

MODULE 1

Production of materials

Throughout history humans have used their ingenuity to make new materials and objects to satisfy their diverse and growing needs—materials such as ceramics and glass, metals and alloys, plastics and synthetic fibres, and inventions such as wheels, weapons, weaving looms, locomotives, motor cars, aeroplanes, telephones, televisions and computers.

When the demands for particular natural resources put strains on their supply, new materials were developed. For example when agriculture expanded greatly in order to feed a growing world population, synthetic fertilisers such as ammonium sulfate and superphosphate were developed to overcome shortages of natural fertilisers (manure and saltpetre). When demand for natural fibres (cotton, wool, silk) put strains on supply, synthetic fibres (rayon, nylon, polyester) were developed. Now that demands for crude oil are likely to deplete supplies within a few decades, attention is turning to developing new sources for the important materials such as plastics we currently get from oil.

In recent decades we have seen the development of many new technologies to meet the expanding demands of a more sophisticated society. When demands for more and more telecommunications put strains on the ability of copper wires to carry the signals, fibre optics were developed. Similarly the demands of the space race of the 1960s and '70s produced strong, light, heat-resistant materials.



The needs of medicine prompted the development of more sophisticated diagnostic tools and materials for artificial body parts, while the development of computers since the 1960s continues to stimulate the production of new high-purity materials.

In this module we shall examine some of the synthetic materials that are in widespread use and some of the ways of making them.

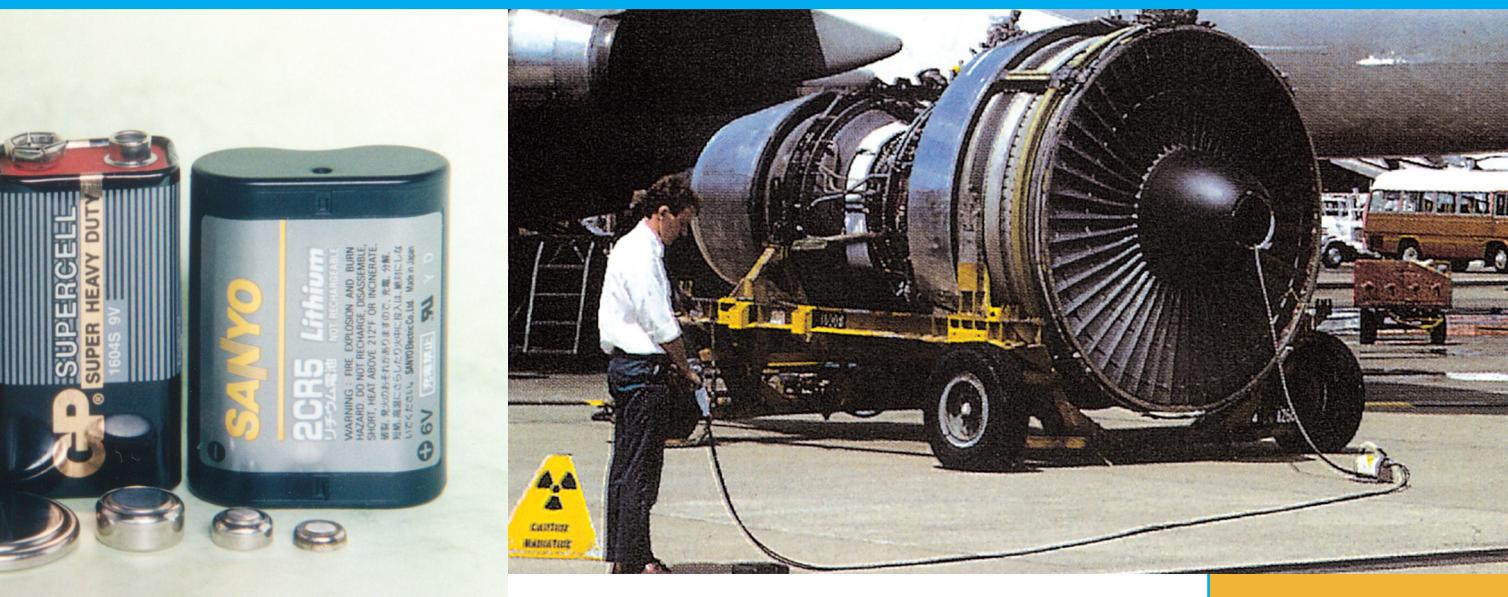
We will start (in Chapter 1) with a survey of some polymers (plastics and fibres) that we make from crude oil. This will lead us into a discussion of possible future trends for such materials, particularly in view of likely depletion of oil supplies and widespread pollution by plastics. Use of plant material as a possible source of liquid fuels will also be considered.

Electrochemical methods (which are processes involving chemical reactions and electricity) are widely used to produce sources of easily portable energy.

Chapter 2 will introduce the basic ideas and describe several widely used batteries.

Chapter 3 will introduce what are called radioactive materials and will describe some of the important roles they play in medicine and industry.

Throughout this module particular attention will be given to new materials and to likely future developments in these areas of chemistry.



MANY EVERYDAY PRODUCTS ARE MADE FROM SYNTHETIC MATERIALS

This colourful picnic ware and the collection of batteries used in a variety of consumer goods are just some of the thousands of products that are made from materials synthesised by chemical reactions.

Synthetic radioactive materials such as caesium-137 are made in nuclear reactors and used to detect structural faults in complex machinery (in much the same way as X-rays detect broken bones in people).



Ethylene, polymers and ethanol

IN THIS CHAPTER

Ethylene from cracking crude oil fractions
 Properties of alkanes and alkenes
 Reactions of alkanes
 Reactions of alkenes
 Industrially important reactions of ethylene
 Polymerisation of ethylene
 Other addition polymers
 Relating properties and uses to structure
 Uses of polyethylene, PVC and polystyrene

Will raw materials run out?
 Condensation polymers
 Structure and possible uses of cellulose
 Biopolymers
 A synthetic biodegradable biopolymer
 Ethanol as a source of ethylene
 Ethanol as a solvent
 Synthesis of ethanol from plant material
 Ethanol as a fuel
 Heat of combustion of ethanol

In Chapter 9 of *Conquering Chemistry Preliminary Course (CCPC)* we saw how crude oil provides us with a variety of products—gases for LPG, petrol for cars, kerosene for jet aircraft, diesel for trucks, lubricating oils and greases and tar (Table 9.6, p. 257 *CCPC*). Crude oil also provides us with the raw materials for making many plastics or *polymers* as they are called technically.

The most widely used starting substance for making polymers is ethylene[†] which is obtained from crude oil, either as a by-product of petrol refining or by the deliberate decomposition of some of its higher boiling point fractions. The term ‘cracking’ is used in these contexts.

1.1 ETHYLENE FROM ‘CRACKING’ CRUDE OIL FRACTIONS

Cracking is the name given to the chemical process of breaking large hydrocarbon molecules into smaller ones; for example breaking dodecane, C₁₂H₂₆ into octane, C₈H₁₈, and butene, C₄H₈. There are two types of cracking: *catalytic cracking* and *thermal cracking*.

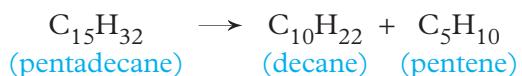
[†] This is the historical name for the compound. Its systematic name is ethene. However, as explained on p. 262 *CCPC* this is one of several compounds where the historical (trivial) name, rather than the systematic name, is the IUPAC-preferred name; hence, it will be used in this book.

Ethylene from catalytic cracking in oil refineries

Oil refineries need to balance their outputs of various products (petrol, diesel, fuel oil etc) to match the demands of the marketplace. As was mentioned on p. 258 of *CCPC*, generally more petrol is required than is obtained from fractional distillation. Hence oil refineries increase the proportion of gasoline by converting some of the lower demand fractions into gasoline. The process is called *catalytic cracking*.

Catalytic cracking is the process in which high molecular weight (*high boiling point*) fractions from crude oil are broken into lower molecular weight (*lower boiling point*) substances in order to increase the output of high-demand products.

The column in which this occurs is called a **cat cracker**. Alkanes with 15 to 25 carbon atoms per molecule are broken into two smaller molecules, one an alkane and the other an alkene; for example:



The alkene further splits into smaller alkenes until either ethylene or propene (or both) is formed; for example,



The overall products of catalytic cracking are alkanes of shorter chain lengths (used for petrol) and small alkenes. The proportions of ethylene to propene to alkanes vary with the reaction conditions.

The catalysts used for cracking alkanes are inorganic compounds called **zeolites**: they are crystalline aluminosilicates (compounds of aluminium, silicon and oxygen with some metal ions attached). The reaction is typically carried out at 500°C in the absence of air and with pressures somewhat above atmospheric.

The ethylene and propene which are by-products of catalytic cracking are starting materials for making plastics (polymers). However this production of ethylene and propene is insufficient to meet current needs for these chemicals. Often some fractions of crude oil are decomposed completely to produce ethylene and propene in a process called steam cracking or thermal cracking.

Ethylene from steam or thermal cracking

Steam cracking or **thermal cracking** is a non-catalytic process in which a mixture of alkanes with steam is passed through very hot metal tubes (700 to 1000°C) and at just above atmospheric pressure to decompose the alkanes completely into small alkenes such as ethylene,

Catalytic crackers at an oil refinery



propene and butene. Some hydrogen is also produced. For example, for the thermal cracking of undecane, C₁₁H₂₄:



Steam is present as an inert diluent; it allows the process to operate at just above atmospheric pressure (which facilitates easy flow of the gases through the hot tubes), while keeping the concentrations of the reacting gases low enough to ensure that the desired reactions occur.

Sometimes the feedstock for thermal cracking is a mixture of ethane and propane obtained from natural gas (which is mainly methane: see p. 268 CCPC). In this case the reactions are:



and



1.2 PROPERTIES OF ALKANES AND ALKENES

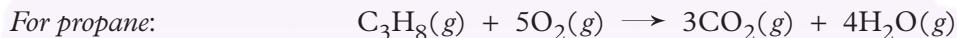
We saw on p. 265 CCPC that alkenes had similar physical properties (boiling points, densities and solubilities) to the corresponding alkanes. This was because alkenes, like alkanes, are *non-polar molecules* with *weak dispersion forces* being the only intermolecular forces involved. Recall that ethylene, propene and the butenes are gases at room temperature (as are the corresponding alkanes). The higher alkenes (like the higher alkanes) are liquids.

However alkenes and alkanes differ markedly in their chemical reactivity.

1.3 REACTIONS OF ALKANES

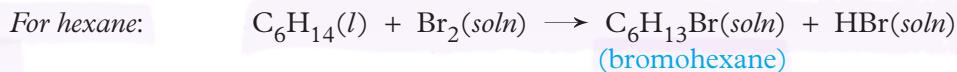
For alkanes there are only two important reactions:

- 1 Alkanes burn in air to form carbon dioxide and water. In doing so they liberate large amounts of heat, for example:



It is this combustion reaction that makes alkanes useful to us as fuels (Chapter 9 CCPC).

- 2 Alkanes react with chlorine and bromine when the mixtures are exposed to ultraviolet (u.v.) light, for example:



A reaction such as these in which an atom in a molecule is replaced by another atom or group of atoms is called a **substitution reaction**.

A variety of other products can be formed by these reactions, depending upon the conditions used, but for our present purposes the key point to note is that alkanes do not react with (decolourise) chlorine or bromine solutions in the absence of u.v. light but that they do react (quite slowly for the liquid ones) in the presence of u.v. light. This contrasts with the behaviour of alkenes (below).

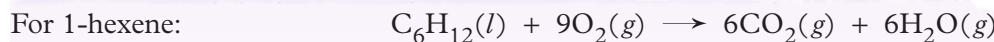
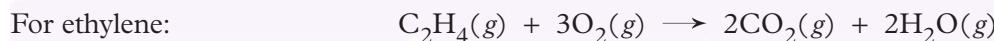


Exercises

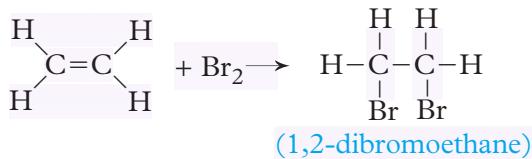
- 1 a Write an equation (in terms of molecular formulae) for the catalytic cracking of
 - i butadecane, C₁₄H₃₀, into a C₈ alkane and a C₆ alkene
 - *ii dodecane, C₁₂H₂₆, into a C₇ alkane and a C₅ alkene
- b Draw structural formulae and name the products of your reactions in (a).
- 2 Write equations to show the decomposition of the alkenes in Exercise 1 to propene and/or ethylene.
- *3 Why is it necessary to exclude air from catalytic and thermal cracking?
- 4 Write an equation for thermal cracking of hexadecane, C₁₆H₃₄ (to form ethylene, propene and perhaps hydrogen); more than one equation is possible.
- 5 An oil refinery was processing a Middle East crude oil that contained a high proportion of C₂₀ to C₂₅ alkanes. After fractional distillation (see pp. 256–7 CCPC) the refinery wanted to increase the proportion of the gasoline fraction, C₆ to C₁₂, so it passed the C₂₀ to C₂₅ fraction through a catalytic cracker. Operating conditions were such that this cat cracker produced a mixture of C₆ to C₁₂ alkanes along with C₂ to C₅ alkenes.
 - a How would the refinery separate this mixture into a portion that could be added to its gasoline output, a portion that contained C₄ and C₅ alkenes that could be further cracked, and a gaseous mixture of ethylene and propene? Some contamination of the gasoline portion with C₅ alkenes and vice versa would cause no problem.
 - b Write equations for the cracking of one of the starting alkanes and for the complete cracking of one of the C₅ alkenes.
 - *c Draw a flow chart for the complete processing of this C₂₀ to C₂₅ fraction.
- 6 Write equations for the combustion of:
 - a butane
 - b hexane
 - *c octane
- 7 Write equations for the reaction of butane with chlorine in the presence of u.v. light. How many monosubstituted chloro-compounds (that is, compounds with only one Cl atom per molecule) can be formed? Draw their structures.
- 8 a When ethane is reacted with bromine in the presence of u.v. light, under certain conditions compounds having two Br atoms per molecule are formed. Draw structures to show that two such compounds (isomers) are possible.
b Under other conditions compounds with three Br atoms per molecule are possible. How many isomers with three Br atoms are possible?

1.4 REACTIONS OF ALKENES

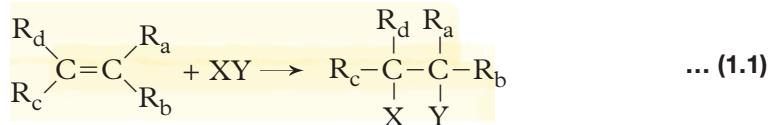
Alkenes burn in air to form carbon dioxide and water in the same way as alkanes do; for example:



The presence of the double bond in alkenes makes them much more reactive than alkanes. There are many substances which react with alkenes by opening out the double bond to form two single bonds: these are called **addition reactions**, the simplest one being between bromine and ethylene:



The general form of addition reactions is:



where XY is a molecule such as Cl_2 , Br_2 , H_2 , HCl , HBr , HOH (H_2O) and where R_a , R_b , R_c and R_d represent the rest of the alkene molecule—either H atoms or what are called **alkyl groups**.

An **alkyl group** is an alkane molecule with one hydrogen atom missing; it does not exist on its own, but is part of another molecule.

Alkyl groups are named by deleting the *ane* from the parent alkane and adding *-yl*. The simplest alkyl groups and their parent alkanes are shown in Table 1.1.

TABLE 1.1 Names and formulae of simple alkyl groups

Alkane	Name	Alkyl group	Name
CH_4	methane	CH_3-	methyl
CH_3-CH_3	ethane	CH_3-CH_2-	ethyl
$\text{CH}_3-\text{CH}_2-\text{CH}_3$	propane	$\text{CH}_3-\text{CH}_2-\text{CH}_2-$	propyl
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$	butane	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-$	butyl

Addition reactions of alkenes are summarised in Figure 1.1. Although ethylene is used as the alkene (for simplicity), *all* alkenes undergo these reactions.

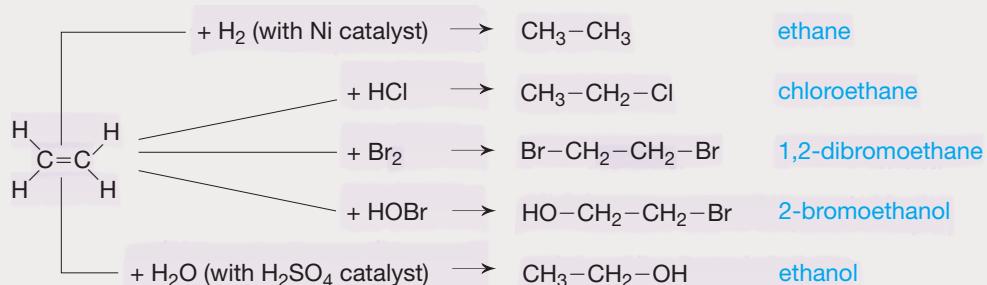


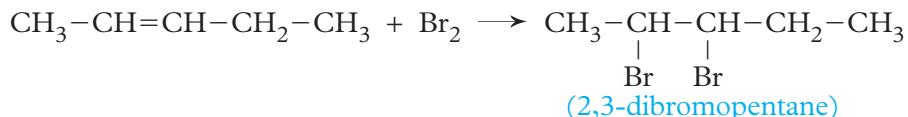
FIGURE 1.1
Common addition reactions of alkenes
(examples of Reaction 1.1)

Laboratory test for alkenes

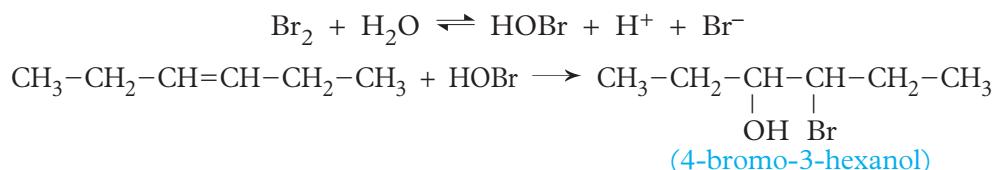
Reaction with bromine is often used in the laboratory to distinguish between alkenes and alkanes. The bromine can be used either in a non-aqueous solvent such as chloroform or hexachloroethane or as an aqueous solution called bromine water. In either case drops of the bromine solution are added to the colourless sample to be tested with gentle shaking. If the sample decolorises

the bromine solution, the sample is an alkene; if the sample takes on the brown colour of the bromine (that is, does not react with the bromine), it is an alkane. The test must be performed in subdued light because in the presence of ultraviolet light (for example sunlight) alkanes will react slowly with bromine (previous section).

As an example, 2-pentene will decolorise drops of a solution of bromine in hexachloroethane, the reaction being:



Alternatively 3-hexene will decolorise drops of bromine water, the reaction being:



On the other hand pentane and hexane will not decolorise either solution.

While the aqueous bromine solution is more convenient to use, the chemistry is a little more complicated than for the non-aqueous solution.

Exercises

9 Write balanced equations for the combustion (in excess oxygen) of:

- a** propene **b** 1-pentene ***c** 1-octene

Use molecular formulae for the carbon compounds.

10 Write equations for the reaction of **(i)** hydrogen (using a catalyst) **(ii)** chlorine **(iii)** bromine water, with each of the alkenes

- a** propene **b** 2-butene ***c** 1-pentene

Use structural formulae for the carbon compounds.

11 Write equations for the reaction of hydrogen chloride with:

- a** propene **b** 1-butene ***c** 3-hexene

If two products are possible, give both.

12 Write equations for the reaction of aqueous acid solution with:

- a** propene ***b** 2-butene

If two products are possible, give both. Name all your products.

13 Draw structural formulae for the products of the following reactions:

- a** 1-butene with

i bromine **ii** hydrogen bromide **iii** water (with H⁺ catalyst)

- b** 2-pentene with

i bromine water **ii** hydrogen (with Ni catalyst)

14 Compounds A, B and C are either octane or 2-hexene.

- a** When a few drops of a solution of bromine in chloroform were added to compound A and the mixture shaken, there was no apparent reaction. When a solution of bromine in water was added to another sample of the same compound, again after



shaking the mixture there was no apparent reaction. What do you conclude about the compound?

- b** When similar tests were performed on a different compound, B, this compound decolorised both of the bromine solutions. What do you conclude about compound B?
- c** The same two tests were performed on compound C on a sunny patio outside the laboratory. Compound C slowly decolorised both bromine solutions. When the tests were repeated inside the laboratory in very subdued light, neither solution was decolorised. Explain these results and draw a conclusion about the nature of compound C.

1.5 INDUSTRIALLY IMPORTANT REACTIONS OF ETHYLENE

The reactive double bond in ethylene means that it can easily be converted into a range of very useful products such as ethanol and the starting materials for several important plastics (polymers) as shown in Figure 1.2. Let us look at some of these reactions in more detail.

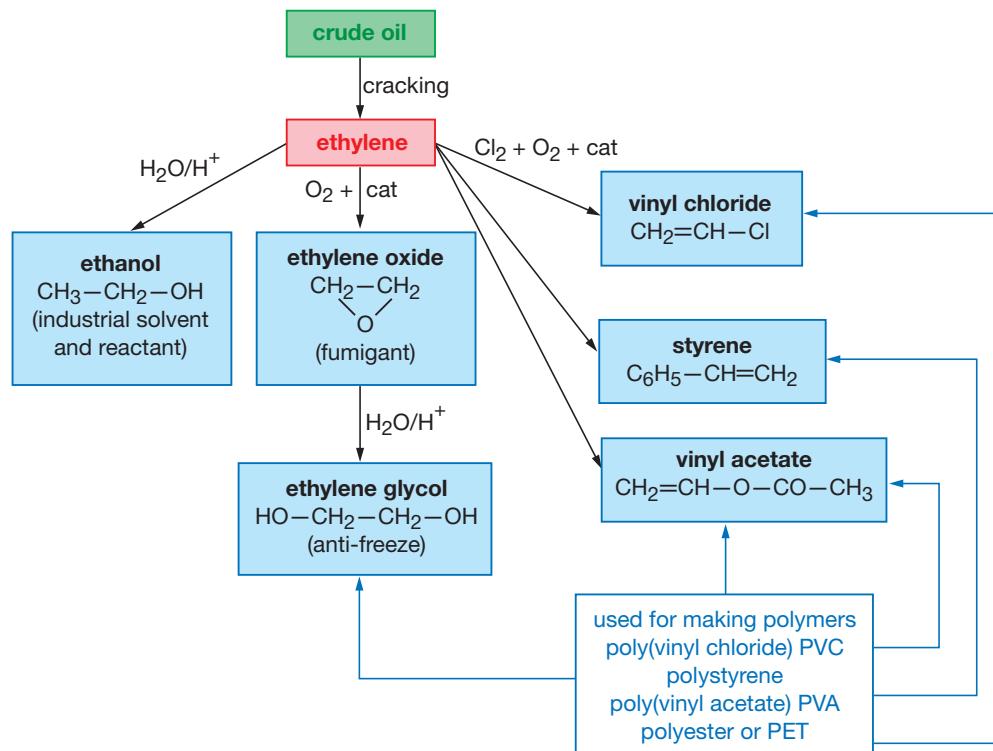
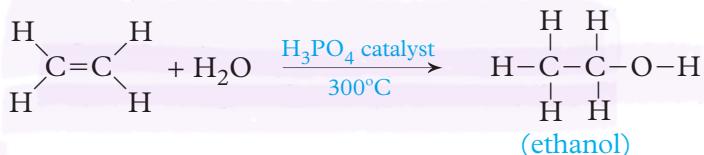


FIGURE 1.2
Important industrial chemicals made from ethylene (cat = catalyst)

1 Reaction of ethylene with water to form ethanol

Industrially ethylene is converted to ethanol by heating it with water (steam) at 300°C and at high pressure and using phosphoric acid as a catalyst:



This addition of a water molecule across a double bond is called a **hydration reaction**. It is a special type of *addition reaction*.

Ethanol is widely used in industry as a reactant and as a solvent in the synthesis of products ranging from pharmaceuticals and perfumes to varnishes and plastics. In the home it is used as an antiseptic and as a solvent in such items as food colourings and flavourings and in many medications.

The alcohol in alcoholic beverages is made by fermentation (discussed below), not by the above industrial process. Similarly the ethanol that is currently being added to petrol is made by fermentation.

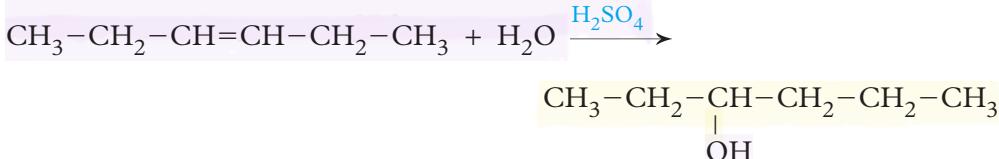
Ethanol belongs to a group of compounds called **alkanols**: they can be regarded as alkanes with one H atom replaced by an OH group: for example methanol, CH_3-OH , from methane, CH_4 ; ethanol (above) from ethane, CH_3-CH_3 .

To name an alkanol

- Delete the e of the parent alkane and add **-ol**: methanol, ethanol, propanol, butanol and so on, and
- Add a number prefix to denote the position of the alcohol group (as the OH is called) in the same way as a number was used for the position of the double bond on p. 265 CCPC[†]. No number is needed for methanol or ethanol. (Why?)

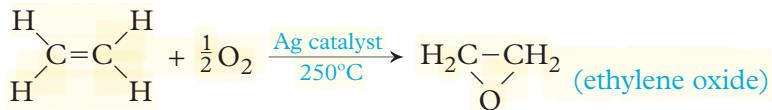
Alkanols are a sub-group of a class of compounds called **alcohols**. *Alcohols (and therefore alkanols) contain the –OH functional group* (centre of reactivity, p. 267 CCPC).

In the laboratory liquid alkenes are converted to the corresponding alkanols by heating with dilute sulfuric acid, the H^+ from H_2SO_4 being the catalyst for the reaction; for example 3-hexene can be converted to 3-hexanol:

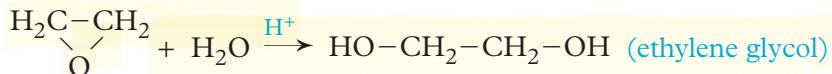


2 Catalysed reactions of ethylene with oxygen

Ethylene glycol (systematic name 1,2-ethanediol) is used in large quantities for the manufacture of polymers (polyester fibres and PET, poly(ethylene terephthalate) plastics) and as an automotive antifreeze. It is made from ethylene. The first step is to react ethylene with oxygen in the presence of a silver catalyst to form ethylene oxide:



While some ethylene oxide is used as a fumigant, much larger amounts are converted to ethylene glycol by treating it with dilute acid solution:



[†] Remember, CCPC is the abbreviation being used for *Conquering Chemistry Preliminary Course*. Page numbers refer to the fourth edition, 2004.

Other catalysed reactions are used to convert ethylene to the starting materials for making a variety of other plastics as indicated in Figure 1.2. For example to form vinyl chloride, the starting material for making the very common plastic, poly(vinyl chloride), PVC, ethylene is heated to 150°C with chlorine and oxygen in the presence of a copper chloride catalyst:

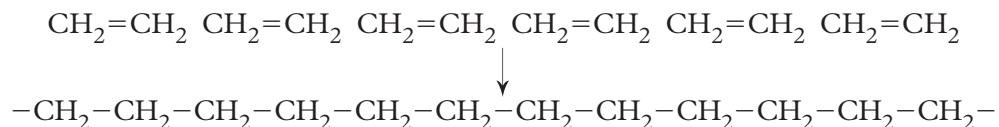


The most important reaction of ethylene is its conversion to polyethylene (or polyethene) in a reaction which is called *polymerisation*.

1.6 POLYMERISATION OF ETHYLENE

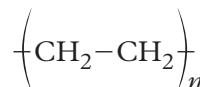
Polymerisation is a chemical reaction in which many identical small molecules combine together to form one large molecule. The small molecules are called **monomers** while the large product molecule is called a **polymer**.

The monomer ethylene polymerises to form the polymer, polyethylene:



These polymers are essentially long alkane molecules: each molecule contains from a few hundred to a few thousand monomer units.

The structure is frequently written in an abbreviated form:



where n is the number of monomer units in the molecule—say about 300 to 3000.

Polyethene is the systematic name for this substance but *polyethylene* is the IUPAC[†] preferred name. *Polythene* was the trade name for the product patented by the chemical manufacturer ICI (Imperial Chemical Industries Pty Ltd).

Polyethylene is called an **addition polymer**. This means that it forms by molecules adding together without the loss of any atoms. Basically each double bond ‘opens out’ to form single bonds with the neighbouring molecules.

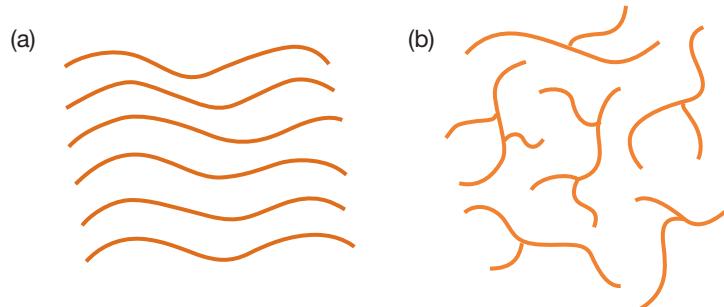
There are two processes used to make polyethylene.

- In the older gas phase process (still widely used) high pressure (1000 to 3000 times atmospheric) and high temperature (300°C) along with an initiator (an organic peroxide, a compound containing a $-\text{O}-\text{O}-$ group, or sometimes oxygen gas) are used. The product has significant **chain branching**. This means that at some carbon atoms one hydrogen atom is replaced by an alkyl group (Table 1.1). Consequently the alkane chains cannot pack close together or in an orderly way: this is called *low density polyethylene* (LDPE). In this process the ‘initiator’ is not strictly a catalyst because it gets incorporated into the actual polymer formed—one initiator molecule per one or two polymer molecules, meaning per 2000 or 3000 monomer units.

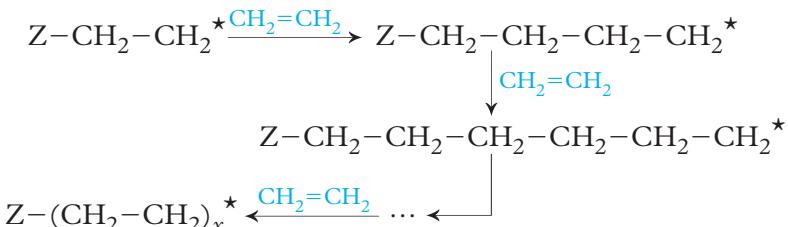
[†] International Union of Pure and Applied Chemistry; this body, among other things, formulates rules for the naming of compounds.

The second (newer) process uses pressures of only a few times atmospheric and temperatures of about 60°C and uses a catalyst which is a mixture of titanium(III) chloride and a trialkylaluminium compound such as triethylaluminium, $(\text{CH}_3-\text{CH}_2)_3\text{Al}$. This **Ziegler-Natta process** as it is called forms unbranched polyethylene molecules which are able to pack closely together in an orderly fashion. This product, called *high density polyethylene* (HDPE), is more crystalline and has a higher density than the branched-chain product. Figure 1.3 illustrates the difference between linear and branched chains. The properties and uses of the two forms of polyethylene will be discussed below.

FIGURE 1.3
Different arrangements of polymer chains:
(a) crystalline linear chains as in HDPE,
(b) amorphous (non-crystalline) branched chains as in LDPE

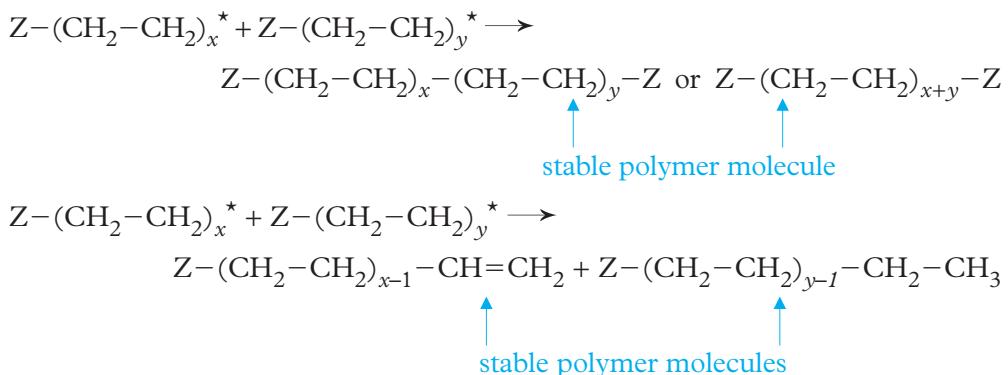


In both these processes the initiator or catalyst activates an ethylene molecule by attaching to it. An ordinary ethylene molecule then attaches to this, forming a new activated species. Polymerisation continues by ethylene molecules one after the other adding to the growing chain:



Z is all or part of the catalyst molecule * indicates an activated species

Finally the process stops by two such activated chains colliding with each other; they either join together to form a stable polymer molecule or they exchange a hydrogen atom to form two stable molecules:



Because activated chains of variable lengths can collide (different values of x and y) and because of the two possible processes, the polymer molecules formed have different chain lengths (different values of x or y or $x+y$) and so different masses. *Hence in any polymer sample there is a distribution of molecular weights as*

shown in Figure 1.4. Consequently we talk about the **average molecular weight** of a polymer; this is the average relative mass of all of the molecules present in the sample.

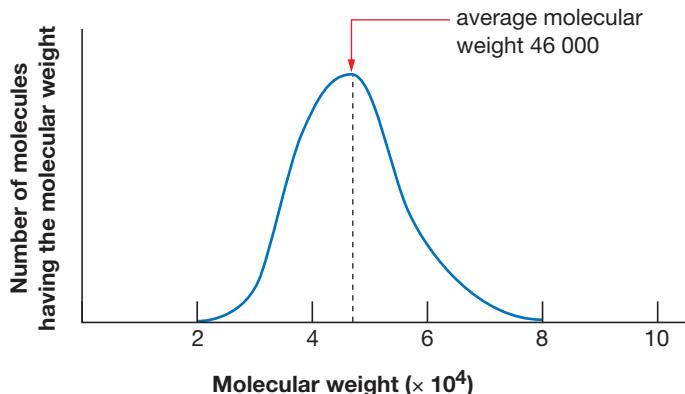


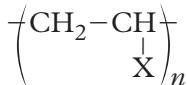
FIGURE 1.4
A typical molecular weight distribution for a polymer. The graph shows the number of molecules having a particular molecular weight as a function of molecular weight

1.7 TWO OTHER ADDITION POLYMERS

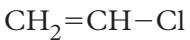
Several other common polymers are addition polymers made from monomers in which one of the H atoms of ethylene has been replaced by a different atom or group such as Cl or CH_3- . We can represent such monomers as $\text{CH}_2=\text{CH}-\text{X}$ and the polymer as:



As with polyethylene, we can abbreviate this to:



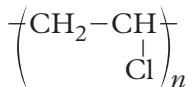
PVC, or poly(vinyl chloride), is made from the monomer, *vinyl chloride*,



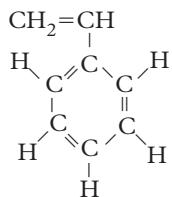
The systematic name for this monomer is *chloroethene* and therefore for the polymer is poly(1-chloroethene)[†]. Apart from polyethylene this is the cheapest and most widely used polymer. It has the structure:



which can again be abbreviated to



Another common addition polymer is *polystyrene*, made from the monomer *styrene* which has the structure:

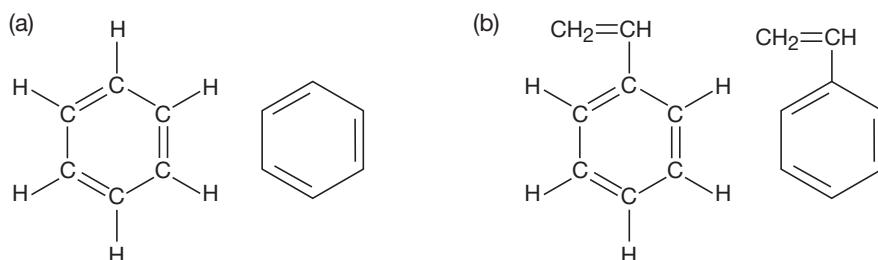


[†] The 1- is not necessary in chloroethene. Why? It is included in the name of the polymer to indicate that the Cl atoms are on alternate C atoms and never on adjacent Cs.

The side group here—the X above—is the so-called *phenyl group*. It comes from the compound benzene, C_6H_6 , in the same way as alkyl groups come from alkanes—by removal of a hydrogen atom. Benzene is a cyclic hydrocarbon with six C atoms in a planar hexagonal ring and with a H atom attached to each C. We can think of the C—C bonds as being alternate double and single bonds though this is not an accurate description of the true structure. The phenyl group can replace an H atom in ethylene in the same way as Cl does.

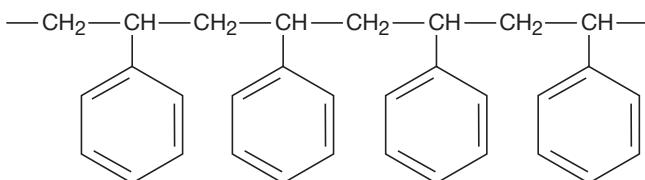
The above structure for styrene is cumbersome to draw, so chemists have a shorthand way of drawing benzene rings (or phenyl groups): they just draw the ring structure, leaving out the C and H atoms. It is understood that there is a C atom at every apex of the structure and attached to it are sufficient H atoms to bring the valence of the C up to its usual 4. The full and abbreviated structures for benzene and styrene are in Figure 1.5.

FIGURE 1.5
Full and abbreviated
structures for (a) benzene
and (b) styrene



Styrene is the common name for this monomer; its systematic name is *phenylethene*. The IUPAC preferred name is styrene.

A segment of the structure of polystyrene is:



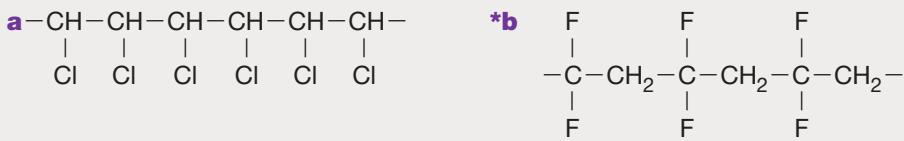
Naming polymers

So far we have had polyethylene, poly(vinyl chloride) and polystyrene. Polymers are named by putting ‘poly’ in front of the name of the monomer, but when do we use brackets around the monomer name and when not? Brackets are used:

- when the monomer name is more than one word, as in poly(vinyl chloride), PVC or
- when the monomer name begins with a number, as in poly(1-chloroethene), the systematic name for PVC.

Exercises

- 15** Would you expect 1,1-dibromoethene, $CH_2=CBr_2$ to form an addition polymer? If so draw a segment of its structure. Include at least four monomer units.
- 16 a** A sample of PVC has an average molecular weight of 7.2×10^4 ; what is the average number of monomer units in a molecule of this sample?
b What would be the average molecular weight of a sample of polystyrene in which the average number of monomer units per molecule was 800?
- 17** Draw the structure of the monomer you would use to make the following polymers:



- 18 Perspex, commonly used as a substitute for glass, is an addition polymer of methyl methacrylate, $\text{CH}_2=\text{C}-\text{CO}-\text{O}-\text{CH}_3$
- $$\begin{array}{c} | \\ \text{CH}_3 \end{array}$$

Draw a segment of the structure of this polymer.

- 19 Using information in Table 1.3, draw segments of the structures of polypropylene, polytetrafluoroethylene and polyacrylonitrile.

Table 1.2 summarises information about the three addition polymers described so far. Their uses and the way these uses depend upon properties will be discussed in Section 1.10.

TABLE 1.2 Common addition polymers, the monomers they are made from, and some of their uses

Polymer	Name and structure of the monomer	Common uses
polyethylene	ethylene (ethene) $\text{CH}_2=\text{CH}_2$	<i>LDPE</i> : milk bottles, soft toys, wrapping film (cling wrap) <i>HDPE</i> : kitchen utensils and containers, more rigid toys, rubbish bins, tougher carry bags
poly(vinyl chloride) PVC	vinyl chloride (chloroethene) $\text{CH}_2=\text{CH}-\text{Cl}$	electrical insulation, garden hoses, drainage and sewerage pipes, household guttering and downpipes
polystyrene	styrene (phenylethene) $\text{CH}_2=\text{CH}$ 	car battery cases, tool handles, modern furniture, CD cases, disposable drink cups (both foam and clear), foam packing material

1.8 SOME FURTHER ADDITION POLYMERS†

Table 1.3 presents information on four further addition polymers in widespread use in the everyday world.

TABLE 1.3 Another four addition polymers, the monomers they are made from, and their common uses

Polymer	Name and structure of the monomer	Common uses
polypropylene	propylene (propene) $\text{CH}_2=\text{CH}-\text{CH}_3$	motor car bumpers, rope and twine, household goods, moulded chairs, carpets
polyacrylonitrile (acrylics)	acrylonitrile (cyanoethene) $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$	as a wool substitute in clothing, blankets, soft furnishings, carpet
poly(vinyl acetate), PVA	vinyl acetate $\text{CH}_2=\text{CH}-\text{O}-\text{CO}-\text{CH}_3$	vinyl coatings on upholstery fabrics, paint, adhesives
polytetrafluoroethylene, PTFE (Teflon™)	tetrafluoroethene $\text{F}_2\text{C}=\text{CF}_2$	high-grade electrical insulation, non-stick surfaces on cookware, pipe thread sealant

† not required for NSW HSC

1.9 RELATING PROPERTIES AND USES TO STRUCTURE

In selecting a polymer for a particular use important properties to consider are:

- melting or softening point
- stability to heat and light
- chemical stability
- mechanical strength
- flexibility or rigidity.

Another factor is cost: we generally select the cheapest polymer that will do the job.

As with all compounds, the properties of polymers are affected by their structure. Important structural features for addition polymers are:

- average molecular weight (or chain length)
- crystallinity (extent of chain branching)
- chain stiffening
- cross-linking.

Average molecular weight

The average molecular weight of a polymer reflects the number of monomer units that combine to make one polymer molecule. This depends upon the conditions used in the polymerisation process. Not all the molecules in a batch of polymer have the same molecular weight: there will be a range of different chain lengths as was explained in Section 1.6, and this is why we need to talk about the *average* molecular weight.

For a given type of polymer, the longer the polymer chain (higher the molecular weight) and the smaller the spread of molecular weights, then the higher the melting point and the harder the substance is.

Chain branching

As already mentioned, we can get **chain branching** in polyethylene. If polyethylene forms in long unbranched chains then these chains are able to intertwine and align closely. This leads to an orderly arrangement; the substance is crystalline. A high degree of crystallinity leads to high density, a high melting point and a relatively hard and tough material. On the other hand, if there is a lot of chain branching then the molecules are not able to get so close to one another, they are not able to align themselves in an orderly fashion and so the material is non-crystalline or amorphous as shown in Figure 1.3. This leads to low density, low melting point, greater flexibility and softness. High density polyethylene is easily recognised by the way it ‘crackles’ when it is crumpled. Low density polyethylene is much softer and ‘clingy’. Gladwrap™ and similar wraps are low density polyethylene.

Chain stiffening

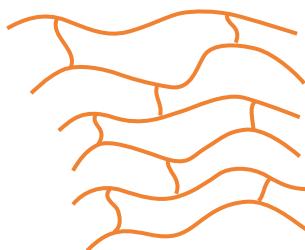
Chain stiffening of an addition polymer involves putting a bigger side-group into the linear chain to reduce its flexibility. Changing from H of polyethylene to CH₃ of polypropylene stiffens the chain only slightly. When the side-group is changed

to a chlorine atom (PVC) or to a benzene ring in polystyrene, both much bigger than a CH_3 group, the ability of the chain to ‘flop around’ is greatly restricted. The material becomes stiffer and much more rigid. PVC without additives (plasticisers) to soften it is quite rigid. Polystyrene, which contains a benzene ring, is a hard plastic used for screwdriver handles, car battery cases, some plastic furniture and the like. Polyethylene, even the high density form, is never as hard or as rigid as polystyrene or unplasticised PVC because it lacks chain stiffening.

However when polystyrene is formed with gas being blown through it, it forms soft beads or foam. The softness however is due to the gas trapped inside the beads, not to the polymer itself.

Cross-linking

The rigidity or hardness of a polymer can be increased by what is called **cross-linking**. This is a process in which two or more linear chains are joined together to form a more extended two-dimensional network as shown in Figure 1.6. Cross-linking is much more common in the condensation polymers to be discussed below than in addition polymers. However it does occur in the vulcanising of rubber. Natural rubber is an addition polymer of polyisoprene: it is rather soft and sticky. If it is heated with a few per cent sulfur, the sulfur forms $-\text{S}-\text{S}-$ bridges between pairs of linear chains. This introduces considerable cross-linking into the material and makes it harder and more ‘springy’ (elastic).



The four properties just discussed can all be controlled in the manufacture of these various polymers. It is therefore possible to ‘tailor-make’ molecules—to make materials with specific physical properties.

Solubility of addition polymers

None of the polymers mentioned so far contains OH groups or exposed O atoms and so these polymers cannot form hydrogen bonds with water. Although some of them contain polar C–Cl or C≡N bonds, there are many more non-polar bonds. Consequently these polymers are quite insoluble in water and are generally hydrophobic (water repelling): this means that they are not easily wetted by water.

Stability

Most of the bonds in these polymers are strong C–C and C–H bonds and so these molecules are fairly stable. Polytetrafluoroethene (Table 1.3) has



The addition polymer poly(vinyl chloride) or PVC is widely used for plumbing fittings, particularly for drain pipes

FIGURE 1.6
Cross-linking joins long chains to one another: this can make the polymer more rigid (polystyrene) or elastic (rubber)

C–F bonds which are much stronger than C–H bonds. This makes the polymer the most stable of those discussed so far. On the other hand PVC has C–Cl bonds which are weaker than C–H bonds. PVC is vulnerable to attack by ultraviolet light (which can break C–Cl bonds) and so special additives are needed to protect PVC exposed to sunlight (though PVC is extremely stable underground or in the dark).

When heated to high temperatures, PVC decomposes to form hydrogen chloride which is extremely corrosive: it is the cause of much of the damage that results from fires involving PVC. Acrylics, when heated strongly, decompose to form hydrogen cyanide which is an extremely poisonous gas; this is of considerable concern with the increasing use of acrylics in furnishings and carpets.

1.10 USES OF POLYETHYLENE, PVC AND POLYSTYRENE

Having seen how structural features affect properties of polymers, we can now look at how these properties determine which polymers will be used for particular purposes.

Low density polyethylene, LDPE

Low density polyethylene, because of its extensive chain-branching, lack of stiffening side groups and lack of cross-linking, is relatively soft and very flexible with a fairly low melting point; it is not particularly strong. These properties make it well suited for making wrapping materials and disposable shopping bags, flexible toys, milk bottles and squeeze bottles in both the laboratory and the home.

High density polyethylene, HDPE

High density polyethylene has virtually no chain branching. This means that molecules can pack closely together in an orderly fashion, which results in this polymer being harder and stronger and having a higher melting point than LDPE. HDPE is widely used to make kitchen utensils and containers, tougher carry bags, more rigid toys, a variety of building products, ‘wheely’ bins for household waste and recycling, and pipes for transporting natural gas to households (replacing older steel and copper ones). The absence of chain stiffening and cross-linking limits the hardness and brittleness of HDPE.

Poly(vinyl chloride), PVC

Poly(vinyl chloride), with its Cl side groups producing considerable chain stiffening and with its polar C–Cl bonds producing quite strong intermolecular forces, is a hard inflexible polymer. Its C–Cl bonds make it vulnerable to attack by ultraviolet (u.v.) light so it degrades fairly quickly in daylight; for outdoor use PVC needs an inhibitor added to it to absorb the u.v. light. The rigidity of PVC can be adjusted quite considerably by adding non-volatile plasticisers to it. Consequently some formulations of PVC are quite soft and can be used for electrical insulation and garden hoses; PVC is the common insulation on household electrical wiring. More rigid formulations are used for many household items, for drainage and sewage pipes, for household guttering and down-pipes and increasingly for window frames.

Both PVC and polyethylene are cheaper than the other common plastics so they tend to be used unless the product requires properties they do not have.

Polystyrene

Polystyrene with its large phenyl side group is the most stiffened of the common plastics. Hence it is very hard and rigid. With only C–C and C–H bonds it is also very stable to heat and u.v. light. With minimal chain branching it is very crystalline and can be formed into very clear transparent objects. It is widely used for making tool handles, car battery cases, high quality modern furniture and assorted ornaments, CD cases and clear disposable drink glasses.

Despite its inherent hardness polystyrene is used to make foam drink cups, bean-bag filler and foam packing materials, both moulded-to-fit ones and pellets. These uses arise because, if gas is bubbled through the styrene mixture as it is polymerising, a very light-weight foam is formed which solidifies as a very spongy material. The sponginess arises from the gas bubbles that are trapped inside the polymerised material. It is the compressibility of the gas that gives polystyrene foam its softness and lightness; the actual polystyrene is still quite hard.

WEBSITES

For further information about structure and uses of polymers:

<http://www.pscl.ws/macrog/index.htm>

(scroll down a bit, then click on a level. Level One is very good for uses of polymers.)



<http://www.pacia.org.au>

(click on *Education*, then, on the left side of the screen under *Education and Resources for Students*, click on *Orica Chem Fact Sheets*; select *Polyethylene* or *Polypropylene* or any other chemical of interest.)

<http://www.kcpc.usyd.edu.au/discovery/Syllabus.html>

(click on *Addition polymerisation scenic route*. Lots of interesting information though much of it is outside the HSC syllabus.)

Exercises

20 Arrange the three polymers, polyethylene, PVC and polystyrene in order of increasing chain stiffness. Explain your reasoning. Which of these would you expect to be the most flexible or pliable and which the least? Explain why.



21 Draw a section of a polyethylene molecule with chain branching.

22 What type(s) of intermolecular forces would you expect in:

- a polyethylene b poly(vinyl chloride) *c polystyrene?

Draw a diagram to illustrate for (b)

23 Which of LDPE, HDPE, PVC or polystyrene would be most suitable for making each of the following products? Give your reasoning. If you are unable to make a clear choice discuss the possibilities.

- a disposable juice bottles
- b reusable juice bottles (for daily use in school lunch packs)
- c plastic raincoats
- d transparent protective covers for outdoor light bulbs
- *e outer casings for desktop computers and printers
- *f self-assembly toys for young children such as buildings, boats, robots and dolls.
- *g insulating sheath for keeping a wine bottle cool

1.11 WILL RAW MATERIALS RUN OUT?

The raw materials for making the polymers just described come from crude oil (basically ethylene and propene). There is considerable concern that the world is going to use up all its available oil reserves within the next few decades. Some analysts predict that supplies will be effectively used up by the middle of this century: others suggest a few decades later. How long oil supplies will last depends upon our rate of consumption—whether it continues to increase rapidly as it has done in the last half century or whether our use starts to decline.

By far the major use of crude oil is as a fuel for cars, planes and trains. Currently there is pressure to reduce energy use and to develop alternative fuels, first because of the greenhouse problem (p. 288 CCPC) and secondly because as supplies of oil diminish the cost will increase. However progress in this direction has been slow.

Currently the petrochemical industry (mainly plastics) consumes only about 3 to 5% of the total oil used in the world today.

Some scientists argue that because oil supplies are going to run out in the foreseeable future, we should be developing alternative sources of the raw materials for plastics. They point to ethanol obtained from agricultural crops as a possible source of ethylene for making polymers.

Others argue that as oil supplies diminish, costs will increase and oil will become too expensive to use as a fuel: overall energy use will fall and alternative fuels will become cost effective. The petrochemical industry will be less affected by price rises (because the cost of raw materials is a smaller proportion of the cost of the finished products) and so will still be able to afford to use oil. Consequently, these people argue, the remaining oil will become the exclusive domain of the petrochemical industry and will last for many more decades.

Regardless of which argument is correct, it would be prudent for the plastics industry to develop alternative sources of ethylene and propene.

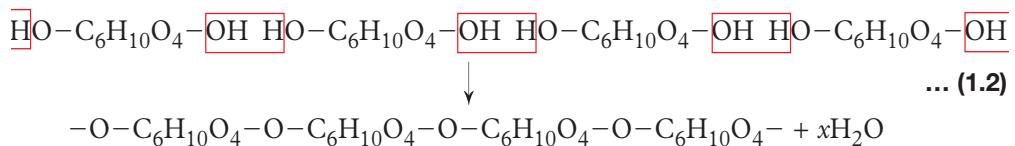
Ethanol is the prime candidate for an alternative source of ethylene. Ethanol can be produced by fermentation of starch and sugars from a variety of agricultural crops and it can be easily converted to ethylene. We will discuss this approach in Section 1.16.

There is however an even more tantalising source for starting materials for making many of the polymers that are so useful today, and that is cellulose. Cellulose is a major component of plant material, whereas starch and sugars are minor components. In order to explore the possible use of cellulose for making petrochemicals, we need to look at the general structure of natural polymers (starch, cellulose, proteins). This leads us to what are called *condensation polymers*.

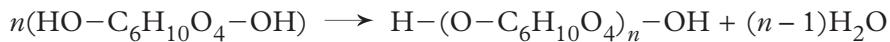
1.12 CONDENSATION POLYMERS

Condensation polymers are polymers that form by the elimination of a small molecule (often water) when pairs of monomer molecules join together.

Cellulose is a naturally occurring condensation polymer. The monomer from which it forms is glucose. To illustrate condensation polymerisation let us write glucose, which has the molecular formula $C_6H_{12}O_6$ as $HO-C_6H_{10}O_4-OH$. The polymerisation occurs by the elimination of water molecules from between pairs of glucose molecules:



Alternatively we can write this as:

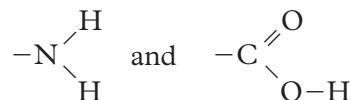


This is saying that n molecules of glucose combine to form one molecule of cellulose (which contains n glucose units) by eliminating $(n-1)$ molecules of water.

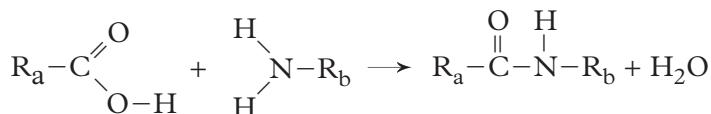
A synthetic condensation polymer is *nylon-6*. This is a particular type of nylon formed from the monomer 6-aminohexanoic acid which has the structure:



This can be written as $\text{H}_2\text{N}-(\text{CH}_2)_5-\text{COOH}$. This molecule contains two functional groups (pp. 266–7 CCPC), the **amine group** $-\text{NH}_2$ and the **carboxylic acid group** $-\text{COOH}$. Although written in these ways for convenience, their full structures are:



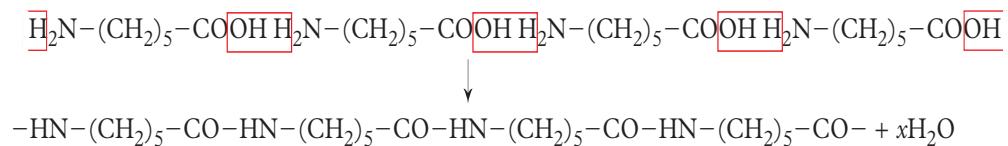
Carboxylic acids react with amines:



where R_a and R_b are the rest of the molecules (commonly alkyl groups). For convenience this reaction is often written as:



Molecules of 6-aminohexanoic acid having both functional groups can react with one another to form a polymer. The polymerisation reaction is:



The chemical bond that has formed here is the same as occurs when proteins form: a carboxylic acid group $-\text{COOH}$ combines with an amine group $\text{H}_2\text{N}-$ to form what is called an **amide link** $-\text{CO}-\text{NH}-$. In biochemical contexts this is called a **peptide link**. In nylon-6 all the monomer units are identical. Nylon-6 was the first nylon to be made but it is not the common nylon today. Nylon is actually a trade name. The generic name is **polyamide**.

Proteins are condensation polymers made from amino acids. **Amino acids are compounds with a $-\text{COOH}$ group at one end and a $-\text{NH}_2$ group at the other.** When proteins form from amino acids, different amino acids are strung together sequentially in the one chain. The properties of the protein depend as much upon the *sequence* of amino acids as upon the number of them in the chain. Proteins will be discussed in Chapter 14. 6-aminohexanoic acid is an amino acid, though not a

naturally occurring one, and therefore it is not involved in any proteins.

The condensation polymer made from ethylene glycol and terephthalic acid is known as **polyester** when used as a fibre (such as terylene) and as PET or poly(ethylene terephthalate) when used for drink bottles. This polymer plus nylon are the main synthetic condensation polymers in use today.



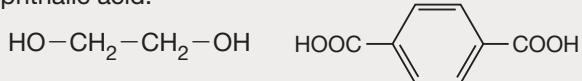
The condensation polymers nylon (left) and polyester (right) are widely used for carpets and textiles because they form as linear (unbranched) molecules that stick together via hydrogen bonding to form fibres

Exercises

- 24** What would be the average molar mass of cellulose that contained on average 300 glucose units per molecule? What would have been the mass of the glucose from which this cellulose had been formed?
- 25** The structure for cellulose can be written as $\text{H}-(\text{O}-\text{C}_6\text{H}_{10}\text{O}_4)_n-\text{OH}$. Write the structure of nylon-6 in the same way.
- 26 a** Poly(ethylene glycol) or Carbowax can be considered a condensation polymer formed from ethylene glycol, $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$. Draw a structure for a segment of this polymer. Include at least four monomer units.
b Carbowax can also be considered as an addition polymer of ethylene oxide. Explain how this can be so. (Carbowax is made by polymerising ethylene oxide, not from ethylene glycol.)
- 27** Glycine is the simplest amino acid: $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$. Draw a structure for the simplest possible protein, a condensation polymer formed from glycine.
- 28 a** What is the essential feature that a molecule must have in order for it to be involved in the formation of a condensation polymer?
b Would it be possible to make a condensation polymer from each of:
i 1-propanol, $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH}$
ii 1-chloropropanol, $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$
iii 1,3-dichloropropanol, $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Cl}$

either alone or with some other compound? Explain why or why not and if some other compound is needed, suggest a possibility.

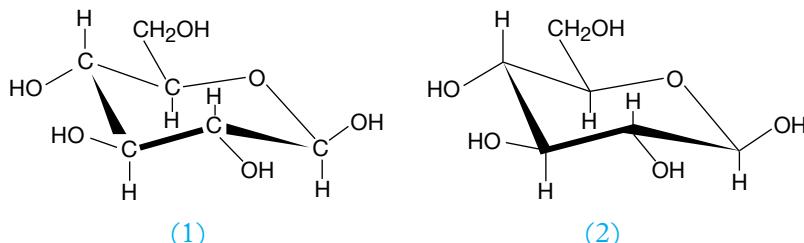
- 29** Poly(ethylene terephthalate), polyester or PET, is made from ethylene glycol and terephthalic acid:



Draw a segment of this polymer, including two of each of the monomer units.

1.13 STRUCTURE AND POSSIBLE CHEMICAL USES OF CELLULOSE

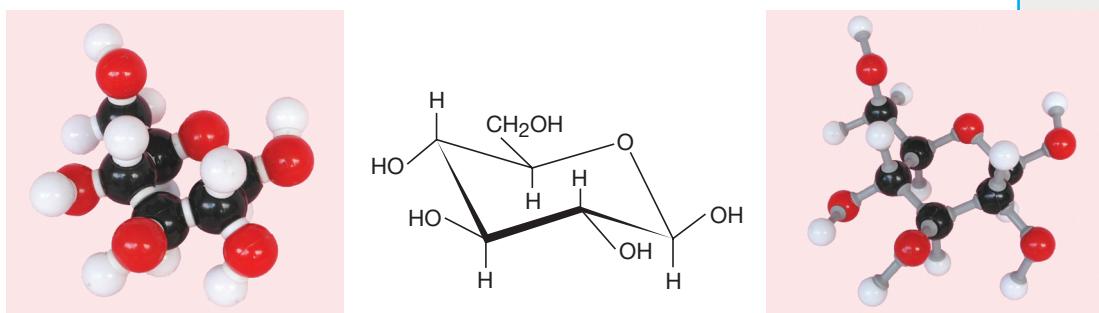
As already mentioned, cellulose is a polymer of which the monomer units are glucose which earlier we wrote as HO-(C₆H₁₀O₄)-OH. The structural formula for glucose is (1):



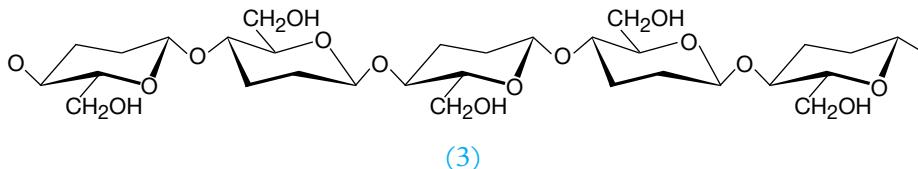
It has 5 carbon atoms and an oxygen atom forming a puckered ring; there are OH groups on 5 of the C atoms. The side of the ring (top or bottom) on which each OH group is positioned is important: interchange an OH and an H on the one C atom and you get a different compound (galactose or mannose, for example). Because structure (1) is quite cluttered, chemists commonly abbreviate it to (2) above, that is we leave out the ring C atoms: it is understood that there is a C atom at every apex of the structure.

Figure 1.7 shows space-filling and ball-and-stick models of β-glucose, the form that is used to make cellulose. An explanation of the β in β-glucose is given in Section 13.8†.

FIGURE 1.7
Space-filling and ball-and-stick models of β-glucose along with the structural formula oriented in approximately the same way



When glucose molecules combine to form cellulose, the OH on the right-hand C atom of one molecule (as drawn above) combines with the OH of the left-hand carbon atom of the next glucose molecule; this forms structure (3).



This is the structure of the product in Equation 1.2.

For clarity several of the H and OH groups have been omitted from each ring. The important points to note are:

- for bonding to occur alternate glucose units must be inverted (tipped ‘upside down’)

† part of the option, Forensic Chemistry: not required for the HSC core.

- this bonding produces a very linear molecule. The geometry of the rings and the C–O–C bond angles cause this linearity.

Cellulose is the major component of plant material or of *biomass*.

Biomass is material produced by living organisms; mainly it is plant material though the term also includes animal excreta and material made by algae.

Cellulose as a source of chemicals

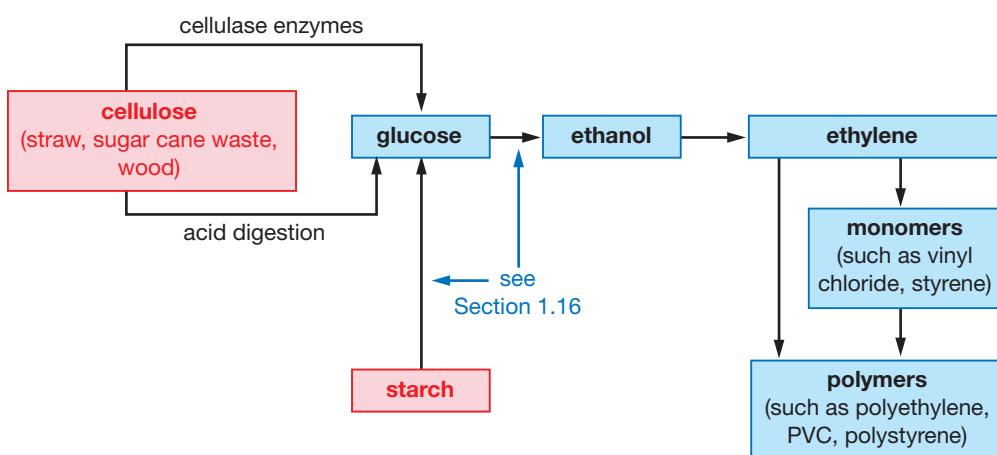
Cellulose is widely used as cotton, particularly for textiles, and as paper and cardboard. But can it be used as a source of chemicals?

As we shall see in Section 1.16, starch is a useful alternative source for some chemicals we currently make from petroleum, notably ethanol and ethylene. Starch is also a polymer of glucose, though there is a subtle difference between its structure and that of cellulose and this leads to quite different properties and chemical reactivity. The structures of starch and cellulose will be discussed in more detail in Section 13.9. Plants produce far more cellulose than starch, so there would be great benefits if we could use cellulose as a source of materials we currently make from oil.

Each glucose unit of cellulose has six carbon atoms joined together (Figure 1.7 and structure (3) above), so it could be regarded as a basic structure for making starting molecules for petrochemicals—molecules such as ethylene (2 C atoms), propylene (3 C atoms) and butene (4 C atoms, a starting point for synthetic rubber).

Figure 1.8 is a flow chart that shows how cellulose and starch could be converted into ethylene which could be used to make many of the polymers we currently make from ethylene derived from oil.

FIGURE 1.8
Possible production of polymers from non-oil sources such as cellulose and starch



Unfortunately it is much more difficult to break cellulose into glucose than it is to break up starch. This is because the long near-linear chains of cellulose hydrogen bond to one another to form very compact fibres, making it hard for chemicals to ‘get at’ the glucose–glucose links. However, there are two processes for breaking cellulose into glucose:

- 1 *digestion by cellulase enzymes*. These enzymes exist in bacteria (present in the first stomach of herbivores) and in certain fungi. The process can be performed industrially by first treating finely ground cellulose-containing materials (such as grain husks and stalks, bagasse and old newspapers) with

sodium hydroxide solution (or sometimes just hot water) to swell (open up) the cellulose fibres, then digesting them with cellulase enzymes to produce a solution of glucose.

- 2 *digestion with strong acid.* This involves heating a suspension of cellulose-containing materials (those mentioned above plus wood chips) with moderately concentrated aqueous sulfuric acid solution which breaks cellulose into glucose. Insoluble matter, particularly lignin from wood pulp, is filtered off, many impurities are removed, then the acid is neutralised to produce a solution of glucose.

In both cases the solution of glucose can be treated with yeast to form ethanol and if required this can be dehydrated to ethylene (Section 1.16).

While this conversion of cellulose to ethanol and then to ethylene does work, it has the major disadvantage that if much of the energy required for the process (keeping reaction mixtures hot and driving the process machinery) comes from oil, then more oil would be used making ethylene in this way than is used by cracking the oil directly to ethylene (Section 1.1). Making ethanol from cellulose is considerably more expensive than making it from starch or sugars, despite the lower cost of the starting cellulose-containing material. Nevertheless considerable scientific effort is currently being directed into developing more efficient ways of using cellulose as an alternative source of chemicals we now obtain from oil.

1.14 BIOPOLYMERS

Biopolymers are polymers that are made totally or in large part by living organisms.

Originally the word meant biologically-synthesised polymers such as cellulose, starch, proteins and nucleic acids. However the word now includes polymers that are chemically-modified versions of natural polymers and polymers that can be produced by ‘manipulating’ biological organisms.

Partially synthetic biopolymers based on cellulose have been used commercially for nearly a century.

Some biopolymers that have been made from cellulose (itself a biopolymer) are:

- *rayon*, also called *viscose rayon* or just *viscose*. This is a reconstituted cellulose; cellulose that is unsuitable for spinning into thread for fabric weaving, such as wood pulp, waste paper and sometimes straw, is treated chemically and mechanically to produce fibres that can be used to make fabric. Rayon generally has a silky look and feel.
- *cellophane*. This is a form of rayon that is produced as a thin transparent film which is widely used for packaging.
- *cellulose nitrate*. This is a synthetically modified cellulose that was widely used for photographic and movie film early last century: it was also used as an explosive (gun cotton) and as a plastic called *celluloid*. Unfortunately it was highly flammable and was soon replaced by other plastics.
- *cellulose acetate*. This is much less flammable than cellulose nitrate and is still widely used, for example for overhead projector slides.

In cellulose nitrate and acetate the three OH groups on each glucose unit of the cellulose molecule (can you identify them in (1) and (2) in Section 1.13?) are replaced by --ONO_2 (nitrate group) and --O--CO--CH_3 (acetate group) respectively.

- *carboxymethyl cellulose, CMC*. This is another cellulose-based biopolymer; in it the $-\text{CH}_2\text{OH}$ side chain on each glucose unit has been replaced by $-\text{CH}_2-\text{COOH}$. CMC is used as a thickener in many foods, because the supply of natural alginate thickeners obtained from seaweed cannot keep up with increasing demand.

Cellulose has been fairly widely used as a raw material for making products that people need or want. However, to date it has not been practical to use cellulose to synthesise polymers or other substances that we currently make from petroleum.

Moves from natural to synthetic polymers

The commercial use of biopolymers such as cotton (cellulose), wool and silk (protein) has been declining as the petroleum-based polymers such as polyester (or PET) and polyamide (nylon) have been taking over. Similarly natural rubber has been quite dramatically supplemented by a synthetic, SBR, styrene-butadiene rubber which is a co-polymer (two monomers) of styrene and butadiene. Again the starting materials come from crude oil.

A problem

There is a major problem with petroleum-based polymers: they are not **biodegradable**. This means that when they are discarded into the environment or put into rubbish dumps, they are not decomposed naturally by the action of living organisms such as bacteria or fungi. Carelessly discarded synthetic plastics are causing harm and often death to marine and bird life and remain eyesores in landscapes almost indefinitely.

One approach to building biodegradability into synthetic polymers has been to alternate biopolymer sections with synthetic sections in the same polymer molecule: biological decay of the biopolymer sections leads to disintegration of the whole polymer. Another very recent approach has been to develop biopolymers that have similar properties to the synthetic polymers but which still retain biodegradability.

1.15 A SYNTHETIC BIODEGRADABLE POLYMER

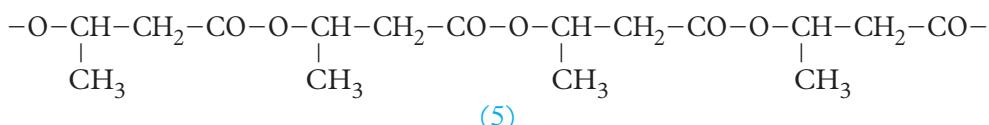
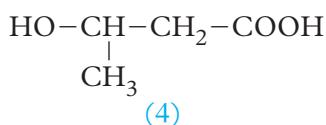
There is a range of microorganisms (for example from the *Alcaligenes*, *Clostridium*, *Rhizobium* and *Streptomyces* genera (groups)) that under suitable conditions can make polymers that have similar properties to polypropylene with the important exception that they are biodegradable (polypropylene is not). The biopolymer formed is a poly(3-hydroxyalkanoate) or PHA. Some explanations about naming are shown in Table 1.4.

The simplest PHA is PHB, poly(3-hydroxybutanoate): the 3 means that the hydroxy group is on the third carbon counting from the carboxylic acid group. The monomer, 3-hydroxybutanoic acid, sometimes called β -hydroxybutanoic acid, has structure (4) and the polymer structure (5).

TABLE 1.4 Some general classes of carbon compounds

Class of compound	General formula ^a	Example
alkane	R—H	CH ₃ —CH ₂ —CH ₃ propane
alkanol (alcohol)	R—OH	CH ₃ —CH ₂ —OH ethanol
alkanoic acid (carboxylic acid)	R—COOH or R—C=O O—H	CH ₃ —COOH acetic acid
alkanoate (ester) (acid combined with alcohol)	R—COO—R' or R—C=O O—R'	CH ₃ —COO—CH ₂ —CH ₃ ethyl ethanoate

^a R is any alkyl group (Table 1.1); R' is another alkyl group (same as or different from R).



The polymer is a polyester (same chemical linkage as in PET, Section 1.12). Although PHB has quite a different chemical structure from polypropylene, its physical and mechanical properties are very similar.

To produce PHB a culture of a microorganism such as *Alcaligenes eutrophus* is placed in a suitable medium and fed appropriate nutrients so that it multiplies rapidly and grows into a large quantity. Then the ‘diet’ is changed to restrict the supply of one particular nutrient (such as nitrogen): under these conditions the organism is no longer able to increase its population but instead begins to make the desired polymer which it stores for later use as an energy source. The amount of PHB that the organism can produce is from 30 to 80% of its own dry weight. The organism is then harvested and the polymer separated out.

PHB is much more expensive to make than oil-based polymers with similar properties. However, there is a slowly growing demand for it where biodegradability is a prime consideration. Such applications include disposable nappies and packaging in the form of bottles, bags and wrapping film, particularly packaging for medical and hospital supplies.

WEBSITES

For further information about the conversion of cellulose to ethanol and about PHB:

<http://www.kcpc.usyd.edu.au/discovery/Syllabus.html>

(click on *Condensation polymers scenic route*, then *Converting cellulose to ethene*; alternatively click on *Biosynthesis of polymers* for information on PHB)

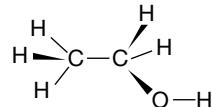
<http://www.personal.psu.edu/users/e/r/erd127/index.htm>

(at the bottom of the page click on any of the named processes for making ethanol from wood (cellulose)).



1.16 ETHANOL AS A SOURCE OF ETHYLENE

As explained in Section 1.11, there are good reasons for wanting an alternative source of ethylene for the plastics industry. Ethanol is such a source; it has the structure:



We saw in Section 1.5 that ethanol is an alkanol, meaning that it is an alkane with one H atom replaced by an OH (or alcohol) functional group. The geometrical arrangement of the bonds in the molecule is tetrahedral around each carbon atom and bent around the oxygen atom. This geometry is better shown in the ball-and-stick and space-filling models of ethanol in Figure 1.9. However for printing convenience we generally draw it with bonds at right angles:

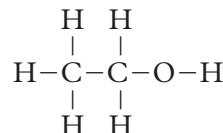
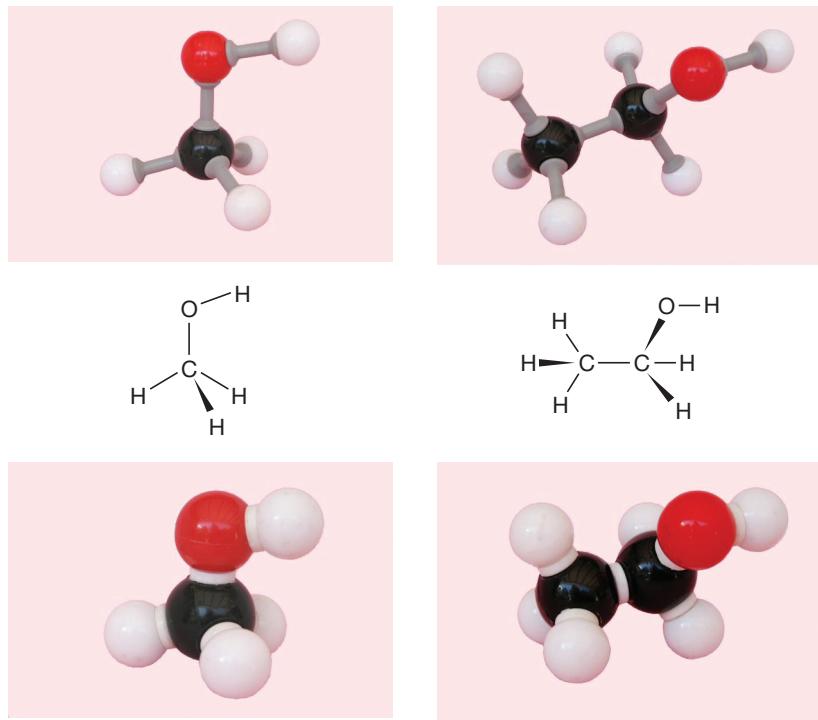


FIGURE 1.9
Ball-and-stick and space-filling models of methanol (left) and ethanol (right)



Ethylene is made from ethanol by dehydration.

Dehydration is a chemical reaction in which water is removed from a compound.

Ethanol is dehydrated by heating it with concentrated sulfuric or phosphoric acid which acts as a catalyst:



The reverse reaction, the addition of water to ethylene, is called *hydration*. It was introduced in Section 1.5. Hydration also needs heat and a catalyst which is generally dilute aqueous sulfuric acid:



These two reactions, *dehydration* and *hydration*, are quite general reactions: they apply to *any* alkanol or alkene respectively. For example 1-pentanol can be dehydrated to 1-pentene and 3-hexene can be hydrated to 3-hexanol. (Naming of alkanols was explained in Section 1.5.)

1.17 ETHANOL AS A SOLVENT

As mentioned in Section 1.5 ethanol is widely used as a solvent. In the home it is a common solvent in:

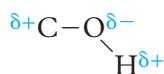
- cosmetics (perfumes, deodorants, after-shaves)
- food colourings and flavourings (cochineal, vanilla essence)
- medicinal preparations (antiseptics)
- some cleaning agents.

It is also widely used as a solvent in industry.



Ethanol is the solvent in many consumer products such as perfumes

Ethanol is a good solvent for both polar and non-polar substances. It dissolves polar substances such as chloroform, CHCl_3 , and common ether, $\text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$, because its OH end is very polar; the C–O and O–H bonds are polar, because O is much more electronegative than C or H (p. 189 CCPC). The partial charges on the ethanol molecule are:



Ethanol is therefore a good solvent for polar substances (p. 199 CCPC). In addition ethanol can form hydrogen bonds with many other substances (pp. 190–2 CCPC) and this increases its ability to dissolve such substances—for example glucose and sucrose, carboxylic acids, amino acids and some proteins. Because of hydrogen bonding ethanol is miscible with water in all proportions (from 100% water through to 100% ethanol).

Because of its alkyl part, the CH_3-CH_2- , which is non-polar, ethanol often dissolves non-polar substances also. Dispersion forces form between this hydrocarbon tail and the non-polar solute. Non-polar iodine readily dissolves in ethanol as do short-chain hydrocarbons such as pentane and heptene.

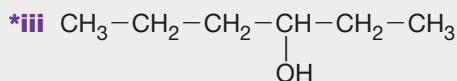
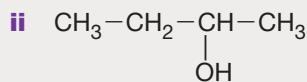
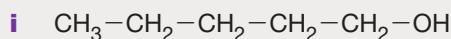


Exercises

30 a Draw structures of the following alkanols:

i 2-butanol **ii** 3-pentanol ***iii** 1-hexanol

b Name the following compounds:



31 Explain why ethanol has a much higher boiling point than propane (78°C compared with -42°C) despite having similar molecular weights (46 and 44 respectively).

***32** Offer an explanation for the fact that iodine is more soluble in ethanol than it is in water.

33 Urea, $\text{H}_2\text{N---CO---NH}_2$, has a much higher solubility in ethanol than heptane does. Offer an explanation: a diagram may help.

34 The dehydration of ethanol and the hydration of ethylene discussed above are general reactions for all alkanols and alkenes respectively. Hence write equations (using structural formulae) for:

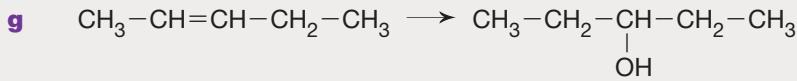
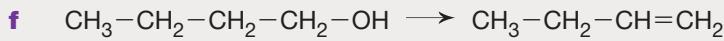
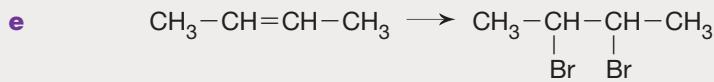
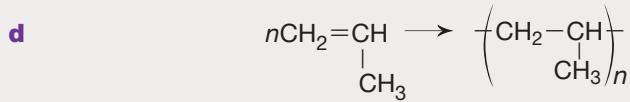
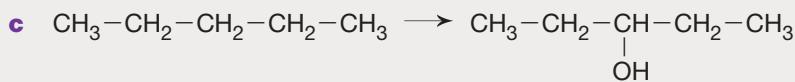
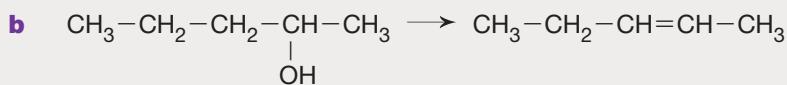
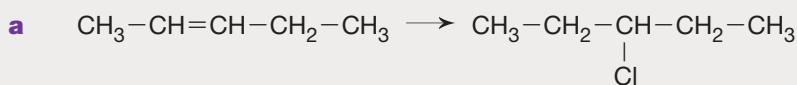
a the dehydration of 1-propanol and 2-propanol

b the hydration of 2-butene

***c** the dehydration of 3-heptanol

***d** the hydration of 3-hexene

35 What type of reaction (substitution, dehydration, addition, hydration, polymerisation) is each of the following?



1.18 SYNTHESIS OF ETHANOL FROM PLANT MATERIAL

Until about sixty years ago the major source of ethanol was fermentation of starches and sugars from plant material. With the dramatic increase in use of motor cars after World War II and the rapidly growing demand for high quality petrol for them, the amount of crude oil being refined increased greatly. In addition, processes were developed to increase the yield of petrol from refining (catalytic cracking, Section 1.1). The result was that large supplies of quite cheap ethylene became available as a by-product. In addition this ethylene was available close to the places of greatest demand for ethanol, the industrial cities. Hence it became more economic to produce ethanol from ethylene. Today fermentation provides only a small proportion of industrial alcohol, though it still provides all the beverage alcohol.

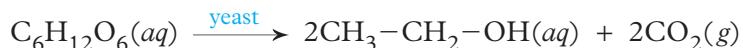
If it becomes necessary to produce ethylene for plastics from ethanol, then fermentation will again become a very important industrial process.

Fermentation is a process in which glucose is broken down to ethanol and carbon dioxide by the action of enzymes present in yeast.

For fermentation:

- suitable grain or fruit is mashed up with water
- yeast is added
- air is excluded, and
- the mixture is kept at about blood temperature, 37°C.

Enzymes (biological catalysts) in the mixture first convert any starch or sucrose in the mixture into glucose and/or fructose, then other enzymes convert glucose or fructose into ethanol and carbon dioxide:



Bubbles of carbon dioxide are slowly given off: hence the name, *fermentation*.

Yeast can produce ethanol contents up to about 15%. Alcohol concentrations above this level kill the yeast and stop further fermentation. To produce higher alcohol contents it is necessary to distil the liquid.

If the aqueous mixture from a fermentation process is subjected to fractional distillation (p. 15 CCPC), 95% ethanol can be obtained. This is common industrial or laboratory alcohol. To obtain 100% ethanol more elaborate distillation procedures are needed.

Fermentation and distillation have been used to produce ethanol for centuries. Ethanol was one of the earliest organic compounds to be synthesised and obtained in nearly pure form.

‘*Suitable grain or fruit*’ for fermentation is plant material that has a high content of starch or simple sugars (sucrose, glucose, fructose). Starchy grains (such as wheat, maize or corn, barley), tubers (such as potatoes, cassava or tapioca), and fruits (such as grapes, apples) with high simple-sugar contents are commonly fermented to ethanol.

Molasses, the leftover syrup from sugar milling, is also widely used. Sucrose has a very high solubility in water; this means that

Part of CSR's
fermentation and
distillation plant at Sarina
in North Queensland
where molasses left over
from extracting sugar
from cane is fermented
into ethanol

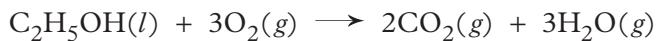


the mother liquor left over after sucrose has been crystallised out still has a high sucrose content, so ethanol can be obtained from an otherwise useless waste product of sugar production. Much of the molasses from the North Queensland sugar industry is used to make ethanol.

The economics of ethanol production change dramatically if sugar cane is grown specifically for conversion to ethanol rather than producing ethanol from a waste product (as Brazil discovered—next section).

1.19 ETHANOL AS A FUEL

Ethanol is a liquid which readily burns:



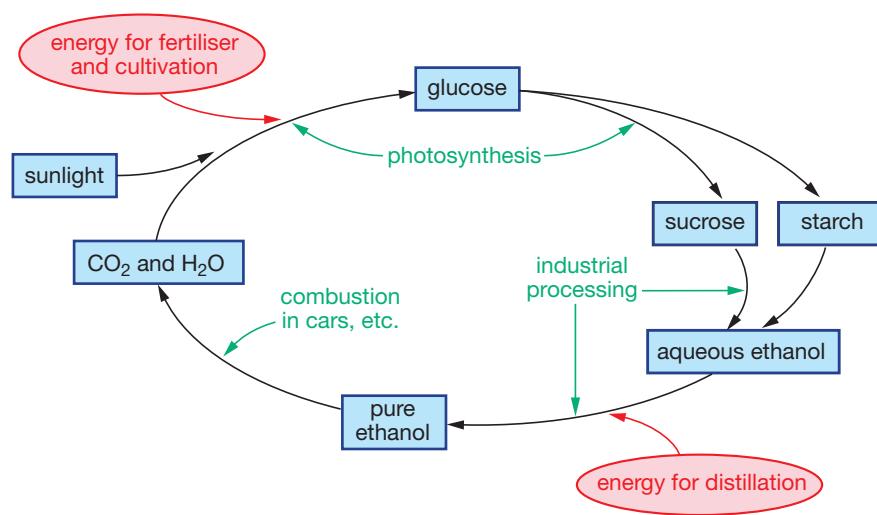
It is also an easily transportable liquid, often used by hikers and campers. Consequently it has often been proposed as a possible alternative liquid fuel for automobiles. It has been used as a ‘petrol extender’ in the past (particularly during World War II) and in a few places in more recent times. One advantage is that petrol containing about 10 to 20% ethanol can be used in ordinary petrol engines without any engine modification. To use 100% ethanol engines need to be modified.

Brazil in the 1970s and '80s adopted ethanol as its major fuel for cars. It grew sugar cane specifically for conversion to ethanol. The purpose was twofold: to reduce consumption of non-renewable crude oil and to address a trade imbalance problem (by replacing expensive oil imports with locally produced fuel). The experiment proved extremely expensive and was virtually abandoned in the 1990s though there are now (2005) moves to re-establish it.

Ethanol as a renewable resource

Ethanol has been promoted as a fuel for motor cars to supplement or replace petrol on the grounds that it is a renewable resource. Basically it is made from carbon dioxide, water and sunlight (via glucose), and when it is burnt it returns to carbon dioxide and water which can be re-converted to ethanol. The cycle is shown in blue in Figure 1.10.

FIGURE 1.10
The ethanol cycle: the blue cycle is ‘greenhouse neutral’; the red inputs mean that using ethanol as a fuel still contributes significantly to greenhouse emissions



Many people in Australia advocate the addition of ethanol to our petrol to reduce our consumption of crude oil, particularly as local reserves of oil are likely to run out within two or three decades. If we want to make oil supplies last longer or save them for petrochemicals, so the argument goes, then we need to find an alternative, preferably renewable, liquid fuel for our cars.

Ethanol has also been advocated as a fuel on the grounds that it is neutral with respect to the greenhouse effect: the carbon dioxide that it liberates when it burns is just that which was used in its synthesis. However this ignores the other energy inputs in the ethanol cycle. The blue cycle in Figure 1.10 is ‘greenhouse neutral’. However the other energy inputs, shown in red in that diagram, are quite significant—the manufacture of most fertilisers has a large fossil fuel input, and the distillation process (to get 95% ethanol from the 15% fermentation product) requires much energy.

Currently ethanol has potential as a liquid fuel, particularly for transport (cars, trains, planes) when oil runs out provided coal is available for making fertilisers and supplying the energy for distillation, though as technology currently stands this would not be much better than oil from a greenhouse gas viewpoint.

The advantages of using ethanol as a fuel are:

- It is a renewable resource and so would reduce the use of non-renewable fossil fuel (provided less fossil fuel was used to make the ethanol than was ‘saved’ by using the ethanol in cars).
- It could reduce greenhouse gas emissions (if the amount of CO₂ not released from oil because of the use of ethanol in cars was greater than the CO₂ released from the fossil fuels used to make the ethanol).

The disadvantages are:

- Large areas of agricultural land would need to be devoted to growing suitable crops with consequent environmental problems such as soil erosion, deforestation, fertiliser runoff and salinity.
- Disposal of the large amounts of smelly waste fermentation liquors after removal of ethanol would also present major environmental problems.

The current situation in Australia

- 1 Ethanol costs more than petrol to produce so the federal government has set up subsidies and excise concessions to encourage the production of ethanol (from crops) to be added to petrol (presumably to reduce oil consumption).
- 2 Car manufacturers accept that up to 10% ethanol in petrol has no detrimental effect on vehicles but have opposed higher concentrations.
- 3 Significant quantities of petrol with 10% ethanol in it are available in some parts of Australia, but there is considerable public suspicion of this blended fuel, largely because of incidents involving some petrol suppliers who put excessive amounts of ethanol in their petrol (to gain from the government subsidies), and because of car manufacturers who have widely claimed that amounts above 10% could damage car engines and may void warranties.
- 4 There are no reliable studies to show whether ethanol as made in Australia from wheat or molasses produces less greenhouse gas in total than does the petrol it replaces.

1.20 HEAT OF COMBUSTION OF ETHANOL

You will recall from p. 280 CCPC that:

The **molar heat of combustion**[†] of a substance is the heat liberated when one mole of the substance undergoes complete combustion with oxygen at standard atmospheric pressure with the final products being carbon dioxide gas and liquid water.

As thus defined *the molar heat of combustion is minus the enthalpy change for the combustion process* (because enthalpy change, ΔH , is always energy absorbed).

In practice, when we burn a fuel the water generally forms as a gas. However the values we tabulate are the ones we would get if the water formed as a liquid. Table 10.1 (p. 281 CCPC) gave molar heats of combustion for some common substances. In particular for ethanol the molar heat of combustion is 1360 kJ mol⁻¹. This means that for:



Example 1 illustrates how heats of combustion can be measured in a school laboratory.

[†] Sometimes this is just called heat of combustion. It is preferable to include the ‘molar’.

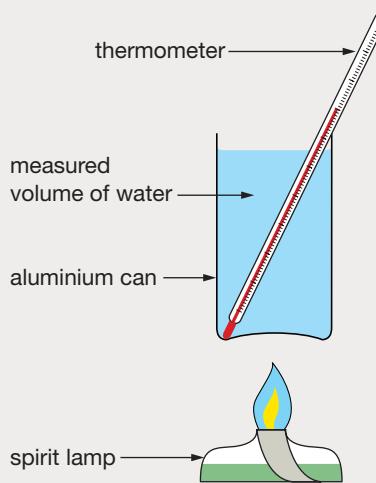


Example 1

The apparatus in Figure 1.11 was used to measure the heat released when ethanol burns in air. Initially the small spirit burner, partly filled with ethanol, had a mass of 155.66 g. The aluminium drink container with its top cut out contained 250 g water at 19.5°C and was suspended above the burner with a clamp in a retort stand. The spirit lamp was lit and used to heat the water in the can (being carefully stirred with a thermometer). When the temperature had risen about 15°C, the flame was extinguished. The maximum temperature that the water reached was 37.3°C. The mass of the spirit burner and its contents at the end of the experiment was 154.75 g. Calculate the heat released per gram of ethanol used, and hence the molar heat of combustion of ethanol. The specific heat capacity of water is 4.18 J K⁻¹ g⁻¹.

FIGURE 1.11

Apparatus for measuring the heat of reaction for combustion of a liquid



The heat absorbed by a substance when its temperature is increased is given by Equation 8.11 on p. 223 of CCPC, namely:

$$q = m C \Delta T$$

So in this example:

$$\begin{aligned}\text{heat absorbed by the water} &= 250 \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} \times (37.3 - 19.5) \text{ K} \\ &= 1.87 \times 10^4 \text{ J} (= 18.7 \text{ kJ})\end{aligned}\quad \dots (1.3)^{\dagger}$$

Let us neglect the heat capacity of the aluminium container and assume that there were no heat losses to the surroundings. On that basis the heat released by the reacting ethanol must be equal to the heat absorbed by the water. That is:

$$\text{heat released by ethanol reacting} = 18.7 \text{ kJ}$$

This is the heat released from burning $(155.66 - 154.75) = 0.91 \text{ g}$ ethanol.

$$\begin{aligned}\text{So heat released per gram of ethanol} &= \frac{18.7}{0.91} \\ &= 20.5 \text{ kJ/g} \\ &= \mathbf{21 \text{ kJ/g}}\end{aligned}$$

(to two significant figures which is all the accuracy of the experiment justifies)

$$\begin{aligned}\text{The molar mass of ethanol, C}_2\text{H}_5\text{OH} &= 2 \times 12.01 + 6 \times 1.01 + 16.0 \\ &= 46.0 \text{ g/mol}\end{aligned}$$

$$\begin{aligned}\text{Therefore heat released per mole} &= 20.5 \times 46.0 \\ &= 943 \text{ kJ/mol}\end{aligned}$$

That is, molar heat of combustion of ethanol = **$9.4 \times 10^2 \text{ kJ/mol}$**

While heat of combustion per mole is useful and convenient for chemists, for ordinary citizens who have to buy fuel by the litre or kilogram, heat per litre or per gram is much more useful. Exercises 40 and 41 will highlight this aspect.

WEBSITES

<http://www.kcpc.usyd.edu.au/discovery/Syllabus.html>

(click on *Ethanol from plants* for information about the process)

For discussions about using ethanol as a fuel for cars and its greenhouse consequences:

<http://www.canegrowers.com.au/>

(click on *Sugarcane Products* then on *Ethanol*)

<http://www.worldofmolecules.com/fuels/ethanol.htm>

(a more balanced presentation of the energy and greenhouse cases)



1.21 OVERVIEW

In this chapter we have seen how crude oil and/or by-products from processing it can be used to make the fibres and plastics that are in widespread use today. We have also seen that oil supplies are likely to run out within a few decades. Ethanol from plant material such as starch and sucrose is a possible alternative source of liquid fuel and of ethylene, the starting substance for many polymers, but there are problems. Cellulose, a much larger fraction of plant material, has not to

† This equation uses the usual value for the specific heat capacity of water, namely $4.18 \text{ J K}^{-1} \text{ g}^{-1}$. The NSW HSC examination data sheet in recent years has given it as $4.18 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$. Use of this value in Equation 1.3 would give: $0.250 \text{ kg} \times 4.18 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1} (37.3 - 19.5) \text{ K}$ which of course still gives $1.87 \times 10^4 \text{ J}$.

date proved a practical alternative source of petrochemicals though progress is being made.

A major problem with the petroleum-based polymers is their lack of biodegradability. Progress has been made in the development of biodegradable substitutes in the form of biopolymers.

Exercises

- 36** If 1.00 kg of a 10% solution of glucose in water in apparatus weighing 350 g was completely fermented, and any gas formed allowed to escape, by what amount would the mass of the apparatus and its contents decrease? What percentage decrease does this correspond to?
- 37** The heat of combustion of ethanol is 1360 kJ/mol. What mass of ethanol needs to be burnt to raise the temperature of 350 g water through 77°C if 50% of the heat released by the ethanol is lost to the surroundings? The specific heat capacity of water is 4.2 J K⁻¹ g⁻¹.
- 38** The heat of combustion of each of three different alkanols was measured as follows. Some alkanol was placed in a small spirit burner and the mass determined. The burner was placed under an aluminium container (of mass 21.7 g) filled with 750 g water. The set up was as in Figure 1.11. The temperature of the water was measured then the burner was lit. The water was gently stirred with the thermometer until the temperature had risen by about 20°C. The burner was extinguished and the maximum temperature reached by the water noted. Results from the three alkanols are tabulated below.

Alkanol	Initial mass ^a (g)	Final mass ^a (g)	Initial temperature (°C)	Final temperature (°C)
methanol	124.3	120.6	20.4	41.3
1-propanol	127.8	125.2	19.7	39.4
2-pentanol	122.6	120.2	21.3	41.5

a mass of the burner plus alkanol

- a** Write equations for the combustion of the three alkanols.
- b** Calculate the heat of combustion per gram of alkanol and per mole. The specific heat capacity of water is 4.2 J K⁻¹ g⁻¹. Ignore the heat capacity of the aluminium container and any heat losses to the surroundings.
- 39 a** The mass of the aluminium container used in Exercise 38 was 21.7 g. The specific heat capacity of aluminium is 0.89 J K⁻¹ g⁻¹. Show that ignoring the heat capacity of the container in your calculations for Exercise 38 introduced negligible errors.
- b** The values you calculated for the molar heat of combustion of the alkanols in Exercise 38 are much less than those tabulated in books of data. Suggest some reasons why the results of these experiments are low.
- 40** Some heats of combustion are: hydrogen, 285 kJ/mol; propane, 2220 kJ/mol; octane, 5460 kJ/mol; ethanol, 1360 kJ/mol. Calculate the heat released per gram for each of these fuels. For a typical coal the value is 35 kJ/g. Arrange these fuels including coal in decreasing order of heat released per gram of fuel. Why is this a better measure of 'heat efficiency' of fuels than molar heats of combustion?
- 41** The result you obtained in Exercise 40 for the heat per gram for octane is typical of all liquid hydrocarbons. On a mass for mass basis, then, how does ethanol compare as a fuel with the liquid hydrocarbons?

Important new terms

You should know the meaning of the following terms:

addition polymer (p. 13)
addition reaction (p. 8)
alcohol (p. 12)
alkanol (p. 12)
alkyl group (p. 9)
amide link (p. 23)
amine group (p. 23)
amino acid (p. 23)
average molecular weight (p. 15)
biodegradable (p. 28)
biomass (p. 26)
biopolymer (p. 27)
carboxylic acid group (p. 23)
cat cracker (p. 6)
catalytic cracking (p. 6)
chain branching (p. 13)

chain stiffening (p. 18)
condensation polymer (p. 22)
cracking (p. 5)
cross-linking (p. 19)
dehydration (p. 30)
fermentation (p. 33)
hydration reaction (p. 11)
molar heat of combustion (p. 36)
monomer (p. 13)
peptide link (p. 23)
polyamide (p. 23)
polyester (p. 24)
polymer (p. 13)
polymerisation (p. 13)
steam (or thermal) cracking (p. 6)
substitution reaction (p. 7)
zeolites (p. 6)
Ziegler–Natta process (or catalyst) (p. 14)

Test yourself

- 1 Explain the meaning of each of the items in the ‘Important new terms’ section above.
- 2 Why do oil refineries carry out catalytic cracking? Name the catalyst used and write an equation for a specific example.
- 3 Name two important by-products from catalytic cracking and state their major use.
- 4 What is the difference between catalytic and thermal cracking? How do the experimental conditions differ for the two processes? What is the major purpose of each process?
- 5 Compare the boiling points and solubilities of alkanes and alkenes. Explain why they are so similar or so different. Which members of each class are gases at room temperature?
- 6 What are the two major reactions of alkanes? Write equations for a specific example of each.
- 7 List five addition reactions of alkenes. Write an equation for a specific example of each, using either propene or a butene as the alkene.
- 8 Name and give formulae for the first six alkyl groups.
- 9 Describe a test for distinguishing between alkanes and alkenes.
- 10 How is ethanol made industrially? Include an equation.
- 11 Why does industry need to convert ethylene to vinyl chloride?
- 12 Write an equation for the polymerisation of ethylene. Name the product.
- 13 Name two other addition polymers and draw structures for them.
- 14 What are the systematic names for vinyl chloride and styrene?

- 15** Draw a structure for styrene and give its molecular formula.
- 16** What structural feature is responsible for the difference between low density and high density polyethylene?
- 17** Use the polymers from Questions 12 and 13 to illustrate what is meant by chain stiffening and describe the effect it has on properties.
- 18** Describe the structure of cellulose and give a molecular formula for it.
- 19** What are the major uses of cellulose?
- 20** Name one condensation polymer (not cellulose) and explain how it is formed.
- 21** Describe some biopolymers that are made from cellulose and give some of their uses.
- 22** What is the biopolymer PHB, how is it made, and why is there interest in its commercial development?
- 23** Explain how we could obtain ethylene from ethanol if oil supplies were to run out.
- 24** What types of compounds dissolve in ethanol? Give some specific examples.
- 25** Describe how ethanol is obtained from plant material. What type of plant material is used?
- 26** How would you measure the molar heat of combustion of a liquid such as 1-propanol?
- 27** On a heat per gram basis, how does ethanol compare as a fuel with liquid hydrocarbons?
- 28** Discuss the advantages and disadvantages of using ethanol as a fuel for motor cars.

Electrochemistry

IN THIS CHAPTER

Displacement reactions

Displacement reactions and the activity series

Valence and oxidation states

Electricity from redox reactions

Some technical terms for cells

Purpose of the salt bridge

Anode and cathode

Some commercial galvanic cells

Rechargeable batteries (cells)

Fuel cells

Gratzel cell

Standard electrode potentials

Calculating EMFs for reactions and cells

Many of the appliances and devices we use in our everyday life need easily portable sources of electricity—batteries, as we call them. Examples range from simple torches, clocks and watches, portable radios and mechanical toys for children to calculators, cameras, cordless drills and shavers and motor car batteries, and more recently to mobile telephones, portable CD players, video cameras and laptop computers. For all of these devices we use batteries. Although there are many different types of battery in use, they all have one feature in common: electricity is generated by chemical reactions.

In this chapter we shall look at how chemical reactions can be made to generate electricity and we shall examine some common batteries in general use.

This area of science that is concerned with the relations between chemistry and electricity is called **electrochemistry**.

We shall begin our study of electrochemistry by looking at the simplest type of chemical reaction that can be used to generate electricity, namely *displacement reactions*.

2.1 DISPLACEMENT REACTIONS

A **displacement reaction** is a reaction in which a metal converts the ion of another metal to the neutral atom.

Examples will illustrate.

- When a reddish-brown copper wire is dipped into a colourless solution of silver nitrate, a black deposit of metallic silver forms on the copper (black because the silver is very finely divided). If we let the reaction proceed for

a sufficiently long time, the solution takes on a bluish colour due to copper ions. This is shown in Figure 2.1(b). The reaction is:

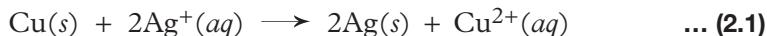
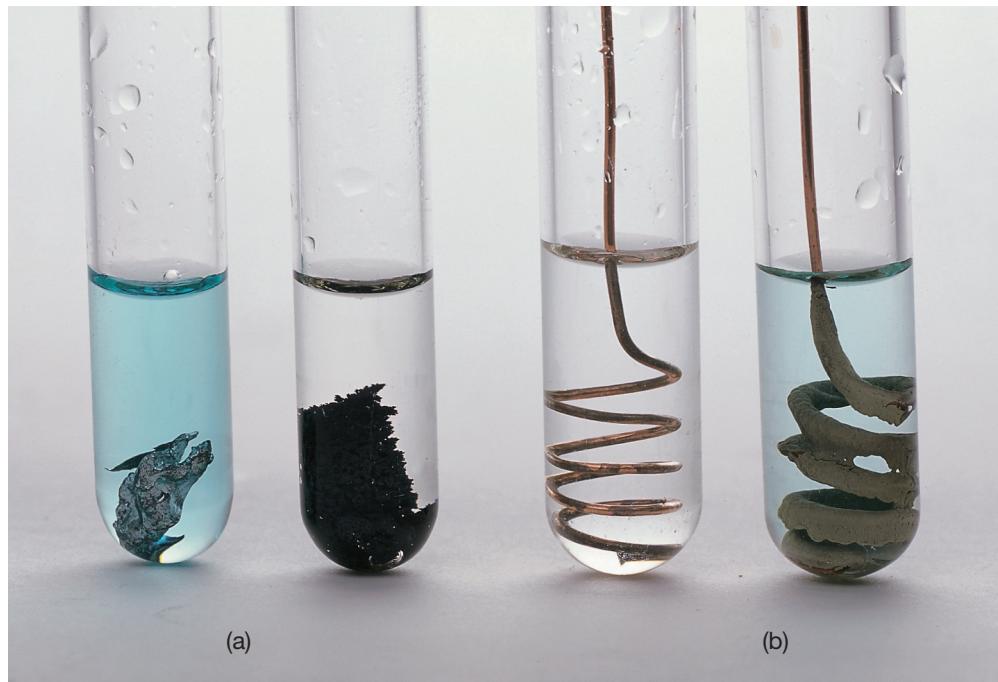


FIGURE 2.1
Two displacement reactions: (a) a granule of zinc dropped into a copper sulfate solution; (b) copper wire dipped into a silver nitrate solution. For each case the left-hand test tube shows the metal just after being dropped into the solution: in the right-hand test tube the metal has been in the solution for ten to twenty minutes



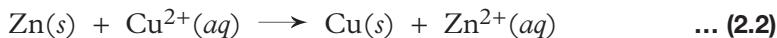
Copper loses two electrons to form Cu^{2+} and hence is *oxidised*. Silver ions gain electrons to form Ag and so are *reduced*.

Recall from p. 117 CCPC the definitions:

Oxidation is loss of electrons.

Reduction is gain of electrons.

- 2 Similarly, when a silvery granule of zinc is dropped into a blue solution of copper sulfate, the zinc gets covered with reddish-brown copper and the blue colour of the solution is discharged (Fig. 2.1(a)) The reaction is:



Zinc metal has been oxidised and copper ions have been reduced.

We can show the oxidation and reduction processes more clearly by writing half reactions (p. 118 CCPC). For Reaction 2.1:



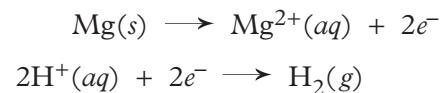
And for Reaction 2.2:



The reaction of metals with dilute acids—that is, with hydrogen ions, (pp. 116–17 CCPC)—can be considered as a special type of displacement reaction. The metal displaces hydrogen gas from a solution of hydrogen ions. For example:



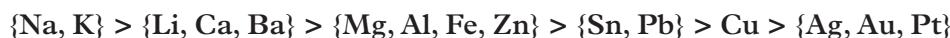
Again we can break this into oxidation and reduction half reactions:



Oxidation–reduction reactions are also called **redox reactions** and **electron transfer reactions**.

2.2 DISPLACEMENT REACTIONS AND THE ACTIVITY SERIES

When we were establishing the activity series for metals on p. 119 *CCPC*, we used reactions with oxygen, water and dilute acids to obtain:



where species within curly brackets had equal activities (based on the limited criteria used there).

This activity series lists metals, from left to right, in order of increasing difficulty of losing electrons—that is, in order of increasing difficulty of oxidation: *a metal on the left loses electrons more easily than a metal to the right of it.* From the series, lithium and calcium lose electrons more easily (are more easily oxidised) than magnesium and iron; zinc is more easily oxidised than copper or silver.

Displacement reactions also show which of two metals is the more easily oxidised—the one that goes into solution. Reaction 2.1 shows that copper is more easily oxidised than silver (because copper goes into solution), so copper is more active than silver. Similarly Reaction 2.2 shows that zinc is more active than copper. In general, of two metals:

The more reactive metal is the one which will displace the other metal from a solution of its ions.

From Reactions 2.1 and 2.2, copper should be to the left of silver in the activity series and zinc should be to the left of copper, which is consistent with what we already have.

Consequently we can use other displacement reactions to sort out some of the ‘equalities’ in the above interim activity series. By observing experimentally which metal will displace which we can show that in terms of activity:



However displacement reactions do not allow separation of the other two equalities, because of interference of the reaction with water. The measurements on galvanic cells referred to on p. 119 of *CCPC* (and to be discussed in Section 2.14) are needed to arrive at the final activity series (Sequence 4.9 in *CCPC* now to be called 2.3):



† based on measurements from galvanic cells, the sequence for the first five metals would be Li, K, Ba, Ca, Na. The sequence presented here gives greater priority to the vigorousness of the reaction with water: as we saw on pp. 115–16 *CCPC*, K and Na react more vigorously than Li, Ba, and Ca.

Hydrogen has been included in Sequence 2.3 on the basis of reactions of metals with dilute acid. Hydrogen has been placed just to the right of all metals that will react with dilute acid to form hydrogen gas (and so just to the left of those that do not so react).

Once it has been established, we can use this activity series to decide which metal (of a given pair) displaces which from solution:

The metal further to the left in sequence 2.3 will displace the other metal from a solution of its ions.

In other words, the metal further to the left loses electrons more easily or is more easily oxidised. Similarly we can use the series to decide whether or not a metal will react with dilute acid to form hydrogen gas: those to the left of H will do so, those to the right will not.

Oxidation and reduction or electron transfer has some implications for valencies and the way we name certain species.

2.3 VALENCE AND OXIDATION STATES

When we were discussing the naming of simple ionic compounds on pp. 76–8 *CCPC*, we talked about the *valence* of various metal ions and of the need with some of these ions to state the valence (in capital Roman numerals) in the name: tin(II) oxide, iron(III) chloride, copper(I) sulfide and the like. What we referred to there as valence is also called the *oxidation state* of the element.

For monatomic ions the **oxidation state** of the element is the charge on the ion (including the sign).

The oxidation state:

- of copper in the oxide Cu_2O ($2\text{Cu}^+ \text{O}^{2-}$) is +1
- of iron in the sulfide FeS ($\text{Fe}^{2+} \text{S}^{2-}$) is +2
- of titanium in the chloride TiCl_3 ($\text{Ti}^{3+} 3\text{Cl}^-$) is +3
- of chlorine in MgCl_2 ($\text{Mg}^{2+} 2\text{Cl}^-$) is -1
- of sulfur in PbS ($\text{Pb}^{2+} \text{S}^{2-}$) is -2.

There are other rules for assigning oxidation states in more complex molecules but they need not concern us at this stage. The only other rule we need is this:

The oxidation state of an element present in its stable elemental state is zero, regardless of the formula of the molecule of the element.

This means, for example, that the oxidation states for elemental zinc, hydrogen, chlorine, phosphorus, sulfur and argon are all zero despite the formulae being Zn , H_2 , Cl_2 , P_4 , S_8 and Ar .

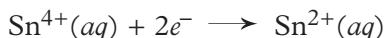
A change in oxidation state of a species corresponds to a loss or gain of electrons:

- An increase in oxidation state corresponds to a loss of electrons and so is oxidation.
- A decrease in oxidation state corresponds to a gain of electrons and so is reduction.

For example the change from iron(II) to iron(III) (+2 to +3) is oxidation (an electron is lost):



while the change from tin(IV) to tin(II) (+4 to +2) is reduction (electrons gained):



The change from bromide to bromine (change of oxidation state from -1 to 0) is oxidation:



while the change from oxygen to oxide (0 to -2) is reduction:



Exercises

- 1 Write equations for the reactions which occur in the following experiments:
 - a When a granule of zinc is dropped into a clear silver nitrate solution, the zinc becomes covered with a black deposit of metallic silver—black because it forms as extremely small particles.
 - b When a clean iron wire is dipped into a blue copper sulfate solution, a brown deposit forms on the wire and the solution loses its blue colour.
 - *c When a piece of aluminium foil is dropped into a clear lead nitrate solution, a black deposit of metallic lead forms on the foil.
- 2 Write oxidation and reduction half reactions for each of the reactions in Exercise 1.
- 3 By referring to the Activity series 2.3, select three metals which will displace:
 - a lead from a solution of lead nitrate
 - b iron from a solution of iron(II) sulfate.

Write balanced equations for these reactions.

- 4 a In which direction (left to right or right to left) will the following reactions occur? If no reaction occurs, write NR.

<p>i $\text{Sn} + \text{Ag}^+ \longrightarrow \text{Sn}^{2+} + \text{Ag}$</p> <p>ii $\text{Fe} + \text{Mg}^{2+} \longrightarrow \text{Fe}^{2+} + \text{Mg}$</p>	<p>*iii $\text{Cu} + \text{Al}^{3+} \longrightarrow \text{Cu}^{2+} + \text{Al}$</p> <p>*iv $\text{Pb} + \text{Ag}^+ \longrightarrow \text{Ag} + \text{Pb}^{2+}$</p>
---	---

b Balance the equations in (a), and write them so that they go from left to right.
- 5 For the reactions in Exercise 4, write oxidation and reduction half reactions; write them in the directions in which the reactions actually occur.
- 6 Which of the following metals liberate hydrogen gas from dilute sulfuric acid:

Ca, Ag, Sn, Al, Hg, Cu, Fe?

Write balanced equations for the reactions that occur. Then write the oxidation and reduction half reactions that make up each of your overall reactions.

- 7 a In each of the following compounds the metal exists as a monatomic ion. What is the oxidation state of the metal in each compound?

<p>i CrSO_4</p> <p>ii Cr_2O_3</p> <p>iii Mn(OH)_2</p>	<p>iv MnO_2</p> <p>v $\text{Ce}(\text{SO}_4)_2$</p> <p>vi V_2O_5</p>
--	--



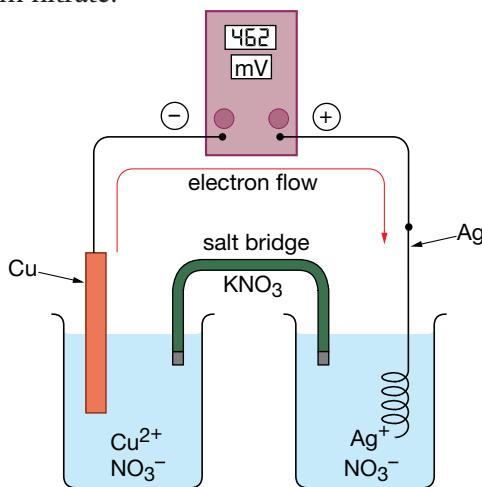
- b** In each of the following compounds the non-metal is present as a monatomic ion. What is the oxidation state of the non-metal in each compound?
- | | |
|-----------------------------|--|
| i KCl | iv Fe ₂ S ₃ |
| ii Na ₂ O | v (NH ₄) ₂ S |
| iii AlF ₃ | vi PbI ₂ |
- B** Does each of the following conversions represent oxidation or reduction of the underlined element, or neither? Explain why.
- | | |
|--|---|
| a <u>Mn</u> Cl ₃ → MnO ₂ | e Fe + S → FeS |
| b Na <u>Br</u> → Br ₂ | * f Ni <u>O</u> (OH) → Ni(OH) ₂ |
| c Fe <u>SO</u> ₄ → FeCl ₃ | * g Fe <u>O</u> → Fe ₂ O ₃ |
| d Cr(<u>NO</u> ₃) ₃ → Cr ₂ (SO ₄) ₃ | |

2.4 ELECTRICITY FROM REDOX REACTIONS

Redox reactions involve transfer of electrons from one reactant to another. An electric current is a flow of electrons through a wire. We can make redox reactions generate electricity by arranging for the oxidation and reduction half reactions to occur at different locations, and by providing a wire for the electrons to flow through. This occurs in all the batteries we use. The following experiment demonstrates the connection between a redox reaction and electricity.

As shown in Figure 2.2, a strip of copper metal is suspended in a beaker of copper nitrate solution, and a spiral of silver wire in a beaker of silver nitrate solution. The two solutions are connected by a U-tube filled with a solution of potassium nitrate held in place by plugs of cotton wool. This U-tube which makes electrical contact between the two solutions is called a **salt bridge**; in order to make electrical contact it must contain some conducting substance such as a solution of potassium nitrate.

FIGURE 2.2
A simple galvanic cell

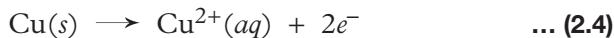


If a voltmeter is now connected across the pieces of metal, it is found that the silver wire is about 0.5 volt positive with respect to the copper; if we connect an ammeter across the terminals, a significant current flows. The electron flow is from the copper through the external circuit (meter and connecting wires) to the silver wire.

If the copper strip and silver wire in Figure 2.2 are connected with a conducting wire, and if the current is allowed to flow for some time, significant chemical change occurs:

- 1 metallic silver deposits on the silver wire—as can be seen by inspection and can be confirmed by weighing
- 2 some of the copper strip dissolves, again as can be confirmed by weighing
- 3 the concentration of silver ions in the right beaker falls appreciably, and
- 4 the concentration of copper ions in the left beaker increases.

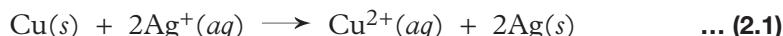
In other words, *electricity has been produced by a chemical reaction*. The voltmeter showed that electrons flowed out of the copper strip into the external circuit then down into the silver wire. The process occurring at the strip of copper metal is therefore:



and the reaction at the silver wire must be:



The overall chemical reaction occurring in our cell is the sum of these two half reactions (with Reaction 2.5 doubled to balance electrons):



This reaction is simply the one that occurred in the test tube in Figure 2.1 when a piece of copper was placed in a solution of silver nitrate; when the reaction occurs in a test tube no electricity is produced.

2.5 SOME TECHNICAL TERMS

We use the name **galvanic cell** or **voltaic cell** for a device in which a chemical reaction occurs in such a way that it generates electricity. Motor car batteries, and dry cells for torches and radios, are galvanic cells.

The conductors of a cell which get connected to the external circuit are called electrodes. In the present cell we talk about the copper electrode and the silver electrode. *Sometimes the term ‘electrode’ is also used to describe the combination of conductor and associated ion through which electrons enter or leave a cell;* in our example we can talk about the copper electrode and the silver electrode, or more precisely about the Cu^{2+} , Cu electrode and the Ag^+ , Ag electrode.

The solution(s) in a galvanic cell is (are) called *electrolyte* solution(s).

An **electrolyte** is a substance which in solution or molten conducts electricity.

In the cell in Figure 2.2 the copper nitrate, silver nitrate and potassium nitrate solutions are electrolyte solutions.

The chemical reactions occurring at the electrodes are called **electrode processes** or **electrode reactions**. Equations 2.4 and 2.5 are the *electrode reactions* of the cell in Figure 2.2.

Cell and battery

The device in Figure 2.2 is a galvanic cell. Similarly the ‘batteries’ we put in torches, calculators and radios etc. are galvanic *cells*. Technically a **battery** is several cells joined together in a common outer casing. The common nine volt battery, used for example in smoke detectors, and car batteries are genuinely *batteries*: in both cases they consist of six cells joined together in the one casing. The common 1.5 V dry cell, the alkaline cell and the 1.2 V nickel–cadmium cell are technically cells, not batteries. Although ‘battery’ is commonly used

instead of ‘cell’ in everyday life, we as chemistry students should be aware of the technical distinction.

2.6 PURPOSE OF THE SALT BRIDGE

If we remove the **salt bridge**, the voltage falls to zero and no current flows. Hence the salt bridge is necessary to make this and many other galvanic cells operate. What then is its purpose?

If the only changes that occurred were the ones already described, namely Equations 2.4 and 2.5, then the beaker containing copper nitrate would end up with an excess of positive ions (the copper ions produced by the electrode reaction), and the silver nitrate beaker would end up with an excess of negative ions (nitrate ions) because some silver ions have been discharged. Now it is quite impossible to have an imbalance of positive and negative ions in any solution, so some other changes must also be occurring. A closer inspection of the solutions shows that the nitrate concentration in the copper nitrate solution has also increased, and in the silver nitrate solution there has been a decrease in nitrate concentration as well as in silver ion concentration. Electrical neutrality of each solution has in fact been preserved. This implies that there has been a migration of nitrate ions away from the silver nitrate solution through the salt bridge and into the copper nitrate solution.

The purpose of the salt bridge is to allow this migration of ions to occur.

Both positive and negative ions migrate through the salt bridge. In Figure 2.2 not only do nitrate ions migrate from the right-hand beaker into the left-hand one, but also positive ions migrate from left to right. Copper ions move into the salt bridge and ‘push’ potassium ions out into the silver nitrate solution. This migration preserves electrical neutrality in both beakers (half-cells).

The electrolyte used in the salt bridge must be one which does not react with any of the ions in the two solutions it is connecting. Potassium nitrate is a good choice because NO_3^- and K^+ do not form any precipitates with other ions. (See the solubility data in Table 8.1 on p. 205 CCPC.) Sodium chloride is often suitable, but not for solutions containing Ag^+ because AgCl would precipitate.

When a galvanic cell produces electricity

- 1 One electrode reaction liberates electrons which flow out of the metal of the electrode and into the external circuit.
- 2 These electrons flow through the metallic conductor of the external circuit to the other electrode.
- 3 The reaction at the other electrode consumes these electrons.
- 4 Ions migrate through the solutions and connecting salt bridge to maintain electrical neutrality.

These processes are true of all galvanic cells and are shown diagrammatically in Figure 2.3.

An electric current through a metallic conductor is a flow of electrons. Through a conducting solution it is a *migration of ions*; negative ions move through the solution in the direction that completes the circuit for the electrons: in Figure 2.3 negative ions move from right to left. Positive ions move in the opposite direction. The ‘connection’ between ions and electrons is made by the electrode reactions which occur where the metallic electrode meets the solution.

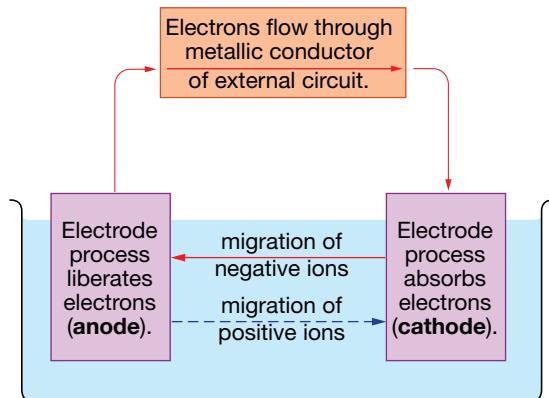


FIGURE 2.3
Schematic diagram of a galvanic cell

The *negative terminal* of a galvanic cell is by definition the *electrode from which electrons flow out into the external circuit* (torch bulb, calculator, radio). *Oxidation* occurs at this *negative electrode* to provide the electrons for the external circuit. The positive terminal of the battery draws electrons back to the cell from the external circuit. Hence the reaction which occurs at the *positive terminal* to do this is *reduction*.

A galvanic cell is an ‘electron pump’; it pumps electrons out of the negative terminal into the external circuit and ‘sucks’ them back into the positive terminal. It can do this because a redox reaction is occurring in the cell.

2.7 ANODE AND CATHODE

Two terms which are frequently used in electrochemistry are anode and cathode. By definition:

The **anode** is the electrode at which oxidation occurs.

The **cathode** is the electrode at which reduction occurs.

An aid to memory is this: **an oxidation** occurs at the anode. In the galvanic cell of Figure 2.2 the copper electrode is the anode (because Cu is being oxidised to Cu^{2+} there), and the silver wire is the cathode (Ag^+ is being reduced to Ag). Hence *in a galvanic cell, the anode is the negative terminal while the cathode is the positive terminal*.

Terms and signs are summarised in Box 2.1.

BOX 2.1 IN A GALVANIC CELL

Electrode reaction	Name of the electrode	Sign of the electrode
oxidation	anode	negative
reduction	cathode	positive

2.8 VARIETY OF GALVANIC CELLS

A great variety of galvanic cells can be made in the laboratory. In addition there is a wide variety of galvanic cells available commercially. Some of these will be discussed in Section 2.9.

In the laboratory we can easily make cells having three different types of electrodes:

- 1** electrodes that consist of a piece of metal dipping into a solution containing the ion of the metal, such as the Cu, Cu^{2+} and Ag, Ag^+ electrodes in Figure 2.2
- 2** electrodes consisting of an inert conductor (a piece of platinum wire or a graphite rod) dipping into a solution containing both an oxidised and a reduced form of the one element, such as a platinum wire dipping into a solution containing both Fe^{2+} and Fe^{3+} ions (Example 1 below)
- 3** electrodes consisting of a gas bubbling into a solution containing the oxidised or reduced form of the gas with an inert conductor (platinum wire) dipping into the solution, such as a chlorine, chloride electrode (Example 2 below) or a hydrogen, hydrogen ion electrode (Section 2.13).

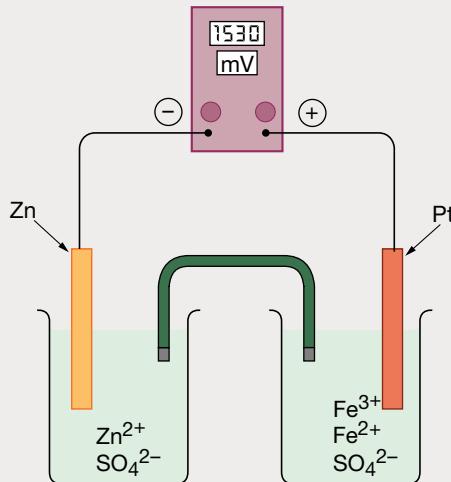
Galvanic cells can be made by combining pairs of electrodes together as the following examples will illustrate.



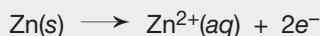
FIGURE 2.4
The galvanic cell for Example 1

Example 1

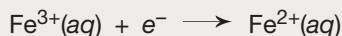
A galvanic cell was made by combining a Zn, Zn^{2+} electrode with a Fe^{3+} , Fe^{2+} electrode as shown in Figure 2.4. As indicated by the voltmeter, the platinum wire (that is, the Fe^{3+} , Fe^{2+} electrode) was positive.



- a** What chemical reaction is occurring at each electrode?
 - b** What is the overall reaction occurring in this cell as it produces electricity?
 - c** In which direction do electrons flow in the external circuit?
 - d** In which direction do ions flow within the cell?
 - e** Which electrode is the anode?
- a** If the platinum wire is positive, the zinc must be the negative electrode, meaning that electrons must be flowing out of the zinc into the external circuit (that's what being the negative electrode of a cell means). So the reaction occurring there must be:



The platinum being positive means that that electrode is absorbing electrons from the external circuit so the reaction must be



- b** The overall reaction will be the sum of these two equations, but before we can add them up we need to have the same number of electrons in each half reaction (because

we cannot have free electrons floating around in a balanced overall reaction). Hence we double the Fe half reaction:



then add the two half reactions to get



- c Electrons flow out of the zinc rod through the external circuit (wires and voltmeter) and into the platinum wire.
- d Negative ions flow away from the platinum wire into the salt bridge and into the zinc solution. This is because as Fe^{3+} ions are reduced to Fe^{2+} there is a decrease in the amount of positive charge near the platinum wire and so there must be a movement of negative charge (ions) away from that region to preserve electrical neutrality. Similarly positive ions move away from the zinc rod into the salt bridge and into the Fe^{3+} , Fe^{2+} solution.
- e Oxidation is occurring at the zinc electrode, so the zinc electrode is the anode (from the definition of anode).

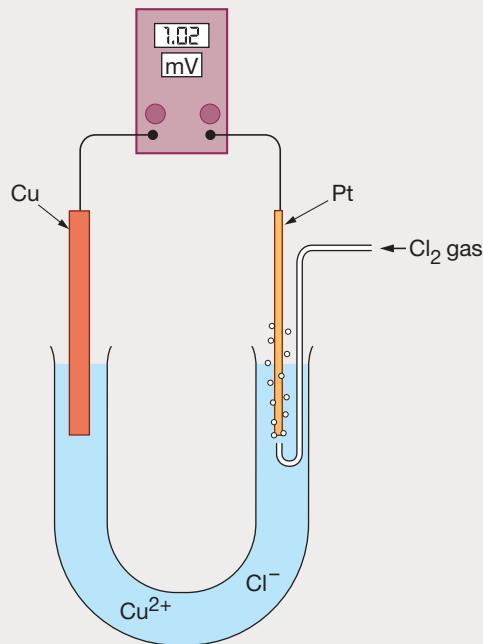
Not all galvanic cells require a salt bridge. Sometimes the one electrolyte can service both electrodes and that makes a salt bridge unnecessary. This is the case in all our commercial cells, but before looking at them let us consider a laboratory example.

Example 2

A galvanic cell was set up as shown in Figure 2.5 by making a chlorine electrode in the right-hand arm of a U tube containing copper chloride solution and dipping a copper rod into the left-hand arm (to make a Cu, Cu^{2+} electrode there). The chlorine electrode consisted of chlorine gas bubbling over a piece of platinum wire immersed in the chloride solution. The platinum wire was positive. What electrode reactions are occurring and what is the overall cell reaction? In which directions do electrons and ions flow as the cell generates electricity? Which electrode is the cathode?



FIGURE 2.5
A galvanic cell without a salt bridge (Example 2)



If the platinum wire is positive, the copper wire is negative, so it must be giving up electrons to the external circuit. So the reaction there is:



(In this type of exercise it is best to start with the negative electrode—that's where the electrons come from—and then you can follow them around the complete circuit.)

These electrons flow through the external circuit to the platinum wire where the electrode reaction absorbs them, so the reaction there must be reduction, namely:



The overall reaction will be the sum of the two electrode reactions:



Electrons flow from copper through the external circuit to the platinum. Negative ions flow from the chlorine electrode through the solution to the copper electrode (and so complete the circuit), while positive ions flow from the copper electrode towards the chlorine electrode, in both cases to preserve electrical neutrality in the solution near the electrodes.

Reduction is occurring at the chlorine electrode, so it must be the cathode.

Exercises

- 9 Write the electrode reactions, and hence the overall reaction, that occur in each of the following galvanic cells as it generates electricity.

Cell a: One electrode consists of a piece of cadmium dipping into a cadmium sulfate solution; it is connected by a salt bridge to another electrode which consists of a strip of magnesium metal dipping into a magnesium sulfate solution. The magnesium is the negative electrode.

Cell b: One electrode consists of a copper wire dipping into a copper sulfate solution; it is connected by a salt bridge to a solution containing both V^{2+} and V^{3+} ions (along with sulfate). A piece of platinum wire dips into this solution. The platinum wire is the negative electrode.

- 10 For each of the cells in Exercise 9 what would happen to the voltage if the salt bridge was removed? Explain why.

- 11 a Draw a diagram showing how you would set up each of the cells in Exercise 9 in the laboratory. Include some form of external circuit (such as a torch bulb or voltmeter).
b On each of your diagrams show the direction of flow of the electrons in the external circuit and the flow of ions within the cell.
c Label the anode and cathode in each cell.

- 12 Would you expect the cell in Example 2 (Fig. 2.5) to continue to function as a galvanic cell if the copper chloride solution was replaced by a solution of:

- a sodium chloride b copper sulfate c sodium sulfate?

Explain why or why not.

- 13 Which of the following reactions could or could not be used as the working reaction in a galvanic cell? Explain.

- a $\text{Mg(OH)}_2(\text{s}) + 2\text{HCl}(\text{aq}) \longrightarrow \text{MgCl}_2(\text{aq}) + 2\text{H}_2\text{O(l)}$
b $\text{Mg(s)} + \text{Pb}^{2+}(\text{aq}) \longrightarrow \text{Mg}^{2+}(\text{aq}) + \text{Pb(s)}$
c $\text{Fe(s)} + 2\text{H}^+(\text{aq}) \longrightarrow \text{Fe}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
d $\text{Pb}^{2+}(\text{aq}) + 2\text{Br}^-(\text{aq}) \longrightarrow \text{PbBr}_2(\text{s})$

14 A cell consists of a zinc rod dipping into a beaker of zinc sulfate solution; a salt bridge connects this beaker to a second beaker which contains a solution of iodine and potassium iodide into which dips a platinum wire. Sketch how this cell would look in the laboratory. Measurements with a voltmeter show that the platinum wire is positive with respect to the zinc rod.

- a** What electrode processes are occurring?
- b** What is the overall cell reaction?
- c** What migration of ions (if any) occurs as current flows?
- d** Which electrode is the anode?

15 Sketch a possible experimental arrangement for each of the following galvanic cells:

- a** a Cu, Cu²⁺ electrode joined by a salt bridge to an Fe, Fe²⁺ electrode
- b** an Al, Al³⁺ electrode connected by a salt bridge to Pb, Pb²⁺ electrode.

Use the activity series to decide which electrode would be positive in each cell. Explain your reasoning. Hence write down the electrode reactions and the overall reaction that occur as each cell generates electricity. On your diagrams show the directions of electron flow and ion migration. Also label the anodes and cathodes.

2.9 SOME COMMERCIAL GALVANIC CELLS

A wide range of galvanic cells is in everyday use. Some are shown on pp. 2–3.

The 'ordinary' dry cell

The ordinary **dry cell** is the most common and the cheapest of the commercially available cells. It is widely used in torches, radios and calculators. The technical name for it is the **Leclanché cell**, named after its inventor. Figure 2.6 shows its structure.

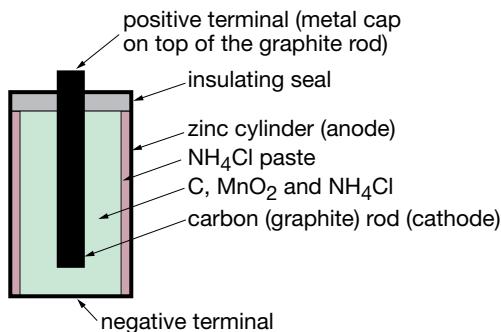
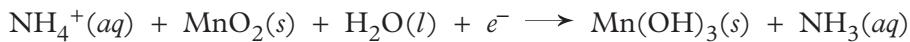


FIGURE 2.6
The common dry cell
(Leclanché cell)

It consists of a zinc outer casing, which is the negative electrode (or anode), an aqueous paste of ammonium chloride (so it is not really 'dry'!), and a mixture of powdered carbon, manganese dioxide and ammonium chloride around a carbon rod which is the positive terminal. Initially no zinc chloride is present, but as the cell is used zinc ions are formed and ammonium ions are discharged. At the negative terminal, the half reaction is:



At the carbon rod (the positive electrode), the reduction half reaction is:



Manganese is reduced from an oxidation state of +4 to +3. This cell operates under slightly acid conditions, because as we shall see in Chapter 5 ammonium

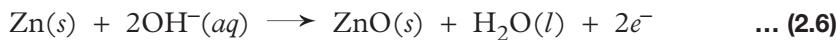
chloride solutions are slightly acidic. This cell initially has a voltage of 1.5 volts but this gradually decreases as the cell is used.

As already stated, this cell is relatively cheap. It was the first commercial battery and therefore had a big impact upon society because it made things such as torches (flashlights), portable radios and battery-operated clocks and toys possible. Today with many other cells available, the Leclanché cell is best used for devices which need only small currents such as radios and liquid-crystal calculators. This dry cell is robust, easy to store and use, and causes minimal environmental problems upon disposal: the manganese(III) is readily oxidised to stable insoluble manganese(IV) oxide and so becomes immobilised, small quantities of zinc are not a problem and ammonium salts and carbon are harmless.

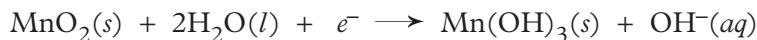
Disadvantages of the cell are that it does not contain a very large amount of electricity for its size, it cannot deliver very high currents and it can develop leaks when it goes flat (the zinc casing gets eaten away during operation).

The alkaline cell[†]

This cell has a similar appearance to that of the Leclanché cell. However, the electrolyte paste contains potassium hydroxide instead of ammonium chloride so it operates under alkaline conditions instead of slightly acidic ones. The electrode processes are basically the same as in the ordinary dry cell, namely oxidation of zinc to zinc(II) and reduction of manganese(IV) to manganese(III). However, because of the strongly alkaline conditions, the details are different. At the negative electrode:



The reaction at the positive electrode is:



Because these reactions occur so readily under alkaline conditions, this cell is able to delivery *higher currents* than the ordinary dry cell without suffering severe voltage drop. Alkaline cells can deliver a *greater total amount of electricity* than Leclanché cells of the same size. Hence alkaline cells are preferred for appliances requiring high currents (photographic electronic flash units) or high total capacity (tape recorders or children's toys).

Alkaline cells appear more expensive than Leclanché cells but on a cost per unit quantity of electricity basis they are comparable. They are relatively small and robust and very practical to use. Their ability to deliver higher currents and a greater quantity of electricity led to the development of portable higher energy-demanding devices such as portable tape recorders and CD players and more elaborate battery-operated toys.

Leakage problems can be more severe (because of the alkalinity of the electrolyte paste) than with Leclanché cells while disposal problems are similarly minimal.

Silver oxide cell

The silver oxide cell is a 'button' cell meaning it is small and looks roughly like a button; some are shown in Figure 2.7. It is widely used in miniature appliances

[†] not required for the NSW HSC but is included here because it is such a common battery

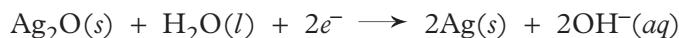
such as watches, hearing aids and calculators. Quite small cells can provide considerable amounts of electricity at a very constant voltage over a long period of time.



FIGURE 2.7
Silver oxide button cells can be made quite small and are commonly used in cameras, calculators, watches and hearing aids

A typical design is shown in Figure 2.8.

The anode reaction is the same as for the alkaline cell, Equation 2.6. The cathode reaction is:



Addition yields the overall reaction:

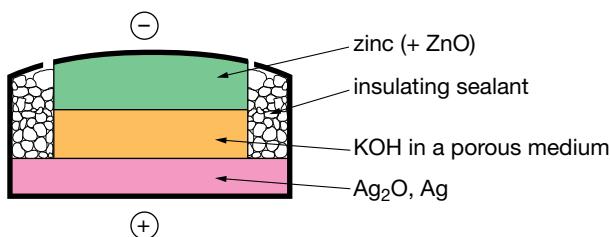


FIGURE 2.8
A silver oxide button cell (for watches, calculators and cameras)

This cell delivers a very constant voltage throughout its lifetime, because as it operates there is no change in the concentration of the electrolyte solution (potassium hydroxide).

Lithium cells

There are many types of lithium cell available commercially; one of the most widely used is the lithium–manganese dioxide cell (generally just called a lithium battery), a use-once-only cell widely used for cameras, watches and electronic devices such as calculators.

Lithium is the ideal metal for making negative electrodes, because it can generate the highest voltage of any metal and, having a low molar mass, it can produce more electrons per gram than any other metal. However it has the disadvantages that it reacts with air and water (p. 115 CCPC) so lithium cells must be water-free and sealed to exclude air.

Lithium–manganese dioxide cell

This cell is shown schematically in Figure 2.9. The negative electrode is lithium while the positive one is manganese dioxide in contact with a metal. Because lithium reacts with water, the electrolyte has to be non-aqueous.

Lithium releases electrons to the external circuit by the reaction

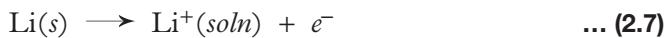
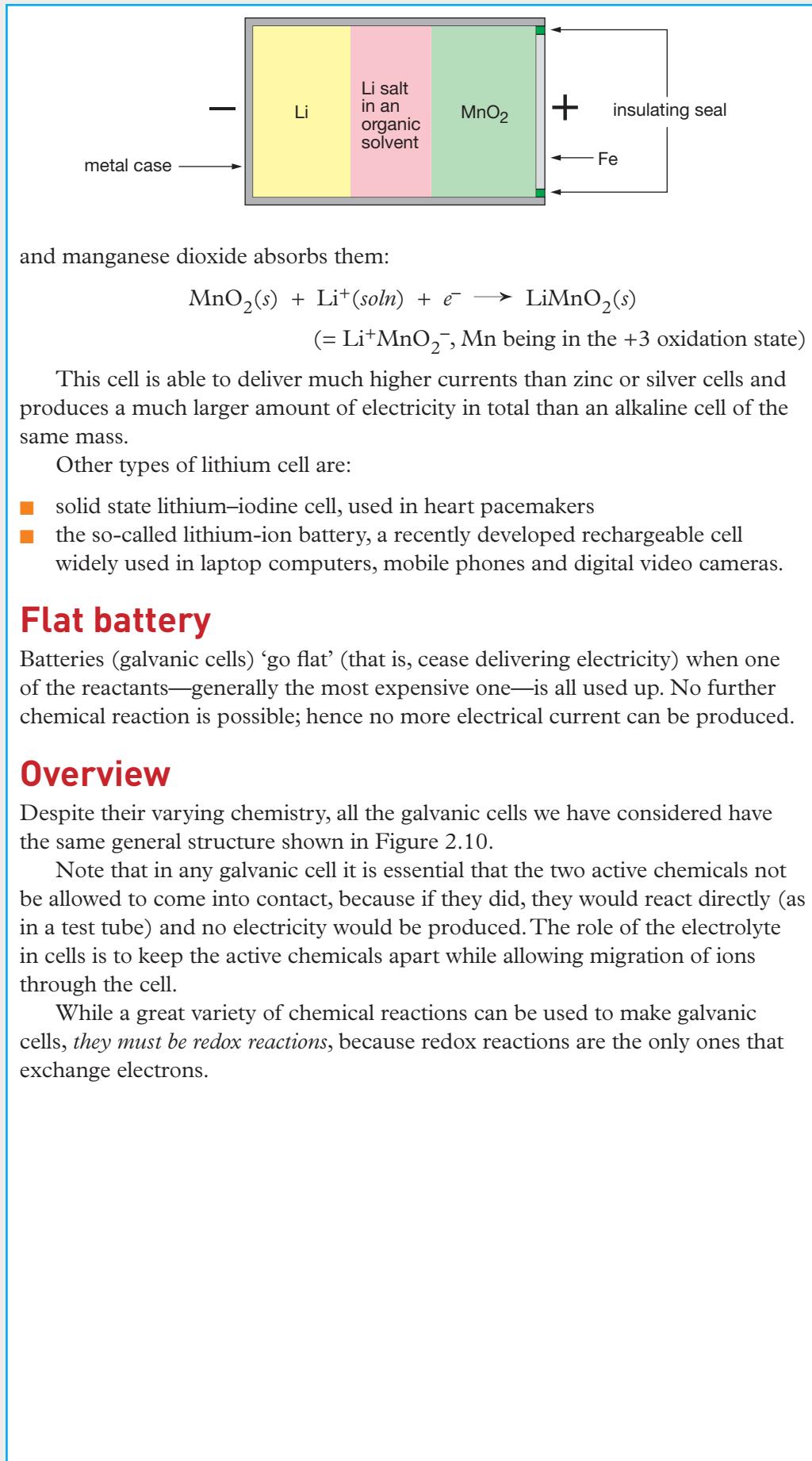
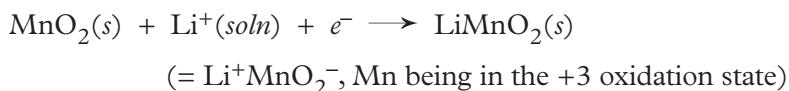


FIGURE 2.9
Schematic drawing of a lithium–manganese dioxide cell



and manganese dioxide absorbs them:



This cell is able to deliver much higher currents than zinc or silver cells and produces a much larger amount of electricity in total than an alkaline cell of the same mass.

Other types of lithium cell are:

- solid state lithium–iodine cell, used in heart pacemakers
- the so-called lithium-ion battery, a recently developed rechargeable cell widely used in laptop computers, mobile phones and digital video cameras.

Flat battery

Batteries (galvanic cells) ‘go flat’ (that is, cease delivering electricity) when one of the reactants—generally the most expensive one—is all used up. No further chemical reaction is possible; hence no more electrical current can be produced.

Overview

Despite their varying chemistry, all the galvanic cells we have considered have the same general structure shown in Figure 2.10.

Note that in any galvanic cell it is essential that the two active chemicals not be allowed to come into contact, because if they did, they would react directly (as in a test tube) and no electricity would be produced. The role of the electrolyte in cells is to keep the active chemicals apart while allowing migration of ions through the cell.

While a great variety of chemical reactions can be used to make galvanic cells, *they must be redox reactions*, because redox reactions are the only ones that exchange electrons.

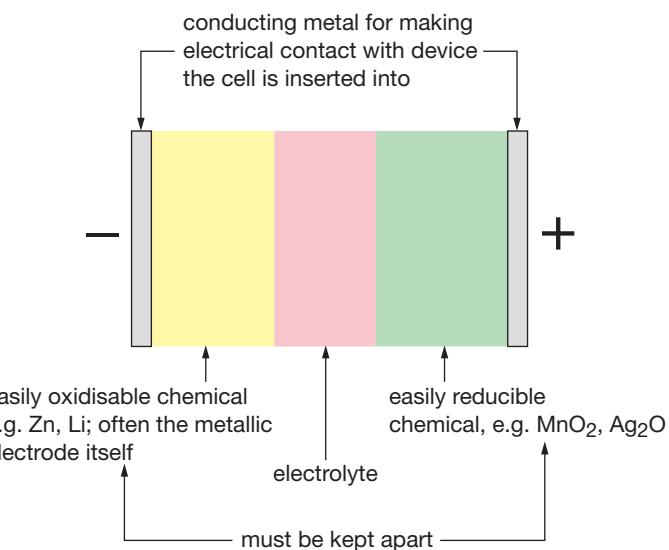


FIGURE 2.10
The general structure of galvanic cells

The batteries described in this section are ‘use once only and throw away’ type cells. They cannot be recharged. We shall look at the reason for this after we have considered some cells that can be recharged.

FOR INVESTIGATION

Prepare a table that compares the chemistry of the ordinary dry cell, the alkaline cell, the silver oxide button cell and the lithium–manganese dioxide cell. Then search out information in order to prepare another table in which you compare the relative costs and practicality (including uses), impact on society and environmental impact of these cells.



WEBSITES

<http://www.powerstream.com/BatteryFAQ.html>

(a good introduction to common types of cells)

<http://www.eveready.com/learning/howbatterieswork.asp>

(general information on commercial batteries with a good simple account of the alkaline battery)



Exercises

16 Use the information in Section 2.9 to write the overall reaction for the Leclanché cell and for the alkaline cell.



17 The mercury cell is a button cell similar to the silver oxide cell, but with Hg, HgO replacing Ag, Ag₂O; the mercury electrode is positive. The solid state lithium–iodine cell consists of a lithium anode and a cathode which is a solid solution of iodine in a polymer: the electrodes are separated by a thin film of crystalline lithium iodide.

Write the electrode reactions for these cells. Hence write the overall cell reactions.

18 a Initially an ordinary dry cell consists of an outer zinc cylinder surrounded by a protective wrapping. Explain why this cell has a greater tendency to leak chemicals after it has ‘gone flat’ than when it was new.

b Why would you expect a leaking alkaline battery to cause more damage than a leaking ‘ordinary’ cell?

19 What masses of lithium, zinc and cadmium need to be oxidised to produce a mole of electrons? This highlights an advantage of using lithium as an anode in galvanic cells.

2.10 RECHARGEABLE BATTERIES (CELLS)

Some galvanic cells can be recharged by passing an electric current through them in the opposite direction to that in which they delivered current.

Two common rechargeable commercial cells are the lead accumulator (car battery) and the nickel–cadmium cell.

Lead-acid cell (or lead accumulator)

The **lead-acid cell** or **lead accumulator** is the cell in the common motor car battery; it is shown in Figure 2.11(a). Six such cells are joined together in series to make a car battery as in Figure 2.11(b). In the one cell the positive and negative electrodes each consists of several plates joined together to maximise the area of contact between electrode and electrolyte which allows the cell to deliver a large current. The electrode plates are close together: this also increases the current the cell can deliver.

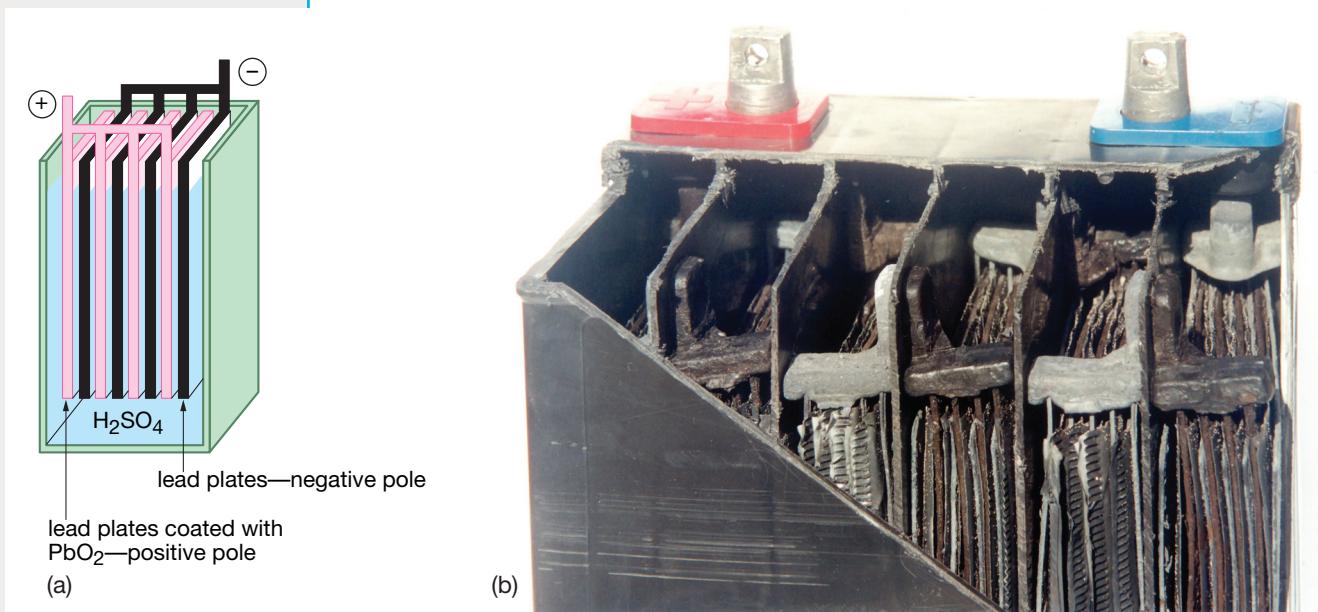
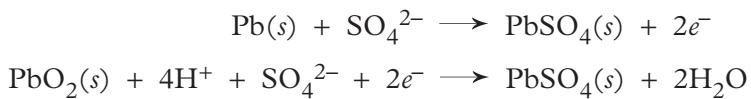


FIGURE 2.11

The lead accumulator: (a) a single 2 V cell, (b) a 12 V car battery which is six such cells joined together. The electrode plates are close together (to generate high currents) and so are separated by thin perforated plastic film (partly cut away in some cells here). As the photo shows, after heavy use the plates buckle with heat and eventually short circuit through the plastic film and so the battery becomes unserviceable.

Figure 2.12 shows the cell schematically. In the charged state the negative electrode is lead while the positive is lead coated with lead(IV) oxide, PbO₂. The electrolyte is approximately 5 mol/L sulfuric acid. As the cell generates electricity, both electrodes become coated with insoluble lead sulfate, and the concentration of the sulfuric acid solution decreases. The electrode reactions are:



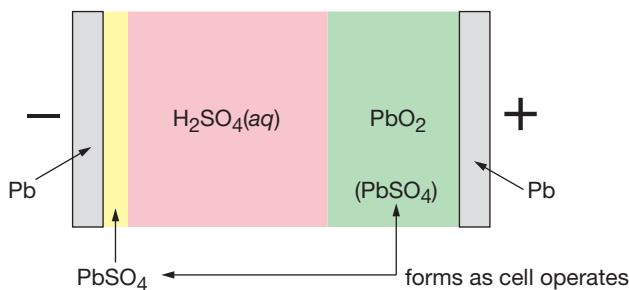


FIGURE 2.12
A schematic diagram of the lead–acid cell

This cell has a voltage of approximately 2 V. To recharge it, a voltage somewhat greater than 2 V is applied, with its positive connected to the positive of the lead–acid cell. This reverses the directions of the above half reactions. The cell is capable of being charged and discharged many times.

Recharging a galvanic cell is simply reversing the spontaneous chemical reaction that occurred when the cell delivered current.

Nickel–cadmium cell[†]

The nickel–cadmium cell consists of a cadmium, cadmium hydroxide negative electrode and a nickel, nickel oxyhydroxide, NiO(OH) , nickel hydroxide, Ni(OH)_2 , positive electrode, both in contact with an aqueous potassium hydroxide paste as electrolyte as shown schematically in Figure 2.13. Both the cadmium hydroxide and nickel oxyhydroxide are present as (insoluble) solids. The electrode reactions are:

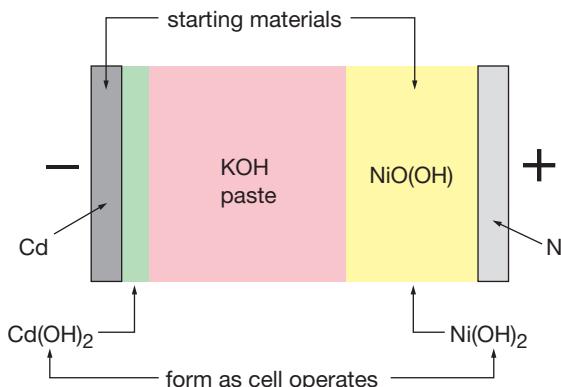
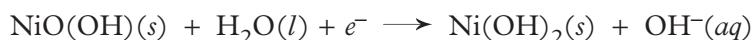


FIGURE 2.13
A schematic drawing of the nickel–cadmium cell

Cadmium is oxidised from the zero to +2 oxidation state while nickel is reduced from the (unusual) +3 oxidation state to the +2 state.

Nickel–cadmium cells are generally designed to look very similar to ordinary cells or alkaline cells (so they can simply replace them). They have a voltage of 1.2 V.

To recharge a nickel–cadmium cell a voltage somewhat greater than 1.2 V is applied, with the positive of the applied voltage connected to the positive (nickel) electrode of the cell. This reverses the above electrode reactions and restores the cell to its original state, ready to be used again.

[†] not required for the NSW HSC but included here because it is such a widely used battery

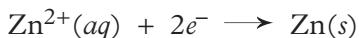
Nickel–cadmium cells are available as general purpose cells of various sizes for direct replacement of dry cells and alkaline cells and also as specially prepared packs for use in specific appliances such as cordless drills (8×1.2 V here) and video cameras (5×1.2 V here)



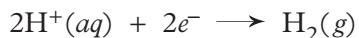
Recharging a galvanic cell is simply reversing the spontaneous chemical reaction that occurred when the cell delivered current.

Why are some cells non-rechargeable?

Some commercial galvanic cells can be used once only and then have to be thrown away. This is because if we attempt to recharge them, we do not simply reverse the cell reaction but instead bring about a different reaction. For example to recharge the Leclanché cell, we need to bring about:



However when a current is passed through this cell the reaction that occurs is:



This is not only ineffective for recharging the cell, but is quite dangerous (because of the explosive nature of hydrogen).

There are now alkaline cells that are rechargeable. Reaction 2.6 in alkaline solution can be reversed by recharging but there are difficulties of the cell overheating and exploding, so alkaline cells were generally considered to be non-rechargeable. However some alkaline cells are now being made with improved conductivity to overcome the problem, and by using chargers specially built for them (pulsed current at carefully regulated voltages), these alkaline cells can be recharged a limited number of times. Note carefully that only *rechargeable* alkaline cells should be recharged and *only* by using a dedicated recharger.

2.11 FUEL CELLS

A **fuel cell** is a type of galvanic cell that can be recharged simply by adding more chemical (fuel) to it.

Fuel cells can operate indefinitely as long as we keep supplying the fuel to them. The reason for this is that fuel cells operate without the electrodes undergoing any change in the electrode reactions. This contrasts with rechargeable

cells, such as the nickel–cadmium cell and the lead–acid cell, where the electrodes undergo changes which have to be reversed in order to recharge those cells.

The *hydrogen–oxygen fuel cell* shown in Figure 2.14 is a typical example. The electrodes are porous carbon with a coating of a catalyst. Hydrogen and oxygen flow slowly across the separate electrodes while there is a potassium hydroxide solution between the electrodes.

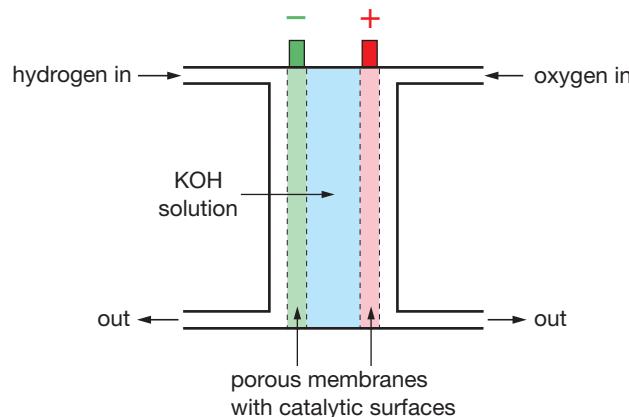


FIGURE 2.14
A hydrogen–oxygen fuel cell

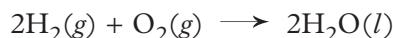
At one electrode, hydrogen is oxidised:



This makes that electrode negative. At the other electrode, oxygen is reduced:



This is therefore the positive electrode. To write the overall reaction, we balance electrons by multiplying Equation 2.8 by 2, then by adding it to Equation 2.9 to get (after cancelling $2\text{H}_2\text{O}$ on each side):



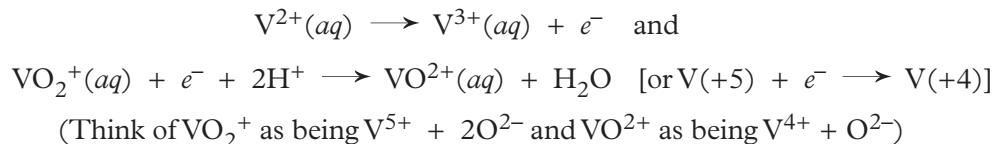
Both hydrogen, which is the fuel, and oxygen have to be supplied continuously to the cell. The product, water, dilutes the KOH electrolyte which therefore has to be slowly replenished during operation. It is because the electrodes undergo no permanent chemical change during cell operation (in contrast to rechargeable cells) that the cell can be operated indefinitely by merely keeping up the supply of fuel and oxygen.

The big advantage of fuel cells is that they provide direct conversion of chemical energy to electrical energy and this can, in principle, be done with 80–100% efficiency. The main problem with fuel cells is developing catalytic electrodes that can provide sufficiently fast electrode reactions for the cells to produce the high currents which are often required. This still remains the main stumbling block to the widespread use of fuel cells.

Vanadium redox cell

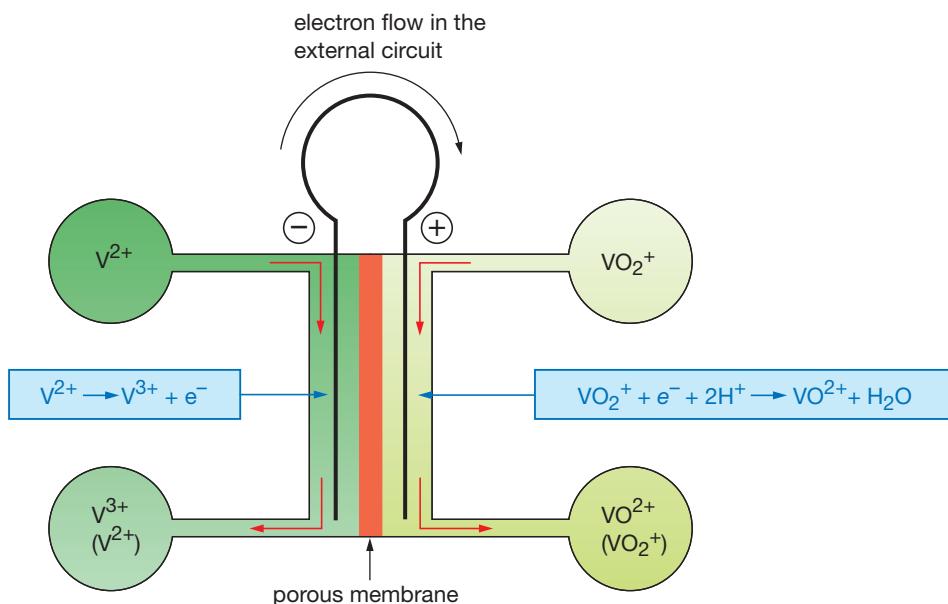
This is a recently developed cell that is showing great potential for the storage of electricity in the form of certain vanadium solutions. The quantities of electricity it can store are in the order of megajoules rather than the kilojoules of the other storage batteries. The electricity can be recovered by using the solutions to operate a galvanic cell.

This cell uses two redox half reactions involving vanadium species in oxidation states 2 and 3 and in 5 and 4 respectively:



The cell is shown schematically in Figure 2.15.

FIGURE 2.15
A schematic drawing of a vanadium redox cell



There are two electrode compartments separated by a porous membrane. A solution of VSO_4 flows through the anode compartment where V^{2+} oxidises to V^{3+} releasing electrons to the external circuit. A solution of $(\text{VO}_2)_2\text{SO}_4$ [i.e. $\text{V}(+5)$] flows through the cathode compartment where VO_2^+ takes electrons from the electrode and so is reduced to VO^{2+} [i.e. to $\text{V}(+4)$]. Sulfate ions migrate through the porous membrane to preserve electrical neutrality.

The cell operates in a flow mode with reactant solutions being recirculated until the concentrations of V^{2+} and VO^{2+} drop considerably (as V^{3+} and VO^{2+} are formed).

The cell is recharged by passing an electric current through it (in the reverse direction) and also by reversing the solution flow. This reverses the two half reactions (that is, converts V^{3+} back to V^{2+} and VO^{2+} back to VO_2^+). Because there are no changes to the electrodes during operation, the cell can also be recharged by replacing the spent solutions with fresh ones (with the old ones being regenerated at a more convenient time or place).



Exercises

- 20** As a lead accumulator discharges, it uses up the sulfuric acid electrolyte. Explain why it is not possible to recharge this cell simply by adding extra sulfuric acid.
- 21 a** A methanol–oxygen fuel cell has been developed. Its construction is similar to the cell in Figure 2.14. The fuel is methanol, the electrolyte is sulfuric acid and oxygen gas (from air) is the other reactant. Deduce the half reactions for this cell (methanol is oxidised to carbon dioxide), and hence the overall reaction.
- b** Suggest an advantage that this cell has over the one in Figure 2.14.
- 22** Is the vanadium redox cell a fuel cell or just a rechargeable cell? Explain.

2.12 THE GRATZEL CELL

Photovoltaic cells are devices that generate electricity when light falls upon particular surfaces, usually silicon ‘doped’ with small amounts of other elements. They are quite different from galvanic cells. However in recent years a photovoltaic cell has been developed that has some electrochemistry involved in it. It is called the **Gratzel cell**, or more technically, a **liquid junction photovoltaic device**.

The Gratzel cell is shown schematically in Figure 2.16. The photosensitive material is a thin layer of titanium dioxide, TiO_2 (red in the diagram) on the surface of a thin sheet of glass (green in the diagram); this glass is made electrically conducting by the depositing of platinum on it (black). A thin film of a solution of potassium iodide and iodine separates this ‘electrode’ from another sheet of conducting glass (the other electrode).

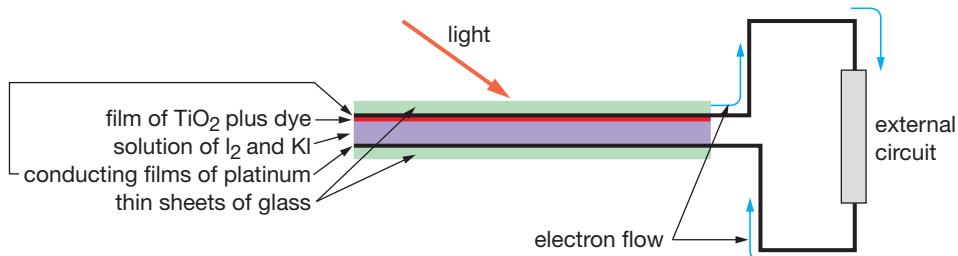
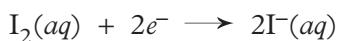


FIGURE 2.16
The Gratzel cell

When light hits the TiO_2 an electron is released: it flows through the external circuit to the other sheet of glass. The electron released by the TiO_2 is replaced by oxidation of iodide:



and so the TiO_2 can continue emitting electrons as light shines on it. The circuit is completed on the bottom sheet of glass by the iodine absorbing the returning electrons:



Doubling the first equation and adding it to the next two shows that there is no net change to the chemicals involved so the device can operate indefinitely. The only change has been the conversion of light energy into a flow of electricity through the external circuit.

Titanium dioxide is sensitive to only a narrow wavelength range of light so it is usually mixed with a suitable dye to extend its range across most of the solar spectrum.

The layers of material used in this device are extremely thin, so much so that the device is nearly transparent (though darkish looking) and so can be used as watch faces which generate enough power to run the watch. Gratzel cells are also being used as ‘smart windows’—windows that let light into a room but at the same time generate electricity for the house.



FOR INVESTIGATION

Prepare a table that compares the chemistry of the lead–acid cell, a fuel cell, the vanadium redox cell and the Gratzel cell. Then search out information in order to prepare another table in which you compare the relative costs and practicality (including uses), impact on society and environmental impact of these cells.



WEBSITES

<http://www.science.org.au/nova/023/023key.htm>

(fuel cells)

<http://www.h2fc.com/technology.html>

(fuel cells)

<http://www.ceic.unsw.edu.au/centers/vrb>

(vanadium redox cell: look in the picture gallery as well as reading the text)

2.13 STANDARD ELECTRODE POTENTIALS

Often chemists want to measure and compare voltages of cells and use them to get a measure of the relative activity of metals in cells. To do this it is not necessary to tabulate voltages of all possible cells but rather to assign voltages to electrodes; that is, to list what are called *electrode potentials*. However before doing this we need to clarify the meaning of ‘voltage’.

Voltage and EMF

As can be verified by anyone who has watched a motor mechanic put a voltmeter across the terminals of a car battery while the starter motor is being operated, the voltage delivered by a galvanic cell is not constant, but depends upon the amount of current being drawn. The greater the current being delivered, the lower the cell voltage. If we are going to compare voltages of cells, we need to standardise the conditions under which they are measured. Hence we introduce a term called electromotive force or EMF.

The **electromotive force** or **EMF** of a galvanic cell is the potential difference (voltage) across the electrodes of the cell when a negligibly small current is being drawn. It is the maximum voltage that the cell can deliver.

Modern solid-state digital voltmeters are high-resistance devices which measure voltage while drawing a negligibly small current. Hence such voltmeters give a good approximation to the EMF of the cell.

Strictly speaking, for comparative purposes we should talk about the EMFs of galvanic cells rather than just ‘voltages’.

Standard hydrogen electrode

For reference purposes we tabulate EMFs of electrodes relative to one particular electrode. The chosen reference electrode is the **standard hydrogen electrode**. This consists of a piece of platinum metal immersed in a 1.000 mol/L solution of hydrogen ions (hydrochloric acid) and through which hydrogen gas is bubbled at a pressure of 100.0 kPa. A typical hydrogen electrode is shown in the left-hand

beaker in each of the cells of Figure 2.17. The half reaction associated with this electrode is:

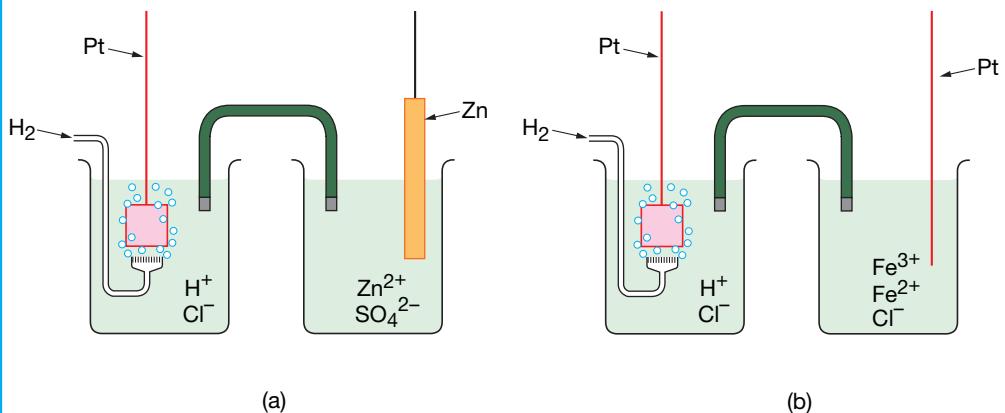
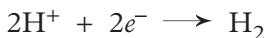


FIGURE 2.17
Cells used for measuring the standard electrode potentials for the Zn^{2+} , Zn and Fe^{3+} , Fe^{2+} , Pt electrodes

We specify a concentration of 1.000 mol/L for hydrogen ion and a pressure of 100.0 kPa for hydrogen gas because cell EMFs depend upon concentration and upon the pressure of any gas involved.

Measuring standard electrode potentials

Electrode potentials are measured relative to the standard hydrogen electrode.

Each of the other electrodes we are interested in is connected in turn to this standard hydrogen electrode, via a salt bridge, to make a cell as shown in Figure 2.17, and the cell voltage (EMF), including its sign, is measured.

As cell EMF depends upon electrolyte concentration and gas pressure, we also require that the ion associated with the electrode be present at a concentration of 1.000 mol/L and any gas involved be present at a pressure of 100.0 kPa for consistency in tabulated data. These conditions, 1.000 mol/L for solutes and 100.0 kPa for gases comprise, what we call the **standard state**.[†] EMFs of such cells are called standard electrode potentials.

The **standard electrode potential**, E° , of an electrode is the potential of that electrode in its standard state relative to the standard hydrogen electrode.

E° is the EMF of the cell formed by combining the electrode with a standard hydrogen electrode, and its sign is the sign of the electrode relative to the hydrogen electrode. We use the superscript $^\circ$ of E° to denote that the value refers to the standard state.[‡]

Standard electrode potentials are sometimes called *standard redox potentials* or *standard reduction potentials*.

If conditions are not those of the standard state, we just use the term **electrode potential**. Its value would be different from the *standard electrode potential*.

[†] Defining the standard state for solutes as 1.000 mol/L is not strictly correct, but it suffices for present purposes.

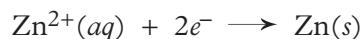
[‡] An older standard state is still in widespread use. It is based on a pressure of 1.000 atmosphere which is a non-systematic unit of pressure that is gradually being phased out:

1 atmosphere = 101.3 kPa. A superscript o is used to denote that older standard state. E° is the standard electrode potential based on a standard state of 101.3 kPa, while $E^{\circ\circ}$ refers to the newer standard state (100.0 kPa). You will see E° in many texts. The numerical value, to the accuracy used in elementary texts such as this one, is the same for both standard states.

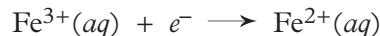
The cell shown in Figure 2.17(a) has an EMF of 0.76 volt with the zinc rod being negative with respect to the platinum of the hydrogen electrode. Hence we say that the Zn^{2+} , Zn electrode has a standard electrode potential of -0.76 volt. The cell in Figure 2.17(b) has an EMF of 0.77 volt, with the platinum wire dipping into the Fe^{3+} , Fe^{2+} solution being positive relative to the wire of the hydrogen electrode; hence the standard electrode potential of the Fe^{3+} , Fe^{2+} electrode is $+0.77$ volt (V).

Standard electrode potentials are assigned not only to the electrodes but also to the *reduction* half reactions associated with the electrodes.

Not only do we say that the Zn^{2+} , Zn electrode has a standard electrode potential of -0.76 V, but we also say that the reduction half reaction:

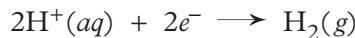


has a standard electrode potential of -0.76 V. Similarly, the reduction half reaction associated with the Fe^{3+} , Fe^{2+} electrode:



has a standard electrode potential of $+0.77$ V.

Because of the way standard electrode potentials are defined, the H^+ , H_2 electrode has a standard electrode potential of zero; similarly the associated reduction half reaction:



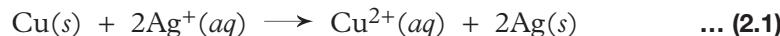
also has a standard electrode potential of zero.

It is important to note that electrode potentials or redox potentials refer to *reduction* half reactions only (and not to oxidation half reactions). We can talk about voltage (or EMF) of an oxidation half reaction but we must *never* call it an electrode potential; that term is reserved for reduction half reactions.

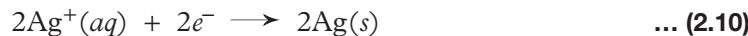
Standard electrode potentials for some common electrodes (or electrode reactions) are given in Table 2.1. Such a table of standard electrode potentials can be used to calculate EMFs of redox reactions or of cells and to determine the relative oxidising or reducing strengths of different substances.

2.14 CALCULATING EMFs FOR REDOX REACTIONS AND CELLS

Just as half reactions can be added to form complete redox reactions, so too standard electrode potentials can be combined to calculate EMFs of complete reactions. As an illustration, let us calculate the EMF of the first reaction we discussed in Section 2.1:



We first break it into its half reactions:



Since the required reaction (Equation 2.1) is made by adding these half reactions, it follows that:

TABLE 2.1 Standard electrode potentials at 25°C^a

Oxidised form + ne ⁻	→	Reduced form	E ^o (V)
F ₂ + 2e ⁻	→	2F ⁻	+2.87
H ₂ O ₂ + 2H ⁺ + 2e ⁻	→	2H ₂ O	+1.78
Au ⁺ + e ⁻	→	Au	+1.69
MnO ₄ ⁻ + 8H ⁺ + 5e ⁻	→	Mn ²⁺ + 4H ₂ O	+1.51
PbO ₂ + 4H ⁺ + 2e ⁻	→	Pb ²⁺ + 2H ₂ O	+1.46
Cl ₂ + 2e ⁻	→	2Cl ⁻	+1.36
O ₃ + H ₂ O + 2e ⁻	→	O ₂ + 2OH ⁻	+1.24
Cr ₂ O ₇ ²⁻ + 14H ⁺ + 6e ⁻	→	2Cr ³⁺ + 7H ₂ O	+1.23
O ₂ + 4H ⁺ + 4e ⁻	→	2H ₂ O	+1.23
MnO ₂ + 4H ⁺ + 2e ⁻	→	Mn ²⁺ + 2H ₂ O	+1.22
Ag ₂ O + 2H ⁺ + 2e ⁻	→	2Ag + H ₂ O	+1.17
Br ₂ + 2e ⁻	→	2Br ⁻	+1.09
NO ₃ ⁻ + 4H ⁺ + 3e ⁻	→	NO + 2H ₂ O	+0.96
NO ₃ ⁻ + 3H ⁺ + 2e ⁻	→	HNO ₂ + H ₂ O	+0.93
2Hg ²⁺ + 2e ⁻	→	Hg ₂ ²⁺	+0.92
Hg ²⁺ + 2e ⁻	→	Hg	+0.85
NO ₃ ⁻ + 2H ⁺ + e ⁻	→	NO ₂ + H ₂ O	+0.80
Ag ⁺ + e ⁻	→	Ag	+0.80
Fe ³⁺ + e ⁻	→	Fe ²⁺	+0.77
O ₂ + 2H ⁺ + 2e ⁻	→	H ₂ O ₂	+0.70
MnO ₄ ⁻ + 2H ₂ O + 3e ⁻	→	MnO ₂ + 4OH ⁻	+0.60
I ₂ + 2e ⁻	→	2I ⁻	+0.54
O ₂ + 2H ₂ O + 4e ⁻	→	4OH ⁻	+0.40
Ag ₂ O + H ₂ O + 2e ⁻	→	2Ag + 2OH ⁻	+0.34
Cu ²⁺ + 2e ⁻	→	Cu	+0.34
SO ₄ ²⁻ + 4H ⁺ + 2e ⁻	→	H ₂ SO ₃ + H ₂ O	+0.17
Sn ⁴⁺ + 2e ⁻	→	Sn ²⁺	+0.15
S + 2H ⁺ + 2e ⁻	→	H ₂ S	+0.14
S ₄ O ₆ ²⁻ + 2e ⁻	→	2S ₂ O ₃ ²⁻	+0.08
2H ⁺ + 2e ⁻	→	H ₂	0.00
Pb ²⁺ + 2e ⁻	→	Pb	-0.13
Sn ²⁺ + 2e ⁻	→	Sn	-0.14
Ni ²⁺ + 2e ⁻	→	Ni	-0.26
Co ²⁺ + 2e ⁻	→	Co	-0.28
PbSO ₄ + 2e ⁻	→	Pb + SO ₄ ²⁻	-0.36
Cd ²⁺ + 2e ⁻	→	Cd	-0.40
Fe ²⁺ + 2e ⁻	→	Fe	-0.45
2CO ₂ + 2H ⁺ + 2e ⁻	→	H ₂ C ₂ O ₄	-0.49
Zn ²⁺ + 2e ⁻	→	Zn	-0.76
2H ₂ O + 2e ⁻	→	H ₂ + 2OH ⁻	-0.83
Al ³⁺ + 3e ⁻	→	Al	-1.66
Mg ²⁺ + 2e ⁻	→	Mg	-2.37
Na ⁺ + e ⁻	→	Na	-2.71
Ca ²⁺ + 2e ⁻	→	Ca	-2.87
Ba ²⁺ + 2e ⁻	→	Ba	-2.91
K ⁺ + e ⁻	→	K	-2.93
Li ⁺ + e ⁻	→	Li	-3.04

oxidising strength increases

reducing strength increases

On the large, side arrows, ‘oxidising strength’ refers to the oxidised form of the redox half reaction and ‘reducing strength’ refers to the reduced form.

a State symbols (phase descriptors) have been omitted in order not to clutter up what is already a complex table. All ions are present as aqueous solutions; other substances are present in their stable pure forms at 25°C and 100 kPa.

$$\left\{ \begin{array}{l} \text{Standard EMF} \\ \text{of the complete} \\ \text{reaction} \end{array} \right\} = \left\{ \begin{array}{l} \text{Standard EMF} \\ \text{of the reduction} \\ \text{half reaction} \end{array} \right\} + \left\{ \begin{array}{l} \text{Standard EMF} \\ \text{of the oxidation} \\ \text{half reaction} \end{array} \right\} \dots (2.12a)$$

or in symbols:

$$\text{EMF}^{\circ}(\text{total}) = \text{EMF}^{\circ}(\text{red}) + \text{EMF}^{\circ}(\text{oxid}) \dots (2.12b)$$

Now the standard EMF of the reduction half reaction in Equation 2.10 is simply the standard electrode potential of the Ag^+ , Ag electrode, E°_{Ag} , which is $+0.80\text{ V}$. Because the oxidation half reaction is the reverse of the reduction half reaction, the EMF of the oxidation half reaction is *minus* the standard electrode potential of the corresponding reduction half reaction. Hence in our particular case:

$$\text{EMF}^{\circ}(\text{oxid}) = -E^{\circ}_{\text{Cu}} = -(+0.34\text{ V}) \quad (\text{from Table 2.1})$$

$$\begin{aligned} \text{Hence } \text{EMF}^{\circ}(\text{total}) &= E^{\circ}_{\text{Ag}} + (-E^{\circ}_{\text{Cu}}) \\ &= 0.80 - 0.34\text{ V} \\ &= 0.46\text{ V} \end{aligned}$$

Reaction 2.10 is actually *twice* the reaction written in Table 2.1. Note carefully that

doubling the half reaction does not alter E° .

This contrasts with ΔH° 's (p. 277 CCPC). The reason is that E° is a type of *energy per electron*. It does not matter how many electrons are in the reaction written—the energy per electron is unaltered. Changing the direction of the half reaction does change the sign of its EMF° . In this regard EMF° behaves like ΔH .



Example 3

Using standard electrode potentials from Table 2.1, calculate the standard EMF of the reaction:



This reaction is made up of the following half reactions:

$$\begin{aligned} \text{Ni(s)} &\longrightarrow \text{Ni}^{2+}(\text{aq}) + 2e^- \quad \text{EMF}^{\circ} = -E^{\circ}_{\text{Ni}} \\ &= -(-0.26)\text{ V} = +0.26\text{ V} \end{aligned}$$

$$\begin{aligned} \text{Cl}_2(\text{g}) + 2e^- &\longrightarrow 2\text{Cl}^-(\text{aq}) \quad \text{EMF}^{\circ} = E^{\circ}_{\text{Cl}} \\ &= +1.36\text{ V} \end{aligned}$$

By Equation 2.12:

$$\begin{aligned} \text{EMF}^{\circ}(\text{total}) &= +0.26 + 1.36 \\ &= \mathbf{1.62\text{ V}} \end{aligned}$$

In summary: to calculate the EMF of a redox reaction, we use Equation 2.12 together with the fact that the EMF of an oxidation half reaction is *minus* the electrode potential of the corresponding reduction half reaction.

Having seen how to calculate the EMF of a redox reaction, we need to explore exactly what it means. While chemists often talk about the EMF of a

reaction, what they really mean is ‘the EMF of the galvanic cell in which that reaction occurs’. The EMF of Reaction 2.1 is really the EMF of the cell shown in Figure 2.2. *With regard to sign, it is the voltage of the piece of metal where the reduction half reaction is occurring relative to the other electrode*—in this case, the voltage of the silver wire *relative* to the copper wire.

For Reaction 2.13 the galvanic cell it refers to would be like the one in Figure 2.5 with a piece of nickel and a nickel chloride solution replacing the copper and copper chloride solution respectively. Our calculation shows us that the chlorine electrode (the piece of platinum wire) is positive relative to the piece of nickel.

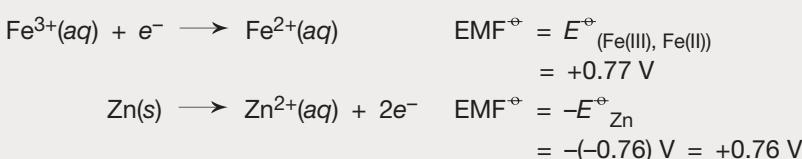
To calculate the emf of a galvanic cell

We first write the redox half reactions associated with the cell, then follow the above procedure. If we are told which electrode is positive, we write a reduction half reaction for that electrode (*and oxidation for the other*) and proceed as above. Alternatively, we write reduction at the electrode with the higher electrode potential.

Example 4

Calculate the standard EMF of the galvanic cell in Figure 2.4.

We are told that the Fe^{3+} , Fe^{2+} electrode is positive, so we write the half reactions:



By Equation 2.12:

$$\begin{aligned} \text{EMF}^\ominus_{(\text{cell})} &= 0.77 + 0.76 \\ &= \mathbf{1.53 \text{ V}} \end{aligned}$$

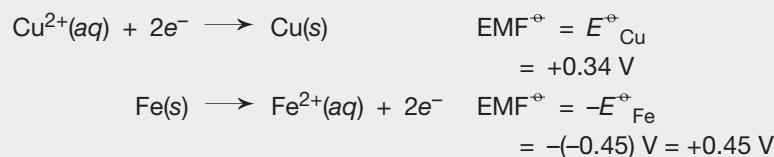
(with the Fe^{3+} , Fe^{2+} electrode, the Pt wire, being positive relative to the Zn)

Example 5

Calculate the EMF of a cell made by connecting a Cu, Cu^{2+} electrode to a Fe, Fe^{2+} electrode.



Since we are not told which electrode is positive and hence at which electrode reduction is occurring, we use the suggestion above of writing reduction at the electrode with the higher electrode potential. From Table 2.1 copper has the higher electrode potential (+0.34 V compared with –0.45 V), so we write:



By Equation 2.12:

$$\begin{aligned} \text{EMF}^\ominus_{(\text{cell})} &= 0.34 + 0.45 \\ &= \mathbf{0.79 \text{ V}} \end{aligned}$$

(with the copper wire being positive relative to the iron one)

This example shows that when considering a galvanic cell with electrodes A and B, Equation 2.12(a) can be written as:

$$\text{EMF}^{\circ}_{\text{(cell)}} = \left\{ \begin{array}{l} \text{standard electrode} \\ \text{potential of} \\ \text{electrode A} \end{array} \right\} - \left\{ \begin{array}{l} \text{standard electrode} \\ \text{potential of} \\ \text{electrode B} \end{array} \right\} \dots (2.14)$$

where $\text{EMF}^{\circ}_{\text{(cell)}}$ is the voltage of electrode A relative to electrode B. If we know the values of the two electrode potentials, it is convenient (though not essential) to make A the more positive electrode.

This equation is particularly useful when we want to calculate an electrode potential from a measured cell EMF and a known electrode potential as in Exercise 28(b) below.

Finally, concerning the significance of the sign of the calculated EMF of the reaction (or of the cell):

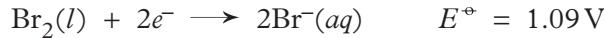
If the EMF of a redox reaction calculated by Equation 2.12 is positive, then the reaction occurs as written; if the calculated EMF turns out to be negative, then the reaction does not occur as written, but rather occurs in the reverse direction.

A consequence

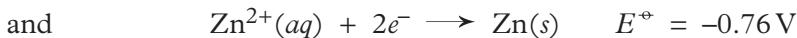
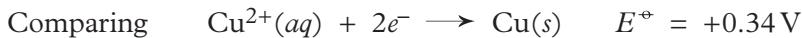
A consequence of that last calculation is this:

When comparing two reduction half reactions, the one with the larger standard electrode potential has the greater tendency to occur. As it occurs it drives the other half reaction in the reverse direction.

For example,



The first half reaction (with the higher E°) occurs as written and drives the other one in the reverse direction: Cl_2 oxidises Br^- to Br_2 (and is itself reduced to Cl^-).



the first half reaction goes as written and drives the second one in the reverse direction: Cu^{2+} oxidises Zn to Zn^{2+} (and the Cu^{2+} is itself reduced to Cu) or, stated differently, Zn reduces Cu^{2+} to Cu and is itself oxidised to Zn^{2+} .

We can generalise from these examples:

The greater the standard electrode potential, the greater is the oxidising strength of the oxidised form (left-hand side) of the redox half reaction.

Alternatively, the algebraically smaller the standard electrode potential, the greater is the reducing strength of the reduced form (right-hand side) of the redox half reaction.

These trends are shown by the red arrows in Table 2.1.

Exercises



23 Three galvanic cells were set up, each having a standard hydrogen electrode as one of its electrodes with the other electrode being:

- i** gold in contact with a Au^{3+} solution
- ii** cadmium in contact with a Cd^{2+} solution
- iii** a chlorine electrode (Cl_2 , Cl^- in contact with a platinum wire).

In all these cells solutes were present at a concentration of 1.00 mol/L and any gases were present at pressures of 100.0 kPa. The standard EMFs of these cells were **i** 1.99 V (gold positive) **ii** 0.40 V (hydrogen electrode positive) **iii** 1.36 V (chlorine electrode positive).

- a** Use these results to calculate the standard electrode potentials of the three electrodes.
 - b** Write the half reactions these standard electrode potentials refer to.
- 24 *a** What are the two different meanings of the word *electrode*? (Section 2.5)
- b** Many electrodes are of the types *metal conductor, metal ion solution*. Give six examples of such electrodes.
 - c** Some electrodes are of the type *inert conductor (platinum or graphite) in contact with a solution containing both oxidised and reduced forms of a redox couple*. List three such electrodes. For each give its electrode (reduction) reaction.

25 a For each of the reactions below, calculate the standard EMF:

- i** $\text{Cu}^{2+} + \text{Ni} \rightarrow \text{Ni}^{2+} + \text{Cu}$
- ii** $\text{Cd} + 2\text{H}^+ \rightarrow \text{H}_2 + \text{Cd}^{2+}$
- iii** $\text{Pb} + \text{Mg}^{2+} \rightarrow \text{Pb}^{2+} + \text{Mg}$
- iv** $\text{Al}^{3+} + \text{Br}^- \rightarrow \text{Al} + \text{Br}_2$
- v** $\text{Ag}_2\text{O} + \text{H}^+ + \text{Sn} \rightarrow \text{Ag} + \text{Sn}^{2+} + \text{H}_2\text{O}$
- vi** $\text{Fe}^{3+} + \text{Br}^- \rightarrow \text{Fe}^{2+} + \text{Br}_2$

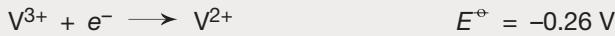
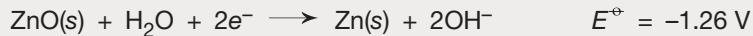
- b** Balance any of the above equations that are not already balanced.
- c** In which direction (left to right or right to left) does each of these reactions go?

26 Use Table 2.1 to calculate the standard EMF of each of the following cells; state clearly which electrode is positive:

- a** a nickel, nickel ion electrode connected with a salt bridge to a silver, silver ion electrode
- b** an aluminium, aluminium ion electrode connected to a silver, silver ion electrode
- c** an $\text{Fe}^{3+}, \text{Fe}^{2+}$ electrode connected to a chlorine, chloride electrode

27 a Sketch what each of the cells in Exercise 26 would look like in the laboratory.
b Write the overall reaction that occurs in each of these cells as it generates electricity.

28 a Calculate the standard EMFs for the silver oxide cell, the lead–acid cell and the vanadium redox cell using Table 2.1 and the following:



- b** The nickel–cadmium cell has an EMF of 1.25 V. The electrode potential for the cadmium, cadmium hydroxide electrode is –0.76 V. Calculate the electrode potential for the nickel hydroxide, oxyhydroxide electrode.

Important new terms

You should know the meaning of the following terms.

anode (p. 49)	galvanic cell (p. 47)
battery (p. 47)	Gratzel cell (p. 63)
cathode (p. 49)	lead–acid cell (lead accumulator) (p. 58)
displacement reaction (p. 41)	Leclanché cell (p. 53)
dry cell (p. 53)	liquid junction photovoltaic device (p. 63)
electrochemistry (p. 41)	oxidation [†] (p. 42)
electrode (p. 47)	oxidation state (p. 44)
electrode potential (p. 65)	photovoltaic cell (p. 63)
electrode reaction (process) (p. 47)	redox reaction [†] (p. 43)
electrolyte (p. 47)	reduction [†] (p. 42)
electromotive force (EMF) (p. 64)	salt bridge (p. 46)
electron transfer reaction (p. 43)	standard electrode potential (p. 65)
fuel cell (p. 60)	standard hydrogen electrode (p. 64)
	standard state (p. 65)
	voltaic cell (p. 47)

Test yourself

- 1 Explain the meaning of each of the items in the ‘Important new terms’ section above.
- 2 Write equations for three displacement reactions involving metals and metal ions.
- 3 Write oxidation and reduction half equations for the complete equations you wrote in Question 2.
- 4 Why do oxidation and reduction always occur together in the one chemical reaction?
- 5 How can you use the Activity Series 2.3 to decide which metal will displace which other metal from solution?
- 6 Name three metals that will displace copper from a copper sulfate solution, and four metals which will displace silver from silver nitrate solution.
- 7 What is the oxidation state of **(a)** chromium in Cr_2O_3 **(b)** titanium in TiCl_4 and **(c)** iodine in MgI_2 ?
- 8 When tin(IV) is converted to tin(II) is the process oxidation or reduction or neither? Explain why.
- 9 What type of reaction can be used to make a galvanic cell? Why not other types?
- 10 Sketch a simple laboratory galvanic cell. Show the electrode reactions, the flow of electrons, the flow of ions, and identify the anode and cathode.
- 11 What is the purpose of a salt bridge in a galvanic cell?
- 12 Describe the structure of an ordinary dry cell (Leclanché cell) and explain its chemistry.
- 13 Sketch a silver oxide button cell and write the electrode reactions for it.

[†] These terms were introduced on pp. 117–18 CCPC: they are repeated here because they were not strictly part of the *Preliminary Course* syllabus.

- 14** How do we recharge certain galvanic cells? Name two everyday rechargeable cells.
- 15** Why do we use the term ‘EMF’ instead of ‘cell voltage’?
- 16** What is a standard hydrogen electrode? Draw a diagram of one.
- 17** Describe how you would measure the standard electrode potential of the Ag^+ , Ag electrode.
- 18** Standard electrode potentials are assigned to which type of half reaction—oxidation or reduction or both?
- 19** How do we calculate the standard EMF of a redox reaction from standard electrode potentials?
- 20** How do we use the EMF of a reaction to decide in which direction the reaction goes?
- 21** Explain how we calculate the standard EMF of a galvanic cell from electrode potentials. The calculated EMF is the voltage of which electrode (relative to the other)? If the calculated EMF for a cell is negative, what does this mean for the half reactions we wrote?

CHAPTER 3

Nuclear chemistry

IN THIS CHAPTER

Radioactivity
Isotopes and symbols for them
Stable and unstable isotopes
Types of radiation emitted
Alpha-emitting radioisotopes
Beta-emitting radioisotopes
Nuclear fission and nuclear reactors

Transuranic elements
Half-life
Preparation of commercially useful isotopes
Detection of radiation
Uses of radioisotopes

Continuing with the theme of using chemistry to make new materials that are useful to human society, we now turn to what are called radioactive materials. These are particularly useful in medicine (for diagnosis and therapy) and in industry (as tools for monitoring processes).

3.1 RADIOACTIVITY

In 1896 the French physicist, Becquerel, discovered that uranium compounds could darken photographic plates even when the plates were protected by the usual opaque paper. All compounds of uranium had this effect, so it was concluded that it was *atoms* of uranium which were emitting some form of radiation. Several other elements—radium, polonium and thorium—were soon found which had this same property. These elements were called *radioactive*, as they actively emitted radiation. This spontaneous emission of radiation by certain elements is called **radioactivity**.

For some elements *all* isotopes are radioactive, while for others only *one* or *some* isotopes are radioactive. For example, all isotopes of uranium, U, and radium, Ra, are radioactive while rubidium, Rb, and rhenium, Re, each have two isotopes, only one of which is radioactive. Hence we talk about **radioactive isotopes** or **radioisotopes** rather than radioactive elements. Furthermore the radioactive emission comes from the nucleus of the isotope, so scientists talk about **unstable nuclei** (ones that are radioactive) and **stable nuclei** (not radioactive).

Before delving too far into radioactivity, let us recall and extend some of our basic knowledge about atomic structure (from pp. 40–2 and p. 131 CCPC).

3.2 ISOTOPES AND SYMBOLS FOR THEM

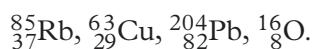
On p. 131 *CCPC* it was explained that **isotopes** are atoms of the one element that differ by having different numbers of neutrons in their nuclei. On p. 42 *CCPC* **atomic number**, Z , of an atom was defined as the number of protons in the nucleus of an atom of the element. **Mass number**, A , was defined as the number of protons plus neutrons in the nucleus of the species concerned.

Isotopes of the one element, then, have the same atomic number but different mass numbers. For example, the stable isotope of rubidium has an atomic number of 37 (37 protons) and a mass number of 85 (37 protons plus 48 neutrons); the radioactive isotope has an atomic number of 37 (otherwise it would not be rubidium) and a mass number of 87 (37 protons plus 50 neutrons).

Isotopes are generally named by their mass number. We talk about rubidium-85 and rubidium-87 or chlorine-35 and chlorine-37. In addition we often use a special symbol for isotopes:

$$_Z^A \mathbf{M}$$

where M is the chemical symbol for the element, A is the mass number and Z is the atomic number. Some examples are



3.3 STABLE AND UNSTABLE ISOTOPES

If we plot the number of neutrons against the number of protons in the nucleus for isotopes that are stable we find, as shown in Figure 3.1, all the points lie in a narrow band—the red shaded area. We say that they all lie in a **zone (or band) of stability**.

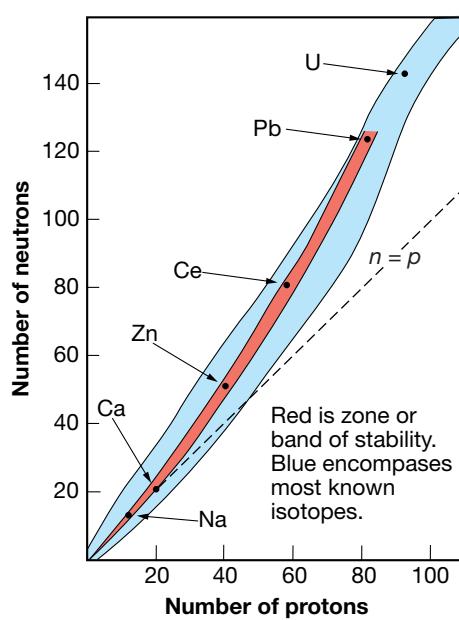


FIGURE 3.1
A graph of number of neutrons versus number of protons for all known isotopes (blue area): the red shaded area is the zone of stability

For light elements (Z less than 20) stable isotopes have a ratio of neutrons to protons of about 1.0. As atomic number increases, this stability ratio of neutrons to protons increases: at $Z = 50$ the ratio is about 1.3 and at $Z = 80$ it is about 1.5. Points for unstable nuclei lie outside this zone of stability. In addition we find that there are no stable isotopes with atomic numbers greater than 83 (bismuth).

In summary:

An isotope is unstable

- if its atomic number is greater than 83, or
- if its ratio of neutrons to protons places it outside the zone of stability of Figure 3.1.

In unstable nuclei the number of neutrons can be greater or less than the value that gives stability.

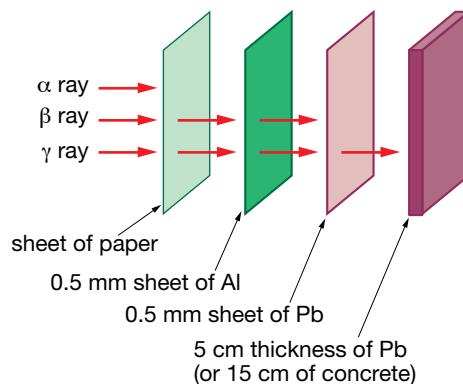
We have said that unstable nuclei undergo radioactive decay. Just what does this mean?

3.4 TYPES OF RADIATION EMITTED

It was found that the various radioactive substances could produce three different types of radiation which were originally called alpha (α), beta (β) and gamma (γ) rays because their true identities were unknown.

Alpha rays or particles were relatively heavy positively charged particles which had low penetrating power; a sheet of paper could stop them. **Beta rays or particles** were much lighter negatively charged particles with greater penetrating power; they could pass through a sheet of paper and even through 0.5 mm of aluminium but could not penetrate a 0.5 mm thickness of lead. **Gamma rays** were like X-rays in that they seemed to be genuine radiation rather than particles. They carried no charge and were extremely penetrating; they could be stopped only by several centimetres of lead or many centimetres of concrete. The relative penetrating power of α , β and γ rays is shown in Figure 3.2.

FIGURE 3.2
Relative penetrating power of α , β and γ rays



Eventually it was discovered that *alpha rays or alpha particles are helium nuclei* (2 protons and 2 neutrons stuck together), and that *beta particles (rays) are simply electrons*. *Gamma rays are a type of electromagnetic radiation* like radio waves, light and X-rays. Gamma rays have shorter wavelengths than the other forms of this radiation and therefore carry large amounts of energy. The properties of these particles are summarised in Table 3.1.

3.5 ALPHA-EMITTING RADIOISOTOPES

The common radioisotopes of uranium and radium are alpha emitters.



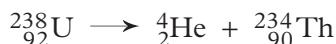
An important question is: what has happened to the uranium nucleus after it has lost a helium nucleus? The uranium nucleus originally contained 92 protons

TABLE 3.1 Types of radioactive emissions

Name	Symbols	Identity	Relative charge ^a	Relative mass ^b	Penetrating power
alpha	α , ${}_2^4\text{He}$	helium nucleus	+2	4	low
beta	β , ${}_{-1}^0e$	electron	-1	1/2000	moderate
gamma	γ	electromagnetic radiation	0	0	high

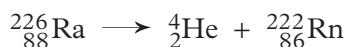
^a relative to the charge on a proton taken as +1^b on the relative atomic mass scale (pp. 130–2 CCPC)

and 146 neutrons. If it loses 2 protons and 2 neutrons, we have left a nucleus with 90 protons and 144 neutrons. Now, the number of protons determines what element it is (p. 41 CCPC). From the Periodic Table we see that 90 protons in the nucleus (i.e. atomic number 90) means that the substance is now thorium. At last then we have achieved the medieval alchemists' dream of transmuting one element into another! As uranium disintegrates (spits out a helium nucleus), it is transformed into thorium. Hence we can complete our **nuclear equation** by writing:



In these nuclear equations we write the atomic number as a subscript on the left of the symbol and the mass number as a superscript, also on the left (Section 3.2). In such equations the atomic and mass numbers must balance, as they represent numbers of protons and neutrons. That is the reason we wrote thorium-234 above: there are several other isotopes of thorium but when uranium-238 disintegrates it can only form thorium-234 because the mass numbers must balance.

Similarly for alpha emission from radium: it will form a nucleus with $88 - 2 = 86$ protons. From the Periodic Table, this is radon, Rn. The particular isotope formed is the one with mass number $226 - 4 = 222$.



This type of radioactive disintegration, alpha emission, is shown in Figure 3.3(a).

Radioisotopes that emit alpha particles often emit gamma rays as well. These gamma rays carry away the excess energy from the reaction. Most of the heavy elements have alpha-emitting radioisotopes—thorium, radon, polonium, plutonium.

3.6 BETA-EMITTING RADIOISOTOPES

Just as alpha particles come from the nucleus in radioactive decay, so too do beta particles (electrons) come from the nucleus and *not* from the electron cloud surrounding the nucleus. It at first seems puzzling that a nucleus which contains only protons and neutrons can emit electrons! However this happens because a neutron 'decomposes' into a proton and an electron:



Putting the atomic and mass numbers on the symbols we have:

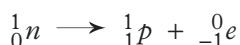
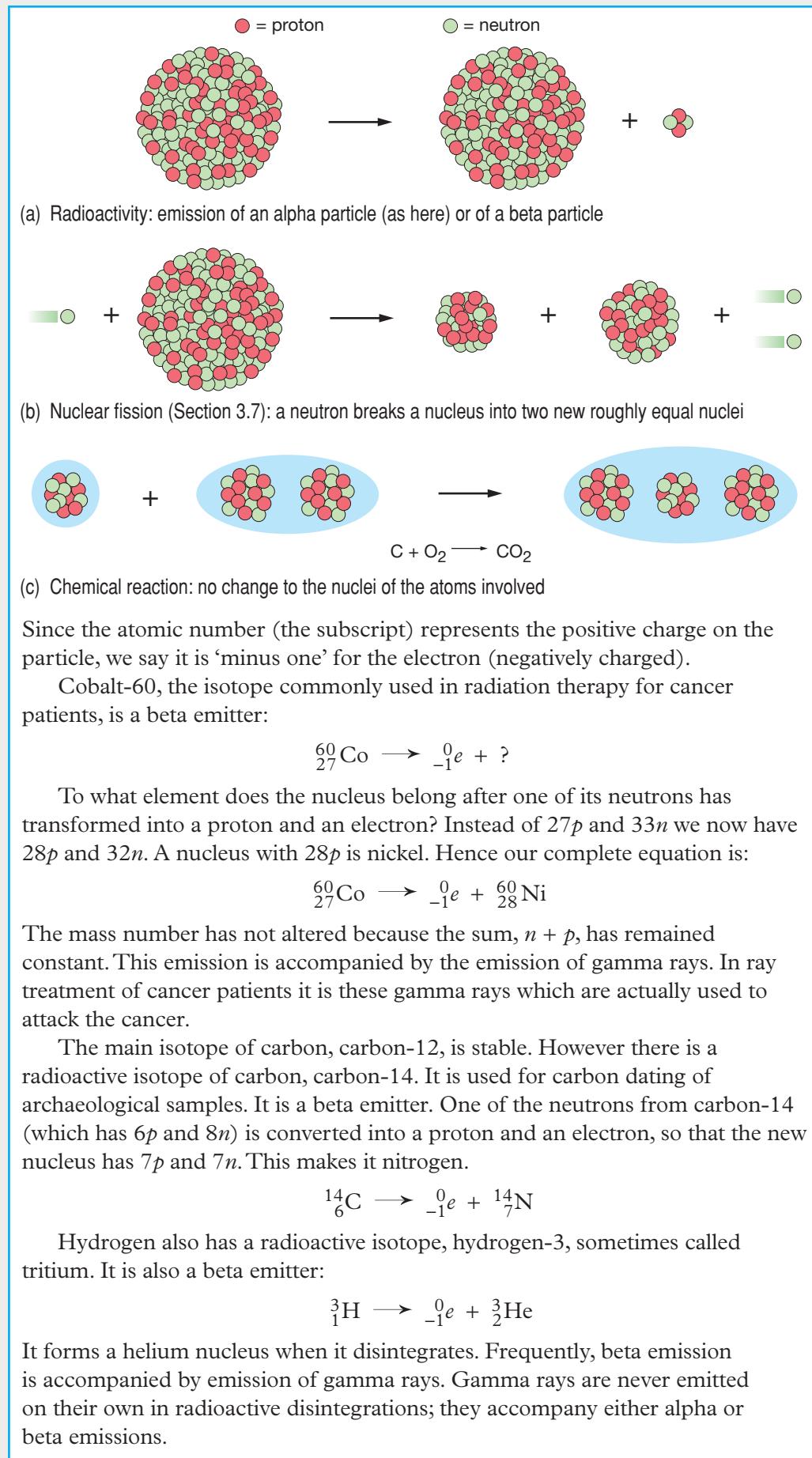


FIGURE 3.3

The difference between nuclear reactions (a) and (b) and a chemical reaction (c). The electron clouds are not shown in the nuclear reactions



FOR INVESTIGATION[†]

Alpha and beta emissions are the only two decay processes for *natural* radioactive nuclei. Some artificial radioactive isotopes decay by positron emission and electron capture. Search out what these two processes are, including the ultimate fate of the positron.



† not required for NSW HSC

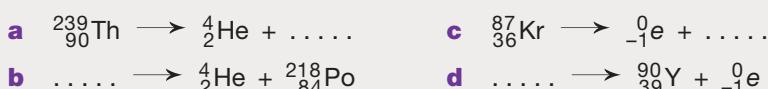
A reaction in which a change occurs to the nucleus of an atom is called a **nuclear reaction**.

Alpha and beta emissions are nuclear reactions. In ordinary *chemical reactions* there are no changes to the nuclei of the atoms involved, just rearrangement of ions or of electrons (for example, as in precipitation and redox reactions). This is illustrated in Figure 3.3.

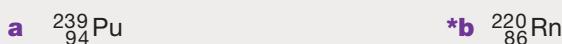
Exercises

- 1 Write the symbol of the type A_ZM for each of the following isotopes:
- a C (6 protons, 6 neutrons)
 - b S (16 protons, 16 neutrons)
 - c Cl (17 protons, 20 neutrons)
 - d iodine-127 (53 protons)
 - *e zinc (30 electrons, mass number 65)
 - *f radium-226 (88 electrons)

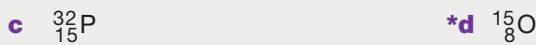
- 2 Complete the following equations for radioactive disintegrations:



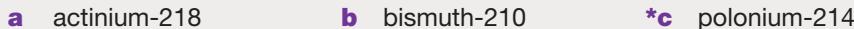
- 3 Write equations for radioactive disintegration of the α -emitters:



and of the β -emitters:



- 4 Use a Periodic Table to decide what element is formed when each of the following undergoes α -decay.



What element is formed when each of the following undergoes β -decay?



- 5 How do you expect alpha, beta and gamma particles to be affected by an electric field? Draw a diagram.

- 6 How does (a) a beta emission and (b) an alpha emission affect the neutrons to protons ratio in a nucleus? Explain, using a specific example for each.

- 7 By comparing each of the following isotopes with data for the element in the Periodic Table, decide whether you would expect it to be stable or not. Give your reason. Which, if any, would you expect to be beta emitters?

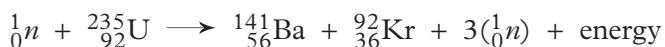


3.7 NUCLEAR FISSION AND NUCLEAR REACTORS

Radioactive disintegration is one type of nuclear reaction: it involves the splitting off of a small fragment (alpha or beta particle) from certain nuclei. Another type of nuclear reaction is nuclear fission.

Nuclear fission is the process in which neutrons bombard atoms and cause them to split into two roughly equal fragments. Nuclear fission is sometimes referred to as *splitting the atom*. It is illustrated in Figure 3.3(b).

Uranium-235 provides the commonest example of nuclear fission:



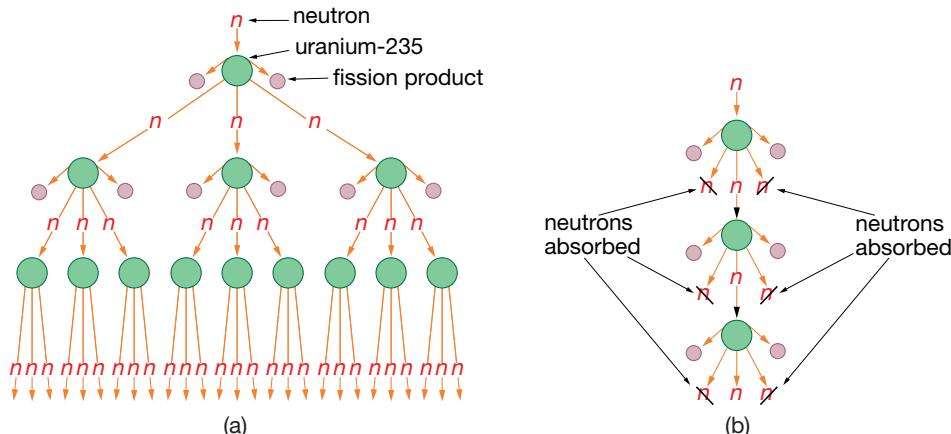
Nuclear fission is the basis of both atomic bombs and nuclear power stations. The amount of energy released per gram of uranium is enormous—far, far greater than is released in normal chemical reactions such as burning a gram of coal or petrol.

If all of the neutrons formed in the above fission reactions are allowed to hit further uranium atoms, the number of neutrons builds up rapidly so that the rate of energy release accelerates dramatically and an enormous explosion results: this is an *atomic bomb*. It is illustrated in part (a) of Figure 3.4.

However if all but one of the neutrons released is absorbed by some other material, so that only this one neutron is allowed to carry on the reaction, then we get a steady and controlled rate of reaction. This constitutes a *nuclear reactor* and is shown in part (b) of Figure 3.4.

FIGURE 3.4

Nuclear reactions: (a) as in atomic bombs where all neutrons released can initiate further fission reactions, (b) as in nuclear reactors where all but one of the emitted neutrons are captured so that a steady reaction proceeds

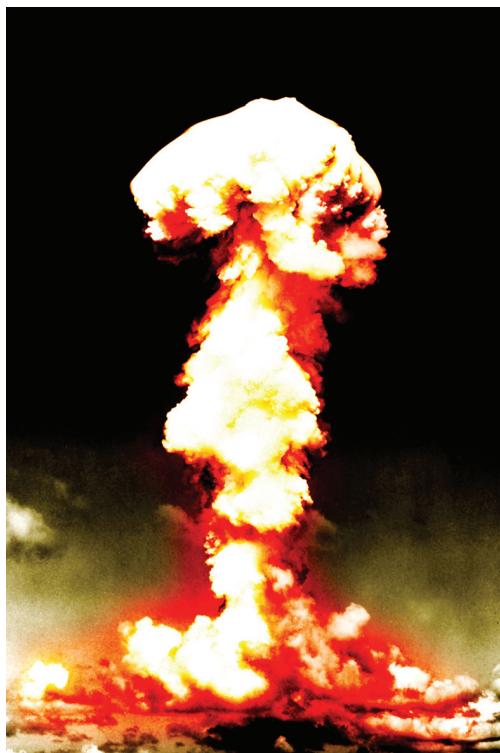


A **nuclear reactor** is a structure in which controlled nuclear fission occurs. It can be used to generate electricity (as done in many countries such as several European ones, Japan and the USA) or to produce radioactive isotopes for medical and industrial uses (so used in most countries including Australia).

Nuclear reactors have produced several new elements and can be used to make new isotopes of naturally occurring elements.

3.8 TRANSURANIC ELEMENTS

Some isotopes such as ${}^{235}\text{U}$ when hit by neutrons undergo fission. Others however undergo nuclear reactions that produce new elements. For example



LEFT An atomic bomb blast

ABOVE The nuclear power station and reprocessing plant at Sellafield in the UK

^{238}U is not **fissionable** (or not **fissile**), meaning that it does not split when hit by a neutron. Instead it forms a new element neptunium, Np:



Neptunium rapidly decays to plutonium Pu which is much more stable:



Neither neptunium nor plutonium exist in nature. They are artificial elements which are made in nuclear reactors.

Most of the new elements that have been made have atomic numbers greater than that of uranium (92) which has the largest value of the naturally occurring elements. These artificial elements with atomic numbers greater than 92 are called **transuranic elements**. One transuranic element is americium, the isotope that is used in domestic smoke alarms. It is made by bombarding plutonium with neutrons:



Scientists have been able to produce about 23 transuranic elements with atomic numbers up to 118. The first few were made by bombardment of other nuclei with neutrons in nuclear reactors as just described. Later ones were made by bombarding heavy nuclei with high speed positive particles such as helium or carbon nuclei; for example californium was made by bombarding uranium-238 with carbon:

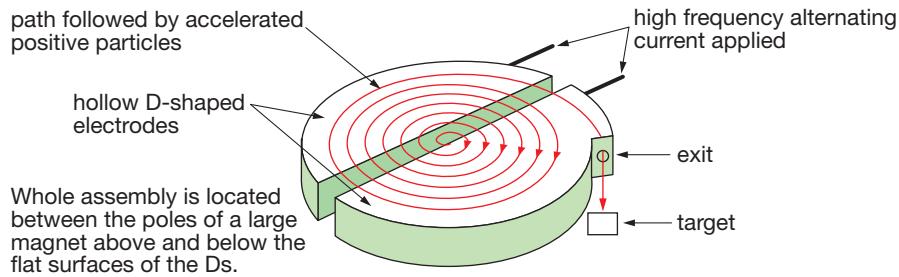


High speed positive particles are produced in machines called *linear accelerators* and *cyclotrons*.

In a **linear accelerator** positive particles are accelerated in a straight line along the axes of a series of cylinders made alternatively positive and negative so the particles are always being pushed from behind by a positive cylinder and pulled from in front by a negative one. This means that linear accelerators are often more than a kilometre in length.

Cyclotrons also accelerate positive particles by passing them through alternating positive and negative fields, but they use in addition a strong magnetic field to constrain the particles to a spiral path as shown in Figure 3.5. This makes the machine more compact. There are cyclotrons in major hospitals in Sydney, Melbourne and Brisbane; they are used to produce short-lived isotopes for medical diagnosis (Section 3.12 and Table 3.3).

FIGURE 3.5
Basic design of a cyclotron



The first of the transuranic elements were made in the 1940s (in nuclear reactors) with others (up to 105) being made, often from high speed positive particles, in the 1950s and '60s. Element 106 was made in 1974 almost simultaneously by Russian and US teams of scientists. Elements 107, 108 and 109 were made in the 1980s, 110 and 111 in 1994, 112 in 1996 and 114, 116 and 118 in 1999.



WEBSITE

<http://www.webelements.com>

(for information on transuranic elements including how each was made, just click on the required element in the Periodic Table)



Exercises

- 8** When uranium-235 undergoes fission, some groups of products which are formed (in addition to those mentioned in Section 3.7) are:
- cerium-144, selenium and 4 neutrons ($4n$)
 - ruthenium-112, cadmium and $3n$
 - iodine-131, yttrium and $2n$
 - molybdenum-99, tin and $4n$.

Write balanced nuclear equations for these fission reactions.

- 9** Some transuranic elements can be made as follows:
- curium-242, by bombarding plutonium-239 with helium nuclei
 - californium-245, by bombarding curium-242 with alpha particles: a neutron is emitted
 - seaborgium-263, Sg, by bombarding californium-249 with oxygen nuclei: several neutrons are released in the process.

Write nuclear equations for these processes.

- 10** Chadwick discovered neutrons by bombarding beryllium with alpha particles. Write a nuclear equation for the reaction that occurred.
- 11** Suggest a reason for nuclei such as helium and carbon having to be accelerated to high speeds to bring about nuclear transformations whereas neutrons do not need to be so accelerated.

3.9 HALF-LIFE[†]

An important property of radioisotopes is their stability, or in other words how long they survive before completely decaying to other isotopes. This is measured by what is called their *half-life*.

Radioisotopes differ greatly in the rate at which they disintegrate. Some, such as sodium-24, will completely disintegrate in a few days, while others, like cobalt-60, take many years. Others, like plutonium-239 (a by-product of nuclear reactors), take tens of thousands of years. Some such as uranium-238 and 235 take billions of years. We use the term ‘half-life’ to characterise the rate at which radioisotopes disintegrate.

The **half-life** of a radioisotope is the time required for half the atoms in a given sample to undergo radioactive decay; for any particular radioisotope, the half-life is independent of the initial amount of the isotope present.

The half-life of iodine-131 is 8 days. If we start with 1 g of iodine-131, then after 8 days we will have only 0.5 g left (the other half gram will have decayed into xenon). After a further 8 days, half of this 0.5 g will have decayed, leaving us with only 0.25 g. After a further 8 days, the amount of iodine-131 left will be 0.125 g. After a total of 40 days (five half-lives), of our original 1 g, there will be only 0.031 g left.

The half-lives of some common isotopes are given in Table 3.2.

TABLE 3.2 Common isotopes, the radiation they emit and their half-lives^a

Name	Radiation emitted	Half-life
*carbon-14	β	5.7×10^3 years
fluorine-20	β, γ	11 seconds
*hydrogen-3 (tritium)	β	12.3 years
molybdenum-99	β, γ	2.7 days
phosphorus-32	β	14 days
*plutonium-239	α, γ	2.4×10^4 years
*potassium-40	β	1.3×10^9 years
*radium-226	α, γ	1.6×10^3 years
sodium-24	β, γ	15 hours
strontium-90	β	28 years
sulfur-35	β	87 days
*uranium-238	α, γ	4.5×10^9 years

* denotes a naturally occurring isotope

a Other isotopes are listed in Table 3.3

[†] Half-life is not mentioned in the NSW HSC syllabus, but it is hard to appreciate why different isotopes are used for different purposes (Section 3.12 and Table 3.3) without some understanding of the term: hence its inclusion here.

3.10 PREPARATION OF COMMERCIALLY USEFUL ISOTOPES

There are only about 50 naturally occurring radioactive isotopes. However about 2000 radioisotopes have been created, mostly in the normal operation of nuclear reactors. Most synthetic radioisotopes have quite short half-lives (hours to seconds) and are either annoying by-products that have to be managed or just laboratory curiosities. However, about twenty radioisotopes have found widespread use in medicine and industry. There are two common methods for producing radioisotopes: (1) from nuclear reactors and (2) in cyclotrons.

Radioisotopes from nuclear reactors

Nuclear reactors are convenient sources of neutrons (Section 3.8), and so are used to make radioisotopes that can be prepared by neutron bombardment. Suitable target nuclei are placed in the reactor core where they are bombarded by neutrons to produce the required isotope. For example cobalt-60, which is used for cancer treatment, is made by placing normal cobalt-59 in a reactor where it captures a neutron.

Sometimes the required isotope is a direct product of uranium fission as in the case of the precursor of technetium-99*m*.

Technetium-99*m*

Technetium-99*m*[†] is widely used in medicine for diagnosis. Its half-life is only 6 hours. Consequently it has to be produced at the hospital needing it rather than transported from a nuclear reactor. Technetium-99*m* is formed by the radioactive decay of molybdenum-99 which is a fission product of uranium-235. Molybdenum-99 has a half-life of 66 hours: this is long enough for it to be transported from the Lucas Heights reactor (south of Sydney) to all major hospitals in Australia.

Molybdenum-99 is prepared by placing special pellets of UO₂ in the reactor core for about a week. The UO₂ contains about 2% ²³⁵U: some of this undergoes fission to ⁹⁹Mo. This molybdenum is extracted, adsorbed onto alumina and packaged into small glass tubes about the size of a person's thumb for despatch to hospitals. ⁹⁹Mo decays to ^{99m}Tc continuously. At the hospital ^{99m}Tc is extracted from the alumina by flowing normal saline solution through it. The ^{99m}Tc is then chemically bound to biologically significant molecules for the diagnostic test to be performed.

The ⁹⁹Mo parent or 'cow' is eluted or 'milked' every day for about a week by which time its activity has become too low for practical use.

Figure 3.6 shows a technetium-99*m* generator.

Radioisotopes from cyclotrons

Some radioisotopes for medical use have to be prepared in a cyclotron (Fig. 3.5). That means they are prepared by bombarding a suitable target nucleus with a small positive particle such as a helium or carbon nucleus. Fluorine-18 is

[†] The *m* denotes that it is an unstable form of the isotope which decays to a more stable form. It is this unstable form that is used in medical diagnosis.

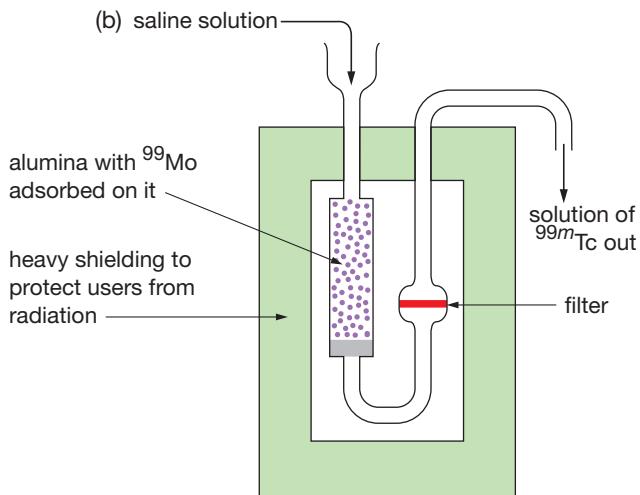


FIGURE 3.6
 (a) A technetium-99m generator: it is heavily shielded to protect users from the radiation emitted by the molybdenum-99 it contains. (b) shows schematically how the technetium-99m is eluted without removing the molybdenum source from its shielded container

prepared by bombarding nitrogen with helium nuclei:



Iodine-123 is also prepared in a cyclotron.

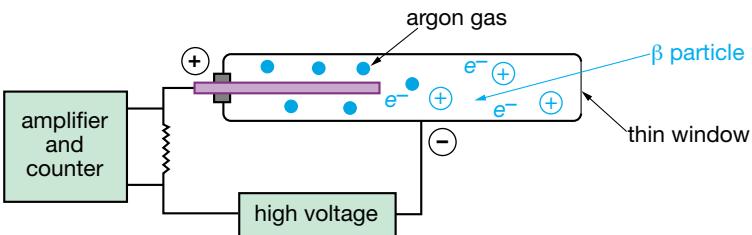
Some commercial radioisotopes and their uses are listed in Table 3.3.

3.11 DETECTION OF RADIATION

Emissions from radioisotopes can be detected and measured by the following devices:

- 1 **Photographic film.** Darkening of such film was the way radioactivity was first detected. The method is still used today in some *radiation badges* worn by laboratory workers handling radioactive substances; the amount of darkening of the film is a measure of the amount of radiation that the worker has received.
- 2 **Cloud chamber.** This is an instrument which contains a supersaturated vapour of water or alcohol. When radiation passes through it, it ionises some of the air; the ions formed act as nuclei upon which droplets of liquid form. In this way the path of the radiation is made visible. Alpha particles form straight dense tracks; beta particles form less dense zig-zag tracks while gamma rays generate even fainter tracks.
- 3 **Geiger-Müller counter.** This device also uses ionising properties of radiation. It is particularly good for measuring beta particles, though it can be made to work for alpha and gamma rays too. The beta ray enters through the thin end window of the Geiger tube, Figure 3.7, hits a gas molecule (generally argon) and ionises it by knocking an electron out of it. The high voltage accelerates this electron towards the central electrode and as it gains speed (energy) it ionises more argon atoms in its path, so that there is a cascade of electrons reaching that electrode. This constitutes an electrical pulse which is amplified and measured either by generating clicks in an audio amplifier or by operating an electronic digital counter. The positive argon ions move more slowly towards the negative case to complete the circuit.
- 4 **Scintillation counter.** This instrument uses the fact that when certain substances are irradiated with alpha, beta or gamma rays (different substances for each type of radiation), they emit a flash of light which can be

FIGURE 3.7
A Geiger-Müller counter



collected and amplified in a photomultiplier. The electrical signal generated then operates an electronic counter.

3.12 USES OF RADIOISOTOPES

Radioisotopes are widely used in medicine and industry.

Medical uses

1 Cancer treatment. One method of treating cancer is to irradiate the affected areas of the body with gamma rays which kill cancer cells (along with some 'good' cells as well). As mentioned in Section 3.6 the common source for this radiation therapy is cobalt-60. This isotope is made by neutron bombardment of normal cobalt-59; it disintegrates by beta emission to form nickel-60: it is the gamma rays that accompany this beta emission that attack the cancer because they are able to penetrate quite deeply into body tissue.

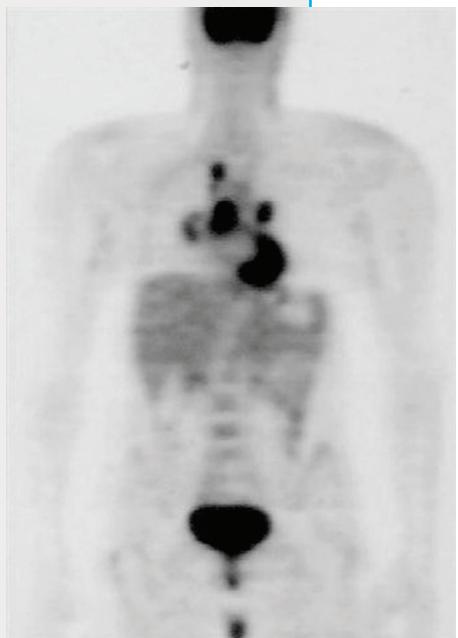
Cobalt-60 is used because the gamma rays carry a suitable amount of energy to destroy certain biological molecules, and because cobalt-60 has a suitable half-life: it is sufficiently long for the radiation source to have a reasonable lifetime in the equipment (about 4 to 6 years) but short enough for the source to emit a reasonable intensity of radiation.

A more recent development in cancer treatment is *in situ* radiation in which a radioactive source, often iridium-192, encased in a thin sealed container is surgically implanted beside the affected organ for a period of time; this technique concentrates the radiation on the cancer and minimises damage to other tissue.

2 Diagnosis. Several radioisotopes are used for medical diagnosis. A widely used one is technetium- $99m$ (Table 3.3). If incorporated into some blood serum and injected into a patient's bloodstream, its distribution throughout the body can be measured with a scintillation counter and used to detect blood clots, constrictions and other circulation disorders. In a different form it can be taken up by heart tissue and so used to assess damage after a heart attack. It can also be used to detect brain tumours.

A property of technetium- $99m$ which makes it particularly suitable for medical diagnosis is its short half-life of 6 hours: it rapidly decays and so causes minimal damage to the patient.

Technetium- $99m$ is also used to diagnose thyroid abnormalities. One method of treating over-active thyroid glands is to have the patient ingest some iodine-131 which accumulates in the gland and being a beta emitter irradiates and so destroys some of the gland.



Positron emission tomography (PET) using ^{18}F bonded to glucose can be used for the early detection of secondary cancers (black spots) after removal of a melanoma (skin cancer)

TABLE 3.3 Some radioisotopes produced by the Australian Nuclear Science and Technology Organisation (ANSTO)^a

Radioisotope	Radiation emitted	Half-life	Uses
technetium-99m	γ	6 h	medical diagnosis for heart, bone, lung, brain, thyroid, blood flow
iodine-131	β, γ	8 d	treatment of diseases of the thyroid
iridium-192	β, γ	74 d	used as an internal radiotherapy source
fluorine-18	$\beta^+ b$	1.8 h	positron emission tomography (PET) to study brain function and to diagnose epilepsy, heart diseases and certain types of cancer
iodine-123	E.C. ^b , γ	13.2 h	diagnosis of thyroid diseases and some cancers
cobalt-60	β, γ	5.3 y	gamma radiation for cancer treatment
caesium-137	β, γ	30 y	thickness gauges in industry radiography of machinery and welds irradiation of food (not in Australia—yet)
americium-241 ^c	α	432 y	smoke detectors
gold-198	β, γ	2.7 d	radio-tracer to follow movements of sewage and other wastes through waterways movement of sand in river beds and ocean floors (erosion)
zinc-65 and manganese-54 (produced together)	$\beta^+ b$ E.C. ^b	244 d 312 d	follow heavy metals in waste water from mining

a ^{18}F and ^{123}I are produced at the National Medical Cyclotron near Royal Prince Alfred Hospital, Sydney; the others are made at the Lucas Heights reactor by placing suitable substances in the reactor core.

b β^+ is positron emission; E.C. is electron capture. See For Investigation in Section 3.6.

c distributed but not made by ANSTO

Industrial uses

- 1 Thickness gauges.** A radioactive source and a detector arranged as in Figure 3.8 can be used to monitor and control the thickness of materials such as steel sheets, paper, aluminium foil and plastic film in factories. With fixed geometry for the source and detector and the same material passing between them, the amount of radiation received by the detector depends upon the thickness of the material: thicker material absorbs more radiation and so the signal drops. This can be built into a feed-back loop to control the manufacturing process.

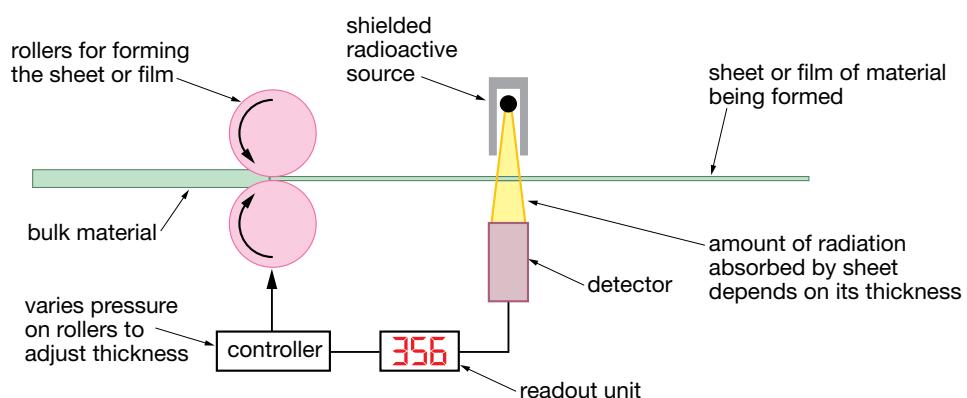


FIGURE 3.8
Thickness gauges using radioactive sources are widely used in industry to monitor and control the thickness of materials ranging from paper to plastics to steel

For this purpose an isotope with a fairly low energy emission but a long half-life is used—low energy because we want the thin film to be able to absorb a significant proportion of it, and long half-life so we do not have to replace the source too frequently. Low energy emissions also mean that safety precautions are minimal. Strontium-90 (half-life 28 years), caesium-137 (half-life 30 years) and cobalt-60 (half-life 5.3 years) are often used.



FOR INVESTIGATION

Select one use of a radioisotope in each of medicine and industry. Collect information on how the isotope is used and how its use relates to its properties. Find information to analyse the benefits of using the isotope for that purpose and to discuss problems (including safety and environmental consequences) associated with that use.

- 2 Leak detectors.** Leaks can be detected in water pipes or underground oil pipelines by adding a suitable radio tracer to the liquid and scanning along the pipe. No radiation will be detected from the isotope inside the pipe, but if the tracer leaks into the soil surrounding the pipe it can be detected and the leak located. For this use a short-lived isotope is needed, so that after the leak has been found the radioactivity quickly decays, the water or oil becomes safe to use again and the environment is quickly decontaminated. Sodium-24 with a half-life of 15 hours is widely used.
- 3 Irradiation of medical supplies and food.** Because gamma radiation is particularly effective in destroying large biological molecules such as DNA, it has been widely (and successfully) used for several decades to kill bacteria and so sterilise medical supplies such as dressings and bandages. In more recent years there have been moves to irradiate food in order to destroy micro-organisms and so minimise spoilage and extend shelf life. Many countries have approved irradiation of specified foods: Australia (as at early 2005) has approved the irradiation of only herbs, spices and certain herbal infusions (but not tea).

Arguments in favour of irradiating food are that by destroying bacteria and moulds it makes food safer and it keeps food ‘fresher’ for longer and so reduces wastage. Arguments against are that it does not necessarily kill all dangerous organisms, it destroys some of the vitamin content of the food, it may lead to the formation of harmful compounds in the food, and it can lead to laxity with food hygiene standards.

Food irradiation requires gamma rays of sufficient energy to destroy bacteria but not enough energy to make the food radioactive (carbon-12 and oxygen-16 are easily converted to radioactive isotopes), and the source must have a reasonably long half-life (to minimise replacement). Caesium-137 and cobalt-60 are widely used.

Domestic smoke alarms[†]

Simple domestic smoke alarms contain a small source of alpha particles (often americium-241). These alpha particles ionise air, the ions are collected by an

[†] not required for the NSW HSC

electrode and the resulting electrical current measured. When smoke (small solid particles) is present in the air, it prevents ions reaching the electrode causing a reduction in the electrical current which triggers an alarm.

WEBSITES

<http://www.ansto.gov.au>

(a variety of information about many aspects of nuclear science. For information about industrial and medical uses move your mouse over *Publications and media* to highlight it, click on *Brochures, fact sheets and links*, then scroll down either to *Brochures* (and click on *Medical and Industrial Isotopes (PDF)(html)*) or to *Information* (and click on *Nuclear Medicine (html)*). You can get to this latter site directly from www.ansto.gov.au/info/reports/radboyd.html.)

<http://www.uic.com.au/nip26.htm>

(nuclear medicine)

<http://www.uic.com.au/nip27.htm>

(industrial uses)

<http://education.jlab.org/glossary/cyclotron.html>

(simple account of a cyclotron)



3.13 BENEFITS AND PROBLEMS

There are both benefits and problems associated with the use of radioisotopes in industry and medicine.

The *benefits for industry* include the ability to make monitoring equipment that is more sensitive, precise and reliable than earlier equipment, to do things more efficiently and reliably (such as sterilisation of medical supplies) and to do things that were not otherwise possible (such as examine buildings and machinery for weld and structural faults).

The *benefits for medicine* are that radioisotopes have opened up a wide range of non-invasive diagnostic procedures that otherwise would not be possible (on organs such as heart, brain, kidney, thyroid) and have allowed the introduction of radiation therapy for treating many forms of cancer; in many cases this has proved the most effective treatment.

Problems

The problems with using radioisotopes are the same for industry and medicine. They arise from the fact that *radiation from radioisotopes is harmful to people* (and all other life forms). Alpha, beta and gamma radiation from radioactive substances can cause undesirable reactions in living tissue and so upset the delicate balance that exists among the numerous complex chemical reactions that are always occurring in living cells. Such radiation can cause:

- *tissue damage* (which is immediate and can show up as skin burns and/or nausea, if exposure is mild, or as radiation sickness that can lead to death if exposure is high)

A simple domestic smoke alarm that uses americium-241

- *cancer* (particular leukaemia and lung cancer) which generally does not show up until ten to twenty years after exposure, and
- *genetic damage* which leads to deformities in offspring.

To avoid the harmful effects of radiation people working with radioisotopes must observe a set of stringent safety precautions.

Safety precautions

The following are some of the safety precautions that must be observed when handling radioactive materials:

- 1 Radioactive materials must always be stored in well-shielded containers.
- 2 Equipment that uses radioactive materials must be designed to ensure that radiation is directed only where it is required and that there is no stray radiation escaping from it.
- 3 People using such equipment or materials must be well trained to handle such things in a safe manner.
- 4 Such people must always wear appropriate safety clothing which depending on the radioisotope in use may vary from gloves and face mask to specially laundered laboratory coats and overshoes, lead-lined aprons and, in the extreme, full protective body suits.
- 5 People working in and around radiation facilities must wear radiation monitors (badges) that record the cumulative amount of radiation they have received.
- 6 Proper procedures for safe storage and disposal of radioactive wastes must be established along with stringent accounting of quantities received and despatched.
- 7 Clear and unambiguous signs must be displayed in any location where radiation equipment or materials are being used or stored.

This is the international radiation hazard sign.
It must be displayed in any location where radioisotopes are used.



Exercises

- 12 After some nuclear testing in the Pacific Ocean, certain North Queensland pastures (and consequently the milk of cattle which grazed on them) became contaminated with iodine-131. If the levels of activity were 64 times greater than was acceptable, how long did the dairy farmers have to wait before they could safely market their milk again? The half-life of iodine-131 is 8 days.
- 13 After reprocessing a nuclear fuel, scientists had samples of two radioactive isotopes to look after. Isotope A had an activity of 1000 disintegrations per second (dps) and a half-life of 30 s. Isotope B had an activity of 10 dps and a half-life of 1500 years. An activity of 1 dps was considered safe. Which isotope would present the greater problem for long-term storage? Explain.

- 14** Why is it necessary to produce technetium-99*m* at or close to the hospital using it?
- 15** When using a Geiger–Müller counter, why is it necessary to maintain a fixed geometrical arrangement between sample and detector in order for measurements to be comparable?
- 16** Write nuclear equations for:
- the conversion of cobalt-59 to cobalt-60 by neutron bombardment
 - the decay of cobalt-60 by beta ray emission
 - the fission of a uranium-235 nucleus into a molybdenum-99 nucleus and another nucleus and three neutrons
- 17** Why is iodine-123 preferred over iodine-131 for diagnosis of possible problems with the thyroid gland whereas iodine-131 is preferred for irradiation of an overactive thyroid?

Important new terms

You should know the meaning of the following terms:

alpha rays (particles) (p. 76)
atomic number[†] (p. 75)
band of stability (p. 75)
beta rays (particles) (p. 76)
cloud chamber (p. 85)
cyclotrons (p. 82)
fissile (fissionable) (p. 81)
gamma rays (p. 76)
Geiger–Müller counter (p. 85)
half-life (p. 83)
isotope (p. 75)

linear accelerator (p. 82)
mass number[†] (p. 75)
nuclear equation (p. 77)
nuclear fission (p. 80)
nuclear reaction (p. 79)
nuclear reactor (p. 80)
radioactive isotopes (p. 74)
radioactivity (p. 74)
radioisotope (p. 74)
scintillation counter (p. 86)
stable nuclei (p. 74)
transuranic elements (p. 81)
unstable nuclei (p. 74)
zone of stability (p. 75)

Test yourself

- Explain the meaning of each of the items in the ‘Important new terms’ section above.
- Give the isotopic symbol for the chlorine isotope that has 17 protons and 20 neutrons in its nucleus.
- Explain how you can predict whether a particular isotope is likely to be stable or radioactive.
- Describe the nature and relative penetrating powers of alpha, beta and gamma particles (rays).
- Why do we talk of radioisotopes and not just radioactive elements?
- Write nuclear equations for the emission of α -particles from $^{235}_{92}\text{U}$ and $^{226}_{88}\text{Ra}$.
- How does a nucleus which contains only protons and neutrons emit an electron?

CHAPTER
3

[†] These terms were introduced in CCPC but are listed here because it is important that you know their meanings.

- 8** Write nuclear equations for the emission of a β -particle from $^{60}_{27}\text{Co}$ and $^{14}_{6}\text{C}$.
- 9** Explain what is meant by nuclear fission. Give at least one equation to illustrate it.
- 10** What is the essential difference between a nuclear reactor for generating electricity and an atomic bomb?
- 11** Describe two methods for preparing transuranic elements.
- 12** List four practical applications of radioisotopes, two medical and two industrial.
- 13** What properties of particular isotopes make them suited to each of the uses you listed in Question 12?

EXTENDED RESPONSE EXAM-STYLE QUESTIONS FOR MODULE 1

MODULE
1

Questions in this section are in a similar style to that currently being used in the extended response questions in the New South Wales HSC Chemistry examination: they use the HSC list of verbs (such as **account** for, **analyse**, **assess**, **compare**, **contrast**, **demonstrate**, **describe**, **discuss**, **evaluate**, **explain**, **identify**, **justify**, **outline**, **propose**, **summarise**) and relate closely to items in the syllabus document. They place heavy emphasis upon recall of learnt information. Practice is the best way of developing skill in answering this type of exam question.

The actual HSC exam will be a mixture of this type of question and ones similar to the problem-solving exercises located within the chapters of Conquering Chemistry. The Revision Tests that follow these sets of questions at the end of the modules are similar mixes.

Marks (shown at the right-hand end of the question) are assigned to each question in order to indicate how much detail is required in your answer (that is, how much time you should spend on each question). The marks are on the HSC exam basis of 100 marks for three hours work (or 1.8 minutes per mark).

	MARKS
1 Outline the importance of the cracking of hydrocarbons to our industrialised society.	4
2 Demonstrate that displacement reactions are electron transfer reactions.	4
3 Distinguish between stable and unstable (radioactive) isotopes and outline the way scientists decide whether a particular isotope will be stable or not.	5
4 Outline the structure, sources and uses of cellulose and assess its potential as a source of chemicals that we currently obtain from oil.	7
5 Discuss the advantages and disadvantages of using ethanol as a fuel or fuel additive for motor cars.	5
6 Demonstrate the usefulness of radioisotopes in industry and in medicine.	5
7 Describe, with a diagram, a galvanic cell that you have set up in the laboratory and explain the flow of electrons and ions through it; identify its anode and cathode.	6
8 Compare and contrast the physical and chemical properties of alkanes and alkenes.	7
9 Assess the need for alternative sources of chemical compounds presently obtained from oil.	4
10 Compare and contrast the chemistry of either the vanadium redox cell or some other fuel cell with that of the lead–acid cell.	6
11 Outline the use of one radioisotope in medicine or industry and describe the properties that make it particularly suited for that use.	4
12 Explain, with an example, how oxidation states allow chemists to decide whether or not a reaction involves electron transfer.	3
13 Describe the method of production and uses of a biopolymer that has come into commercial use in only the last twenty years and evaluate its significance for society.	7

- | | |
|---|----------|
| 14 Describe an experiment you have performed to measure and compare the heats of combustion of three alkanols. List the major sources of error in your experiment and outline steps you took to minimise them. | 7 |
| 15 Use two specific examples to demonstrate how the use of a particular polymer for a particular purpose depends upon its properties which in turn depend upon its chemical structure. | 4 |
| 16 Demonstrate the importance of ethylene as an industrial chemical. | 4 |
| 17 Discuss the benefits and problems associated with the use of radioisotopes in medicine. | 5 |
| 18 Describe the chemical structure and uses of three addition polymers. | 6 |
| 19 Describe the structure and chemistry of the ordinary dry cell and assess its importance to society over the last hundred years or so. | 5 |
| 20 Evaluate the claim that ethanol is a renewable fuel. | 5 |

REVISION TEST FOR MODULE 1

MODULE
1

Total marks: 50 Suggested time: 90 minutes

Table 2.1 on p. 67 may be used if needed

MULTIPLE CHOICE QUESTIONS (1 mark each)

Select the alternative **a**, **b**, **c**, or **d** which best answers the question.

- 1 For the galvanic cell consisting of a zinc, zinc ion electrode connected by a salt bridge to a nickel, nickel ion electrode, the standard EMF (voltage) is:
a 0.50 V with the Ni positive **c** 1.02 V with the Ni positive
b 0.50 V with the Zn positive **d** 1.02 V with the Zn positive
- 2 The compound which could *not* be the monomer for making a polymer is:
a $\text{CH}_2=\text{CH}-\text{CN}$ **c** $\text{CF}_2=\text{CF}_2$
b $\text{CH}_3-\text{CH}_2-\text{COOH}$ **d** $\text{Cl}-\text{CH}=\text{CH}-\text{Cl}$
- 3 The property of beta particles that is used to detect them in a Geiger–Müller counter is:
a a flow of beta particles constitutes an electric current
b their great penetrating power
c they darken photographic plates
d they ionise argon gas at low pressure
- 4 The compound $\begin{array}{c} \text{H} \\ | \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ | \\ \text{Cl} \end{array}$ can be prepared by reacting:
a propene with chlorine
b propane with chlorine in the dark
c propene with hydrogen chloride
d 2-propanol with chlorine
- 5 The reaction that goes in the direction shown is:
a $2\text{Ag}(s) + \text{Sn}^{2+}(aq) \rightarrow 2\text{Ag}^+(aq) + \text{Sn}(s)$
b $\text{Pb}(s) + \text{Fe}^{2+}(aq) \rightarrow \text{Pb}^{2+}(aq) + \text{Fe}(s)$
c $\text{Mg}^{2+}(aq) + \text{Fe}(s) \rightarrow \text{Mg}(s) + \text{Fe}^{2+}(aq)$
d $\text{Fe}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Fe}^{2+}(aq) + \text{Cu}(s)$
- 6 In the following nuclear equation:
$${}_{86}^{222}\text{Rn} \rightarrow {}_2^4\text{He} + {}_y^z\text{X}$$

a $z = 218$ and $y = 88$ **c** $z = 226$ and $y = 84$
b $z = 218$ and $y = 84$ **d** $z = 226$ and $y = 86$
- 7 The heat of combustion of 2-propanol is 33.5 kJ/g. The enthalpy change for the combustion reaction is:
a $-1.54 \times 10^3 \text{ kJ/mol}$ **c** $-2.01 \times 10^3 \text{ kJ/mol}$
b $+2.01 \times 10^3 \text{ kJ/mol}$ **d** $+1.54 \times 10^3 \text{ kJ/mol}$

- 8** The substance that ethylene cannot easily be converted to is:
- a** ethylene glycol
 - c** propylene (propene)
 - b** ethanol
 - d** chloroethane
- 9** Some isotopes of lead and strontium are ^{206}Pb , ^{212}Pb , ^{214}Pb , ^{88}Sr , ^{90}Sr and ^{94}Sr . The *least* stable of these isotopes for each element are:
- a** ^{214}Pb and ^{94}Sr
 - c** ^{206}Pb and ^{88}Sr
 - b** ^{214}Pb and ^{90}Sr
 - d** ^{212}Pb and ^{94}Sr
- 10** Ethanol would be a good replacement for petrol as a liquid fuel for cars because:
- a** it is easily made from cellulose which is a major component of plant material
 - b** it can be used in current petrol engines after suitable modification to the engines
 - c** its formation by fermentation is a natural process which produces a concentrated solution from which pure ethanol is separated with little expenditure of energy
 - d** its large-scale production would cause far less environmental damage than does extraction and refining of crude oil

SHORT ANSWER AND EXTENDED RESPONSE QUESTIONS

The number of marks for each part of each question is shown at the right-hand end of the question. Marks allocated are based on the HSC scale of 1 mark per 1.8 minutes.

- | | MARKS |
|---|----------|
| 11 Demonstrate the difference between addition and condensation polymers. | 4 |
| 12 a The mass of ethanol that had to be burnt in air to heat 575 g of water from 18.6°C to 31.2°C was 1.65 g. The specific heat capacity of water is $4.2 \text{ J K}^{-1} \text{ g}^{-1}$. Calculate the molar heat of combustion of ethanol. | 2 |
| b The value obtained in (a) is much lower than tabulated values. Suggest two possible reasons for this. | 2 |
| 13 Describe an experiment you have performed to measure the voltage (EMF) of a cell made up of two metal, metal ion electrodes. On a diagram of your cell show the directions of electron and ion flows and label the anode and cathode. Suggest reasons why your measured voltage differed from that calculated from standard electrode potentials. | 6 |
| 14 a Industrial ethanol is generally made from ethylene. It is also possible to make ethylene from ethanol. Write equations for these two reactions and give the experimental conditions needed for each of them. Which catalyst, if any, is required for each reaction? | 2 |
| b To which general classes of reaction do the reactions in (a) belong? For one of these classes give another example <i>not</i> involving any of the reactants or products of the reactions in (a). | 2 |
| 15 Describe, with examples, how commercial radioisotopes are produced. | 4 |
| 16 a Two current or future concerns about the synthetic polymers in widespread use today are (i) uncertainty about future sources of raw | |

materials and (ii) disposal problems. Explain what these problems are and how they arise. **2**

- b** Discuss one recent development in polymer science that has potential for alleviating both of these concerns. Refer to at least one specific substance and include details of how it can be made. **4**
- 17** Outline the structure and operating principle of one instrument used to measure radiation from radioactive sources. **3**
- 18** Describe an experiment you have performed to distinguish between alkanes and alkenes. Include at least one chemical equation. **3**
- 19** Compare and contrast the chemistry, uses and environmental impacts of either the common dry cell or the lead–acid cell with one other commercial galvanic cell you have studied. **6**

MODULE 1 AND THE NEW SOUTH WALES HSC SYLLABUS

This section allows you to check that *Conquering Chemistry* has covered all necessary material for Module 1 of the New South Wales Higher School Certificate HSC Course.

Syllabus content

The following table lists (for Module 1) the items from the *students learn to* column of the HSC syllabus and shows where they are treated in *Conquering Chemistry (CCHSC)*.

Location of HSC Course material in *Conquering Chemistry* for Module 1

Syllabus reference	Sections where found in CCHSC
Students learn to	
9.2.1 Fossil fuels provide both energy and raw materials such as ethylene, for the production of other substances	
■ identify the industrial source of ethylene from the cracking of some of the fractions from the refining of petroleum	1.1
■ identify that ethylene, because of the high reactivity of its double bond, is readily transformed into many useful products	1.4, 1.5
■ identify that ethylene serves as a monomer from which polymers are made	1.6
■ identify polyethylene as an addition polymer and explain the meaning of this term	1.6
■ outline the steps in the production of polyethylene as an example of a commercially and industrially important polymer	1.6
■ identify the following as commercially significant monomers: – vinyl chloride – styrene by both their systematic and common names	1.8
■ describe the uses of the polymers made from the above monomers in terms of their properties	1.9, 1.10
9.2.2 Some scientists research the extraction of materials and energy from biomass to reduce our dependence on fossil fuels	
■ discuss the need for alternative sources of the compounds presently obtained from the petrochemical industry	1.11
■ explain what is meant by a condensation polymer	1.12
■ describe the reaction involved when a condensation polymer is formed	1.12
■ describe the structure of cellulose and identify it as an example of a condensation polymer found as a major component of biomass	1.12, 1.13
■ identify that cellulose contains the basic carbon-chain structures needed to build petrochemicals and discuss its potential as a raw material	1.13

Syllabus reference	Sections where found in CCHSC
Students learn to	
9.2.3 Other resources, such as ethanol, are readily available from renewable resources such as plants	
■ describe the dehydration of ethanol to ethylene and identify the need for a catalyst in this process and the catalyst used	1.16
■ describe the addition of water to ethylene resulting in the production of ethanol and identify the need for a catalyst in this process and the catalyst used	1.16
■ describe and account for the many uses of ethanol as a solvent for polar and non-polar substances	1.17
■ outline the use of ethanol as a fuel and explain why it can be called a renewable resource	1.19
■ describe conditions under which fermentation of sugars is promoted	1.18
■ summarise the chemistry of the fermentation process	1.18
■ define the molar heat of combustion of a compound and calculate the value for ethanol from first-hand data	1.20
■ assess the potential of ethanol as an alternative fuel and discuss the advantages and disadvantages of its use	1.19
■ identify the IUPAC nomenclature for straight-chained alkanols from C1 to C8	1.5
9.2.4 Oxidation-reduction reactions are increasingly important as a source of energy	
■ explain the displacement of metals from solution in terms of transfer of electrons	2.1
■ identify the relationship between displacement of metal ions in solution by other metals to the relative activity of metals	2.2
■ account for changes in the oxidation state of species in terms of their loss or gain of electrons	2.3
■ describe and explain galvanic cells in terms of oxidation-reduction reactions	2.4, 2.6
■ outline the construction of galvanic cells and trace the direction of electron flow	2.4, 2.6
■ define the terms anode, cathode, electrode and electrolyte to describe galvanic cells	2.5, 2.7
9.2.5 Nuclear chemistry provides a range of materials	
■ distinguish between stable and radioactive isotopes and describe the conditions under which a nucleus is unstable	3.1, 3.3
■ describe how transuranic elements are produced	3.7, 3.8
■ describe how commercial radioisotopes are produced	3.10
■ identify instruments and processes that can be used to detect radiation	3.11

Syllabus reference	Sections where found in CCHSC
Students learn to	
<ul style="list-style-type: none"> ■ identify one use of a named radioisotope: <ul style="list-style-type: none"> – in industry – in medicine ■ describe the way in which the above named radioisotope is used and explain its use in terms of its chemical properties 	3.12 3.12

Compulsory experiments

The table below lists the compulsory experiments (from the right-hand column of the syllabus), along with places where you can find procedures for these experiments (in *CCHSC BLM*) and the location of relevant information in *CCHSC*.

CCHSC is an abbreviation for this book *Conquering Chemistry HSC Course*.

CCHSC BLM is *Conquering Chemistry HSC Course Blackline Masters* by Debra Smith, McGraw-Hill, Sydney, 2003.

Information about compulsory experiments for Module 1

Experiment	Location in CCHSC BLM	Related material in CCHSC ^a
1 Plan and perform an experiment to compare the reactivities of alkenes and the corresponding alkanes with bromine water.	Module 1 Worksheet 2 (p. 6)	Section 1.4 Chapter 1 Exercise 14 Revision Test Question 18
2 Plan and perform an experiment to ferment glucose and monitor mass changes.	Module 1 Worksheet 7 (p. 21)	Section 1.18 Chapter 1 Exercise 36
3 Determine and compare the heats of combustion of three liquid alkanols.	Module 1 Worksheet 8 (p. 23)	Example 1 in Section 1.20 Chapter 1 Exercises 38, 39 Exam-style Question 14
4 Identify the simplest conditions under which a galvanic cell can be produced.	Module 1 Worksheet 9 (p. 25)	Sections 2.4 and 2.6 and Figure 2.11 may help.
5 Measure cell voltages (EMFs) for several galvanic cells made from metal, metal ion solution electrodes.	Module 1 Worksheet 11 (p. 31)	Revision Test Question 13
^a Exercises, Exam-style and Revision test questions are listed here, because their answers at the back of the book often contain helpful information.		

Other items in the student activity (right-hand) column

The table below lists (in abbreviated form) the non-experimental items in the student activity (right-hand) column of the syllabus and indicates where in *Conquering Chemistry* relevant information is located.

Location of material for other Module 1 activities

Syllabus item	Relevant material in CCHSC
9.2.1	<ul style="list-style-type: none"> ■ ... write equations to represent all chemical reactions encountered ... ■ Experiment 1 (see above) ■ analyse information ... to model the polymerisation process
9.2.2	<ul style="list-style-type: none"> ■ use available evidence ... development and use of a named biopolymer ...
9.2.3	<ul style="list-style-type: none"> ■ process information ... to model ... addition of water to ethylene ... dehydration of ethanol ■ process information ... industrial production of ethanol from sugar cane ■ process information ... use of ethanol as an alternative car fuel ... success of current usage ■ Experiment 2 (see above) ■ present information ... balanced equation for fermentation of glucose ... ■ Experiment 3 (see above)
9.2.4	<ul style="list-style-type: none"> ■ Experiment 4 (see above) ■ Experiment 5 (see above) ■ gather ... structure and chemistry of a dry cell or lead-acid cell and evaluate it ... in comparison to ... in terms of ... ■ solve problems ... to calculate the potential E^\ominus requirement of named electrochemical processes ...
9.2.5	<ul style="list-style-type: none"> ■ process information ... to describe recent discoveries of elements ■ use available evidence ... benefits and problems ... use of radioactive isotopes

Prescribed focus areas

The five prescribed focus areas of the syllabus are:

- 1** the history of chemistry
- 2** the nature and practice of chemistry
- 3** applications and uses of chemistry
- 4** implications for society and the environment
- 5** current issues, research and development.

As with most modules, the material of Module 1 (in this book and in the syllabus) relates strongly to focus areas 2 and 3. However there are many opportunities in Module 1 for involving areas 4 and 5.

For area 4, implications for society and the environment, there are:

- plastics with issues of resource depletion and environmental contamination
- ethanol as a fuel and its economic and environmental consequences
- environmentally safe disposal of commercial galvanic cells
- the environmental problems associated with the manufacture, use and disposal of the radioisotopes widely being used in industry and medicine.

For area 5, current issues, research and development, there are:

- the development of new biodegradable biopolymers
- current controversies over the addition of ethanol to petrol
- production of newer types of galvanic cells such as lithium batteries, vanadium redox cells and the Gratzel cell, and
- controversies about the nuclear reactor being built in Sydney's far-south suburbs (needed to produce some of the radioisotopes required by industry and medicine).

There is little scope in this module for discussing area 1, history of chemistry.