hydrogen, liquid (−253°C)	142	ethanol	23 485	methanol	727
		LP gas	25 600	ethanol	1367
				hydrogen	286

Section 5.6 **Molar volume** describes the relationship between standard conditions and the volume of a gas (page 321).

2 The energy density. This indicates the amount of energy released per kilogram of fuel. Transport may be a major cost in supplying a fuel. The higher the energy density of a fuel the more cost effective it is to transport.

figure es.7 Transport is a major cost related to fuel supply, especially when safe transport requires the use of purpose-built vehicles.

3 The ease of transport. How easy a fuel is to transport will be determined by such things as whether the fuel is a solid, a liquid or a gas. Highly volatile fuels may require specialised containers. Some dangerous fuels can only be transported along designated routes and cannot travel through residential areas. Some fuels can be easily transported using permanent pipelines.

figure es.8 Pipelines allow some gaseous and liquid fuels to be transported efficiently and without the safety concerns of road transport.

4 The availability of a fuel, which also can determine its uses. In Australia, most of our electrical power stations are coal fired while in other countries oil or natural gas use is more widespread. Many of our power stations are built within easy access to coal mines to reduce transport costs.

figure es.9 The national electricity grid allows electricity to be produced in remote areas near coal mines and then supplied to cities using high voltage power lines.

5 Environmental concerns, including methods of obtaining fuel (for example mining), transport and waste products created as the fuel is used. Some fuels are considered cleaner than others and special precautions need to be taken when using dirty fuels.

figure es.10 Oil spillage has resulted in major environmental damage, harming sea life and birds and destroying fishing industries.

Cells and batteries

Historical development

The earliest battery is credited to Count Alessandro Volta. He investigated reports of animal electricity made by Galvani, who noted that when two different metals were placed in contact with a frog leg, the muscles twitched. Volta found the electric current was generated from the different metals, rather than the frog. He built a voltaic pile—a stack of round copper and zinc plates, separated by cardboard moistened with salt solution (figure es.11). He showed that this arrangement was able to generate an electric current, and that the two different metals were oppositely charged.

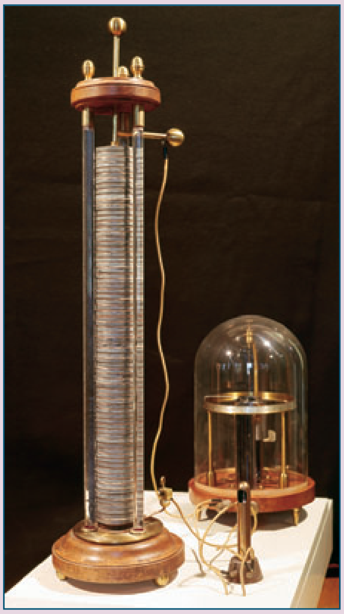


figure es.11 A voltaic pile

* Section 7.4 **Ease of oxidation** describes electrochemical cells and the reactions that provide their energy (page 348).

Other cells and batteries

Volta made a great breakthrough, but his battery was not portable. Thomas Edison designed the first dry cell, in which the electrolyte between the electrodes was a moist paste. Since then, cells and batteries have been designed for a variety of purposes. Rechargeable Ni–Cad cells power many electronic devices. High-powered lithium cells in corrosion-resistant cases are used in heart pacemakers to keep people alive. Motor vehicles use rechargeable lead–acid batteries. These are able to supply a large current for the starter motor of the car and power all the electrical systems in the car. Figure es.13 shows a car battery and part of the electrical system of a car.

The following half equations show what occurs when a car battery is producing electricity. At the anode, the lead plates are oxidised according to this half equation:

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$$

At the cathode, lead oxide is reduced to Pb^{2+} ions, which combine with sulfate ions from the electrolyte solution:

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$$

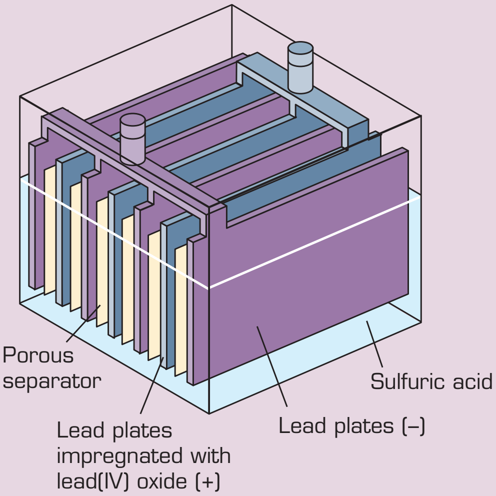


figure es.12 This diagram shows the construction of the six cells in a car battery.

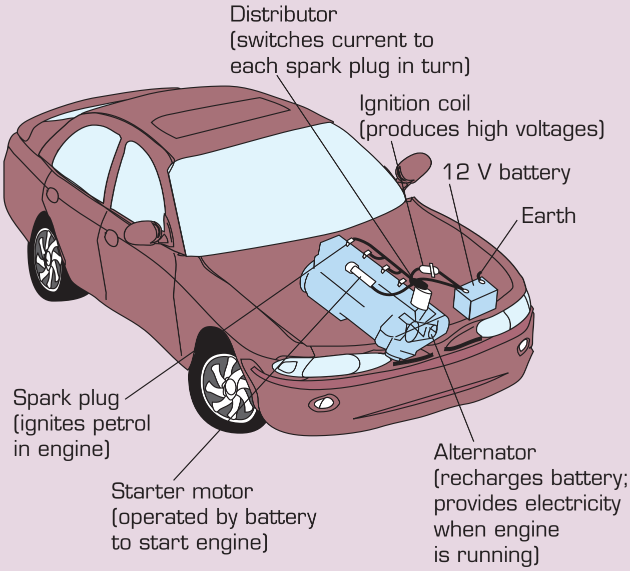


figure es.13 Part of the electrical system of a car. The car battery supplies over 100 amps of current to the starter motor for several seconds. The alternator recharges it when the engine is running.

* Chapter 7 **Redox reactions** describes redox reactions and electrochemical cells (page 338).

In most cars, the battery is not used to run the car, just for the electrical systems. New hybrid cars are available in Australia. These have both a petrol motor and a bank of batteries to electrically drive the car. Such cars reduce the level of pollution in city areas.

In all cells and batteries, the electrical energy is released by a spontaneous, exothermic reaction.

* Section 11.3 **Spontaneous reactions** describes the factors which determine whether or not a reaction will be spontaneous (page 433).

A mysterious discovery—the Baghdad battery

In 1938, a German archaeologist discovered some unusual jars found near Baghdad. These jars are thought to be about 2000 years old. They consist of an earthenware pot containing a cylindrical copper container. The top is sealed with a tar stopper through which an iron rod is inserted (figure es.14). When the copper container is filled with a liquid such as vinegar or grape juice, the device produces about two volts. No one knows how this power source was discovered or what the primitive cell was used for. It is possible to use this cell to electroplate objects with gold, which suggests the possibility that some museum pieces thought to be gold are silver that has been plated.

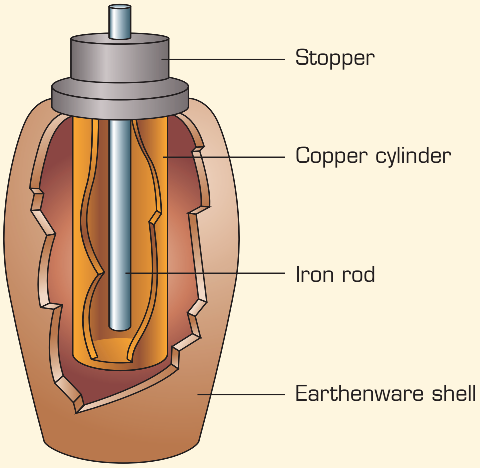


figure es.14 The structure of devices found near Baghdad. Was this the world's first battery?

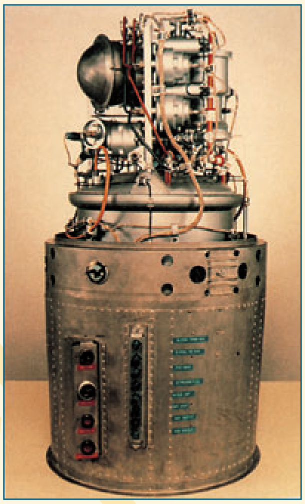


figure es.15 This fuel cell was used to supply the Apollo space program.

Fuel cells

Combustion engines and furnaces have the advantage of a continuous supply of fuel. They can produce energy as long as a supply of fuel is provided. For battery-operated devices, this is not so. Once the chemicals stored in the cell have been converted into products, the battery is said to be flat. In most cases, it is then thrown away. With the cost of the chemicals, this is an expensive form of energy. Some batteries can be recharged, by having the chemical reaction reversed. They are more convenient and economical.

Combustion is an inefficient reaction because a large percentage of the energy produced is lost in the form of heat. Batteries are more efficient at converting chemical energy to electrical energy. It would be good to be able to combine the convenience and efficiency of batteries with the continual fuel supply of combustion.

Fuel cells do just that. First designed in 1839 by Sir William Grove, fuel cells can produce more than double the useful energy from a given amount of fuel as combustion. As they operate at lower temperatures, pollutants such as NO_x are not produced. With no moving parts, they have no noise or vibration, and suffer less wear and tear. However, they are more costly and have a lower power density, i.e. they produce less energy for a given volume or mass, than other energy sources. This is partly because less effort has been made to develop them.

NASA has used fuel cells aboard spacecraft (shown in figure es.15). They are beginning to be used worldwide for various applications. The Australian Technology Park in Sydney has a 200 kW fuel cell using natural gas. Around the world, small systems are in use or being developed for houses, vehicles and electronic devices such as laptops. A small system would be ideal for isolated areas of Australia that are not connected to the main power grid.

How fuel cells work

As shown in figure es.17, fuel (hydrogen) is supplied to the anode through an inlet and oxygen is supplied to the cathode. Sandwiched between the anode and the cathode is the electrolyte. In this case, a solution of potassium hydroxide is used.

At the anode, hydrogen gas reacts with the hydroxide ions from the electrolyte, supplying electrons to the cathode.

$$H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$$

At the cathode, the half reaction is

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

Other fuel cells with different fuels, electrolytes and electrodes have been developed.

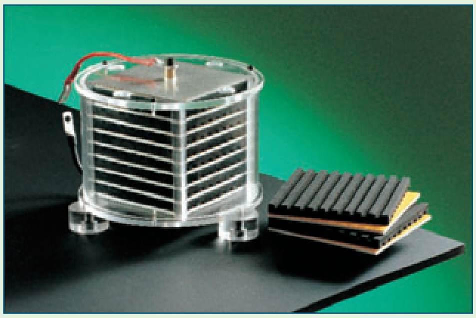


figure es.16 A model of another type of fuel cell. This one is a ceramic fuel cell.

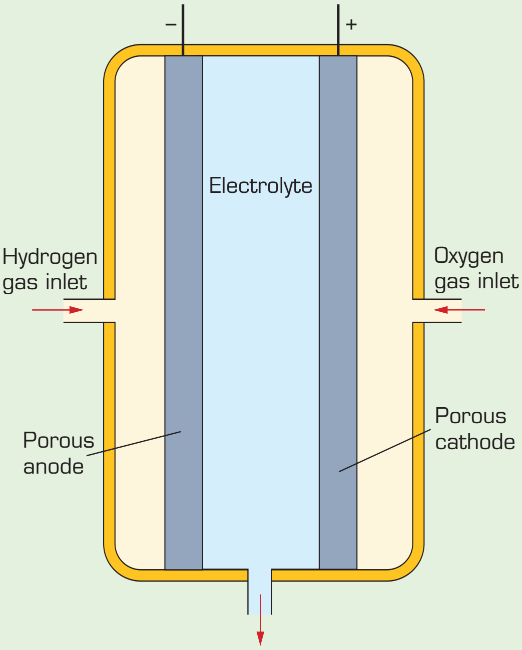


figure es.17 A hydrogen–oxygen fuel cell.

Experimental investigations

The experimental investigation of this context may give you a starting point from which to plan an investigation of your own. Here are some ideas to get you started.

1. Methanol, ethanol and 1-propanol were used as fuels. You could continue the series and investigate 1-butanol and 1-pentanol. Compare their combustion properties as well as their heats of combustion.
2. The alcohols investigated are primary alcohols (the hydroxide group is attached to an end carbon). How do 1-propanol and 2-propanol compare as fuels?

3 Fuels not only vary in the amount of energy that they produce but also in the rate at which they produce it. By using a spirit burner, some fuels could be measured for their heat released over a period of time, say 10–20 minutes. Fuels could be compared using the units kJ per minute.

4 Candles come in a wide range of types at vastly different prices. The combustion properties of different brands of candles could be observed to allow comparison of performance and value for money.

Discuss the plans for your investigation with your teacher and perform a complete risk assessment to ensure that your investigation is carried out safely and that materials used as fuels are not hazardous.

Consider this

Use the information presented in the context and related chapters to answer the following questions.

1 Acid rain is caused when oxides of nitrogen and sulfur form during combustion. Write equations showing the formation of NO, NO_2, SO_2 and SO_3 during combustion. Write equations to show how the resulting compounds form acids.

2 Write thermochemical equations for the combustion of each of the fuels in table es.1.

3 Hydrogen gas produces a relatively large amount of energy per gram. Despite this, hydrogen gas is not frequently used. Consider the energy per litre for this fuel and suggest why it is used as a fuel so infrequently.

Further investigations

1 The combustion engine used in cars is designed to provide optimal fuel to air ratios and economical fuel use. Research and consider the design of a car engine. Explain how the engine is designed to carry out the mixing of air and fuel, and the combustion reaction as efficiently as possible. How do various features contribute to the efficient operation of the vehicle? Your answer should consider how developments, such as electronic fuel injection and other recent developments, are an improvement over carburettors. Present your findings in a poster.

2 A number of different electrochemical cells and batteries have been discussed in this context. Select one of these and report on the historical development and chemistry involved in the cell or battery. Consider the advantages and disadvantages of this type of cell. Present your research in the form of a display. It may contain a model, a poster or a PowerPoint presentation.

energy from food

Living things need energy to enable their cells to function, allowing them to sense changes around them, react through movement and thought, and enabling internal activities of the body to take place. The fuel supply for living things is the food they consume.

figure ef.1 Food for the body is like coal for a furnace. It supplies the energy needed to drive the body like an engine.

Food as fuel

The fuel a car uses is petrol and one of its main components is octane. The combustion of octane to produce energy is described by the reaction:

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

Ethanol can be used as a fuel. It can be used in spirit burners like those used for camping or to keep food warm at the dinner table. An ethanol–petrol blend is being used to conserve oil reserves. The combustion of ethanol can be described by the reaction:

$$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

There are no flames or smoke but living things use the energy produced by foods in a similar process. Cellular respiration involves the breaking down of glucose and can be described by the reaction:

$$C_6H_{12}O_6(g) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l); \Delta H = -2803 \text{ kJ mol}^{-1}$$

Each of the reactions described above involves a reaction between a fuel and oxygen. They all produce carbon dioxide and water, and energy is released. If glucose was burned in air, the reaction taking place could be described by the same reaction and the amount of energy released would be almost the same as during cellular respiration. The release of energy from food during cellular respiration, the combustion of octane, ethanol and any other fuels are all redox reactions. Each of these fuels is oxidised during combustion.

* Section 7.1 **Oxidation and reduction** describes combustion reactions as redox reactions (page 338).

* Section 11.1 **Enthalpy** describes how energy is released during exothermic reactions (page 424).

Glucose is obtained as the body breaks down food during digestion. Food substances are broken down into small molecules such as glucose so that they can be absorbed into the bloodstream. The bloodstream takes the glucose to the cells that need it and respiration takes place to enable the cells to convert the energy to a usable form. In the muscles, this energy becomes the mechanical energy required for movement; in the nerve cells it becomes the electrical energy for the complex messages sent around the body. In specialised cells chemical energy is stored through the production of enzymes and other chemicals. Most of the energy produced is simply the thermal energy that keeps us warm.

Your weight is affected by the balance between the amount of energy you consume as food and the amount of energy you expend during daily activities. If you consume more energy than you use, the excess is stored in fats and your weight increases. If you use more energy than you consume, fats are broken down to supply the energy needed and your weight decreases. A sensible diet means finding a balance between how much you consume and the amount of energy that you use in a given day.

Table ef.1 shows the approximate energy value of some common foods. It is easy to see why a diet rich in processed snacks and sweet foods will result in weight gain compared with one that concentrates on lean meats, fruit and vegetables. You will notice that the units of energy used in this table are kilojoules. Occasionally you may hear the energy in food described in terms of calories. A calorie is the amount of energy required to increase the temperature of one gram of water by 1°C. One calorie is the equivalent of 4.18 J. A Calorie (with a capital letter) is in fact a kilocalorie (1000 calories). Currently, kilojoules are the most commonly used units of energy content in foods.

figure ef.2 Which of these foods are high in energy and which are low in energy?

table ef.1 The approximate energy content of some foods.

Food	Energy value (kJ g^{-1})
butter/margarine	30
peanuts	24
chocolate	22
potato chips (packet snacks)	21
cheddar cheese	17
sugar (most sweets)	16
jam	12
bread	12
chicken (grilled, lean)	5
steak (grilled, lean)	11
potato (boiled)	4
milk	3
most fresh fruit	2
most vegetables	1

Experiment ef.1
Marshmallow energy

Purpose

To measure the heat released during the combustion of a marshmallow.

Method

1. Weigh and record the mass of the marshmallow.
2. Using the retort stand and clamp, fix the steel can so that it is just above a crucible.
3. Place 100 mL of water in the can and measure its temperature.
4. Holding it in the tongs, light the marshmallow in the Bunsen burner and place it in the crucible to burn, heating the water.
5. Gently stir the water with the thermometer until the water has increased in temperature by about 20°C. Datalogging using temperature probes could also be used to monitor the rise in temperature of the water.
6. Extinguish the burning marshmallow, allow it to cool, and weigh the remains.

Calculations

1. Calculate the temperature rise of the water and the corresponding mass of marshmallow burned.
2. The heat energy absorbed by water can be found using the relationship

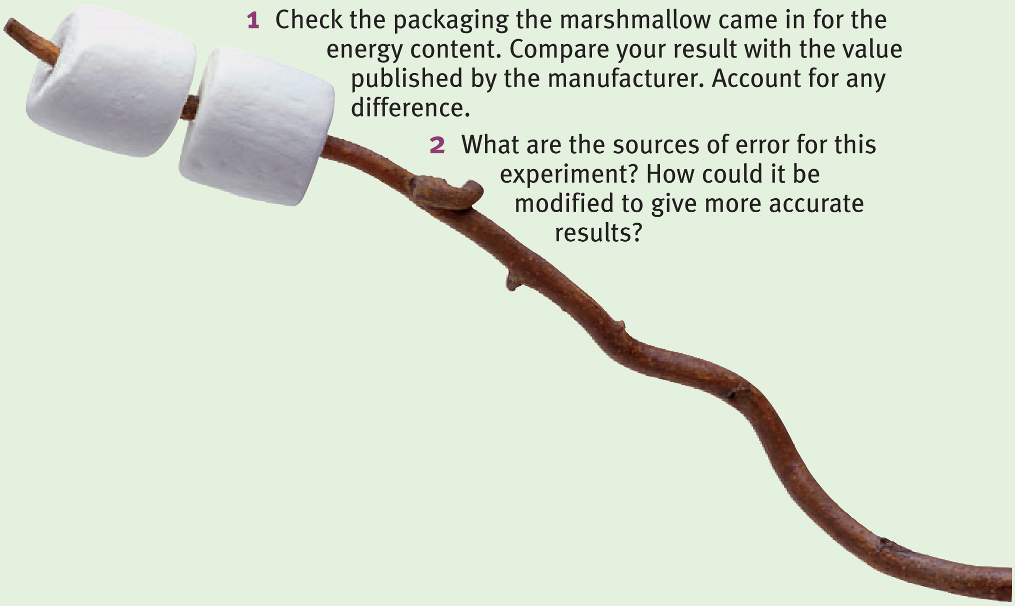
$$\underset{\text{(joules)}}{\text{heat energy}} = \underset{\text{(g)}}{\text{mass of water}} \times \underset{(^\circ\text{C})}{\Delta T} \times \underset{(4.18\ \text{J g}^{-1}\,^\circ\text{C}^{-1})}{\text{specific heat of water}}$$

Using this relationship, calculate the amount of heat energy supplied by the marshmallow.

3. Calculate the energy released per gram of the marshmallow burned (kJ g^{-1}).

Discussion

1. Check the packaging the marshmallow came in for the energy content. Compare your result with the value published by the manufacturer. Account for any difference.
2. What are the sources of error for this experiment? How could it be modified to give more accurate results?



materials

- a marshmallow or alternative foodstuff
- 250 mL measuring cylinder
- retort stand and clamp
- steel can
- crucible
- thermometer
- tongs
- Bunsen burner
- electronic balance

safety

- Wear safety glasses and a laboratory coat for this experiment.

* Section 11.2 **Specific heat capacity** describes the type of calculations used in these experiments (page 429).

Experiment ef.2

Heat of combustion of vegetable oil

materials

- small beaker (30 mL)
- wire bent to form a wick holder
- wick (4 cm)
- vegetable oil
- 250 mL flask
- thermometer (0–50°C)
- retort stand, clamp
- aluminium foil

safety

- Wear safety glasses and a laboratory coat for this experiment.
- Take care with naked flame.

Purpose

To determine the heat of combustion of a vegetable oil.

Method

1 Three-quarters fill the beaker with vegetable oil.

2 Bend the wire to form a wick holder. Hook the free ends of the wire over the rim of the beaker to hold the wick in place. Make sure that the bottom end of the wick is dipping into the oil (see figure ef.3). This is called the oil burner.

3 Weigh the oil burner. Record its mass.

4 Add 100 mL water to the flask and clamp it to the retort stand, ensuring that the bottom of the flask is about 1 cm above the burning wick (see figure ef.4).

5 Measure the temperature of the water in the flask.

6 Light the wick soaked with vegetable oil. Try to reduce drafts by minimising movement around the area of the investigation.

7 Stir the water in the flask occasionally as the oil burner heats it. Datalogging using temperature probes could be used to monitor the rise in temperature of the water over about 10 minutes.

8 When the temperature of the water has risen by about 20°C, blow out the flame. Record the temperature.

9 After the oil burner has cooled to room temperature, weigh it and record the mass.

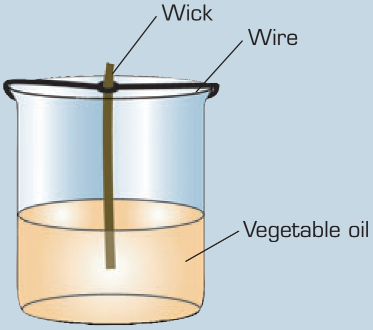


figure ef.3

Calculations

1 Calculate the temperature rise of the water and the corresponding mass of oil burned.

2 The heat energy absorbed by water can be found using the relationship

$$\underset{\text{(joules)}}{\text{heat energy}} = \underset{\text{(g)}}{\text{mass of water}} \times \underset{(^\circ\text{C})}{\Delta T} \times \underset{(4.18\ \text{J g}^{-1}\,{}^\circ\text{C}^{-1})}{\text{specific heat of water}}$$

Using this relationship, calculate the amount of heat energy supplied by the vegetable oil.

3 Calculate the energy released per gram of the oil burned (kJ g^{-1}).

Discussion

1 Any pure, edible fat or oil will provide about 37 kJ g^{-1}. How does this compare with the results that you calculated?

2 Account for any differences between the expected result and your experimental results.

3 Suggest any modifications to this investigation to reduce error.

4 Your results would have been more accurate if calibrated equipment was used. Explain how you could calibrate your equipment. Hint: Use a substance with a known heat of combustion (e.g. ΔH of ethanol = 29.7 kJ g^{-1}).

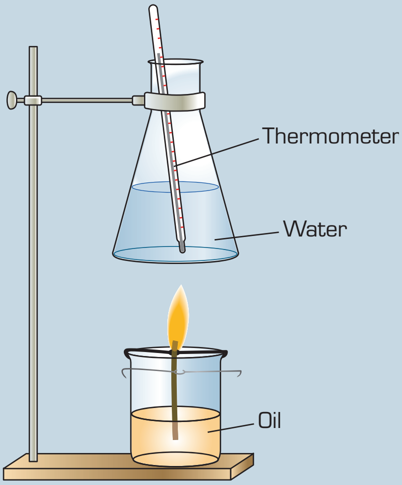


figure ef.4

Experiment ef.3

Energy content of food

materials

- calculator

Introduction

One instrument used for measuring the energy change during a chemical reaction is the bomb calorimeter (figure ef.5). It is particularly useful for measuring the energy content of food, as it can be used to measure the amount of energy released as a food sample undergoes combustion. The heat of combustion is defined as the energy released when a specified amount of a substance (one mole, one gram or one litre) is completely burned in oxygen.

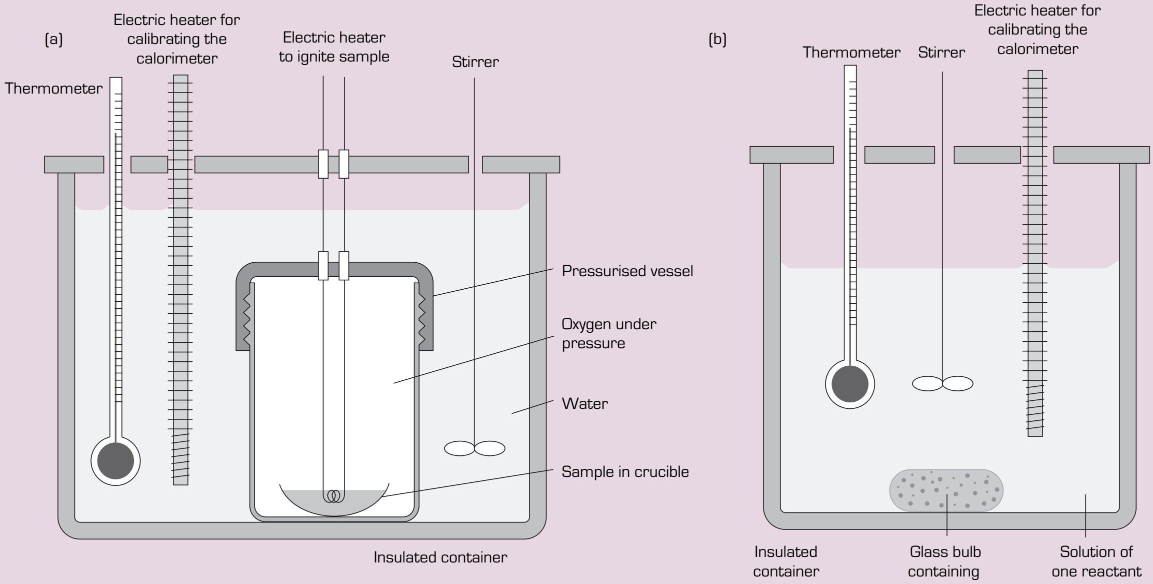


figure ef.5 The structure of a bomb calorimeter.

Bomb calorimeters contain a large, insulated reservoir of water. The heat released or absorbed during the chemical reaction causes the temperature of the water to change and this temperature change can be measured.

Purpose

Bomb calorimeters are highly sophisticated pieces of equipment and are not usually accessible in a school environment. In this investigation, you will carry out a virtual investigation to determine the energy content of pizza. The following experimental data was collected during an experiment in which a sample of packaged frozen pizza was totally consumed by combustion in a bomb calorimeter.

table ef.2

Calibration data		Combustion of pizza sample	
voltage	2.40 V	temperature before combustion	22.6°C
current	3.50 A	temperature after combustion	27.4°C
temperature before calibration	19.0°C	mass of pizza	65.0 g
temperature after calibration	22.6°C		
time of calibration	3.00 min		

Calibration

The reservoir of water is used to absorb or release energy during a chemical reaction, but the calorimeter itself can also absorb or release energy into the water. This energy is taken into account by calibrating the calorimeter.

Calorimeters are calibrated electrically by releasing a known amount of electrical energy in the calorimeter and measuring the change in temperature, ΔT. The energy required to raise the temperature of the calorimeter and its contents by 1°C is called the **calibration factor** or **calorimeter constant** for that particular calorimeter and can be calculated using the following formulae.

E (energy input in J) = V (potential difference in V) × I (current in A) × t (time in s)

Calorimeter constant = $\frac{E}{\Delta T}$, where ΔT is the change in temperature in °C

Use the information in table ef.2 to determine the calorimeter constant of the calorimeter used.

Energy released by a food sample

Using the calorimeter constant and the change in temperature for the combustion of the sample of pizza, calculate the energy change of the reaction.

E = calorimeter constant × ΔT

Energy content of a food sample

The nutrition guide on packaged food will state the energy content of that particular food.

Chemists may express the energy content of a substance in joules per mole, joules per litre or joules per gram. The nutrition guide provided by the manufacturers of foods normally describes energy content in terms of serving size (often 100 g) or simply per gram. Use the amount of energy calculated for the sample of pizza to calculate the energy (kilojoules) per gram.

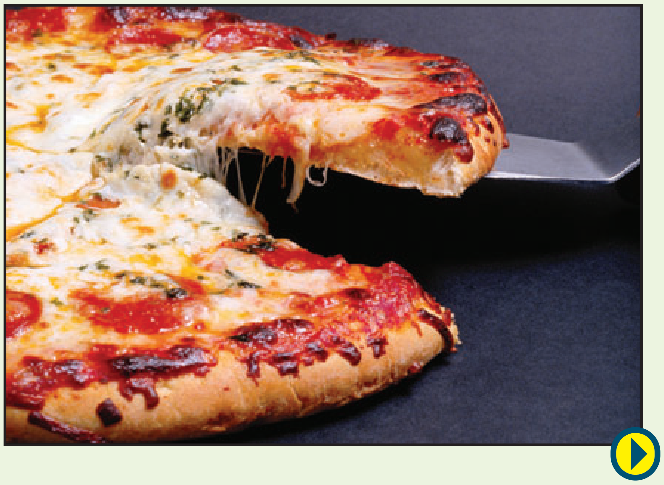
$$\text{Energy content} = \frac{\text{energy (kJ)}}{\text{mass of sample (g)}}$$

Questions

1 The nutrition guide on the packaged pizza stated that the energy content is 0.36 kJ g^{-1}. How does this compare with the energy content you have calculated from the results?

2 What possible sources of error could account for any discrepancy between the value derived from the experiment and the manufacturer's claims?

3 What precautions would manufacturers of food products need to take to ensure that the claims on their packaging were accurate?



Bomb calorimetry calculations

Determining the energy content of a substance using bomb calorimetry involves three steps.

1. Calculate the calibration factor.
2. Use the calibration factor to determine the energy change for the reaction performed.
3. Express this as an energy change as required, e.g. J g^{-1}.

Questions

Using the method outlined above and the information in the following tables determine the energy content of the food products tested in a bomb calorimeter.

table ef.3

Calibration data		Combustion of McDuff's Chunky Soup sample	
voltage	2.40 V	temperature before combustion	23.5°C
current	3.20 A	temperature after combustion	24.9°C
temperature before calibration	15.2°C	mass of pizza	73.0 g
temperature after calibration	23.8°C		
time of calibration	3.00 min		

table ef.4

Calibration data		Combustion of donut sample	
voltage	2.30 V	temperature before combustion	24.0°C
current	3.65 A	temperature after combustion	38.9°C
temperature before calibration	21.0°C	mass of pizza	58.0 g
temperature after calibration	24.5°C		
time of calibration	3.00 min		

Balancing energy intake

The three groups that most food substances fall into are carbohydrates (which include sugars and starches), lipids (which include fats and oils), and proteins (which the body uses to make new cell materials). The amount of energy available in each of these substances is shown in table ef.5.

table ef.5 The energy content of carbohydrates, fat and protein.

Nutrient	Heat of combustion (kJ g^{-1})	Available energy (kJ g^{-1})
carbohydrate	17	17
fat	39	37
protein	24	17

The heat of combustion, as found through calorimetric processes, is sometimes higher than the actual energy content available to the body. This is because not all nutrients available from food are absorbed during digestion and some substances, such as fibre and protein, are not completely oxidised in the body.

The vegetable oil used in Experiment ef.2 is very little else other than lipid. The glucose used in Experiment ef.3 is a carbohydrate. In Experiment ef.1 peanuts, like most foods we eat, are made up of a certain amount of each food group. The actual energy content of a particular food will depend on how much of each food type it contains. Fatty foods tend to have higher energy content since fat has virtually twice the available energy of the other food groups. The typical composition of some foods and their overall energy value is included in table ef.6.

table ef.6 Some foods, their composition and energy content.

Food	Carbohydrate (%)	Fat (%)	Protein (%)	Energy value (kJ g^{-1})
butter	0	80.3	0	29.9
chicken (fried)	0	17.6	29.4	12.1
steak (grilled, lean)	0	14.1	28.2	10.8
potatoes (boiled)	22.0	0	2.0	4.2
apple	13.8	0	0	2.3
bread	53.2	4.0	8.0	11.7
egg (boiled)	0.6	11.8	12.5	6.7
wine	4.2	0	0	3.5

The rate at which energy supplied by food is consumed depends on several factors. The amount of activity a person is involved in is one factor. Their age, sex, body size and level of fitness are also factors. An average teenager will require anywhere from about 6000 to 12 000 kJ per day depending on their activities.

table ef.7 The energy used by a person performing various activities.

Activity	Energy use (kJ h^{-1})
sitting	420
standing	590
vacuuming	1000
lawn-mowing (power)	1030
walking (5 km h^{-1}, leisurely)	1200
jogging (8 km h^{-1})	2060
running (13 km h^{-1}, mod. fast)	4050
tennis (singles)	1900
swimming (leisurely)	1700

figure ef.6 The rate of a person's energy expenditure depends on their age, sex, size and level of physical activity.

Experimental investigations

1 The experiments of this context could be adapted to measure the energy content of other types of food. Devise methods to experiment on foods such as dry biscuits, pasta or rice. What preparation would be needed to test fruits or vegetables? Test out your proposals and compare the measured values with published values.

2 Perform a series of experiments similar to those in this context to compare the energy content of various brands of similar products. Do different brands differ in their energy value? Which provide the better value for money?

Further investigations

1 Some living things undergo anaerobic respiration. In this case, energy is released from food without oxygen being present. Find out what organisms use this type of respiration. How is the reaction that takes place different to cellular respiration? How have people put this process to use?

2 Over a period of weeks, log your physical activities and the foods you consume. Use the tables in this context and your own research to estimate your energy consumption and expenditure. Could any weight change you experience over this period be predicted from your calculations? Describe ways in which this experiment could be improved.

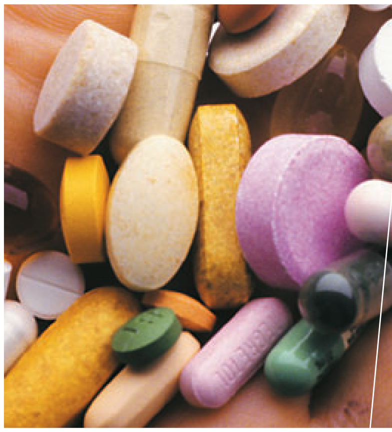
3 There are many different suggested diets in publication at any time—high protein/low carbohydrate diets, high carbohydrate/low protein diets, non-dairy, high fibre, toxin-cleansing or cabbage soup diets. Find out the details of some of these diets and evaluate them. Do they work? Why do they work? Are they nutritionally safe?

Contexts

Wine analysis
Quality control
Pharmaceuticals
Forensic chemistry

Chapters

12 Qualitative and quantitative testing
13 Volumetric and gravimetric analysis
14 Instrumental and specialised techniques



area of Study 6

Qualitative and quantitative techniques

wine analysis

The manufacture of wines in Australia is a growing multi-million dollar industry. Winemaking is becoming a more scientific process, in which chemistry is fundamental to its understanding as well as to the analytical processes involved. Due to increased consumer demand for a greater variety of quality wines, science is assisting in the production of better wines for the consumer, together with better processes and analytical techniques for the winemaker.

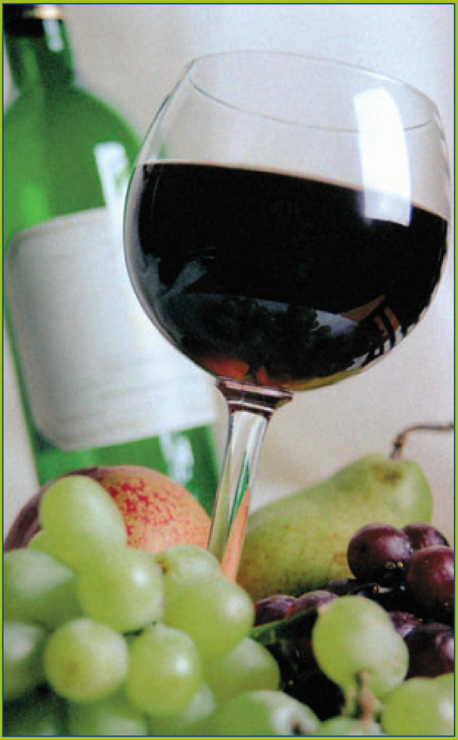


figure wa.1 Wine is an alcoholic beverage made from grapes. The range of wines produced today is vast.

figure wa.2 Wine tasting is a favourite pastime for many.

The winemaking process

A brief look

The winemaking process will vary depending on whether the wine is red, white or sparkling, and then there are also fortified wines such as port and sherry to consider. Below is a general outline of the winemaking process.

1. The ripe grapes are picked and crushed in a press.
2. The crushed grapes and juice are drained from the stems and seeds. At this stage the juice is referred to as the must. The skin is left with the must for red wine. For white wines the skin is separated and only the pulp is used. Red wines are fermented with their skins to give colour and tannins to the wine.
3. The must is added to a vat, barrel or tank along with yeast to ferment for two to four weeks. To ensure the process is proceeding correctly, the fermenting must is checked regularly for acceptable pH levels. Temperature is also closely controlled.
4. The wine is stored in oak barrels or stainless steel tanks for ageing, which can take from a few months to several years.
5. The wine is racked (by siphoning or pouring) to remove it from the lees (impurities, including the yeast, insoluble salts and remnants of grapes). Some winemakers leave the wine in contact with the lees to allow more flavour to develop.
6. The wine is bottled. Further ageing may occur in the bottle.

Tannins are phenol-based plant acids. They are a major component in red wines, giving them their astringent taste, although tannins do soften with ageing.

figure wa.3 The location of the vineyard has a large impact on the taste of the wine.

figure wa.4 The bottling of wine is an automated process in many wineries. After bottling, further ageing may occur, particularly for red wines.

Fermentation

Grapes are naturally high in sugar (glucose, $C_6H_{12}O_6$). When yeast is added to the must, it feeds on the sugar, undergoing anaerobic respiration. Yeast does not contribute to the taste of wine; however, the type of yeast is selected to suit the type of wine being produced. The temperature must be carefully controlled during winemaking for ideal growth of yeast. The reaction equation for this process is given below.

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

Anaerobic respiration is a process in which energy is produced from glucose in the absence of oxygen.

* Section 9.3 **Alcohols** outlines the properties of ethanol and investigates its production from sugars (page 395).

The products formed are alcohol (ethanol, C_2H_5OH) and carbon dioxide. Fermentation is complete when all the glucose has been consumed. By-products such as lactic acid, acetic acid, ethyl acetate, glycerol and other alcohols are also formed and can affect the quality and taste of the wine.

figure wa.5 For sparkling wines, extra yeast and sugar is added to the bottle and the mixture is allowed to undergo a second fermentation. The carbon dioxide produced is trapped, resulting in bubbles.

figure wa.6 The ageing of wine in oak barrels gives it a more full-bodied and complex flavour. Most ageing occurs in stainless steel vats, some of which are lined in oak to develop a fuller flavour.

Ageing

The ageing of a wine results in a smoother and more complex-flavoured wine. This ageing process is a set of chemical reactions between components of the newly made wine. The length of ageing depends upon the type of wine. Some, such as most white wines, require no ageing; others, such as red wines benefit from ageing to soften and concentrate the tannins. All wines have an ideal ageing time and beyond this the quality of the wine will decline.

* Section 9.4 **Derivatives of alcohols** describes the products of the oxidation of alcohols (page 398).

Quantitative analysis of wine

Analysis occurs at every stage of winemaking, from the grape to the finished product. Tests conducted on wine include alcohol content, free and total sulfur dioxide, total acidity, volatile acidity, pH, sugar content, and the presence of metals and contaminants.

A dicarboxylic acid is a carboxylic acid that has two carboxyl groups and therefore two protons that can ionise.

Total acidity

There are several acids present in wine, many of which form during the fermentation process. There are two main acids present in wine that occur naturally in the grape (fixed acids). Tartaric acid is the primary and strongest acid, giving wine its crisp, tart flavour. Malic acid is the other main acid. Both of these acids are weak dicarboxylic acids. Citric acid is also present in significant amounts and gives wine its fruity taste.

Other acids present in the wine, but only in small amounts, include acetic, formic, lactic, butyric, lauric and succinic acids. Most of these acids are referred to as volatile acids as they can be altered during the winemaking process, often by evaporation. It is important that the wine has the correct level of acid, as too much will cause it to taste tart and sour, while too little will leave the wine tasting flat.

The acidity of wine is referred to as total acidity (TA) and is expressed in grams per litre or as a percentage. TA will vary depending on the wine. Sweet wines for example tend to have a higher TA of 7.0–8.5 g L^{-1}, while dry wines have a TA of 6.0–7.5 g L^{-1}. To determine the total acidity of wine an acid–base titration is performed and is measured assuming that all the acid present is tartaric acid.

Total acidity is a measure of all the acid content of wine. It is also referred to as titratable acidity, as the acidity of wine is determined by titration.

* Section 9.5 **Reactions of organic acids** describe some chemical properties of acids found in foods (page 401).

figure wa.7 Tartaric acid is found in grapes, but no other fruit. Malic acid is a common acid found in fruit.

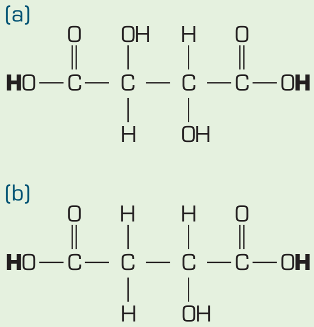


figure wa.8 The structural formula of (a) tartaric acid and (b) malic acid. Each has two ionisable protons (shown in bold).

pH

Total acidity and pH are two different ways of representing the acidity of wine. Even if the amount of acid is within range, pH must also be correct. The acceptable pH range of a wine varies between 3.0 and 3.6. Like other elements of wine it must be carefully balanced to maintain the quality and taste of the wine—wine with a low pH will taste sharp and wine with a high pH risks spoiling by bacterial growth. pH also affects how a wine ages and how it keeps its colour. pH levels can be adjusted during the winemaking process.

* Section 8.5 **The pH scale** describes pH and how it can be measured (page 376).

Sulfur dioxide content

Sulfur dioxide (SO_2) is added at several stages during the winemaking process to assist in the prevention of bacterial growth, to extract red pigments from the grape skins and to reduce oxidation of the grape juice or wine. The production of the vinegary taste of wine is due to the presence of ethanoic (acetic) acid. Sulfur dioxide minimises the formation of ethanoic acid by acting as a reductant and preventing the oxidation of ethanol. Winemakers test for free and total sulfur dioxide as some of the SO_2 added combines with other wine components. Sulfur is often added as potassium or sodium metabisulfite, which reacts with the water and acids in the wine to produce sulfur dioxide according to the following reactions.

$$K_2S_2O_5(aq) + H_2O(l) \rightarrow 2KHSO_3(aq)$$
$$KHSO_3(aq) + H_3O^+(aq) \rightarrow SO_2(g) + 2H_2O(l) + K^+(aq)$$

* Chapter 7 **Redox reactions** describes what occurs during a redox reaction and how to balance redox reaction equations (page 338).

Total sulfur dioxide is determined using a redox titration. It is important the titration is performed quickly to reduce the loss of sulfur dioxide gas.

The half equations for the titration reactions are

$$SO_2(aq) + 2H_2O(l) \rightarrow HSO_4^-(aq) + 3H^+(aq) + 2e^-$$
$$I_2(aq) + 2e^- \rightarrow 2I^-(aq)$$

* Section 13.3 **Volumetric analysis** describes the process of titration and provides you with experimental opportunities to practice titrations (page 466).

Experiment wa.1

Determination of sulfur dioxide in wine

Purpose

To determine the mass of sulfur dioxide in wine by performing a redox titration.

Method

1. Record the brand of wine to be analysed.
2. Use a pipette to transfer a 20.00 mL volume of wine to each of three 250 mL conical flasks.
3. Add about 12 mL of 1 M sodium hydroxide solution to each flask and allow the flasks to stand for 15 minutes.
4. Fill a burette with standard iodine solution. Record the initial burette reading and the concentration of the solution.
5. To one flask, add about 10 mL of 2 M sulfuric acid and 1–2 mL of starch indicator solution. Immediately titrate the mixture with the iodine solution. The end point occurs the moment the mixture turns permanently blue. Record the final burette reading.
6. Repeat Step 5 using the two other flasks.

Discussion

Your experimental determination of the amount of sulfur dioxide in the wine sample will be in mol L^{-1}. Currently in Australia, the total sulfur dioxide content of most wines is limited to a maximum of 250 mg L^{-1}. From your results, determine total sulfur dioxide content in mg L^{-1}. Your results could also be expressed as parts per million (ppm). Compare your experimental results with accepted values. Suggest reasons for any inconsistencies.

* Section 13.4 **Titration techniques** describes how to perform a redox titration (page 474).

materials

- 60 mL white wine
- 40 mL of 1 M sodium hydroxide solution
- 100 mL standard iodine solution (approx. 0.005 M)
- 30 mL of 2 M sulfuric acid
- starch indicator
- 3 × 250 mL conical flasks
- 20 mL pipette
- pipette filler
- 25 mL measuring cylinder
- burette and stand
- small funnel
- white tile

safety

- Wear safety glasses and a laboratory coat for this experiment.
- Iodine solution stains skin, clothing and bench surfaces.
- Sodium hydroxide solution and sulfuric acid are corrosive.

Alcohol content

The consumable alcohol formed during fermentation is ethanol (C_2H_5OH), but it does not actually contribute to the taste of the wine if in the correct amount. All wine labels will show the percentage by volume of alcohol, which may vary between 9% and 14.5%.

The amount of alcohol (ethanol) present may be determined in several ways. One way is to use a back titration, as outlined in Experiment wa.2.

Experiment wa.2

Determination of the alcohol content of wine

Purpose

To use a back titration to determine the alcohol content of wine.

Method

1. Record the brand of wine to be analysed and the manufacturer's specification of the alcohol content.
2. Use a pipette to transfer 10.00 mL of wine to a 250 mL volumetric flask. Make up the volume to 250.0 mL using de-ionised water and mix thoroughly.
3. Place 20.00 mL aliquots of the diluted wine into each of three 250 mL conical flasks.
4. Record the concentration of the standard potassium dichromate solution supplied. Place a 20.00 mL aliquot of this solution in each flask. Wearing gloves and using a measuring cylinder, slowly add approximately 10 mL of 40% sulfuric acid solution to each flask.
5. Stopper each flask loosely and heat for 10 minutes in a water bath at 45–50°C. (It is important that the water bath is maintained within this temperature range. Too high and the ethanol is further oxidised to ethanoic acid, too low and oxidation of the ethanol may be incomplete).
6. After heating for 10 minutes, add about 2 g of potassium iodide to each flask.
7. Fill a burette with standard sodium thiosulfate solution. Record the initial volume of solution in the burette and the concentration of the solution.
8. Titrate the contents of each conical flask with the sodium thiosulfate solution, adding 1–2 mL of starch indicator when the brown colour of the solution develops a green tinge. The equivalence point of each titration is reached when the blue colour of the starch–iodine complex just disappears, leaving a clear, green colour. Record the final volume of liquid in the burette. (Early addition of starch will result in an intense blue colour that is slow to fade, making it difficult to accurately determine the end point).

materials

- 10 mL white wine
- 60 mL standard potassium dichromate solution (approx. 0.04 M)
- 100 mL standard sodium thiosulfate solution (approx. 0.1 M)
- 30 mL of 40% sulfuric acid
- 6 g potassium iodide
- 250 mL de-ionised water
- starch indicator
- 10 mL pipette
- 2 × 20 mL pipettes
- pipette filler
- 250 mL volumetric flask
- 3 × 250 mL conical flasks and stoppers
- 10 mL measuring cylinder
- small funnel
- burette and stand
- white tile
- hot-water bath
- thermometer, −10–110°C
- spatula
- electronic balance

Discussion

In the first step of this back titration, ethanol is oxidised to ethanal. The reaction that occurs can be represented by the following equation:

$$\underset{\text{ethanol}}{3C_2H_5OH(aq)} + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow \underset{\text{ethanal}}{3CH_3CHO(aq)} + 2Cr^{3+}(aq) + 7H_2O(l)$$

Excess potassium iodide is then added. The I^- ions react with the excess $Cr_2O_7^{2-}$ ions to produce iodine:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(aq)$$

Next, the iodine is titrated with standard sodium thiosulfate solution. The equation for the reaction is:

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

1. Calculate the amount of $Cr_2O_7^{2-}$ ions, in mol, in each 20.00 mL aliquot of potassium dichromate solution.
2. Calculate the average titre of standard sodium thiosulfate solution and the amount of thiosulfate ions ($S_2O_3^{2-}$) in this titre.
3. Deduce the amount of iodine (I_2) formed during the reaction with excess dichromate.
4. Use the equation for the reaction between $Cr_2O_7^{2-}$ ions and I^- ions to deduce the amount of $Cr_2O_7^{2-}$ ions in excess after oxidation of the ethanol.
5. By subtracting the amount of excess $Cr_2O_7^{2-}$ ions from the original amount of $Cr_2O_7^{2-}$ ions added to the diluted wine (from Question 1), calculate the amount of $Cr_2O_7^{2-}$ ions that reacted with the ethanol.
6. Using the equation for the reaction between ethanol and $Cr_2O_7^{2-}$ ions, find the amount of ethanol in each 20.00 mL aliquot of diluted wine.
7. Calculate the amount of ethanol in the 250 mL volumetric flask.
8. Find the molar mass of ethanol and hence calculate the mass of ethanol in the initial 10.00 mL sample of wine.
9. Given that the density of ethanol is 0.785 g mL^{-1}, calculate the volume of ethanol in the 10.00 mL sample of wine.
10. Determine the percentage (v/v) of alcohol in the wine.
11. Compare your result with the alcohol content of the wine as specified by the label on the bottle. If there is a discrepancy between the two figures, suggest possible reasons for this.

safety

- Wear safety glasses and a laboratory coat for this experiment.
- Potassium dichromate can cause skin irritation. Sulfuric acid is highly corrosive. If either chemical comes in contact with skin, wash immediately with a large volume of water.
- Avoid contact of potassium iodide and sodium thiosulfate with the eyes and skin.

Adjustment of wine elements

Acidity and pH in particular are monitored and controlled during the winemaking process. Excess tartaric acid tends to crystallise at low temperature, and precipitates to form tartrate crystals that can be removed later. Therefore, the wine can be chilled in a process called cold stabilisation to remove tartaric acid when the pH is too low or the total acidity is too high.

Acidity can also be lowered by malolactic fermentation in which malic acid is converted to the milder lactic acid by bacteria, resulting in a smoother tasting wine. Malolactic fermentation is used in the production of red and sparkling wines. Acidity can also be lowered by adding calcium carbonate ($CaCO_3$), which reacts with acids in the wine. A wine with too little acid can have tartaric, malic, citric or a blend of the three added.

Crystals at the bottom of wine are tartrate crystals. Most wineries remove them purely for appearance. The presence of these crystals does not affect the taste or mean an inferior wine.

Experimental investigation

Select a white wine to analyse for total acidity. Total acidity is measured using titration, where all the acid is assumed to be tartaric acid. The wine is usually titrated against a solution of sodium hydroxide. Design an experiment using titration to determine the amount of acid in a sample of wine. Consider the points below.

- The materials needed and the procedure are similar to other titrations you have performed. You will find that only a 10.0 mL of aliquot of wine is required. Choose a white wine for analysis. Red wine is not suitable as its colour masks the colour change of the indicator. Make sure you follow all safety rules, and have your method checked by your teacher.
- Use table 13.4 in Chapter 13 to select an appropriate indicator. If you haven't used that particular indicator before it is a good idea to have a practice titration first so you know what colour change you will be looking for. You may even want to complete a titration curve for the titration.
- Most of the acid present in wine is tartaric acid and it is assumed that when titrating against sodium hydroxide all the reacting acid is tartaric acid. Tartaric acid, a dicarboxylic acid, reacts with sodium hydroxide according to the following equation:

  $$H_2C_4H_4O_6(aq) + 2NaOH(aq) \rightarrow Na_2C_4H_4O_6(aq) + 2H_2O(l)$$

- Your experimental determination of the amount of acid in the wine sample will be in mol L^{-1}. Total acidity is expressed as g L^{-1} or as a percentage. From your results, determine total acidity in both g L^{-1} and as a percentage. Assume the density of wine is 1.00 g mL^{-1}.
- Compare your results with the accepted values of total acidity.

Other investigations

1. Each group could analyse a different wine type (such as chardonnay, moselle or riesling) and compare the results. Compare your experimental values to the accepted values.
2. You could compare a cheap wine with a more expensive wine, an Australian wine with an international wine or wines produced from grapes grown in different regions of Australia. Analyse the pH, total acidity and alcohol content of each.
3. You may know someone who makes homemade wine. Test a sample and compare it to one of the other wines you have analysed.
4. You may find that there are local wineries for you to visit.

Further investigations

There are many other elements involved in the chemistry of wine that you could research, and perhaps even develop into experimental research. Ideas include:

- how acidity is altered
- the formation of different acids as the grape and wine develops
- other analyses performed on wine
- malolactic fermentation
- allowable component levels in wine
- phenols in red wine
- red wine making
- recent advances in winemaking
- the different aspects of chemistry in winemaking.

quality control

Many of the products used in our society have a basis in the chemical industry. They include detergents, adhesives, cosmetics, paper, fabrics, foods, medicines, plastics and paints. Methods of analysis have been developed to ensure that we are getting a product of good quality.

Why monitor the quality?

The testing of chemicals is vital to ensure that:

- raw materials for new products are of the highest purity
- food is not contaminated with pesticides, heavy metals or other dangerous contaminants
- materials for consumer products will be able to withstand the conditions under which they are used
- medicines contain the correct active ingredients in their right amounts
- nutritional information is accurate.

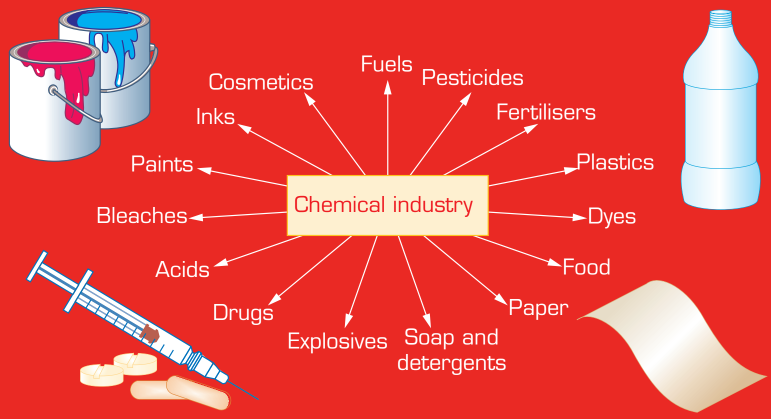


figure qc.1 The quality of all the above products needs to be checked before they can be sold to the consumer.

* Chapter 12 **Qualitative and quantitative testing** describes the properties of substances that are assessed in monitoring quality (page 440).

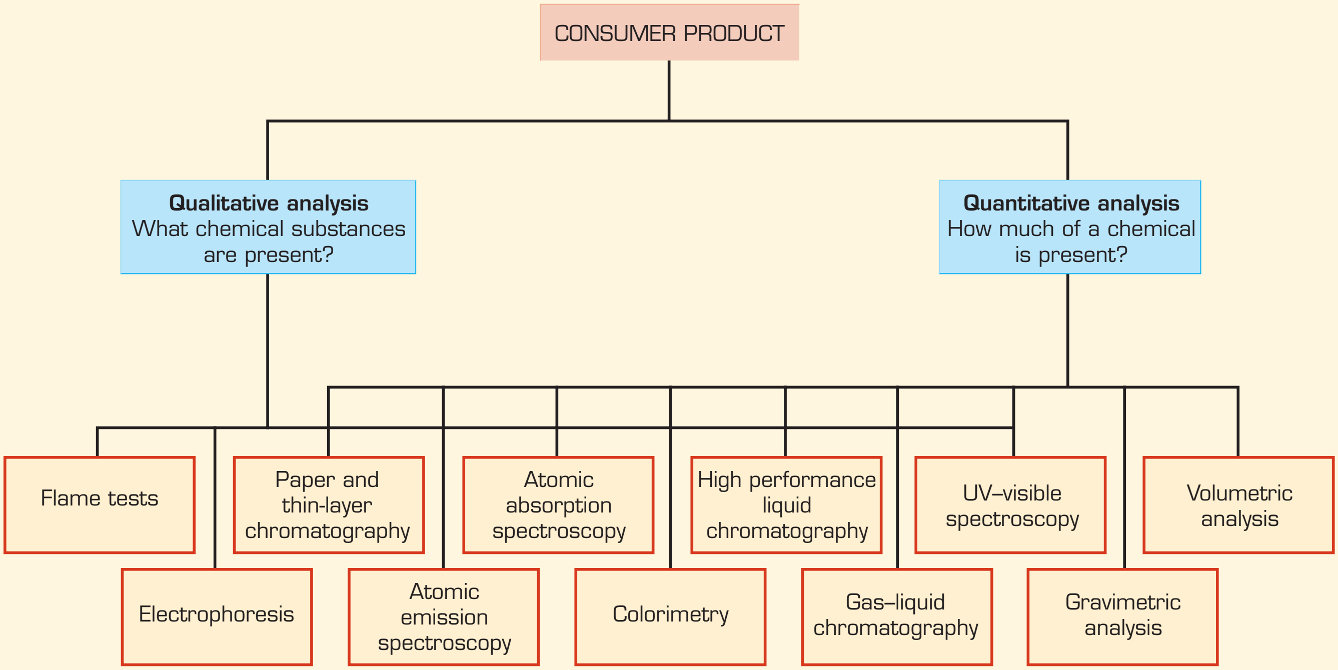


figure qc.2 Consumer products can be analysed by various techniques.

Chapter 13 **Volumetric and gravimetric analysis** (page 456) and Chapter 14 **Instrumental and specialised techniques** (page 488) describe the techniques of figure qc.2.

The term for checking consumer goods to ensure efficient production methods and suitable quality is known as quality control. The chapters of this area of study have outlined some of the techniques used in quality control analyses. The techniques are summarised in figure qc.2.

figure qc.3 This scientist is using chromatography to check for pesticides in food.

Some of the investigations in this context encourage you to make a comparison of your test results with the claims of the manufacturers. Products supplied to consumers are likely to have units in one of the forms described in table qc.1.

table qc.1 The units of concentration as often found on the labels of consumer products.

Concentration	Formula	Units
percent by mass	$\text{concentration} = \dfrac{\text{mass of solute (g)}}{\text{mass of solution (g)}} \times 100\%$	w/w
percent by volume	$\text{concentration} = \dfrac{\text{volume of solute (mL)}}{\text{volume of solution (mL)}} \times 100\%$	v/v
mass of solute per volume of solution	$\text{concentration} = \dfrac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100\%$	w/v
mass of solute per mass of solution	$\text{concentration} = \dfrac{\text{mass of solute (mg)}}{\text{mass of solution (g)}} \times 100\%$	mg/g

For example, a bleach contains 42 g of sodium hypochlorite in 1 L of solution. Using the formula for mass of solute per litre of solution:

$$\begin{aligned}\text{concentration} &= \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100\% \\ &= \frac{42\text{g}}{1000\text{ mL}} \\ &= 4.2\text{ g mL}^{-1}\text{ or }4.2\%\text{ (w/v)}\end{aligned}$$

You may select an area of experimental research that uses one or more of these techniques. The examples of the next section are some that you can perform or modify for a subject of interest to you. Most schools do not have access to expensive equipment such as a high performance liquid chromatograph or an atomic absorption spectrometer but you may be able to make contact with a local tertiary institution or specialised industrial laboratory and work out an investigation using their equipment.

Experimental investigations

1 Chromatography: Colour mixture separation

Chromatography can be used to test the mixtures of colours used in items such as inks, ice-blocks, sweets (Smarties or M&Ms work well) or you can extract the pigments from green vegetables. Water-soluble colours can be separated in a similar process to those in Chapter 12. You may need to evaporate and concentrate the substance before performing the experiment. Leafy vegetables need to be chopped and ground up in a mortar and pestle, and about 10 mL of acetone used to extract the colour. Different vegetables could be compared (for example cabbage and silverbeet) or you could compare the inks in different brands of printer cartridges.

Section 12.3 **Chromatography** describes this separation technique (page 443).

2 Gravimetric analysis: determining sulfate content in fertilisers

figure qc.4 Some crops thrive with the addition of sulfur in the form of sulfates to the soil.

To find the proportion of sulfate in a particular fertiliser, start by grinding up a small amount and accurately weigh out about 1.0 g. Dissolve this in 50 mL of deionised water and then filter the mixture. Wash several times and then heat to boiling. Add 5 mL of 2 M HCl solution. Make the solution up to 200 mL using deionised water and gently bring to the boil. Dropwise add 15 mL of 0.5 M barium chloride to the hot solution with stirring and heat for a further minute. When the precipitate settles, add a few more drops of barium chloride and if more precipitate forms add a few more mL. Filter the barium sulfate precipitate under vacuum and wash it with a little warm water. Dry it overnight in an oven. Use the mass of barium sulfate to determine percentage by mass of sulfur in the fertiliser.

Safety: Soluble barium compounds are toxic.

* Section 13.1 **Gravimetric analysis** describes the techniques used to determine the mass of active ingredients (page 456).

3 Volumetric analysis: hydrochloric acid content in brick cleaner

figure qc.5 After the hard work of laying the bricks is done, excess mortar is removed using a brick cleaner with hydrochloric acid as the main ingredient.

Half fill a 250 mL volumetric flask with deionised water and accurately weigh. Add 5 mL of brick cleaner and accurately weigh again to determine the mass of brick cleaner used. Add more deionised water, mixing thoroughly, to make 250 mL of solution. Titrate 20 mL aliquots of this solution against 0.1 M sodium carbonate using methyl orange as an indicator. Use your results and the following equation to determine the percentage, by mass, of HCl in the brick cleaner.

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

Compare your results with the manufacturer's claims. You could also compare the HCl content of different brands of brick cleaner to determine the one of best value.

Safety: Brick cleaner has a high concentration of hydrochloric acid which is corrosive. Methyl orange may cause irritation to skin and eyes. Always add concentrated acid to water—never the reverse.

* Section 13.3 **Volumetric analysis** describes acid–base titrations (page 466).

4 Volumetric analysis: aspirin in a pain reliever

Dissolve one aspirin tablet in about 10 mL of methylated spirits in a 100 mL flask. Add 20 mL of deionised water and two or three drops of phenolphthalein indicator. Titrate this solution against approximately 0.1 M standardised sodium hydroxide until the first sign of permanent pink. This process should be repeated several times for accuracy. Use your results and the following equation to calculate the amount of aspirin in a tablet.

$$CH_3COOC_6H_4COOH(aq) + NaOH(aq) \rightarrow CH_3COOC_6H_4COONa(aq) + H_2O(l)$$

Compare this figure with that specified by the manufacturer. Compare different brands of aspirin.

Safety: Methylated spirits is highly flammable. Sodium hydroxide solution is highly corrosive.

figure qc.6 Aspirin is one of the most commonly used products for relieving minor pain. If the pain persists, see your doctor.

5 Volumetric analysis: ethanoic acid in vinegar

Dilute vinegar by pipetting 25.00 mL of vinegar into a 250 mL volumetric flask. Add deionised water up to the calibration line and mix thoroughly. Titrate 20.00 mL aliquots of this solution against approximately 0.1 M standardised sodium hydroxide using phenolphthalein indicator. Use your results and the following equation to calculate the amount of ethanoic acid in the vinegar.

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

You could compare the ethanoic acid content of different brands of vinegar.

Safety: Sodium hydroxide solution is highly corrosive. Phenolphthalein may cause irritation to skin and eyes.

6 Volumetric analysis: ammonia in household cleaner

Place a 250 mL volumetric flask on an electronic balance, zero the balance. Add about 8 mL of the household cleaner to the flask and record the mass. Add deionised water up to the calibration line and mix thoroughly. Titrate 20.00 mL aliquots of the solution against approximately 0.1 M standardised hydrochloric acid solution using methyl orange as an indicator. Use your results and the following equations to calculate the amount of ammonia (percentage by mass) in the cleaner.

$$NH_3(aq) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$$
$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

Compare this figure with that specified by the manufacturer. You could repeat this process for different brands and types of ammonia cleaners.

Safety: Hydrochloric acid is corrosive. Ammonia vapour irritates the skin, eyes and respiratory system. Methyl orange may cause irritation to skin and eyes.

7 Volumetric analysis: nitrogen content of lawn food

Accurately weigh out about 1.3 g of fertiliser, transfer it to a 250 mL volumetric flask, add deionised water up to the calibration line and mix thoroughly to dissolve any ammonium compounds. Pipette 20 mL aliquots of this solution and 20 mL aliquots of standardised 0.1 M sodium hydroxide solution into each of three 250 mL conical flasks. Add 50 mL of deionised water to each flask and boil the mixtures for about ten minutes (add additional water if necessary) until the vapour no longer turns moist red litmus paper blue, indicating that all the ammonia has been expelled. Titrate the contents of each flask against approximately 0.1 M standardised hydrochloric acid solution using methyl orange as an indicator. The ammonia compounds of the fertiliser were reacted with sodium hydroxide according to the equation:

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(l)$$

Heating the solution expelled the ammonia formed and the amount of hydroxide ions remaining can be used to determine the amount of nitrogen, as ammonium, in the original sample.

Compare this figure with that specified by the manufacturer. You could use the same process to compare different brands of lawn food.

figure qc.7 For a lush lawn, nitrogen-rich lawn food is often fed to grass.

Safety: Hydrochloric acid and sodium hydroxide solutions are highly corrosive. Ammonia vapour irritates the skin, eyes and respiratory system. Methyl orange may cause irritation to skin and eyes.

* Section 13.3 **Volumetric analysis** describes back titrations (page 466).

8 Volumetric analysis: the effervescence of soda water

Soft drinks contain carbon dioxide dissolved under pressure. It is this that gives them their fizz. Soda water does not contain the colours that could confuse the indicator change of a volumetric analysis and is recommended for this experiment. Carbon dioxide will react with sodium hydroxide according to the equation:

$$CO_2(aq) + NaOH(aq) \rightarrow NaHCO_3(aq)$$

Phenolphthalein can be used as an indicator for this reaction. The soda water is best kept under pressure to prevent carbon dioxide loss until just prior to the titration.

Use this information and after consultation with your teacher, design an analysis of soda water and carry it out. You could also compare different brands of soda water with that produced by a soda siphon.

Safety: Sodium hydroxide solution is highly corrosive. Phenolphthalein may cause irritation to skin and eyes.

9 Volumetric analysis: comparing antacids

Here are some of the active ingredients of commercial antacid preparations and their reactions with acids:

sodium citrate	$Na_3C_6H_5O_7(aq) + 3H^+(aq) \rightarrow C_6H_8O_7(aq) + 3Na^+(aq)$
calcium carbonate	$CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(aq) + H_2O(l)$
sodium hydrogen carbonate	$NaHCO_3(aq) + H^+(aq) \rightarrow Na^+(aq) + CO_2(aq) + H_2O(l)$
aluminium hydroxide	$Al(OH)_3(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$
magnesium hydroxide	$Mg(OH)_2(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + 2H_2O(l)$

The human stomach produces hydrochloric acid but if too much is produced it can cause discomfort. Commercial antacid products are meant to neutralise some of this excess acid and reduce the discomfort.

Use this information and, after consultation with your teacher, design an analysis of antacids and carry it out. You could also compare different brands of antacids and comment on their relative effectiveness.

figure qc.8 Especially after a big meal, the stomach can produce too much acid. Antacid products can provide relief by neutralising some of this acid.

10 Volumetric analysis: ascorbic acid in vitamin C tablets

Standardise a 0.05 M iodine solution by titrating 20.00 mL aliquots against approximately 0.1 M standardised sodium thiosulfate solution with 1–2 mL of starch solution as the indicator. Sodium thiosulfate reacts with iodine solution according to the equation:

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

The starch turns black in the presence of excess iodine.
Calculate the concentration of the iodine solution.

Weigh a vitamin C tablet and dissolve it in about 50 mL of deionised water in a 250 mL flask. Titrate this solution against the standardised iodine solution with 1–2 mL of starch solution as the indicator.

Ascorbic acid undergoes oxidation according to the equation:

$$C_6H_4O_2(OH)_4(aq) + I_2(aq) \rightarrow C_6H_4O_4(OH)_2(aq) + 2H^+ (aq) + 2I^-(aq)$$

Use this information and your results to find the amount of ascorbic acid in a vitamin C tablet. Compare this figure with that specified by the manufacturer. You could use the same process to compare different brands of vitamin C tablets.

Safety: Iodine solution can stain skin and clothing. Sodium thiosulfate solution may irritate the skin and eyes.

* Section 13.3 **Volumetric analysis** describes redox titrations (page 466).

11 Volumetric analysis: chlorine in household bleach

Pipette 20.00 mL of bleach into a 250 mL volumetric flask, add deionised water up to the calibration line and mix thoroughly. To 20.00 mL aliquots of this solution add about 5 mL of 1 M potassium iodide solution and about 5 mL of 1 M sulfuric acid solution, turning the solution dark brown due to the formation of iodine. Titrate each mixture against approximately 0.1 M standardised sodium thiosulfate solution until the yellow brown colour has paled. Add 1–2 mL of iodine solution and continue the titration until a blue colour appears.

In this analysis, the hypochlorite ion (OCl^-) of the sodium hypochlorite of the bleach has reacted to produce iodine according to the reaction:

$$OCl^-(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + Cl^-(aq) + H_2O(l)$$

During the titration sodium thiosulfate reacts with the iodine according to the equation:

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

Use this information and your results to find the amount of available chlorine (as OCl^-) in the household beach as a percentage (w/v). Compare this figure with that specified by the manufacturer. You could use the same process to compare different brands of bleach.

Safety: Sulfuric acid solution is highly corrosive. Iodine solution can stain skin and clothing. Sodium thiosulfate, potassium iodide and household bleach may irritate the skin and eyes.

12 Colorimetry: phosphate in laundry powder

Accurately weigh out approximately 0.5 g of laundry powder, dissolve in approximately 20 mL of hot deionised water and make up to 500 mL in a measuring cylinder. Further dilute the laundry detergent by taking 25 mL of this solution and transferring it to another measuring cylinder and making it up to 500 mL with deionised water. This is the unknown solution that will be analysed by colorimetry.

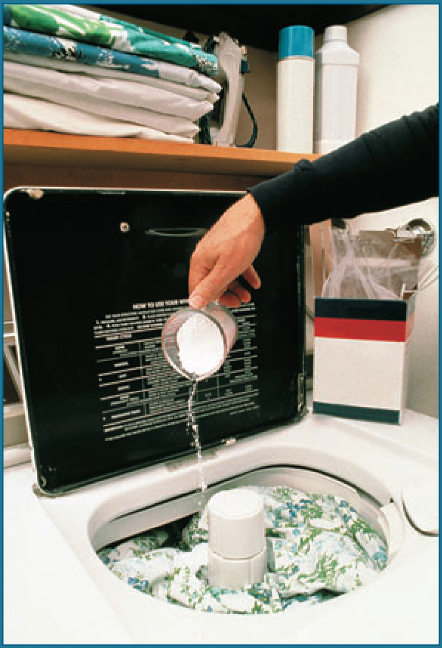


figure qc.9 Cleaners such as detergents and bleaches used in washing clothes vary greatly in quality. The quantitative analysis of these products allows the consumer to determine those that are the best value for money.

Add different amounts of standard phosphate solution (10 mg L^{-1}) to test tubes—20 mL to the first, 15 mL to the second, 10 mL to the third, 5 mL to the fourth and none to the fifth. Add enough water to each test tube to make 20 mL of solution. Add 20 mL of the detergent solution to a sixth test tube. To each test tube add 2 mL of ammonium molybdate and a few crystals of ascorbic acid and mix thoroughly. Heat the test tubes in a beaker of boiling water for about 5 minutes until they turn blue and then remove them all at the same time.

Compare the depth of colours of each test tube to determine the concentration of phosphate in the diluted detergent. If you have a colorimeter available measure the absorbance of each solution, plot an absorbance graph and read from it the unknown phosphate concentration. Use the results of your experiment to determine the amount of phosphate in the original solid sample and the percentage by mass of phosphate in the laundry detergent.

How do your results compare with the manufacturer's specifications?

Safety: Laundry powder is corrosive. Ammonium molybdate is highly corrosive.

* Section 14.3 **Colorimetry** describes this analytical technique (page 491).

13 Colorimetry: iron in food

An analysis of iron in food is described in detail in Section 14.3 Colorimetry. You may like to further investigate the iron content of different food types. You could test whether freshness or processing of certain foods alters their iron content. Does canning, drying or freezing vegetables alter their iron content?

pharmaceuticals

Drugs are substances that alter the physiological or psychological state of the body. They are the active ingredients in medicines—substances which are used to treat, prevent or alleviate the symptoms of disease. There are some substances which are drugs but not medicines, for example alcohol and nicotine. Pharmacy is the science of preparing and dispensing drugs and the term pharmaceutical can be defined as relating to drugs or pharmacy.

figure ph.1 Tablets of all sizes, shapes and colours—the pharmaceutical industry has become a multi-billion dollar business.

Early pharmaceuticals

The use of pharmaceuticals has been recorded as early as ancient Egyptian times 4000 years ago. The Old Testament of the Bible describes the use of fungi and moulds to treat infected wounds. An Indian healer from the sixth century BC recorded a list of 760 medicinal drugs. Early Asian civilisations made quite extensive use of medicinal plants as part of their healing practices (some of which are not legal today because of their recreational misuse). Many tribal medicine men and women used strong herbal drugs to promote trance-like states to add to the mysticism of their healing powers. These early medicines were usually plants whose medicinal benefits were often discovered by accident.

Many of the substances used as medicines in early times have provided the basis for substances still in use today. For example, foxglove plants were commonly used as medicines. Foxglove contains a substance called digitalis, still used today for its properties as a heart stimulant. Ancient Asian medical practitioners used the snakeroot plant, which today provides the basis for a medicine to reduce blood pressure.

figure ph.2 Foxglove has been used since ancient times. The active ingredient, digitalis, is still used today as a heart stimulant.

figure ph.3 Cocaine was once used as a medicine; today it is an illegal drug.

Medicines from natural sources

In recent years, natural medicines have made a remarkable comeback. Many people now choose to see a naturopath for a natural remedy before seeing a doctor for a synthetic medicine. Sales of medicinal products in supermarkets and health-food shops have increased dramatically in the last few decades. Some of the more commonly used natural medicines include:

- echinacea to boost the immune system and help the body fight infection, particularly respiratory infections
- garlic for its antibiotic and antiviral properties, which are particularly useful in fighting colds, sinusitis and other respiratory infections
- ginger for treating nausea, especially motion sickness and morning sickness during pregnancy.

There are over 20 000 common medicinal plants used in various parts of the world listed by the World Health Organization (WHO).

Many pharmaceutical drugs are synthetic versions of the active ingredients from medicinal plants—for example, the cancer medicine Taxol derives from compounds found in yew trees. Although many drugs are based on substances of plant origin, researchers have looked further afield to develop new drugs. Some examples of this include blood pressure medications developed from viper venom, the anti-cancer drug codenamed ET743 developed from sea squirts, and the study of Caribbean sponges to develop the AIDS drug AZT. One of science's major concerns over the loss of species of plants and animals is the loss of potential clues for new drugs to fight diseases for which we currently have no treatment.

figure ph.4 Researchers have become more interested in marine organisms as a possible source of new medicines.

Developing new medicines

There are two elements vital to the development of a new drug:

1. a complete biological understanding of the mechanism of the disease or condition
2. finding a lead compound to use as a starting point in the research.

Finding a lead compound can come from careful study and research, or by sheer good luck. Lead compounds have been discovered by:

- diligent research into the body's chemical processes, e.g. the study of the action of the hormones adrenalin and noradrenalin led to the development of treatments for asthma
- identifying active ingredients in traditional remedies, e.g. the development of aspirin from the traditional remedy from willow bark
- the random screening of a wide range of compounds, including looking for other uses for existing compounds
- by lucky accidents, e.g. the contamination of some bacterial experiments led to the discovery of penicillin
- the use of computer modelling, which can design molecules of a particular shape or size that fit their intended target.

The development of aspirin

The pain-relieving properties of the extract of willow bark have been recorded since ancient times. The bark was commonly made into an infusion (like tea) and then drunk to alleviate symptoms. By the mid 1800s, the active ingredient in willow bark had been identified as salicylic acid. Extracting large amounts of it from willow bark was not practical or cost effective, so a laboratory method was needed to produce it in usable quantities. By 1870 scientists had developed a method to produce it in large quantities, and as a white powder that was easily taken.

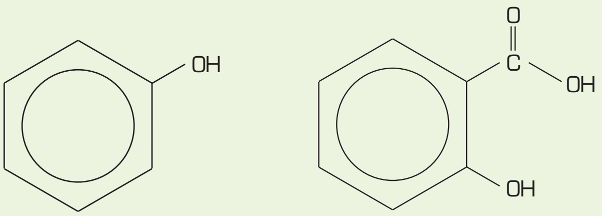


figure ph.5 Phenol and salicylic acid have very similar structures, differing by only one functional group.

The compound phenol was used as a starting point for producing salicylic acid. It was similar in structure and readily available. Using carefully controlled conditions, phenol can be combined with carbon dioxide to produce salicylic acid. The structure of phenol and salicylic acid are shown in figure ph.5.

* Section 2.5 **Organic compounds** describes alcohols and carboxylic acids (page 246).

Esters are organic compounds formed from the reaction of an alcohol with a carboxylic acid.

With a pH of about 2.4, salicylic acid is a relatively strong acid that often caused the unfortunate side effects of irritation (and sometimes bleeding) of the mouth, oesophagus and stomach. Felix Hoffman, a chemist who worked for the Bayer company, decided to try changing the structure to keep the medicinal properties of the molecule but reduce the nasty side effects. His father suffered from very painful rheumatoid arthritis and was a guinea pig for the new substances Hoffman synthesised. In 1898, Hoffman had successfully accomplished his goal. By replacing the alcohol functional group with an ester he produced acetylsalicylic acid, a compound with pain relieving properties, which was gentler on the stomach. He achieved this by reacting acetic anhydride with salicylic acid. Acetic anhydride is formed from the reaction of two acetic acid molecules eliminating a water molecule. The reaction between salicylic acid and acetic anhydride is shown in figure ph.6.

* Chapter 8 **Acids–base reactions** describes the properties of acids such as salicylic acid (page 366).

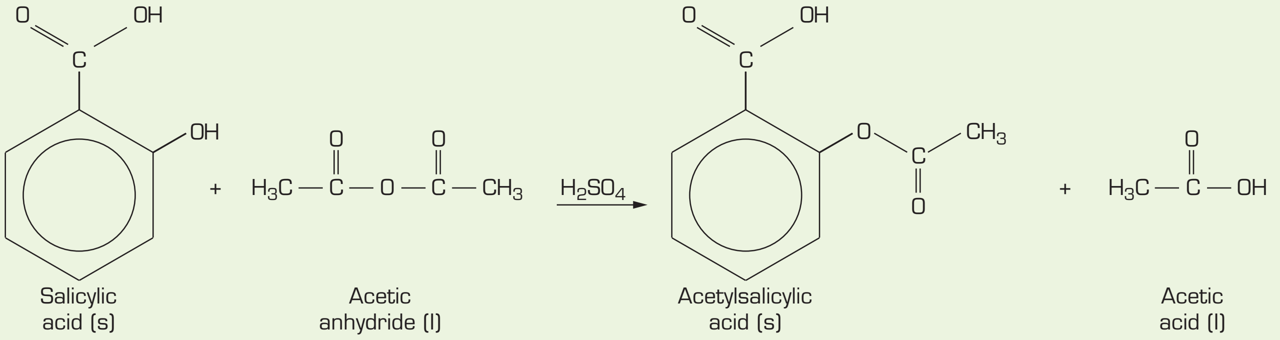


figure ph.6 The reaction between salicylic acid and acetic anhydride produces acetylsalicylic acid and acetic acid.

* Section 9.5 **Reactions of organic acids** describes esterification reactions (page 401).

The Bayer company produced and marketed this product as aspirin. It was originally sold as a powder (as salicylic acid had been) but its solubility in water was quite low. An alternative form of delivery was developed—the tablet. Aspirin was the first medicine marketed in tablet form. It is still widely used around the world and is still marketed in Australia as Bayer aspirin.

Thalidomide—a pharmaceutical disaster story

Developing a new drug for release is a very long and very expensive process. For every new medicine that reaches the market, hundreds of others fail and millions of dollars are spent. In the past, testing procedures have been much less stringent. The drug thalidomide is an excellent example of the need for thorough testing of medicines before they are made available to the public.

Thalidomide was discovered accidentally during a series of experiments investigating new antibiotics. It was tested for various uses including constipation, seizures and influenza, and appeared to have no side effects. It was also noted that it had a calming effect.

In 1957 a West German company developing the drug decided to market thalidomide as a sedative. It was thought to be so safe it was sold over the counter (without prescription) in countries all over the world. (Interestingly, the drug was never approved for use in the USA; the FDA was not happy with the testing that had been done.)

Thousands of pregnant women began taking the drug as it relieved morning sickness. Reports of increased birth defect rates began filtering out, but the drug remained in public use. In the early 1960s, Australian researcher Dr William McBride drew attention to the alarming side effects associated with

figure ph.7 A pharmaceutical disaster. The 'safe' drug thalidomide caused birth deformities in thousands of children around the world.

the use of the drug. The drug was causing terrible deformities in developing foetuses. Around the world, thousands of children were born with serious disabilities, many with seriously shortened arms, legs or both. Some children had little more than stumps for limbs.

The blame was placed on the drug company. In their defence, they cited their animal testing results which did not show these deformities in animal births. Other researchers performed tests and found it difficult to duplicate the abnormalities the drug had caused in human babies. It became clear that the testing procedures were inadequate—relying on animal testing had misled the medical community about the safety of the drug.

As a result of the thalidomide tragedy, the Australian Drug Evaluation Committee (ADEC) was formed. In many countries around the world, the thalidomide incident led to an increase in standards for the testing and approval of new medicines.

Analysis of medicines

It is often useful to know the chemical composition of the active substance in a medicine, especially for research into other uses for the substance and developing new drugs. A variety of qualitative and quantitative techniques can be used to determine the chemical composition of a substance.

figure ph.8 How do we know the chemical structure of the active ingredient in medicines?

Qualitative analysis

The qualitative testing of drugs can determine the types of functional groups present in the drug. Properties of the functional groups can determine the properties of the molecule. For example, salicylic acid:

- is acidic in an aqueous solution
- reacts with an alcohol to produce an ester
- reacts with a neutral solution of iron(III) chloride to produce an intense pink colour.

* Chapter 12 **Qualitative and quantitative testing** describes qualitative testing techniques (page 440).

The acidic nature and reaction which produces an ester are qualitative indications that the substance contains a carboxyl group. The reaction with the iron(III) solution indicates the presence of a phenol group.

A phenol group has an –OH group attached to a benzene ring (see figure ph.5).

* Chapter 2 **Elements and compounds** describes the carboxyl and phenol functional groups (page 226).

Chemical tests provide very basic, limited information. To find out more detail about the molecule, certain instrumental analysis techniques can be used. Some commonly used instrumental techniques include:

- infrared spectroscopy
- mass spectrometry
- nuclear magnetic resonance (nmr) spectroscopy.

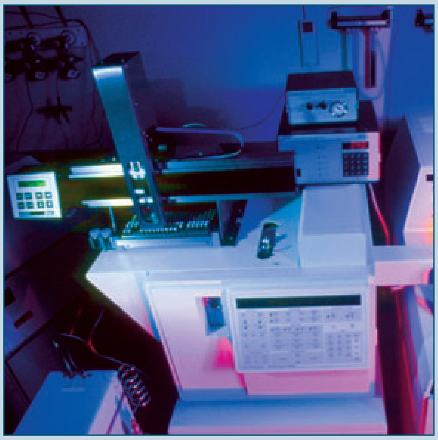


figure ph.9 An infrared spectrometer.

Infrared spectroscopy

The infrared frequency ranges which are absorbed by a compound can be analysed to determine the functional groups present, as they absorb at similar frequencies even if they are in different compounds. An infrared spectrum of salicylic acid provides clear evidence that it contains a hydroxyl group (–OH) and a carbonyl group (C=O).

* Section 14.5 **Infrared spectroscopy** describes how infrared spectroscopy works (page 496).

Nuclear magnetic resonance spectroscopy

This technique analyses the chemical environment of the nuclei of one specific element in the compound. Often that element is hydrogen. The nmr spectrum for salicylic acid provides evidence that it has:

- one proton (hydrogen) in a carboxyl environment
- one proton in a phenolic environment
- four protons which are part of a benzene ring.

This technique provides more detail about the structure of the compound.

* Section 14.6 **Nuclear magnetic resonance spectroscopy** describes this analytical technique (page 499).

Isomers are compounds that have the same molecular formula but different structural formulae or spatial arrangements of their atoms.

Mass spectrometry

The results of nmr and infrared analysis confirm that a hydroxyl group and a carboxyl group are present in salicylic acid attached to a benzene ring. The position of the groups on the benzene ring can vary as the ring contains six carbons. Stated simply, mass spectroscopy identifies the isomeric form of a molecule when more than one structural possibility exists. The results of mass spectrometry for salicylic acid show that the hydroxyl group is on carbon number 2 in the benzene ring.

A combination of the techniques above is used to discover the chemical structure of unknown substances. This is of extreme importance to the pharmaceutical industry. It allows the determination of the structure of a plant or animal substance that shows promise as a medicine or a lead compound for a medicine.

Although the pharmaceutical industry improves on existing drugs constantly, it is always searching for a new medicine to market, especially for conditions that have no suitable drug currently available.

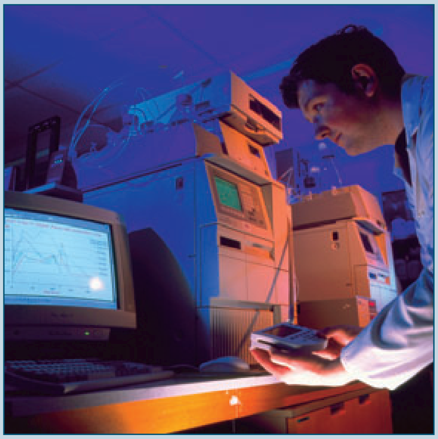


figure ph.10 An nmr spectrometer.

Further investigations

1 Penicillin was a groundbreaking compound in medicine. It became a lead compound for a vast array of antibiotics. Prepare a short report on the history of penicillin from its initial discovery to its widespread use.

2 Aspirin belongs to a class of medicines called analgesics. Two other well-known compounds from this group are acetaminophen and ibuprofen. Research these two substances, indluding their:

- synthesis
- chemical structure
- marketing names
- side effects.

3 Your group has chosen to prepare aspirin (acetylsalicylic acid) for a laboratory assignment. Your chemistry book does not have the instructions for this experiment. Research a reasonably simple method of preparing aspirin and write up experimental instructions, using the same format and headings as you normally use. Make sure you include safety information.

4 You have been hired as a consultant by a chemical company that has stumbled across a new chemical substance that they believe may be effective in acting against certain types of cancer. They are unfamiliar with the procedures associated with the testing and approval required before marketing their new drug. Your job is to prepare a visual presentation for the board of the company detailing what they will need to do to develop and test their substance, and prepare it for approval by the Therapeutic Goods Administration.

5 In Australia, pharmaceutical companies are granted a 20 year patent on new drugs. After this, any other company can manufacture and market the drug under another brand name. In recent years, this has led to a significant increase in the availability of generic drugs on the market. When you give a prescription to a pharmacist, many will ask you if you would prefer a generic brand of the drug. Prepare a factsheet suitable for distribution to the general public explaining generic medicines. Include any differences from the original drug, including cost.

6 In recent years, the body that regulates medicines in Australia, the Therapeutic Goods Administration (TGA) has moved to re-approve the use of thalidomide. Thalidomide was banned in the early 1960s because of its terrible effects on developing foetuses. Based on recommendations from the ADEC, thalidomide may be re-approved as it has been shown to be a very effective treatment in leprosy and possibly certain forms of cancer. Research the facts on this development and write a newspaper article.

7 Coca-Cola is a modern day icon. The company spends millions of dollars yearly on its advertising campaigns. In 1903 the company changed the formula of Coca-Cola—the company substituted caffeine for cocaine. Design a poster that would be suitable to display on the wall of your chemistry classroom comparing the structure and effects of caffeine and cocaine.

forensic chemistry

Forensic science broadly refers to analysis, and is mostly associated with crime. The use of forensic science in solving crime has been around for over two hundred years, but it has only been in the most recent years that considerable advances have occurred. This is the result of new and more accurate techniques, more sensitive analytical instruments such as the mass spectrometer, and also our increased knowledge of science. In particular, DNA analysis has revolutionised the solving of crime.

figure fc.1 Evidence is collected from every crime scene. With advances in analytical techniques, including DNA analysis, criminals are more likely to be identified by the evidence they leave behind.

The term 'forensic' originated from the Latin word *forensis* meaning public forum. The modern equivalent would be a court of law.

The mass spectrometer is a highly sensitive instrument that can identify a specific substance. For example, a paint sample from a hit-and-run victim can be matched exactly to a paint sample taken from a suspect's car.

figure fc.2 Evidence is collected at a crime scene for analysis in the laboratory.

As there are so many aspects to a crime, there are many fields of forensic science. A forensic scientist may specialise in forgery, handwriting analysis, voiceprints, DNA analysis, drugs and arson or many others. The scientists who conduct these analyses therefore come from diverse fields of science, including chemistry, biology, dentistry, pathology, toxicology and entomology. Forensic scientists use the same techniques and apparatus as scientists in other fields.

A forensic chemist specialises in the identification and analysis of substances. Their investigation may be limited if the samples are not pure enough or are contaminated, or if the sample size is extremely small. A forensic chemist at the scene of a crime must be careful not to contaminate or destroy samples. They must draw conclusions and accurately report on findings. The forensic chemist may also be called upon as an expert witness in court to explain the findings. They may be called upon to help with:

- drug identification
- identification of dyes
- identification of unknown substances
- toxicological analysis of food products, drugs and body fluids
- comparison of substances, including paint chips, dyes, lubricants and plastics, to suspected sources
- DNA analysis
- trace evidence, including gunshot residue and the presence of accelerants in arson
- fingerprinting
- fibre analysis, including hair, clothing, rope.

Their main tools are specialised instrumentation and they need to be able to interpret the data (often a spectrum).

* Chapter 14 **Instrumental and specialised techniques** describes the apparatus that a forensic chemist would use to analyse evidence (page 488).

figure fc.3 A forensic chemist often deals with the unknown. Many methods of qualitative and quantitative analyses are used to determine the identity of a substance.

Forensic testing

Identifying food components

During a post mortem examination, the contents of the stomach are analysed. This is used to identify what the person has consumed, which can place them at a certain location or identify if poisons are present. The degree of breakdown of food, particularly carbohydrates, can also assist in determining the time of death. Forensic scientists can also test the stomach contents for protein and lipids from food.

* Section 2.5 **Organic compounds** describes the structure of organic compounds (page 246). Section 10.1 **The structure and properties of polymers** describes the structure of carbohydrates (page 409).

Identification of metals

A metal could be a poison, or a water or soil contaminant. The flame test is a simple test that can be used in the school laboratory to identify the presence of a particular metal in a sample. Experiment 12.1 ‘Flame test’ gives you the opportunity to test for different metals. Although this experiment uses solids, a metal solution can also be tested.

* Section 12.2 **The flame test** describes the technique of flame testing (page 441).

Pigment analysis

A pen is used to forge a cheque. A felt-tip pen is used to write a ransom note. It is possible to identify whether a specific type of pen was used in a crime using a technique called chromatography.

Chromatography is a useful tool for identifying the different components in a mixture. A certain ink or dye is composed of specific pigments in specific quantities. A forensic chemist can test the evidence and compare it to a suspected pen. If the pen used in the crime is the same type as the suspected pen, then the patterns on the chromatogram will be identical. A simple form of chromatography that can be conducted in the school laboratory is paper chromatography. Experiment 12.2 ‘Chromatography of Smarties and felt-tip pens’ will give you the opportunity to use paper chromatography to test for the presence of pigments. The concepts involved are the same as if you were conducting a test using a high performance liquid chromatograph (HPLC).

figure fc.4 The ink from a pen used in a forgery can be analysed by a forensic chemist using chromatography.

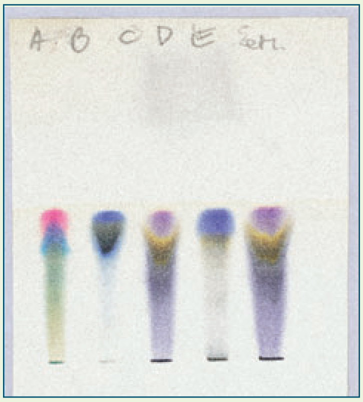


figure fc.5 A chromatogram for a series of pens. The colours are due to the presence of certain pigments.

Section 12.3 **Chromatography** describes the technique of paper chromatography (page 443). Section 14.7 **Chromatography techniques** describes the different chromatography techniques (page 501).

DNA analysis

Everyone’s DNA is unique (except identical twins). DNA can be extracted from a very small sample of human tissue and analysed. The sample may be blood, body cells, semen, saliva or from the root of a hair. The results can be used to match DNA samples and place an individual at the crime scene, as well as to exclude a suspect or identify the victim. Only a few sections of a DNA sequence, which vary greatly between individuals, are compared. The banding on a DNA profile is used to make the comparison.

DNA analysis is pivotal in many criminal cases. In 2000 in the northern NSW town of Wee Waa, around six hundred of the town’s men aged between 18 and 45 agreed to DNA testing. Why? An elderly woman had been raped and existing evidence did not provide any answers. The rapist did leave behind a sample of body fluid, which contained DNA. The town’s men provided saliva samples, along with fingerprints and a photograph. The rapist came forward before testing was completed.

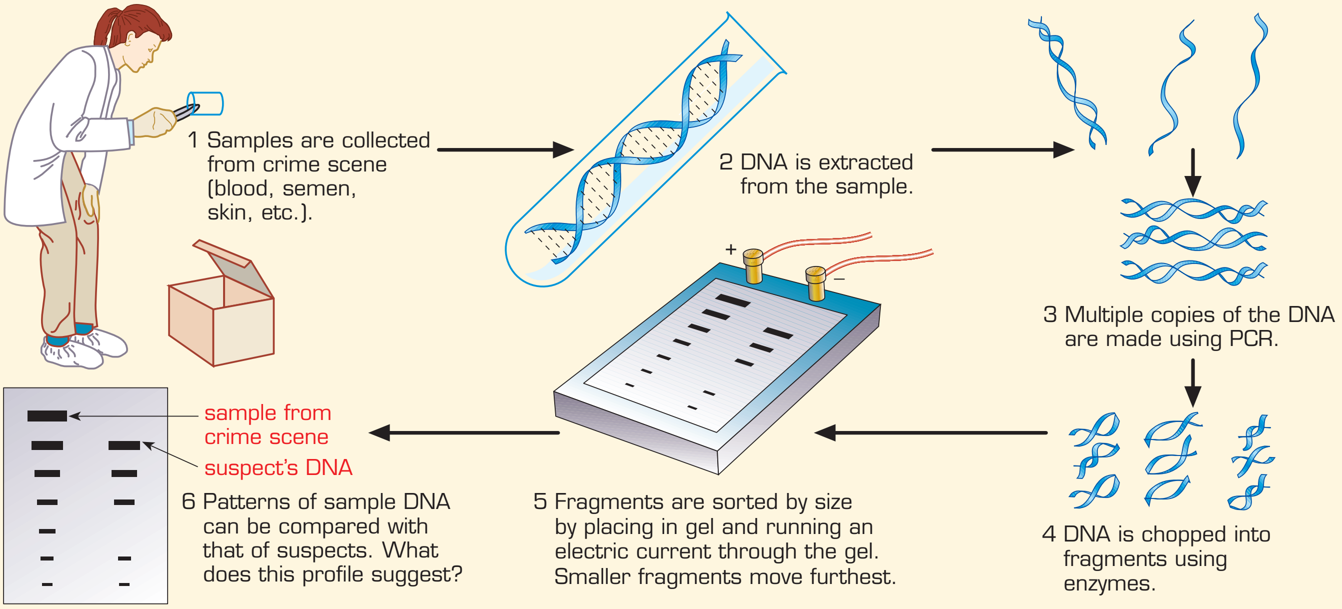


figure fc.6 The process of making a DNA print.

table fc.1 Some areas of forensic chemistry.

Area of investigation	What is tested?	What is being investigated?	Techniques used
drug analysis	• ingredients used in drug production • residues of the drug produced • by-products created during production	• the identity of the compound • the quantities produced • the method of production	• mass spectrometry • thin layer chromatography (separation of sugars used to cut drugs)
fibre analysis	• crystal structure of the fibre • colouring agents used to dye fibres • polymer types	• the identity of fibres used in fabrics and ropes • fibre damage—UV damage, fracture points, shortened polymer lengths	• infrared spectroscopy • infrared microscopy • X-ray diffraction • UV fluorescence • flame analysis • atomic absorption spectroscopy • mass spectrometry • melting point
fats and oils	chemical profiling—different molecular mixtures, qualitative and quantitative	the identity of fats and oils in foods and fuels (theft, arson attacks—fire accelerants)	• infrared spectroscopy • gas–liquid chromatography
DNA analysis	genetic components of hair, skin, blood, semen etc.	the identity of an individual	electrophoresis
soil profiling	• geology and mineralogy of soil • nutrients in soil	• the relationship between drug crops and areas of cultivation • soil transported on shoes, cars and tools of suspects	mass spectrometry
alcohol analysis	blood alcohol levels	whether an individual has been under the influence of alcohol	gas–liquid chromatography

Experimental investigations

1. Conduct chromatography on a range on different substances that contain pigments. Collect different substances, including plants such as silverbeet, red cabbage and flowers. Test a range of solvents and identify the most suitable solvent for different samples. Consider solvents such as methylated spirits and salt solution, always ensuring you undertake the necessary risk assessments. Refer to Experiment 12.3 as a guide for your experimental design.
2. You have been provided with a ransom note written in ink. Your task would be to identify the pen responsible for writing the note, given a range of suspect pens. Use chromatography to analyse a range of pens or inks. Refer to figure 12.6 for a simple diagram of how your experiment could be set up. Again, test a range of solvents and identify the most suitable solvent for different inks. Consider whether the ink is water soluble or not. Compare the colours and distance from the origin of the components of the inks. Do you find that they contain common dyes? Calculate the R_f value for each of the coloured components.
3. Research how to test for carbohydrates, proteins and lipids in food. Make up mock stomach contents of a victim for another group. Test the mock stomach contents for the presence of these nutrients. Investigate the effects of time on the food tests for the mock stomach contents.
4. Your teacher will give you an unknown compound to identify. To make it easier, you may be provided with a set of possible answers. This is a good opportunity for you to use all the chemistry you have learned so far. For example, if it's a solid, does it react with an acid? Does it produce coloured light when placed in a Bunsen flame? Is it water soluble? If so, does a precipitate form when reacted with another solution?

Consider this

1. Refer to the Wee Waa case, and consider the following questions.
   - **a** What forensic evidence could have been collected to help solve the crime? You may like to further research the case.
   - **b** Suggest what analytical techniques would have been used to analyse the evidence.
   - **c** Several men did not agree to participate in the DNA testing program. How does this affect the validity of such a testing program?
   - **d** The testing program caused a lot of debate. Outline the positives and negatives for such a testing program. Consider wider implications; for example, what if the DNA of one of the men matched DNA found at the scene of an unsolved crime elsewhere?

2 Refer to the chromatogram in figure fc.5.

- a Each pen gives a distinctive chromatogram. If the chromatogram of a certain pen matches the chromatogram of a pen used in a forgery, do the test results confirm that it was definitely used in the crime? Explain your answer.
- b What other evidence would a forensic scientist look for related to a forgery?
- c Look again at figure fc.5. Which ink samples are from the same type of pen? Give reasons for your choice.

Further investigations

1. A forensic chemist may specialise within the field of forensic science. Research the possible specialist areas for a forensic chemist. What is their specific role in evidence analysis? What common forms of analyses and techniques do they use?
2. Research the job description of a forensic chemist. Write a biography or a day in the life of a forensic chemist. Be specific about the actual chemistry involved in their profession.
3. Examine a real criminal case. The case may be from a newspaper, a documentary or movie. The case could be current or a past crime. Identify the role of the forensic chemist. What evidence was analysed? What were the findings? How did the evidence lead to the conviction or release of the suspect or suspects?
4. Research criminal cases where forensic evidence is central. Two high profile cases you may like to examine are the disappearance of Azaria Chamberlain, in which her mother was convicted of her murder then later released, or the trial of O.J. Simpson for the murders of his wife and her friend.
5. Research the history of forensic science. Present your information in a timeline. Include data such as the development of analytical techniques and pivotal cases in which forensic evidence has been used for the first time.
6. Examine a fictional criminal case by viewing an episode from a television crime series. Identify the role of the forensic chemist. What evidence is analysed? What were the findings? How did the evidence lead to the conviction of the suspect or suspects? Is the analysis of the evidence realistic or is it just meant for interesting viewing?
7. In a television crime series, you commonly see a forensic scientist testing for blood with a swab that turns pink. Research this test, which is called the Kastle–Meyer test. You will be surprised to find out how simple it is. Identify the limitations of the Kastle–Meyer test.

Contexts

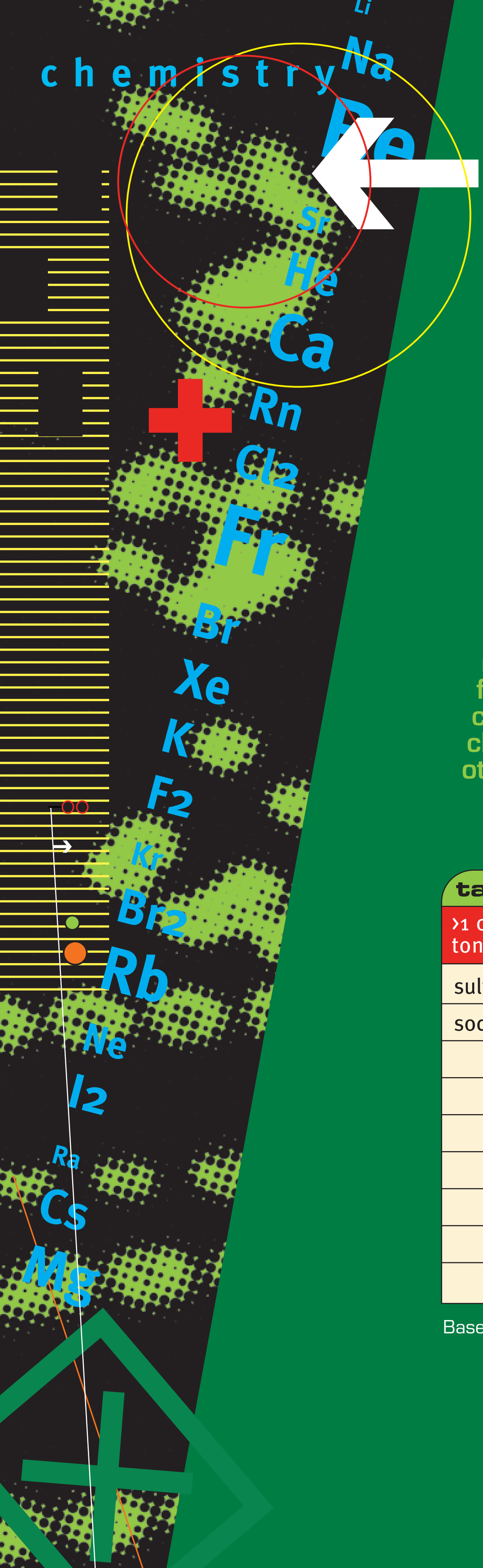
The chemical industry
Food
Marine chemistry

Chapters

15 Reaction rates
16 Reactions of life
17 Reversibility of reactions

area of Study 7

Chemical equilibrium



the chemical industry

Most of the consumer goods we use and enjoy on a daily basis are dependent on the chemical industry. Consider all the things that you and your family purchase at the supermarket, in clothing shops or the hardware store and in restaurants. Table ci.1 shows the main chemicals imported or manufactured in Australia. You would have difficulty finding many of these chemicals in your home but you could easily identify the pharmaceuticals, cosmetics, cleaners, fabrics, fuels, metals, plastics, foods and other goods that are produced from chemicals listed.

table ci.1 Industrial chemicals imported or manufactured in Australia.

>1 000 000 tonnes per year	100 000–999 999 tonnes per year	10 000–99 999 tonnes per year
sulfuric acid	urea	phosphoric acid
sodium hydroxide	nitric acid	hydrochloric acid
	ammonium nitrate	hydrogen peroxide
	ethane	chlorine
	dichloroethene	propene
	carbonic acid	
	calcium oxide	
	calcium hydroxide	
	ammonia	

Based on data collected in 2001–2002.

The chemical connection

figure ci.1 Chemical plants such as this provide a key link between producers of raw materials and the manufacturers of goods.

Figure ci.2 shows the steps involved in taking raw materials and converting them into consumer goods. Most people are aware that our raw materials come from farming and mining, and know about the various manufacturing industries which create the final product, but few would have knowledge of the massive chemical industry that links the two.

The chemical plant

The construction of a chemical plant requires thorough planning. Decisions need to be made regarding the exact method of operation of the plant but a range of other factors also need to be taken into consideration when selecting a location.

For example, many cities have large industrial areas close to rail lines, highways or ports. Raw materials can be easily transported to these sites and products readily removed. Interrelated industries may exist within a short distance of each other so that chemical products can be quickly utilised by the manufacturers of goods.

The method of operation of a chemical plant is dependant upon factors such as the quality of raw materials available, environmental impact and technology available at the time. Chemical plants making the same product will be slightly different depending on local factors.

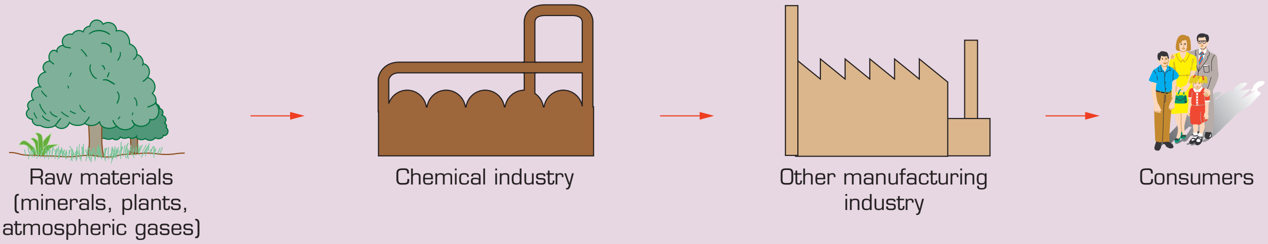


figure ci.2 Manufacturers frequently make use of chemical substances in the process of converting raw materials into consumer products.

Most advances in chemical production are the result of careful research in an effort to discover more efficient methods (for example, improved catalysts) and to protect the environment through stricter control of wastes and pollutants.

Reaction conditions determine the rates of chemical reactions and their equilibrium yields. Careful selection of reaction conditions enable optimum conversion of reactants to products. The conditions for a high yield sometimes oppose a rapid reaction. For example, the high temperatures that tend to increase the rate of reaction may also reduce the equilibrium yield of exothermic reactions.

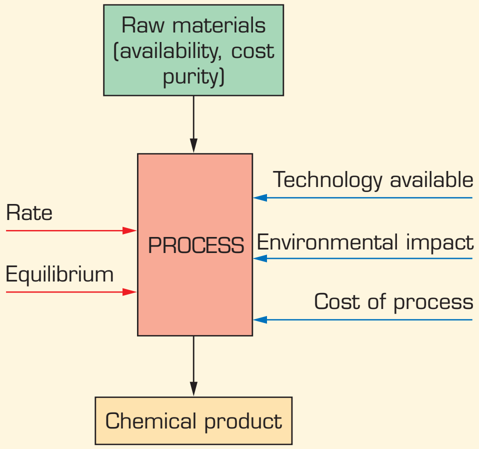


figure ci.3 The production method of a chemical plant is determined by a consideration of a range of factors.

* Section 15.1 **Reaction speed** describes the conditions under which the rate of a reaction varies (page 514).

The operation of a chemical plant

The reaction conditions under which a chemical product is made have to be balanced with the cost of achieving those conditions. The conditions necessary to achieve a maximum yield of product at a reasonable rate include variations to temperature, pressure, amounts of reactants and the use of catalysts. The cost of maximising these conditions is a major concern to the chemical industry. For example:

- increased temperatures through heating can be expensive to achieve
- high-pressure reactions can be costly due to the expense of the equipment needed and operating costs
- the cheapest reactants, in excess amounts, can be used to push reaction equilibrium to products
- some catalysts are expensive and less efficient but cheaper ones may be more cost effective.

The removal of products is another way of driving the reaction equilibrium to produce more products. In the laboratory, we rarely make use of this factor. The small-scale reactions that are undertaken in the laboratory to make fixed amounts of product are a form of batch processing. If the same method was used in a commercial setting the large batches would often be unmanageable.

The industrial production of chemicals most often makes use of a continuous flow process rather than large batches. In this way only a small amount of product is made at any time using smaller, less expensive equipment but the process is continuous. Reactants are fed into the reaction vessel and products are constantly removed. The constant removal of products helps drive the reaction and the small scale allows a degree of control over reaction conditions such as pressure and temperature.

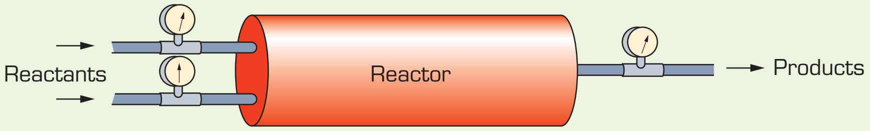


figure ci.4 Continuous flow processing—reactants are continually fed in to give a constant supply of products.

* Section 17.1 **Reversible reactions** (page 554) and Section 17.2 **Le Chatelier's Principle** (page 559) describe the factors accounted for in achieving an acceptable yield at an acceptable rate.

Manufacture of sulfuric acid

As seen in table ci.1 sulfuric acid (H_2SO_4) is produced in large quantities. The amount produced by a country is sometimes used as a measure of its industrial activity since sulfuric acid is used as a starting material in a wide range of industries.

Sulfuric acid is produced industrially by the **Contact process**. There are three main steps to this process.

Step 1: sulfur to sulfur dioxide

The first step in producing sulfuric acid is the combustion of elemental sulfur in a furnace to produce sulfur dioxide.

$$S(l) + O_2(g) \rightleftharpoons SO_2(g)$$

The sulfur is obtained from two main sources: the mining of sulfur deposits, and sulfur recovered from natural gas and crude oil. Sulfur dioxide itself can be collected as it forms during the smelting of sulfide ores of copper, lead and zinc.

figure ci.5 Heavy insulation prevents the costly loss of heat from a sulfuric acid manufacturing plant.

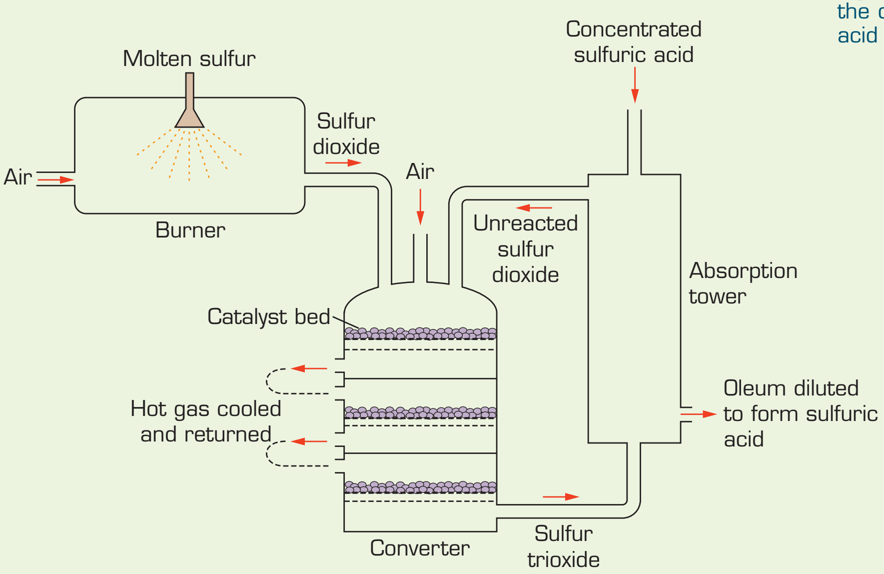


figure ci.6 The manufacture of sulfuric acid by the contact process.

Step 2: sulfur dioxide to sulfur trioxide

In a converter, sulfur dioxide is oxidised by oxygen to sulfur trioxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g);\ H = -197\ \text{kJ mol}^{-1}$$

The catalyst used is vanadium(V) oxide (V_2O_5). The reaction mixture is maintained at 400–500°C. Nearly total conversion to sulfur trioxide is achieved as sulfur dioxide, oxygen and air passes over the catalyst bed at a pressure of 1 atm. The effect of conditions on reaction rate and equilibrium yield (according to Le Chatelier's principle) are summarised in table ci.2.

table ci.2 Reaction conditions and their effects on reaction rate and yield.

Increased reaction rate	Increased yield
Increased temperature increases the number and energy of collisions between reactant particles.	Decreased temperature drives exothermic reactions towards products.
Increased pressure increases the number of collisions of reactant particles.	Increased pressure drives the equilibrium towards products since there are fewer product particles than reactant particles.
A catalyst lowers the activation energy of the reaction, enabling particles of lower energy to react upon collision.	

The conditions used in the manufacture of sulfur trioxide are a compromise between those favouring the greatest rate and those favouring the greatest yield. The catalyst vanadium(V) oxide allows an acceptable rate at lower temperatures. It is not the most effective catalyst but it gives an acceptable rate that is cost effective. An excess of reactants can help drive a reaction, and in this case excess oxygen (present in air) is the cheapest option. The cost of high pressure equipment has been avoided by developing a process which produces high yields at atmospheric pressure.

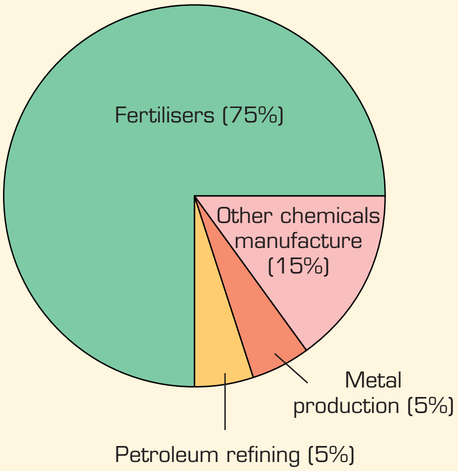


figure ci.7 Industrial uses of sulfuric acid.

Step 3: sulfur trioxide to sulfuric acid

Sulfur trioxide can be converted to sulfuric acid by adding it to water but the heat generated is great enough to vaporise some of the acid formed. Instead, the sulfur trioxide is reacted with concentrated sulfuric acid.

$$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$$

The oleum ($H_2S_2O_7$) produced is carefully mixed with water to produce sulfuric acid.

$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$$

Uses of sulfuric acid

Most of the sulfuric acid produced is used in the production of fertilisers. These include ammonium sulfate, ammonium phosphate and superphosphate. In the nineteenth century, it was discovered that bones treated with sulfuric acid produced an excellent fertiliser. This was the first superphosphate. Today superphosphate is roduced by reacting sulfuric acid with rock phosphate.

$$Ca_3(PO_4)_2(s) + 2H_2SO_4(l) + 4H_2O(l) \rightarrow \underbrace{Ca(H_2PO_4)_2(s) + 2CaSO_4.2H_2O(s)}_{\text{superphosphate}}$$

The products of this reaction are crushed into a powder and sold as a fertiliser.

Some key properties and uses of sulfuric acid are outlined in table ci.3.

table ci.3 Other uses of sulfuric acid.

Properties	Uses
It is a strong acid. - a viscous corrosive liquid - diprotic acid (able to donate two protons) - when added to water large amounts of heat are generated - reacts with water $H_2SO_4(l) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq)$ $HSO_4^-(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + H_3O^+(aq)$	- as a general purpose strong acid - for pickling of iron and steel to remove oxide layer in preparation for galvanising or electroplating—sulfuric acid reacts with the oxide layer to convert it into water and soluble iron sulfate - as an electrolyte in car batteries
It is a strong oxidant. - heating enhances this property - can be reduced to sulfur dioxide (SO_2), sulfur (S), hydrogen sulfide (H_2S) - dilute sulfuric acid reacts with metals to produce hydrogen gas (the hydrogen ions act as an oxidant)	- in reactions with magnesium and copper $Mg(s) + 2H_2SO_4(aq) \rightarrow MgSO_4(aq) + 2H_2O(l) + SO_2(g)$ $3Mg(s) + 4H_2SO_4(aq) \rightarrow 3MgSO_4(aq) + 4H_2O(l) + S(s)$ $4Mg(s) + 5H_2SO_4(aq) \rightarrow 4MgSO_4(aq) + 4H_2O(l) + H_2S(g)$ Magnesium sulfate (also called Epsom salts) is used for medicinal purposes, as a dietary supplement, in agriculture, and even in baths salts. $Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2(g)$ Copper sulfate is used as a pesticide and fungicide in farming.
It is a dehydrating agent. - organic materials such as animal tissues are decomposed by sulfuric acid; for example, sugar is decomposed to carbon and water $C_{12}H_{22}O_{11}(s) \xrightarrow{H_2SO_4} 12C(s) + 11H_2O(l)$	- drying gases and gas mixtures such as air, nitrogen and carbon dioxide by bubbling through concentrated sulfuric acid (for use in reactions where water would interfere) - not suitable for drying bases (for example NH_4) or reductants (for example H_2S).

* Chapter 8 **Acid–base reactions** describes and explains the properties of acids (page 366).

These properties are exploited as sulfuric acid is used in the processing of metals, the refining of petroleum and as an electrolyte in car batteries. It is also used in the production of starting materials. Sulfate compounds are used in the manufacture of pharmaceuticals, cosmetics, rubber goods, detergents, dyes, paper, paints and in glass-making.

figure ci.8 Sulfuric acid is used as a starting material in the manufacture of paints and other common household substances.

Manufacture of ethene

Ethene ($CH_2{=}CH_2$), another chemical produced in large quantities, is derived from natural gas and crude oil. These two materials are a mixture of hydrocarbons and ethene itself is present in only trace amounts. Ethene is produced from crude oil by **fractional distillation** (a separating process) and **cracking** of the hydrocarbons (a process of chemical change).

Section 2.5 **Organic compounds** describes the structure and properties of hydrocarbons including alkenes (page 246).

Fractional distillation begins with crude oil entering the fractionating tower as a mixture of vapour and liquid at 350°C. The temperature decreases up the fractionating tower. Each fraction has a boiling point range at which the vapour condenses and is collected. The lighter gaseous alkanes are collected at the top of the column while heavier liquid alkanes are collected towards the bottom. The heaviest molecules remain at the very bottom of the fractionating column forming bitumen.

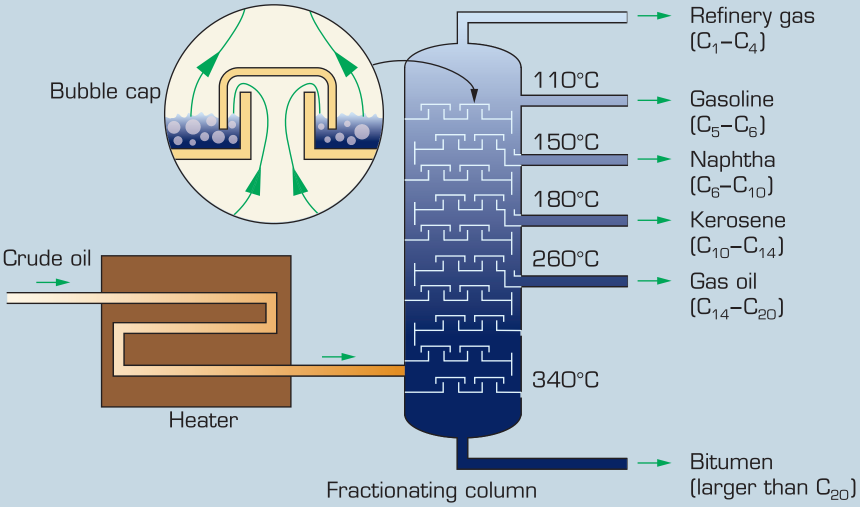


figure ci.9 The separation of crude oil into fractions in a fractionating tower.

Thermal cracking involves the heating of alkanes to sufficiently high temperatures to break the bonds between carbon atoms and form smaller molecules. As smaller alkanes and unsaturated molecules are made, hydrogen gas may also be produced. Unsaturated molecules such as propene, butadiene and ethene are produced by a process known as thermal cracking.

Typical thermal cracking reactions are:

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g);\ \ H = +138\ \text{kJ mol}^{-1}$$
$$C_3H_8(g) \rightleftharpoons C_2H_4(g) + CH_4(g);\ \ H = +81\ \text{kJ mol}^{-1}$$

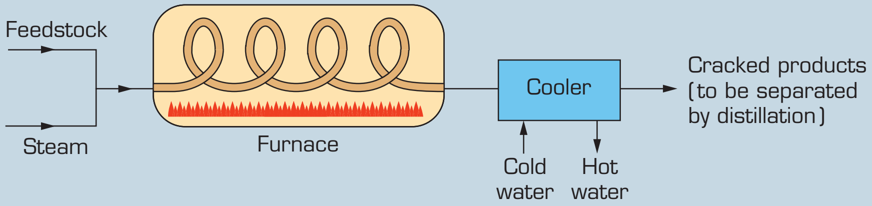


figure ci.10 A thermal cracker. The heat removed from the cracked gases during cooling can be used to produce more steam for the process.

Le Chatelier's principle allows us to predict the conditions for the cracking of hydrocarbons. The reactions are endothermic and so high temperatures will drive the equilibrium position towards products. Since there are a greater number of product particles than reactant particles, low pressures are used to drive the reaction towards the products. Temperatures are maintained at 750–900°C and pressures of less than one atmosphere are used. The conditions favour a fast reaction and the gases are only in the furnace for less than a second to prevent further cracking and the formation of molecules smaller than ethene.

* Section 17.2 **Le Chatelier's Principle** describes conditions that can be used to drive a reaction towards products (page 559).

Another process known as catalytic cracking allows larger molecules in crude oil to be broken down into smaller molecules. These smaller molecules can then be put through the thermal cracking process to produce more ethene. While molecules such as octane (C_8H_{18}) are a component of petrol, the other molecules produced during catalytic cracking can be used as feedstock for the thermal cracker.

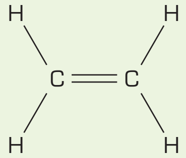


figure ci.11 The double bond of ethene makes it a useful starting material for other compounds.

Properties of ethene

Ethene is a highly reactive, gaseous substance. It is a flammable gas.

The carbon and hydrogen atoms of ethene differ only slightly in electronegativity but the molecule is symmetrical so it is non-polar. Since ethene is a non-polar molecule the only intermolecular forces are weak dispersion forces. It has a boiling point of –104°C and so under normal conditions it exists as a gas.

* Section 2.3 **Covalent bonding** describes the bonding in hydrocarbons and the resulting intermolecular forces (page 233).

Ethene is an unsaturated molecule and it is the double bond that determines its chemical properties. The double bond can be broken and other atoms can be added to ethene by a process known as an addition reaction. For example, if bromine is added to ethene one of the bonds of the double bond is broken and a bromine atom is added to each carbon.

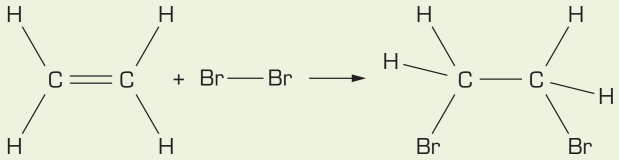


figure ci.12 The addition reaction between bromine and ethene.

This is a significant type of reaction because it means that by adding the right atoms, ethene can be used as a starting material for the production of many other substances. Ethene can even react with other ethene molecules, joining together in a long chain known as polyethene (or polythene).

Chapter 9 **Organic chemistry** describes reactions of alkenes such as ethane as well as reactions of the subsequent products (page 386).

Uses of ethene

Ethene is used as the starting material for a number of reactions, each of which results in useful products.

Ethanol is produced by the fermentation of sugars in the process of making wine, beer and spirits, but ethanol for cleaners, pharmaceuticals, cosmetics and industrial use is manufactured from ethene. The large volumes of ethanol needed for industrial purposes are made by adding water (as steam) to ethene with phosphoric acid as the catalyst.

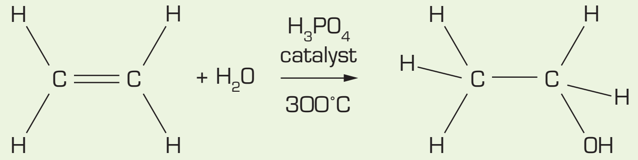


figure ci.13 Ethanol can be formed in large quantities from ethene.

Ethanoic acid can be produced as the ethanol in wine reacts with oxygen. The final mixture is known as vinegar. For industrial use, ethanol can be oxidised to ethanoic acid using a solution of acidified potassium dichromate or acidified potassium permanganate as an oxidant.

$$CH_3CH_2OH(aq) \xrightarrow[H^+]{MnO_4^-(aq) \text{ or } Cr_2O_7^{2-}(aq)} CH_3COOH(aq)$$

Ethanoic acid is commonly called acetic acid and is known for being a weak acid as it only dissociates to a small extent in water.

$$CH_3CH_2OH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq);\ K_a = 10^{-5}\ M$$

Esters are molecules made by reacting together alcohols and carboxylic acids. They are responsible for many of the odours and flavours that we experience. Many are natural but some have been made in the laboratory as close copies of those found naturally. Ethyl ethanoate is the ester formed as ethanoic acid and ethanol undergo a condensation reaction.

Sulfuric acid is used in this process as a dehydrating agent. It removes the water produced, driving the equilibrium to favour the products.

Ethanol can be used to make a whole range of esters using different different carboxylic acids, and others can be made by adding different alcohols to ethanoic acid.

Polyethene is a polymer—a long chain molecule commonly called a plastic. You can find it around your home as sandwich bags, and milk or juice bottles. It is made by adding ethene molecules to each other in a process known as addition polymerisation. The resultant chain can be tens of thousands of carbon atoms long.

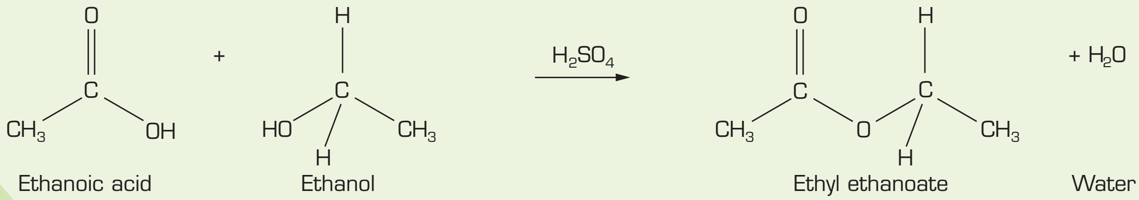


figure ci.14 Ethyl ethanoate smells like apples and can be formed from the reaction between ethanol and ethanoic acid.

The uses of ethene described so far are just a few examples. The double bond in the ethene molecule make it a good starting material for a wide variety of processes. It also has uses of its own. Bananas are often picked green as they are less likely to be damaged in transport in this firmer state. Ethene gas is used to ripen green bananas ready for sale. Apples and other fruit give off ethene gas. If you have a banana that is too green to eat, put it into a paper or plastic bag with an apple for a few hours and it will ripen.

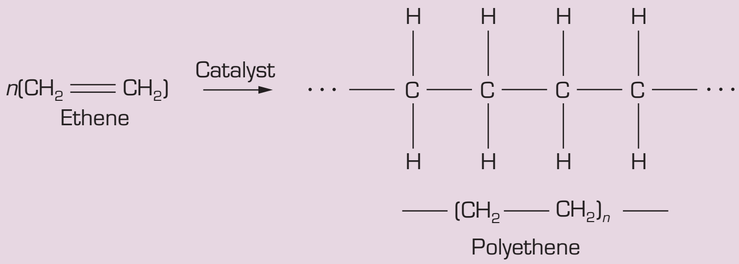


figure ci.15 The addition reaction of ethene to form polyethene.

Section 10.2 **Addition polymerisation** describes this process (page 414).

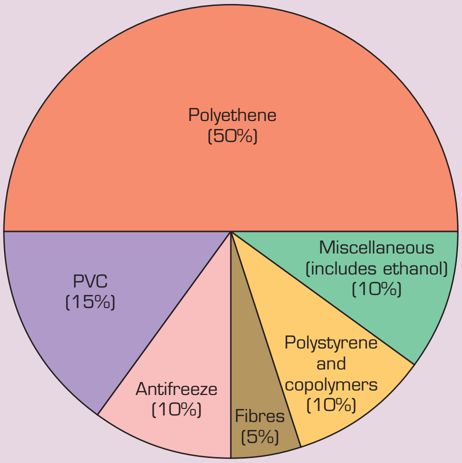


figure ci.16 The uses of ethene.

figure ci.17 Ethene gas is used to ripen bananas after they have been safely transported to their market destination.

Further investigations

1. Research the production of some of the other chemicals listed in table ci.1. Are any of them actually produced using sulfuric acid or ethene? Construct a concept map showing how these production processes are connected.
2. Is there a chemical industry in your area? Find out about the conditions used to run an efficient plant. Present your findings to your class.
3. The production of superphosphate using sulfuric acid is described above. Investigate the production methods of other fertilisers that use sulfuric acid, such as ammonium sulfate and ammonium phosphate.
4. Research how sulfuric acid is used in industries such as petroleum refining and metallurgical processes. Write a report outlining the importance of sulfuric acid to our lifestyle.
5. Ethylene glycol is another chemical produced from ethene. It is used as an ‘antifreeze’. Find out how ethylene glycol is produced from ethene and the properties that enable aqueous solutions of it to have a lower freezing temperature than pure water.
6. Investigate the process of gas-ripening bananas. What chemical reactions are taking place in green bananas? Present your findings on a poster. Other students may be surprised to learn of this process
7. Polyvinyl chloride and polystyrene are other polymers produced from ethene. Find out about the chemical processes behind their manufacture.

food

Food is one of our basic human needs. We all need to eat to survive. Thinking about, talking about and eating food are everyday events for most of us. Most people enjoy eating food and the success of businesses such as supermarkets, restaurants and take-away food outlets depend on this.

Food for life

Food provides the raw material our body needs to supply our cells with energy so that they can function properly. This happens through the process of cellular respiration. As well as providing fuel for cellular respiration, food is a source of materials for many other reactions and processes that keep the body functioning normally. The materials from food that enable this to happen are called nutrients.

figure fd.1 Eating food not only provides us with nutrients; it is often a social occasion.

Essential and non-essential nutrients

Nutrients can be classified as essential or non-essential. Non-essential nutrients are substances that our body can make from other substances if necessary. For example, all carbohydrates are considered non-essential. Other substances in our diet can be converted into the molecules that would normally come from carbohydrates.

Essential nutrients must be present in the food eaten. They can't be made from other substances. All minerals are essential as the human body cannot make them from other materials.

table fd.1 Essential and non-essential nutrients.

Nutrient	Essential	Non-essential
carbohydrate	none	all
protein	the amino acids leucine, isoleucine, valine, lysine, phenylalanine, tryptophan, threonine, methionine	all other amino acids
lipid	arachidonic and linoleic acids	all others
vitamin	A, B group, C, E and K	all others
mineral	all	none

Carbohydrates

Carbohydrates are made up of the elements carbon, hydrogen and oxygen. They vary in size from small individual molecules such as glucose to very large, long-chain molecules such as starch and glycogen. Carbohydrates are a large group of molecules and they have a large range of functions. Some of the more important functions include:

- a fuel for cellular respiration
- energy stores in the form of starch and glucose
- components of the DNA and RNA.

* Section 16.2 **The chemistry of digestion** describes the structure of glucose and starch (page 534).

Many substances contain carbohydrates. We eat carbohydrates directly or feed them (in the form of grain) to animals that we eat, such as sheep and cows. The timber we build houses and furniture from contains carbohydrates. You probably own some clothing which is carbohydrate based—cotton, rayon and linen are all carbohydrates. Even though carbohydrates are in many things, most people associate them with sugary foods such as cakes, chocolates and lollies, or starchy foods such as bread, rice and pasta.

Carbohydrates are made up of individual units called saccharides. They are classified using the number of saccharide units they contain. The most common saccharide unit is glucose. It is the key energy source for most living things.

figure fd.2
Many people associate starchy foods such as this pasta and bread with the term carbohydrate.

* Section 16.1 **Reactions of life** describes the process of cellular respiration (page 532).

figure fd.3 Carbohydrates are generally associated with foods. There are many carbohydrate substances which are not foods, such as paper pulp.

figure fd.4 We feed carbohydrates to stock animals such as cows and sheep. We then use the meat from these animals as a source of protein.

Proteins

Protein is found in all living matter. All cells contain some kind of protein. The light-sensitive cells in your eyes that allow you to read this page are protein based. The nerve tissue, which transmits the optic message, and your brain, which interprets the message, are made of proteins. The muscles which allow you to turn the pages of this book are made of protein.

Proteins contain the elements carbon, hydrogen, nitrogen and oxygen, with other elements such as sulfur. Proteins are the body's only source of nitrogen. Proteins are made up of chains of individual units called amino acids. The types of amino acid present and the order in which they are joined determine what purpose the protein will serve. Considering that there are twenty different amino acids in human proteins and each protein can be tens of thousands of amino acids long, there are a huge number of possible combinations. There are actually thousands of different proteins, each having an important function of its own. Some of these functions are shown in table fd.2.

* Section 16.2 **The chemistry of digestion** describes amino acids and protein structure (page 534).

* Section 16.1 **Reactions of life** describes the role of enzymes in in organisms (page 532).

Proteins are commonly referred to as 'body-building' molecules because of their importance in the structure of cells and tissues, especially muscle tissue.

table fd.2 Examples of some important functions of proteins.

Protein function	Example(s)
major component of enzymes	digestive enzymes
certain hormones	insulin, glucagon (combined action regulates blood glucose level)
component of transport material	haemoglobin
defence and immunity	antibodies
structural: growth, repair, protection, support and movement	bones, teeth, skin, hair, muscle, ligaments, tendons, cartilage, feathers, beaks, etc.
molecules of life	DNA and RNA
toxins	venom of animals such as spiders and snakes

figure fd.5 Bodybuilders often use special protein preparations to help build up their muscles.

figure fd.6 Amino acids from the protein in meat are used as major components in enzymes and provide materials for growth and repair of tissues.

Lipids

This group is often referred to as fats. This is not entirely correct. Chemically speaking, fats are a member of a larger group called lipids. In very basic terms, lipids are a group consisting of fats, oils and waxes. You can generally distinguish between each type of lipid by its state. For example, fats and waxes are generally solids at room temperature, whereas oils are liquids at room temperature. Lipids are made up of carbon and hydrogen, with small amounts of oxygen and sometimes other elements. Most fats and oils are formed by the reaction of a molecule of glycerol with three molecules of fatty acids. Like amino acids, there are many types of fatty acids. The nature of the fat formed is determined by the fatty acids it contains.

Section 16.2 **The chemistry of digestion** describes the chemical structure of lipids (page 534).

Lipids are generally known for their low solubility in water as most of them are non-polar. Think about what happens when you put a greasy dish into the washing up water—the grease doesn't dissolve in the water.

Section 4.1 **Dissolving** describes the solubility of substances (page 286).

Many people think of lipids as bad substances. This is often because of the effects of consuming too much of this group. In fact, an excess of other nutrients is often converted into fat stores under the skin called adipose tissue.

We do need certain lipids in our diet for functions such as:

- structural material in cell membranes and other cell bodies
- solvent for non-polar materials (such as certain vitamins)
- source of energy.

Lipids are especially important in the diet of babies and young children for normal brain development.

figure fd.7 Many of us enjoy eating fried foods; however, they are usually high in fats.

figure fd.8 Lipids are essential to the development of the nervous system, especially the brain, in the early years of life.

Vitamins and minerals

Vitamins are organic substances that are only needed in small amounts. Most important vitamins are an essential part of our diet. Unlike carbohydrates, proteins and lipids, vitamins have no energy value but have many other important functions. In many cases vitamins act as coenzymes. Coenzymes act to help enzymes speed up various chemical reactions.

Some vitamins are water soluble and are flushed out of the body easily. Other vitamins are fat soluble and are not as easily flushed out. They can accumulate in fat tissue, so care must be taken to avoid excessive intake of some vitamins.

Like vitamins, minerals are only required in small amounts, have no energy value and have a wide range of roles in the body. Unlike vitamins, minerals are inorganic substances and are all essential. It is important to make sure that we are getting minerals such as calcium, iron, phosphorous, iodine and magnesium in our diet.

figure fd.9 Many foods contain more than one nutrient. As well as being a good source of the important minerals calcium and phosphorus, milk provides fat, carbohydrate, protein and some vitamins.

table fd.3 The sources for some important vitamins and minerals, and the results of deficiencies.

Vitamin	Major function(s)	Food sources	Deficiency
A	maintain eyesight, skin	green and yellow vegetables, egg yolk, fish	night blindness
B complex	various, e.g. metabolism of nutrients; coenzymes	whole grains, liver, meat, milk, legumes, nuts	various, e.g. beriberi, pellagra, kidney stones
C	formation of cartilage, bones and teeth, antioxidant	fresh fruits and vegetables, e.g. citrus fruits, tomatoes	scurvy, loosening of the teeth
D	bone formation	egg yolk, liver, tuna	rickets
E	prevents damage to cell membranes	vegetable oils, green leafy vegetables, liver	anaemia, especially in infants
K	necessary for blood clotting	green leafy vegetables, liver	increases time taken for blood clotting
Mineral	**Major function(s)**	**Food sources**	**Deficiency**
calcium	formation of bones and teeth, needed for blood, nerves	dairy products, dark green vegetables	stunted growth, convulsions
phosphorus	formation of bones and teeth, maintaining acid–base balance	milk, cheese, meat, chicken	loss of calcium from bones
iron	used in making haemoglobin for red blood cells	green leafy vegetables, eggs, legumes, lean meats	anaemia
sodium	proper nerve function, maintaining blood pressure	table salt, most processed and fast foods	muscle cramping, tiredness
iodine	thyroid gland function	vegetables, dairy products	goitre
magnesium	enzyme function making protein	green leafy vegetables, grains	restricts growth

Food production

Humans were once able to survive by gathering fruit and vegetables that had grown wild. As they started to live in larger groups, people found it convenient and eventually necessary to grow crops. An increasing world population has meant a greater demand for food. This increase in demand can have a negative impact on the environment.

Increased food production needs to be achieved by using existing agricultural land and not by the destruction of important wilderness areas for farms. Sustainable farming practices are needed that make use of methods suited to particular regions without the overcropping of land causing soil degradation. These agricultural processes involve making use of improved crop varieties, planting techniques, fertilisers and pesticides.

Scientists have made use of a knowledge of chemical processes to develop techniques that allow increased food production. This context will concentrate on the use of fertilisers and pesticides to allow farmers to feed an increasing world population.

figure fd.10 An increase in the demand for food dictates that food production processes must be more efficient.

Nutrients for plant growth

Plants are a key part of the cycling of elements through an ecosystem. Plants obtain nutrients for growth from two sources: the atmosphere and the soil. Carbon dioxide is taken from the air by the leaves, and water containing dissolved nutrients is absorbed by roots from the soil as illustrated in figure fd.11

* Section 16.3 **Matter cycles** describes the way certain elements are needed for the survival of living things (page 546).

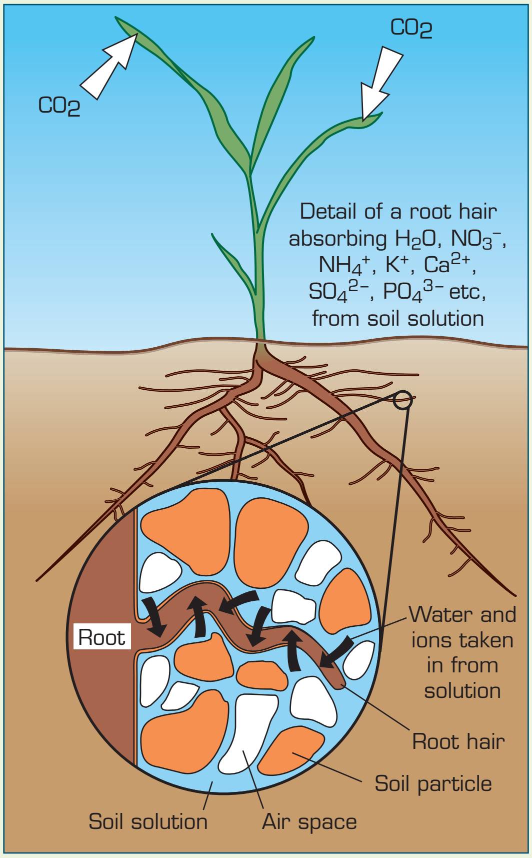


figure fd.11 Apart from carbon dioxide, all nutrients and water are absorbed by the fine root hairs of plants.

figure fd.12 Soil consists of weathered rock and organic matter. Most land plants grow in this thin layer of the Earth's crust.

Soil structure

The outer layer of the Earth's crust, typically 1 m to 2 m in thickness, is the soil. Many areas of Australia have a much thinner layer of soil.

Tiny weathered rock fragments and organic matter make up the soil. It is this porous mixture, and the amounts of air and water it contains determine how successfully plants grow. The coarse rock fragments of soil mainly provide bulk to the soil but the fine clay particles are chemically active. They can bind essential minerals to their surfaces as positive ions. These cations can be exchanged for other cations from the soil solution. For example:

$$\text{clay–Ca}^{2+}(s) + 2NH_4^{+}(aq) \qquad \text{clay–2NH}_4^{+}(s) + Ca^{2+}(aq)$$

This is a reversible process and the direction of the exchange is determined by the concentrations of the cations involved and their attraction for the clay particles. As plants remove nutrients from the soil they are replenished from the store of ions held by the clay particles.

* Secion 17.1 **Reversible reactions** describes the nature of reversible reactions and the factors that influence them (page 554).

Rainfall and the breakdown of decaying organic matter by microbes introduce hydrogen ions (H^+) into the soil. The increased acidity of the soil has an adverse affect on plants in three ways.

1. Hydrogen ions can displace ions such as Ca^{2+} from the clay particles, taking their place. The acidic soil has a lower supply of nutrients stored in it.
2. Clay minerals in the soil are broken down under acidic conditions releasing aluminium ions. Some of these aluminium ions form aluminium oxide which in turn binds with hydrogen ions. These positively charged ions hold anions but repel the positively charged nutrient cations.
3. The high concentration of aluminium ions in acidic soils makes it toxic to plants and restricts plant growth.

Acidic soils can be neutralised by gardeners and farmers by adding materials such as calcium carbonate ($CaCO_3$, chalk) and lime ($Ca(OH)_2$).

* Chapter 8 **Acid–base reactions** describes the neutralisation of acids by carbonates and hydroxides (page 366).

Adding nutrients: fertilisers

Plants depend upon nitrogen in the form of ammonium ions (NH_4^+) or nitrate ions (NO_3^-) in the soil to grow.

* Section 16.3 **Matter cycles** describes the nitrogen cycle (page 546).

Farmers can add nitrogen to the soil and improve crop production by:

- periodically planting crops such as legumes (peas, beans, clover), which have nitrogen-fixing bacteria in nodules on their roots. They can be planted after crops that remove nitrogen from the soil, or alongside crops so that nitrogen is fixed at the same time as it is being removed.
- adding animal manure from livestock. It contains nitrogen compounds and encourages small animals, such as worms, and microorganisms, which break down organic material in the soil and produce more nitrogen compounds. Manure is relatively low in nitrogen by the time it is collected by hosing out animal shelters and so is best used on site, as long-distance transport is uneconomical.
- the application of inorganic nitrogen fertilisers produced by industrial processes. Some common nitrogen fertilisers are listed in table fd.4. It is the addition of fertilisers to the soil that enables the world's people to be fed.

figure fd.13 The nodules on the roots of legumes contain bacteria that fix atmospheric nitrogen.

figure fd.14 Broad beans grown between rows of grapevines fix nitrogen into the soil. They are ploughed back into the soil at the end of winter before the dormant vines come into leaf.

The production of massive quantities of fertilisers is only possible due to efficient methods of making ammonia from nitrogen and hydrogen. This reaction can be represented by the equation

$$N_2(g) + 3H_2(g) \qquad 2NH_3(g);\ \Delta H = -91\ \text{kJ mol}^{-1}$$

* Section 17.1 **Reversible reactions** describes the nature of reversible reactions and the factors that influence them (page 554).

table fd.4 Nitrogen compounds of common fertilisers.

ammonia	NH_3
ammonium sulfate	$(NH_4)_2SO_4$
ammonium nitrate	NH_4NO_3
urea	$(NH_2)_2CO$
ammonium dihydrogen phosphate	$NH_4H_2PO_4$
ammonium hydrogen phosphate	$(NH_4)_2HPO_4$

If nitrogen and hydrogen are combined in the ratio 1:3 and left to react under room conditions very little ammonia forms. The reaction is exothermic, a feature that favours ammonia production, but the equilibrium of this reversible reaction favours the reactants under room conditions.

German chemist Fritz Haber developed a process for ammonia production that is essentially the same one used in modern chemical plants.

The Haber process

BASF (Badische Anilin and Soda Fabrik) in Germany employed Carl Bosch to scale up Haber's process for industrial production. From 1910 to 1912 extensive experimentation took place to find a suitable catalyst. Powdered iron is used today with small amounts of aluminium, potassium, silicon and magnesium oxides to improve its effectiveness. Without a catalyst, temperatures in excess of 3000°C are needed for molecules of hydrogen and nitrogen to break down into their atoms so they can reform as ammonia molecules.

Figure fd.16 shows the action of the iron catalyst, which allows ammonia to form at 500°C and a pressure of 250 atm. These conditions are economically more viable than temperatures of 3000°C without a catalyst.

* Section 15.1 **Reaction speed** describes the factors that affect the rates of reactions including temperature and catalysts (page 514).

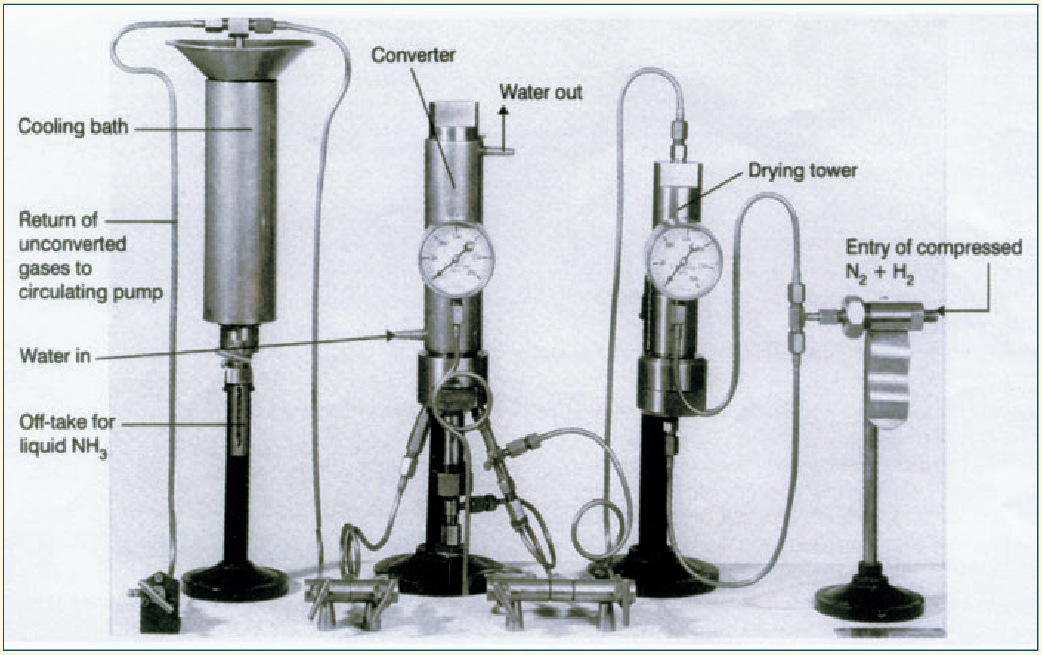
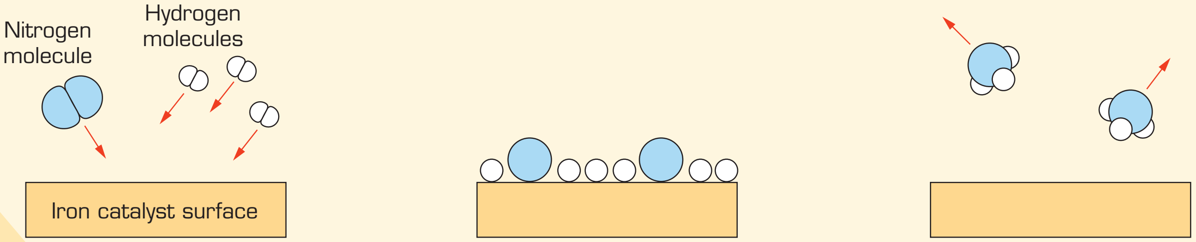


figure fd.15 By 1909 Fritz Haber had produced 100 g of ammonia using this apparatus.



Molecules are adsorbed onto the catalyst and bonds break.

New bonds form to make ammonia molecules.

figure fd.16 As hydrogen and nitrogen adsorb onto the surface of the iron catalyst, the bonds within the molecules break. The free atoms combine to form ammonia.

The presence of the iron catalyst provides a different pathway, with a lower activation energy, for the reaction (figure fp.17). A higher proportion of the reactants have sufficient energy, at lower temperatures, to reach this activation energy and go on to form products (figure fd.18). The reaction can proceed at a greater rate (at that temperature) in the presence of a catalyst than without one.

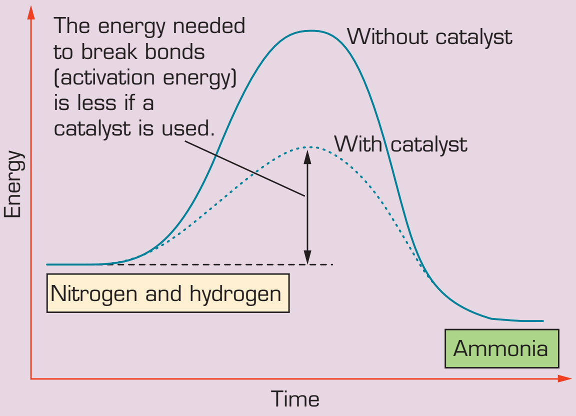


figure fd.17 The presence of a catalyst provides a reaction pathway with a lower activation energy barrier.

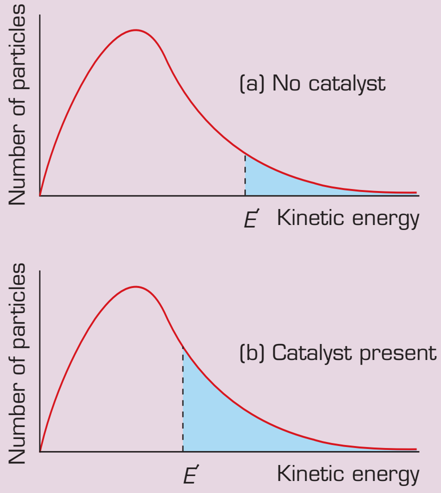


figure fd.18 During a catalysed reaction, more particles have energy above the activation energy barrier.

Competition for crops

The competitors

Growing crops have to compete for space and nutrients with other living organisms. Insects and fungi may use the crops as a food supply since they have taken the place of their natural foods, and other plants competing with the crops become known as weeds. Farmers try to remove these competitors to ensure a maximum crop yield and high-quality produce. They often resort to the use of chemicals (pesticides) to rid their crops of these pests. Pesticides can be broken down into three categories: herbicides, fungicides and insecticides. Herbicides are used to kill weeds that compete with crops for space and soil nutrients; fungicides kill moulds and fungi which cause plants and seeds to rot; and insecticides are used to kill insect pests that eat crops and cause imperfections which are unappealing to consumers.

The chemicals used on crops need to leave the produce safe for human consumption and be gentle to the environment. This is achieved by using chemicals that:

- destroy the pests but are safe for humans
- specifically target the pests and not helpful organisms, such as insects that are the predators of pests
- only require low dosages to eliminate the pest
- quickly break down in the environment to safe levels.

* Sections 2.3 **Covalent bonding** (page 233) and 2.5 **Organic compounds** (page 246) describe the types of molecular compounds used as pesticides.

figure fd.19 Some insects are the predators of the pests which consume crops. An insecticide needs to be harmless to these insects.

DDT (common name: dichlorodiphenyltrichloroethane) was first discovered in 1939 and used as a powerful insecticide. It is highly toxic to insects but low in toxicity to humans. The problem is that it breaks down very slowly. It takes about eight years to break down to half its original amount. DDT is also a non-polar molecule and therefore insoluble in water. It is not excreted in urine and builds up in the fatty tissues of humans and animals. This also means that DDT is concentrated along the food chain as predators

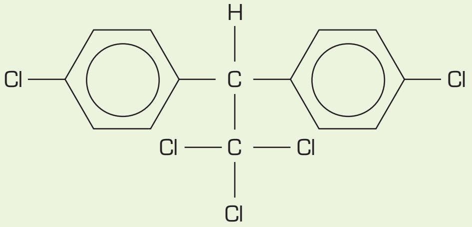
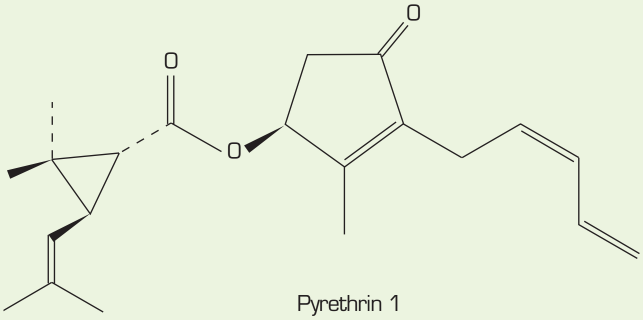


figure fd.20 The molecular structure of DDT.



Pyrethrin 1

figure fd.21 The molecular structure of pyrethrin 1.

consume prey containing it. It was found that DDT could build up to dangerous levels in humans and other animals. Some bird populations were destroyed as a build up of DDT caused the shells of their eggs to be thin and easily broken. The central nervous system of humans is thought to be affected by high levels of DDT.

* Section 16.3 **Matter cycles** describes the cycling of matter and the way substances move through food chains (page 546).

DDT is now banned in many countries including Australia. Farmers are encouraged to use minimal dosages of pesticides, and to use pesticides that are biodegradable and specific to a particular pest. However, DDT can be produced cheaply by a simple one-step process and is still widely used in many developing countries.

Pyrethroids

Many organic gardeners plant chrysanthemums between rows of vegetable plants to ward off insects. They can also be grown around the home to deter mosquitoes. The flower heads of chrysanthemums contain powerful insecticides including one known as pyrethrin 1.

While pyrethrins are effective insecticides, they are harmless to mammals under normal conditions. They make an ideal insecticide except that in the presence of light they undergo oxidation very rapidly. Chemists set about synthesising compounds that were related to pyrethrins and effective against insects, but much more stable.

The first pyrethroid of sufficient stability to make it useful in agriculture was discovered in 1977. Permethrin is a mixture of stereoisomers, molecules of the same formula with the atoms bonded in the same order but the arrangement of atoms in space is different. Biopermethrin is one of the stereoisomers of permethrin. Cypermethrin is another pyrethroid discovered after permethrin. Smaller quantities of this insecticide can be used due to its higher activity.

Pyrethroids work by entering an insect and quickly moving to their site of action—the membranes of nerve cells. They are more soluble in fats than in water and readily move from the aqueous solution of the original pesticide into the fatty tissues of the insect.

Pyrethroids readily break down in mammals into polar substances that remain dissolved in water and are easily eliminated from the body. They can be administered to crops in doses one-fifth the size of other insecticides such as organochlorines and organophosphates. Synthetic pyrethroids last on crops for 7 to 30 days and any that reach the soil rapidly break down in the organic material into inactive polar compounds that do not build up in the environment.

Consider this

1. A soil scientist conducts an experiment in which ammonium nitrate soaks through a clay soil sample. What will happen to the individual ions of ammonium nitrate as they pass through the soil? How could the use of ammonium nitrate as a fertiliser be affected by heavy rain?
2. One of the major costs of using fertilisers is transportation to the site where they are to be used. Calculate the percentage by mass of nitrogen for each of the fertilisers in table fd.4. List the fertilisers in order of transport cost, least costly to most costly.
3. Table fd.5 shows the yield of ammonia from nitrogen and hydrogen under different conditions. What are the conditions for an optimal yield of ammonia? How do they compare with the conditions described for the industrial production of ammonia in this context? Why do you think these conditions are used and not those for the highest yield?

table fd.5 The volume percentage of NH_3 formed when the reaction $N_2(g) + 3H_2(g) \quad 2NH_3(g)$ reaches equilibrium.

Pressure (atm)	NH_3 present at equilibrium (%)					
	100°C	200°C	300°C	400°C	500°C	700°C
10	–	50.7	14.7	3.9	1.2	0.2
25	91.7	63.6	27.4	8.7	2.9	–
50	94.5	74.0	39.5	15.3	5.6	1.1
100	96.7	81.7	52.5	25.2	10.6	2.2
200	98.4	89.0	66.7	38.8	18.3	–
400	99.4	94.6	79.7	55.4	31.9	–
1000	–	98.3	92.6	79.8	57.5	12.9

4. Explain how the experimental yields in table fd.5 are consistent with Le Chatelier's Principle.
5. Why is it better for ecosystems that pesticides be polar substances (or break down into polar substances) rather than be non-polar substances?

Further investigations

1. The use of vitamin supplements has increased greatly in recent years. Most people know that too little of certain vitamins can cause problems in the body. Many people do not realise that taking too much of some vitamins can also cause problems. The local pharmacy has asked you to produce a factsheet suitable to distribute to the general public. The factsheet should describe the need to follow recommended daily doses of vitamin intake and the health problems associated with overdosing of some vitamins.

2 The glucose that occurs in nature is sometimes referred to as dextrose. This name is derived from a property called stereoisomerism. Glucose has a form of stereoisomerism called optical isomerism in which it exists in two forms: D-glucose and L-glucose. Prepare a visual display to explain these terms as simply as possible.

3 Many people use sucrose (table sugar) to sweeten foods or drinks. However the last century has seen an increasing demand for alternatives that provide the sweetness of sugar without the calories. These alternatives are usually called artificial sweeteners. There are several accredited artificial sweeteners.

You have been assigned the task of preparing an information pamphlet comparing sucrose to one of the artificial sweeteners. The pamphlet should include information on:

- how the artificial sweetener is obtained or produced
- its chemical structure
- advantages and disadvantages of artificial sweeteners over sucrose.

4 Besides fats, oils and waxes, there are other types of lipids. Two of these include steroids and phospholipids. Prepare a report on these classes of lipids concentrating on their chemical structure, properties and why they are important.

5 Prepare a poster or wall chart suitable for display in your chemistry classroom comparing a fat-soluble vitamin to a water-soluble vitamin. Your poster should include the chemical structure and chemical role it plays in the body (reactions it is involved in, etc.) for each vitamin.

6 Companion planting is the growing of two or more varieties of plant in close proximity, or alternating their production in a particular area. An example of this is the growing of chrysanthemums with vegetables to protect the vegetables from insect attack. In northern Tasmania, pyrethrin production alternates with poppy production. Find out more about this method of growing plants and why it works. Prepare a brochure that might encourage the use of pesticide-free methods by farmers and home gardeners.

marine chemistry

When we think of protecting the environment, it is often rainforests, trees, rivers, cuddly animals or frogs that come to mind. Sometimes we also consider dolphins or whales, but the significance of the Earth's oceans go largely unnoticed. The oceans are vital for their role in regulating the Earth's climate. They have an essential role in the cycling of nutrients and their capacity to store carbon dioxide may be protecting us from the full force of the greenhouse effect. The unique properties of water, the soup of substances dissolved in what we call ocean and the marine life it supports are a valuable part of our environment, and are worthy of protection.

figure mc.1 Even if you live far from it, the ocean greatly influences the nature of your environment.

Energy distribution

Mars has a very thin atmosphere of carbon dioxide. Whether or not Mars has any water is still the subject of scientific investigation. Certainly there are no oceans of water. The surface temperatures on Mars range from −133°C at the poles to 22°C at its equator. In contrast, the surface temperatures on the Earth range from −30°C to 50°C. These differences can be partially accounted for by the differences in size of the planets and their distances from the Sun. A key difference is the presence of water on the Earth both in the oceans and the atmosphere.

At any point on the surface of Mars the energy received from the Sun is equal to the energy lost into outer space. On Earth the transfer of energy is more complex. As energy from the Sun reaches the Earth a certain amount is reflected back into space, a portion is absorbed by the atmosphere, and some is absorbed by the land and oceans. Due to the spherical shape, more energy strikes the Earth's equatorial regions directly. The energy is spread over a greater area at the poles.

figure mc.2 The temperature variation is greater on Mars than on Earth.

Ocean currents

The formation of ocean currents is a complex process. Cold water has a higher density than warmer water and water of high salinity has a higher density than water of low salinity. Higher density water will tend to sink and water from other areas comes in to take its place. These factors, together with the position of the continents, the sizes of the bodies of water and the rotation of the Earth, have resulted in a complex series of deepwater and surface water currents. Deep ocean currents carry large volumes of water very slowly. Sinking water carrying dissolved materials may not come to the surface again for over 1000 years.

* Section 11.2 **Specific heat capacity** describes the capacity for substances to absorb energy (page 429).

Water has a much higher specific heat capacity than other liquids. It is capable of storing vast amounts of energy from the Sun. Ocean waters around the equator can absorb energy from the Sun and ocean currents carry this energy to cooler regions where it is released. The winters of eastern Europe would be much harsher without warm currents carrying energy there from other parts of the world.

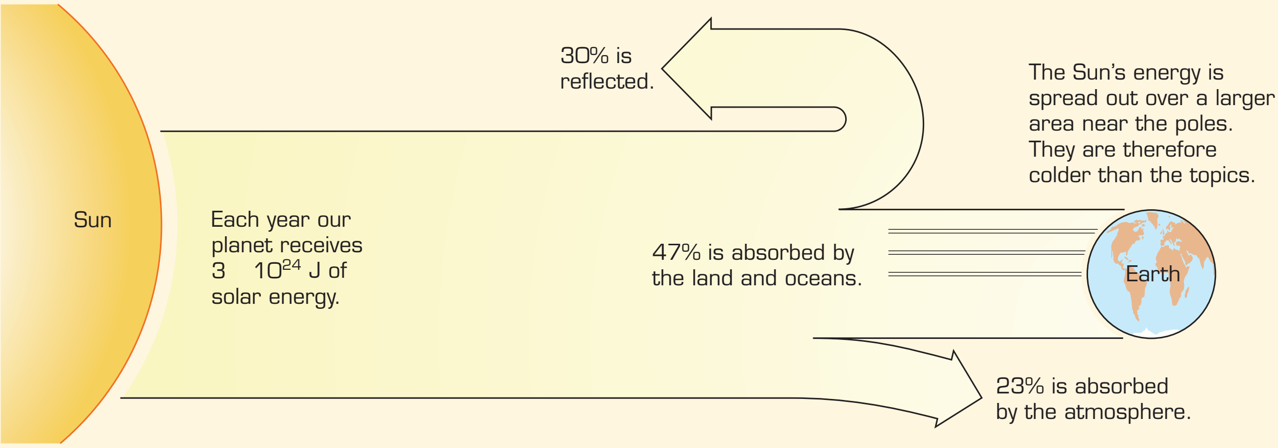


figure mc.3 The energy from the Sun.

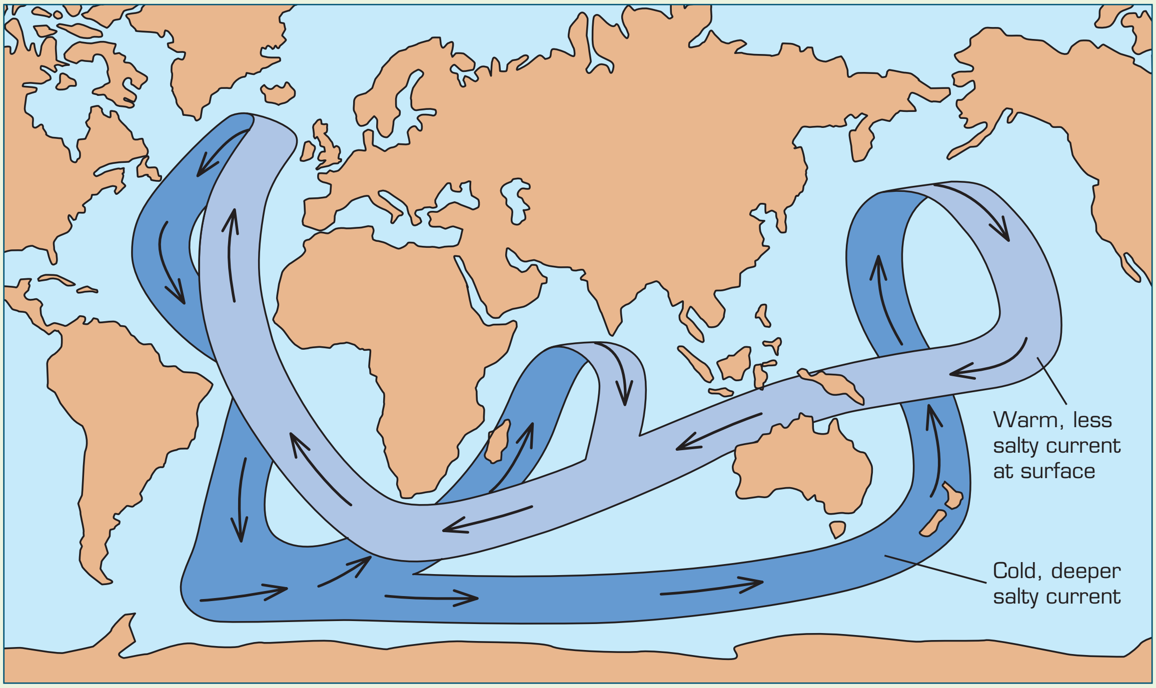


figure mc.4 The movement of water around the Earth due to ocean currents.

table mc.1 The specific heat capacities of some common substances. Water stands out from other substances due to its relatively high specific heat capacity.

Substance	Specific heat capacity ($J\ g^{-1}\ K^{-1}$)
water	4.18
ethanol	2.46
hexane	2.27
propanone	2.18
granite	0.82
copper	0.39
mercury	0.14

Water vapour

Tropical places are saved from scorching temperatures by the evaporation of water. As it evaporates, energy is absorbed, leaving the area cooler than it would be if water was not present. The enthalpy change of vaporisation, ΔH_{vap}, is the measure of energy absorbed as water changes from a liquid to a gas.

* Section 11.1 **Enthalpy** describes the energy changes associated with phase changes (page 424).

The water vapour can then be carried to other cooler regions and there it falls as rain. As water vapour changes into liquid water, energy is released—the same amount of energy as absorbed during vaporisation. The enthalpy change of condensation is $-\Delta H_{vap}$.

While both evaporation and condensation occur in tropical regions, there is an imbalance. Figure mc.5 shows the areas where evaporation exceeds condensation. Energy is removed from these regions to the places where condensation exceeds evaporation.

Water: the temperature regulator

In contrast to a planet like Mars, the temperatures of the Earth are less extreme as water distributes the Sun's energy. The movement of water as a liquid (by ocean currents) and as vapour (by atmospheric currents) allows energy to be transported from areas that receive more of the Sun's energy to regions of the Earth that receive less.

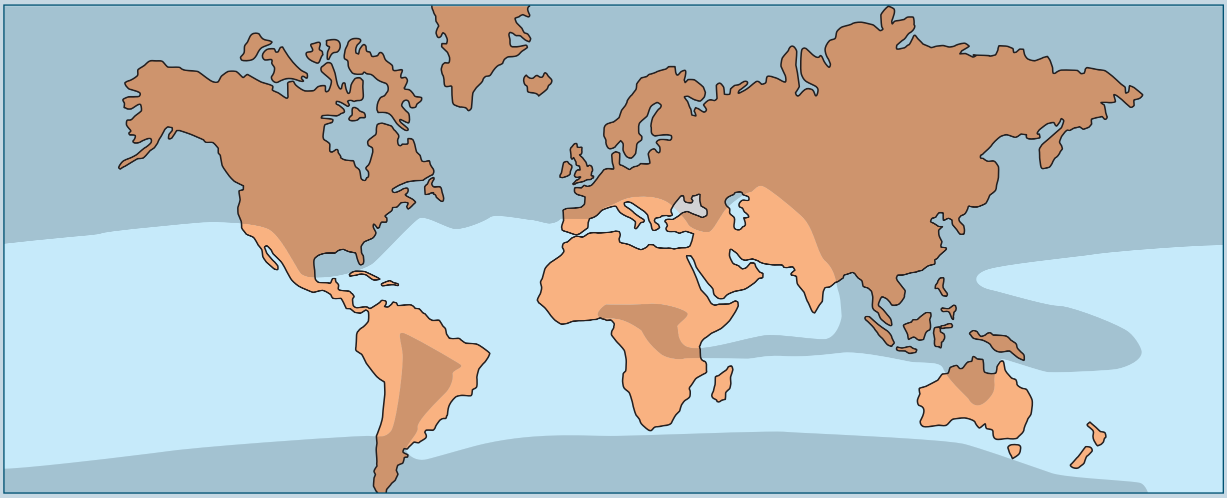


figure mc.5 Water evaporation. The lighter shaded areas denote evaporation exceeding condensation and the darker shaded areas denote condensation exceeding evaporation.

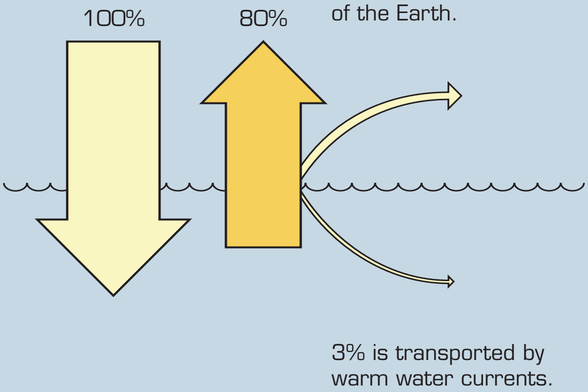


figure mc.6 Solar energy is transported by water to cooler regions of the Earth.

Sulfur

Oxidised sulfur in the atmosphere (mainly SO_2) is responsible for acid rain, a major problem in many countries. The build-up of sulfur dioxide is mainly blamed on the burning of compounds containing sulfur, including fossil fuels and metal ores during smelting, although volcanic activity is also known to release sulfur compounds into the atmosphere. Scientists of the 1960s performed research into the amount of sulfur released and the amount detected in the atmosphere, oceans and around the land. They found that the amounts were out of balance and other sources of sulfur must exist.

* Section 16.3 **Matter cycles** describes the cycling of matter (including sulfur) through ecosystems (page 546).

Dimethyl sulfide, $(CH_3)_2S$, is a substance that is partly responsible for the distinctive smell of the sea. It is produced by algae and seaweeds of the ocean. This volatile substance readily makes its way into the atmosphere where it can be oxidised into compounds that contribute to acid rain. It now seems that a major contributor to acid rain is completely natural and not related to air pollutants.

* Section 7.1 **Oxidation and reduction** describes the process by which an element can be oxidised (page 338).

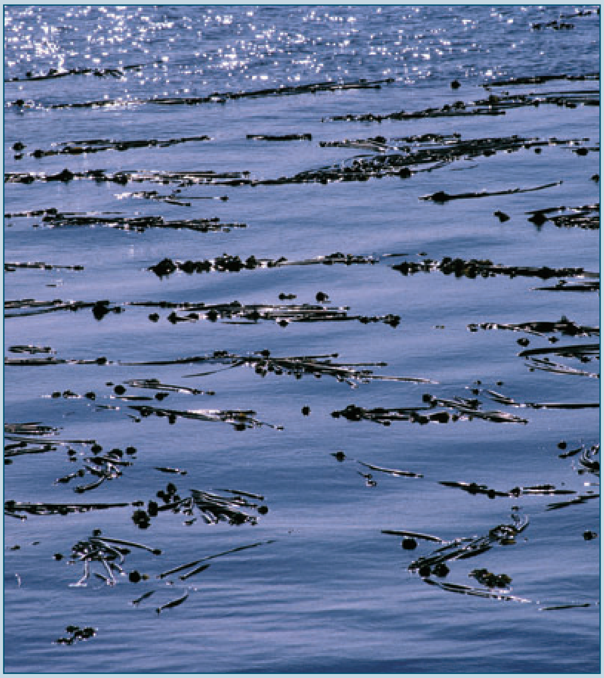


figure mc.7 Seaweeds and microscopic marine algae produce dimethyl sulfide that contributes to the amount of sulfur in the atmosphere.

The carbon dioxide trap

You may recall that while the solubility of solids increases with temperature, the solubility of gases decreases. The gaseous particles have more kinetic energy at higher temperatures, allowing them to escape from the solution. A natural body of water may no longer be able to support aquatic life if the temperature gets too high because insufficient oxygen will be dissolved in it. A cold can of beer will open with a pop but a hot one may spew out a frothy mess as the dissolved carbon dioxide quickly escapes.

* Section 4.1 **Dissolving** describes the solubility of gases (page 286).

Table mc.2 shows a comparison of the solubilities of nitrogen, oxygen and carbon dioxide at different temperatures. There are two things to observe here. The solubility of each gas decreases with increased temperature and the solubility of carbon dioxide is much higher than that of the other gases at the same temperature.

table mc.2 The solubilities of CO_2, O_2 and N_2 at various temperatures under atmospheric pressure.

Temperature (°C)	Solubility (mg per 100 g water)		
	CO_2	O_2	N_2
0	338	6.90	2.88
10	235	5.47	2.28
20	173	4.30	1.89
30	131	3.82	1.65
40	105	3.35	1.46
50	86	3.02	1.35

Increasing the pressure of a gas over a solution will also increase its solubility. This is the method used to carbonate soft drink. Under high pressures (about 14 atmospheres) carbon dioxide can be forced into the flavoured and coloured solution. When the drink is opened the carbon dioxide escapes, causing the bubbles.

The rate at which carbon dioxide is absorbed by the oceans is affected by the marine life present. The process of carbon dioxide dissolving can be described by the equation

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

As carbon dioxide is absorbed into the water some of it is used by phytoplankton during photosynthesis, pushing the equilibrium of this process towards the products. When phytoplankton respire or are eaten by larger animals, carbon dioxide is returned to the water. Carbon dioxide dissolving in sea water comes to equilibrium at a greater rate than a sample of water in a laboratory. Figure mc.8 summarises this process.

Ocean waters in colder areas can absorb higher quantities of carbon dioxide, which are then taken by ocean currents to be stored in deeper waters for long periods of time. Chemical processes, biological processes and ocean currents enable vast amounts of carbon dioxide to be removed from the atmosphere. It is estimated that up to 50% of carbon dioxide released into the atmosphere from the burning of fossil fuels is absorbed by the oceans.

* Section 17.1 **Reversible reactions** describes the factors that effect the equilibrium of chemical systems (page 554).

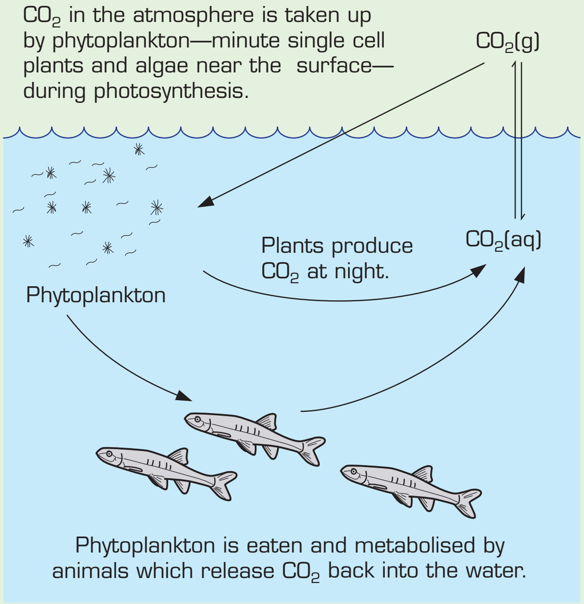


figure mc.8 The dissolving of carbon dioxide in sea water reaches equilibrium faster due to the presence of phytoplankton.

As well as being removed by biological means, carbon dioxide will also react with water, producing a solution containing carbonate ions and hydrogen carbonate ions.

$$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

This removal of carbon dioxide by chemical means will result in more carbon dioxide dissolving to maintain equilibrium.

figure mc.9 The shells of many marine creatures are made up of calcium carbonate.

Marine creatures with shells make use of the carbonate ions in the water. In sea water, calcium carbonate is essentially insoluble. The dissolving of calcium carbonate can be described by the equilibria:

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$

The solubility product for this reaction is given by

$$\begin{aligned} K_{sp}(CaCO_3) &= [Ca^{2+}(aq)] \times [CO_3^{2-}(aq)] \\ &= 5.0 \times 10^{-9}\ \text{mol}^2\ \text{L}^{-2} \text{ at } 298\ \text{K} \end{aligned}$$

*Section 17.4 **Solubility product** describes this concept (page 571).

The low value of the K_{sp} of calcium carbonate indicates its low solubility. Even so, the calcium carbonate of the sea shells will still be in equilibrium with the ions in the sea water, and calcium and carbonate ions will constantly be exchanged between the shells and the sea water.

Consider this

1 Table mc.3 shows the ΔH_{vap} of some different substances, including water. How would rainfall levels be different if, instead of water, the Earth's oceans were filled with propanone?

2 **a** Draw the structural formula for dimethyl sulfide and comment on the shape of the molecule.

b The oxidation of dimethyl sulfide results in the formation $(CH_3)_2SO$ and SO_2. Explain how this is an oxidation process.

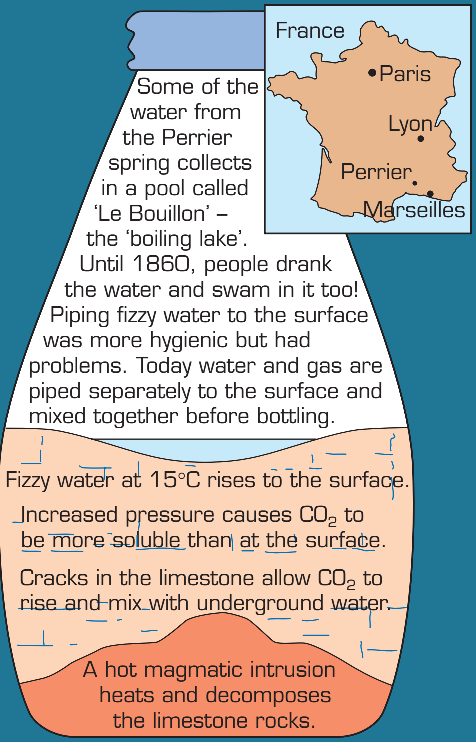
c Sulfuric acid (H_2SO_4) is responsible for acid rain. It is produced as SO_2 and oxygen in the air react to produce SO_3, which reacts with rainwater to produce sulfuric acid. Write reactions for sulfuric acid formation.

table mc.3 Change in enthalpy of vaporisation for a selection of substances.

Substance	ΔH_{vap} (kJ kg^{-1})
water	+2260
ethanol	+840
propanone	+520
hexane	+330
mercury	+300

3 Acid rain is particularly a problem for parts of Western Europe. It is believed that algal activity off the coast of France and Germany could be responsible for up to 25% of acidic pollution in Europe at certain times of the year. This means that 75% comes from other sources. Would an effort to reduce those other sources be warranted if a significant amount is beyond human control?

4 Perrier mineral water is different from most soft drinks and other brands of mineral water as both the water and the carbon dioxide are obtained from underground sources. It is said to be naturally carbonated. Read the information in figure mc.10 and consider the following questions.



Some of the water from the Perrier spring collects in a pool called 'Le Bouillon' – the 'boiling lake'. Until 1860, people drank the water and swam in it too! Piping fizzy water to the surface was more hygienic but had problems. Today water and gas are piped separately to the surface and mixed together before bottling.

Fizzy water at 15°C rises to the surface.

Increased pressure causes CO_2 to be more soluble than at the surface.

Cracks in the limestone allow CO_2 to rise and mix with underground water.

A hot magmatic intrusion heats and decomposes the limestone rocks.

figure mc.10

- **a** Why do you think that the lake collecting water from the Perrier spring was termed the 'boiling lake'?
- **b** The Perrier company decided to pipe water and carbon dioxide separately from the bottom of the lake when they encountered problems obtaining it directly from the ground as carbonated water. What sort of problems do you think they were trying to avoid?
- **c** Write a balanced chemical equation for the decomposition of limestone as it is heated by magma.

5 **a** In the section 'The carbon dioxide trap', there are three equations used to describe the dissolving of carbon dioxide and reactions with sea water. Combine these three into an overall equation for the whole process.

- **b** Some marine creatures produce for themselves a protective shell of calcium carbonate. Describe the effect that this would have on the equilibrium of the reaction that you have written.

6 The remains of dead shellfish and other organisms drift deeper into the depths of the oceans where the temperature is lower, the pressure is higher and the K_{sp} value for the dissolving of calcium carbonate is higher. The process of shells dissolving is described in figure mc.11. On the deep ocean floor there are no sea shells.

In terms of equilibrium conditions, explain why the calcium carbonate of shells dissolves more easily in deep ocean waters.

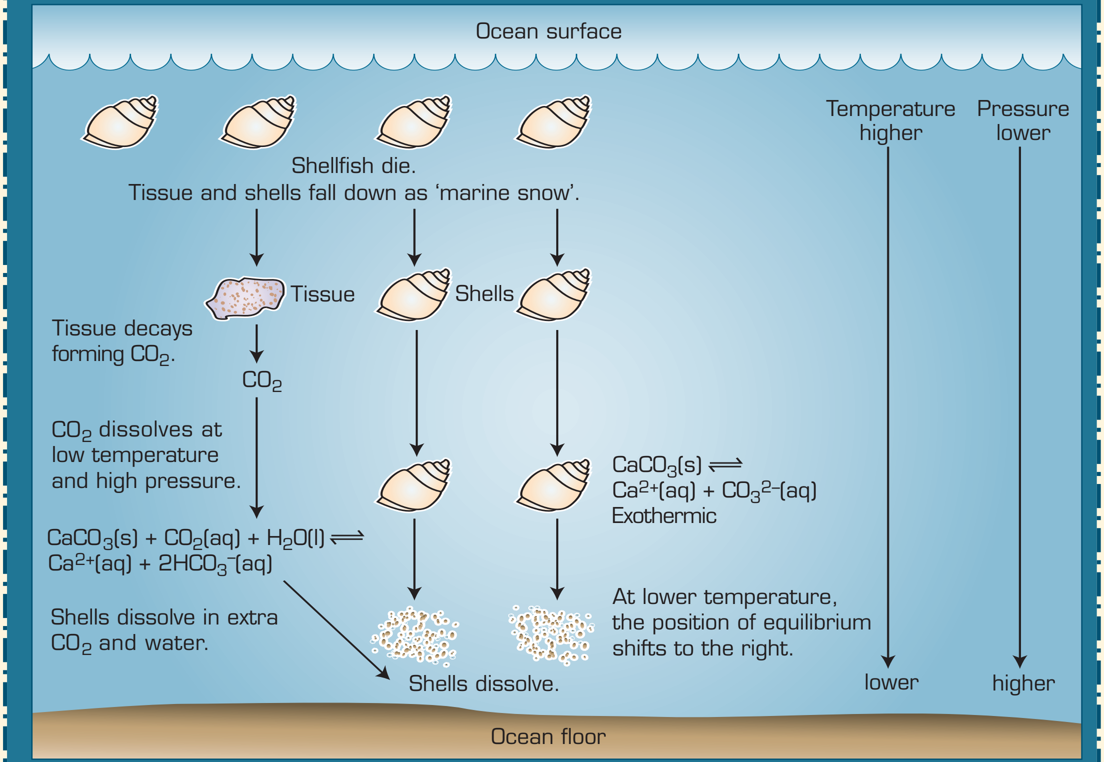


figure mc.11 At deeper levels the shells of marine life become more soluble.

Further investigations

1. Select three different towns around Australia along the same line of latitude. Find out their average temperatures for specific times of the year and account for the differences due to proximity to water and other factors.
2. Another way that water regulates the Earth's temperature is through the polar caps and masses of floating ice called icebergs. Water has unique properties including its high heat capacity and the fact that it is less dense as a solid than as a liquid. This is due to the forces between water molecules. Investigate the difference in properties of salt and fresh water. Find out more about the properties and structure of water, and relate this to the formation of ice on Earth. Relate your findings to the temperature regulation of our planet.
3. Mercury is the nearest planet to the Sun. It has no atmosphere or oceans, and a temperature range of –170°C to 350°C. Investigate the characteristics of Mercury and Earth, and account for the difference in temperature ranges of these planets.