

Option C Energy

C1 Energy sources

C1.1 Energy transformations

Concentrated energy

Energy is the ability to do work. As energy is transferred from one form to another, some does useful work but some will always be lost as heat to the surroundings. The energy that is lost to the surroundings will now be less available to do work and is said to have been **degraded**.

Energy is always transferred in the direction in which it goes from a more concentrated form to a less concentrated (more dispersed) form.

The first law of thermodynamics simply states that energy is conserved – but if energy was transferred without any degradation we would have the basis of a perpetual motion machine because we could continuously transfer energy from one form to another without any losses to a less useful form. In the energy-transfer processes that we will study, some energy will always be lost to the surroundings as low-level heat – this energy is less useful in terms of its potential to do work.

Consider burning coal in a coal-fired power station. Chemical energy is converted to heat energy in a combustion reaction. Some of the heat energy released is dissipated to the surroundings and the rest goes to heat up water to make steam. Some of the kinetic energy of the water molecules in the steam is transferred to a turbine which turns a generator (kinetic energy to electrical energy). In these mechanical components there is friction between moving parts and so some of the energy is again converted to low-level heat energy in the surroundings. The steam then passes through a heat exchanger where it is condensed back to water, with the heat energy being dissipated to the surroundings.

Even the *useful* electrical energy we have obtained from the generator will eventually result in the production of heat – for example, when using some to power a kettle – which will spread out at a low level in the surroundings. When some coal is burned, all the energy released is eventually dispersed in the surroundings – and we cannot get this energy back!

The transfer of heat energy from a hot body to a colder one can be used to do useful work but once the thermal energy is spread out at a low level it is much more difficult to get this energy to do something useful. For instance, there is a lot more energy in a lake at 20 °C than there is in a lump of coal but the energy in the lump of coal is in a much more concentrated form and is therefore more useful. To be useful, the energy has to be in a **concentrated** form.

Learning objectives

- Understand how the quality of energy changes in energy transfer-processes
- Understand what is meant by efficiency and calculate the efficiency of an energy transfer

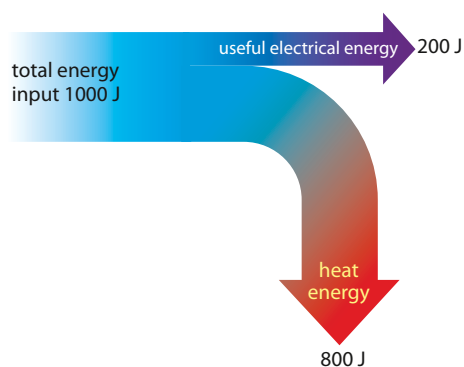


Figure C.1 A Sankey diagram for a solar panel with 20% efficiency.

Efficiency

When comparing energy transformations, it is often useful to know how the amount of useful energy we obtain from a particular transformation compares with the amount of energy put in – the concept of **efficiency** is useful here:

$$\text{efficiency (\%)} = \frac{\text{useful energy out}}{\text{total energy in}} \times 100$$

For instance, if 1000J of light energy from the Sun goes into a solar panel every second and the electrical energy obtained is 200J, then the efficiency of the process is given by:

$$\text{efficiency (\%)} = \frac{200}{1000} \times 100 = 20\%$$

Most of the rest of the energy is transformed into heat and this can be represented in a Sankey diagram (Figure C.1).

? Test yourself

1 Calculate the efficiency of each of the following energy transformations:

	Total energy input	Energy output
a	electric motor 500 J	kinetic energy 350 J heat energy 120 J sound energy 30 J
b	internal combustion engine 1000 J	kinetic energy 180 J heat energy 750 J sound energy 70 J

2 The total kinetic energy of the wind passing through a wind turbine in 1 s is 3000J. The electrical energy obtained per second is 1200J. Calculate the efficiency of the wind turbine.

Learning objectives

- Understand what the desirable characteristics of a useful energy source are
- Understand the difference between renewable and non-renewable energy sources
- Describe the uses of different energy sources
- Discuss the advantages and disadvantages of different energy sources
- Compare different energy sources in terms of energy density and specific energy

C1.2 Energy sources

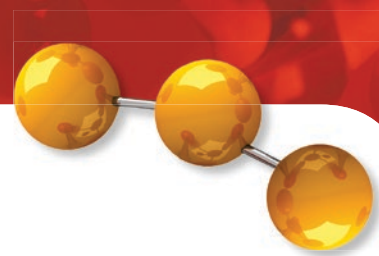
For a particular energy source to be useful it should have the following characteristics:

- it should release energy at a reasonable rate (not too fast or too slow)
- it should produce minimal pollution.

Other desirable qualities of a fuel include being easy to obtain, and being cheap and plentiful.

Sources of energy can be divided into two categories:

- **Renewable energy sources** are naturally replenished – they will not run out.
- **Non-renewable energy sources** are finite – they will eventually run out.



Non-renewable energy sources

These are energy sources that will run out in the (near) future and cannot be easily replaced – they are finite. Examples of non-renewable sources of energy are shown in Table C.1.

Source	Description
fossil fuels	Coal, oil and natural gas. These are burned and the heat used to produce steam, which turns a turbine, which turns a generator to produce electricity.
nuclear fission	A nuclear reaction, in which uranium is bombarded with neutrons, produces heat. The heat can be used to generate steam to turn a turbine, which turns a generator to produce electricity.
electrochemical cells	Batteries are portable sources of energy. A redox reaction generates electricity.

Table C.1 Non-renewable forms of energy.

There is a long-running debate about how long supplies of fossil fuels, especially oil, will last. This depends on existing reserves, the discovery of potential reserves, world population, usage and price. There is, however, little doubt about the fact that oil will one day run out and the timescale for this is likely to be measured in tens of years rather than hundreds.

Renewable energy sources

These will not run out because they are replenished naturally. Examples of some renewable energy sources are given in Table C.2.

Source	Description
solar energy	A huge amount of solar energy reaches the Earth every day but only a tiny fraction is used (Figure C.2). Photovoltaic cells convert energy from the Sun to electrical energy.
wind	Wind is used to turn a turbine to generate electricity (Figure C.2).
hydroelectric	Rivers are dammed and water flows from a higher to a lower level through a turbine (change in potential energy) connected to a generator.
tidal	Uses the rising and falling of tides to turn a turbine.
geothermal	Uses heat from rocks underground. Either hot water from underground is used directly or water is pumped down to generate steam, which is used to turn a turbine.
biomass	Energy from plants. This can be used in various ways – such as growing trees and burning them; growing sugar cane and fermenting the sugar to produce ethanol, which can be used as a fuel additive; producing biogas from decaying matter and burning it.
nuclear fusion	Potentially an unlimited supply of energy – joining hydrogen nuclei together with the release of a large amount of energy.

Table C.2 Renewable forms of energy.



Figure C.2 A wind farm and a solar panel site – the solar panels are mounted on motorised columns to track the Sun across the sky.

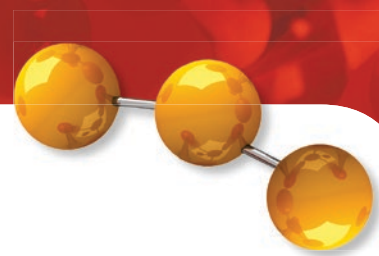
The term 'solar panel' is used in different ways. It is now most often used to describe a panel consisting of linked photovoltaic cells that convert light energy into electrical energy but is also sometimes used to describe a panel that absorbs energy from the Sun to heat water for domestic use.

Advantages and disadvantages of different energy sources

Some advantages and disadvantages of the different energy sources that you will meet in this option are discussed in Table C.3.

Source	Advantages	Disadvantages
solar energy	Energy comes from the Sun – this is free and will not run out in the foreseeable future. Non-polluting in use – e.g. does not produce greenhouse gases. Can be useful in remote locations – e.g. in the desert or on satellites.	Not a very concentrated form of energy and huge banks of solar cells/panels are required. Solar cells and solar panels are expensive to manufacture and buy. Quite a lot of energy and resources needed in manufacture, which can produce pollution. Dependent on the weather and does not produce electricity at night.
burning fossil fuels	Concentrated form of energy – burning fossil fuels can be used to generate the huge amounts of electrical energy required throughout the world each day. Relatively cheap. Gas and oil can be relatively easily transported through pipelines.	Finite – will run out. Greenhouse gases are generated, which can contribute to climate change. Other pollutants such as NO _x and SO ₂ can be produced; these lead to acid deposition. Potential for environmental disasters through extraction of crude oil (e.g. Gulf of Mexico, 2010) and transportation by ship (e.g. Sea Empress, 1996). Coal mining – opencast mining can destroy large areas of land and can be dirty and unsightly for local residents; underground mining can be dangerous.
nuclear fission	Very concentrated form of energy. Does not produce greenhouse gases in operation (although some are produced when fuel is mined/transported to the power station).	Nuclear waste is produced, which is difficult to dispose of safely. Danger of an accident – e.g. Chernobyl, 1986, and Fukushima, 2011 – and the release of radioactivity into the environment. Difficult and expensive to decommission nuclear power stations.
non-rechargeable batteries	They are portable.	They are expensive. Have only a limited lifetime – they run out. Problems with disposal – many contain heavy metals.
rechargeable batteries	They are portable. Can be used over and over again.	They are expensive to buy. They run out and have to be recharged every so often.
hydrogen fuel cells	They are portable. They do not use fossil fuels. They use hydrogen, which can be extracted from water, which is present in virtually limitless supply. They do not produce carbon dioxide in operation.	There are difficulties with storing hydrogen (a flammable gas). How environmentally friendly they are depends on how the hydrogen is produced.
nuclear fusion	Has the potential to produce vast amounts of energy. Does not produce greenhouse gases. Does not produce nuclear waste.	There is no working nuclear fusion power plant – it is very difficult to produce and contain a sustained nuclear fusion reaction that generates more energy than needs to be put in to produce the extremely high temperatures required.

Table C.3 Advantages and disadvantages of different energy sources.



Comparing of the amounts of energy released in combustion reactions

When fuels are burned, energy is released in the form of heat (chemical energy converted to thermal energy). **Specific energy** and **energy density** are sometimes used to compare different fuels.

- $\text{Specific energy} = \frac{\text{energy released from fuel}}{\text{mass of fuel consumed}}$
- $\text{Energy density} = \frac{\text{energy released from fuel}}{\text{volume of fuel consumed}}$

We can calculate the specific energy of hydrogen from its enthalpy change of combustion. The enthalpy change of combustion is the enthalpy change when one mole of substance undergoes complete combustion. For hydrogen the value is -286 kJ mol^{-1} .

One mole of hydrogen (H_2) has a mass of 2.02 g, so burning 2.02 g of hydrogen produces 286 kJ of energy.

$$\text{specific energy} = \frac{286}{2.02} = 142 \text{ kJ g}^{-1}$$

This could also be expressed in other units, such as MJ kg^{-1} . Because there are 1000 kJ in 1 MJ and 1000 g in 1 kg, 142 kJ g^{-1} is equivalent to 142 MJ kg^{-1} .

To calculate hydrogen's energy density, we need to know the volume occupied by one mole of hydrogen.

At 25°C and 100 kPa, the volume occupied by one mole of an ideal gas is 24.8 dm^3 (this can be calculated using $PV = nRT$) and so the energy density of hydrogen can be calculated:

$$\text{energy density} = \frac{286}{24.8} = 11.5 \text{ kJ dm}^{-3}$$

This is equivalent to 11.5 J cm^{-3} or 11.5 MJ m^{-3} .

We can compare these values with those for octane (C_8H_{18}) – a liquid fuel that is a constituent of gasoline:

$$\text{specific energy} = \frac{5470}{114.26} = 47.87 \text{ kJ g}^{-1} \text{ or } 47.87 \text{ MJ kg}^{-1}$$

Octane has a density at 25°C of 0.703 g cm^{-3} , and because

$\text{density} = \frac{\text{mass}}{\text{volume}}$ we can calculate the volume occupied by one mole of octane:

$$\begin{aligned} \text{volume} &= \frac{114.26}{0.703} \\ &= 163 \text{ cm}^3 \text{ or } 0.163 \text{ dm}^3 \end{aligned}$$

$$\begin{aligned} \dots \text{ and the energy density} &= \frac{5470}{0.163} \\ &= 33\,600 \text{ kJ dm}^{-3} \end{aligned}$$

Energy density is sometimes used to describe the energy released per unit mass, rather than per unit volume – it is important to check the units to make sure what the term is describing.

1 MJ is $1 \times 10^6 \text{ J}$.

We usually use the molar volume measured at STP ($22.7 \text{ dm}^3 \text{ mol}^{-1}$) but the problem here is that the standard enthalpy change of combustion is measured at 298 K. We could have made the assumption that the enthalpy change of combustion does not vary much with temperature, in which case we could have calculated the energy density as $\frac{286}{22.7} = 12.6 \text{ kJ dm}^{-3}$

114.26 g is the mass of one mole of octane.

A slightly different answer is obtained if more significant figures are carried through on the calculator.

It can be seen from these values that when hydrogen burns it releases approximately three times more energy per gram than octane, but the energy released per unit volume is more than 2000 times higher for octane. This illustrates a problem with using hydrogen as a fuel – the storage of a large volume of a highly flammable gas.

A typical family car could have an average fuel consumption of 7 litres (dm^3) of gasoline per 100 km – so to travel the same distance more than 1500 litres (dm^3) of hydrogen gas would be required (the size of a trunk/boot of a car is typically about 400 dm^3). One solution to this problem would be to store the hydrogen under pressure but this requires fuel tanks to be made of thicker material which is also heavier and more expensive. Other methods of storage are being investigated such as cryo-compression (storing at low temperature under pressure) and various forms of chemical storage.

When considering the best fuel for a particular job, both the specific energy and the energy density must be considered. When weight is a problem then specific energy is likely to be more important – for instance, the space shuttle used liquid hydrogen as a fuel. When storage volume for the fuel is an issue then energy density becomes more important.

Nature of science

All science has to be funded – either by governments, international organisations or companies. Science should, however, not be biased or be influenced by the vested interests of large international corporations such as oil companies. Scientists can sometimes be put in difficult positions when their findings do not fit with the interests of the people funding their research.

We can understand the non-existence of perpetual motion machines by describing energy as having both quantity and quality. In an energy transfer the total amount of energy transferred is constant but the quality is degraded.

? Test yourself

3 Calculate the specific energy of each of the following fuels:

	Fuel	Formula	Enthalpy change of combustion / kJ mol^{-1}
a	methanol	CH_3OH	-726
b	hexane	C_6H_{14}	-4163
c	benzaldehyde	$\text{C}_6\text{H}_5\text{CHO}$	-3525

4 Calculate the energy density of each of the following fuels – give all your answers in kJ dm^{-3} :

	Fuel	Formula	Physical state at 298 K and 100 kPa	Enthalpy change of combustion / kJ mol^{-1}	Molar volume (dm^3) at 100 kPa and 298 K	Density / g cm^{-3}
a	methane	CH_4	gas	-891	24.8	-
b	ethyne	C_2H_2	gas	-1301	24.8	-
c	benzene	C_6H_6	liquid	-3525	-	0.877
d	ethanol	$\text{C}_2\text{H}_5\text{OH}$	liquid	-1367	-	0.789

C2 Fossil fuels

C2.1 Formation of fossil fuels

The main fossil fuels

The three main fossil fuels are **coal**, **oil** and **natural gas**. They are called **fossil fuels** because they are formed from things that were once alive and have been buried underground for millions of years.

Coal is formed from the remains of plants and trees which fell into swamps millions of years ago. These plants were then covered in layers of sediment and underwent partial decomposition in the absence of oxygen, and under high pressure and temperature, to form coal. Coal can contain up to 95% carbon by mass. The best coals are those with the highest percentage of carbon – these burn most cleanly and release the greatest amount of heat on combustion. Other elements that may be present in coal are hydrogen, oxygen, nitrogen and sulfur.

Crude oil (petroleum) was formed from marine organisms (plankton) that died millions of years ago and sank to the bottom of the sea. These were covered by layers of sediments and underwent chemical processes under conditions of high pressure, moderate heat (between about 60 °C and 170 °C) and the absence of oxygen to convert them into crude oil. Crude oil is a complex mixture of hydrocarbons, including straight and branched-chain alkanes, cycloalkanes and aromatic compounds. Other elements that may be present are nitrogen, oxygen and sulfur.

Natural gas is formed in basically the same way as crude oil and is often found with it. Natural gas consists mostly of methane. Other light hydrocarbons may also be present, as well as hydrogen sulfide.

Fossil fuels are formed by the reduction of biological compounds.

That the reactions involved in the formation of fossil fuels are reduction reactions can be seen by looking at the differences in the oxidation numbers of carbon in biological compounds and fossil fuels. Biological compounds in living organisms that will eventually be converted to fossil fuels include proteins (polymers formed from amino acids) and carbohydrates.

The simplest amino acid is 2-aminoethanoic acid (glycine), the structure of which is shown in Figure C.3. If it is assumed that oxidation numbers are oxygen -2 , hydrogen $+1$ and nitrogen -3 , the average oxidation number of carbon in 2-aminoethanoic acid is $+1$. The oxidation number of carbon in methane is -4 and in coal (assuming that it is pure carbon) is 0 . So, conversion of the amino acid into a fossil fuel involves reduction.

Similarly, the average oxidation number of carbon in glucose ($C_6H_{12}O_6$) is 0 and that in octane (C_8H_{18}) is -2.25 .

Learning objectives

- Understand what is meant by a fossil fuel
- Understand that fossil fuels were formed from biological compounds that contained carbon, hydrogen, nitrogen, sulfur and oxygen
- Understand that fossil fuels were formed in reduction reactions
- Discuss the advantages and disadvantages of fossil fuels

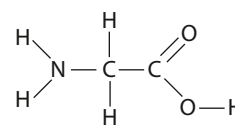


Figure C.3 The simplest amino acid – 2-aminoethanoic acid.

It can also be seen that oxygen is removed when glucose is converted into octane – removal of oxygen is reduction.

It is very difficult to estimate reserves of coal, oil and gas and how long they will last. Factors such as undiscovered reserves, how usage will change, new technologies etc. all have to be considered.

Advantages and disadvantages of fossil fuels

Table C.4 gives details of some advantages and disadvantages of the three main fossil fuels.

Of these fuels, natural gas is currently the cheapest to produce and there is a trend in the USA away from coal-fired power stations to natural-gas electricity generation, driven by price.

Fuel	Advantages	Disadvantages
coal	Supplies should last hundreds of years. Distributed throughout the world. Can be converted into synthetic gaseous and liquid fuels. Can be converted into feedstock for the petrochemical industry. More concentrated source of energy than most renewable sources of energy. Relatively cheap to produce.	Produces greenhouse gases when burned so contributes to climate change. Not as easily transported as oil or gas. Mining is a dirty (slag heaps) and dangerous process. Dirty fuel – pollutants include particulates (fly ash) and sulfur dioxide (acid rain).
oil	Easily transported in pipelines or by tankers. Convenient fuel for internal combustion engine. Source of variety of chemicals for the petrochemical industry.	Produces greenhouse gases when burned so contributes to climate change. Very limited lifespan – supplies could run out in decades. Can produce sulfur dioxide (acid rain) when burned. Environmental problems associated with extraction and transportation in tankers. Only a few countries have reserves.
gas	It is a clean fuel. Easily transported in pipelines and tankers. Releases a higher quantity of energy per kg than coal or oil. Produces less CO ₂ per kJ of energy released. Cheap to produce – comes as a byproduct of coal and oil production.	Produces greenhouse gases when burned so contributes to climate change. Limited lifespan – may be less than 100 years. Only certain countries have reserves. Risk of explosions due to leaks. More difficult to store than coal and oil because it is a gas – must be stored under pressure or cooled to liquefy it.

Table C.4 Advantages and disadvantages of fossil fuels.



In the 1970s people were saying that crude oil would run out in the next 40 years but now, 40 years on, this is still being said. Are these numbers just being used for effect, are estimates being revised in the light of new data or were the scientists in the 1970s simply wrong? There are many different estimates of how long the supplies of crude oil will last; how do we know what to believe?

Learning objectives

- Understand that petroleum is a mixture of hydrocarbons
- Understand that petroleum must be split into fractions before use
- Recall the names of fractions, their relative volatility and uses

C2.2 Petroleum refining

Fractional distillation of crude oil

Petroleum (crude oil) is a complex mixture of thousands of different hydrocarbons.

These hydrocarbons may be alkanes, cycloalkanes (ring compounds) or aromatic compounds (containing benzene rings).

Petroleum is not composed solely of hydrocarbons – it also contains a small proportion of compounds containing nitrogen, oxygen and/or sulfur, as well as carbon and hydrogen.

Petroleum can be separated into a series of simpler mixtures called **fractions** by the process of fractional distillation. The separation process relies on the different components of the mixture having different boiling points so that they condense at different levels in the fractionating column. This process is carried out in an oil refinery and is called **refining**.

The crude oil is heated to about 350 °C in a furnace (Figure C.4). This is high enough to vaporise most components of the petroleum. The liquid–vapour mixture is passed into a fractionating tower which is hot at the bottom and cooler at the top. The lowest-boiling components do not condense at all in the tower and are drawn off at the top as gases (refinery gases). Compounds of intermediate boiling point travel up the column until they condense and are drawn off as liquids. Lower-boiling-point fractions are drawn off higher up the tower. The highest-boiling-point components, which were not vaporised in the furnace, sink to the bottom of the tower and are drawn off there. This fraction, normally just called the **residue**, can be further separated into other fractions using vacuum distillation.

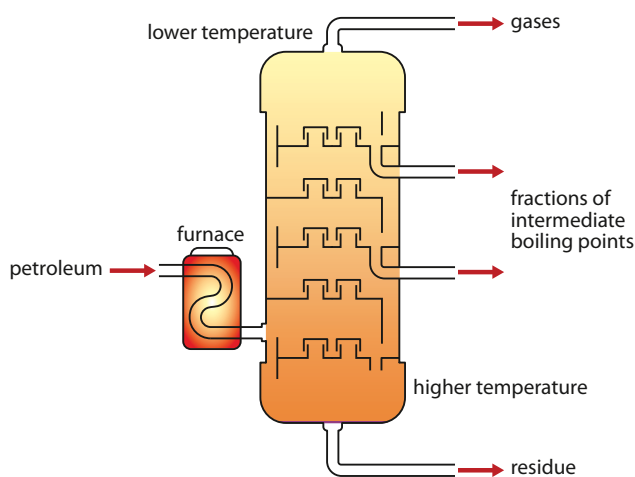


Figure C.4 Crude oil can be separated into fractions using fractional distillation.

Fractional distillation involves separation by physical processes (boiling and condensing) and relies on the different physical properties (boiling points) of the components.

All the fractions obtained from petroleum contain a mixture of compounds and boil over a range of temperatures. For instance, gasoline typically contains hydrocarbons with between five and nine carbon atoms with boiling points in the range 40–200 °C, whereas kerosene contains compounds which have, on average, more carbon atoms per molecule and boils between about 150 °C and 300 °C. Table C.5 shows the names and uses of some fractions.

As the number of carbon atoms in a molecule increases, the strength of the London forces between the molecules increases and the compounds become less volatile (evaporate less easily).

Exam tip

'Crude oil' and 'petroleum' are used interchangeably in the syllabus.

Petroleum has virtually no uses until it is separated into fractions.

Fraction	Uses
refinery gases	Fuel for cooking and heating. Bottled gas. Used for fuel in the refinery.
gasoline	Fuel for cars.
naphtha	Feedstock for petrochemical industry. Converted by catalytic reforming into gasoline. Used as a solvent.
kerosene (paraffin)	Jet fuel. Household heaters and lamps. May also be cracked to produce more gasoline.
diesel oil (gas oil)	Diesel fuel for cars, lorries etc. May be cracked to produce more gasoline.
fuel oil	Fuel for ships and industry. Fuel for home central heating systems.
lubricating oil	Lubricant in engines and machinery. May be cracked.
wax	Candles, petroleum jelly, waxed paper and cardboard in the food industry.
bitumen/asphalt	Tarmac for roads and waterproofing roofs.

Table C.5 Fractions obtained from crude oil. Other names are sometimes used for fractions. Volatility refers to how readily a substance evaporates.

Learning objectives

- Understand that an octane number is a measure of the tendency of a fuel not to auto-ignite
- Understand how octane numbers are related to molecular structure
- Understand that cracking and reforming may be carried out to improve the octane number of a hydrocarbon fraction
- Write equations for cracking and reforming reactions

Octane number is sometimes called 'octane rating'.

C2.3 Octane numbers

The auto-ignition problem

In an internal combustion engine, a fuel–air mixture is compressed in a cylinder and ignited by a spark from a spark plug. The flame spreads smoothly through the cylinder and only a small fraction of the fuel is burning at any one time. However, depending on the fuel used, it can also happen that the fuel explodes in the cylinder – it all burns at essentially the same time. This mini-explosion, often called 'auto-ignition', results in a metallic knocking sound – called 'knocking' or 'engine knock'. Knocking leads to wear in the engine and wastage of petrol.

The tendency of a fuel to auto-ignite and cause knocking depends on the molecular structure of the components of the petrol used. Gasoline mixtures that are rich in straight-chain alkanes, such as heptane, have a high tendency to auto-ignite and cause knocking. The combustion of branched-chain alkanes, such as 2,2,4-trimethylpentane, is much smoother and more controlled. Gasoline mixtures rich in branched-chain alkanes are more efficient fuels and are less likely to cause knocking.

It is convenient to have a measure of the suitability of alkanes as fuels and this is why each compound is given an **octane number**, determined by experiment. Two arbitrary reference points are used in the scale – heptane, which is assigned an octane number of 0; and 2,2,4-trimethylpentane, which is assigned an octane number of 100 (Figure C.5).

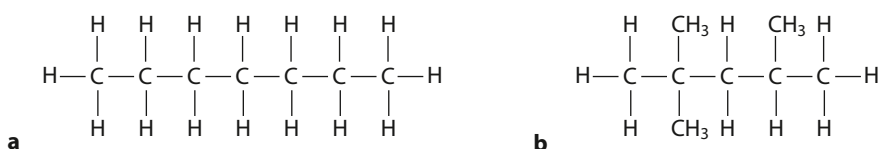


Figure C.5 **a** Heptane, octane number 0, is a poor fuel – it has a high tendency to knock; **b** 2,2,4-trimethylpentane, octane number 100, is a good fuel – it has a low tendency to knock.



The test fuel is placed in a test engine and the compression ratio increased until knocking occurs. The test fuel is then replaced by a series of reference fuels – mixtures of heptane and 2,2,4-trimethylpentane – until a fuel is found that has the same tendency to auto-ignite/knock as the test fuel. So an octane number refers to the performance of a fuel relative to heptane and 2,2,4-trimethylpentane.

An octane number is a measure of the tendency of a fuel not to undergo auto-ignition (cause knocking) in an engine. The higher the octane number, the lower the tendency to undergo auto-ignition/cause knocking.

Modern car engines usually need petrol with an octane number of 90+.

The octane number is affected by various structural features:

- straight-chain alkanes have the lowest octane number and this number decreases as the number of carbon atoms in the chain increases – for instance, pentane has an octane number of 62 and hexane an octane number of 25
- branched-chain alkanes have higher octane numbers than straight-chain alkanes – for example, 2-methylhexane, an isomer of heptane (octane number 0), has an octane number of 44
- as the degree of branching increases so does the octane number – 2,2-dimethylpentane has an octane number of 93, whereas its isomer with three branches, 2,2,3-trimethylbutane, has an octane number of 113
- straight-chain alkenes have higher octane numbers than straight-chain alkanes
- cycloalkanes have higher octane numbers than straight-chain alkanes
- aromatic compounds generally have the highest octane numbers.

Increasing the octane number of fuels

The original solution to increasing the octane number of fuels was to add an anti-knock compound, the most common of which was lead tetraethyl $[\text{Pb}(\text{C}_2\text{H}_5)_4]$. However, concerns about the toxicity of lead have resulted in leaded gasoline being phased out in most countries. In addition, leaded fuels cannot be used with catalytic converters because they poison the catalyst. Other solutions have included adding MTBE (methyl tertiary-butyl ether) but there has been growing concern about its use in the US because of contamination of drinking water – contamination with MTBE makes the water undrinkable (unpleasant taste and odour). It is also suspected that MTBE could be a human carcinogen. MTBE has been largely replaced by ethanol in the US but not in other countries. Another solution to improving the octane number of gasoline is to increase the concentration of benzene and other aromatic compounds. However, benzene is also a known human carcinogen and therefore most countries set limits on the concentration of benzene in fuel. Not all countries, however, set limits and these limits vary considerably between countries.

Catalytic cracking

Catalytic cracking increases the yield of gasoline from a refinery by breaking down long-chain molecules from the less valuable fractions obtained from petroleum into shorter ones. Shorter-chain alkanes

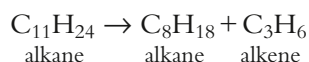
‘Compression ratio’ is the ratio of the volume of an engine cylinder when the piston is at the bottom of its stroke compared to when it is at the top of its stroke – the higher the compression ratio, the greater the likelihood of knocking.



The numbers used here are all research octane numbers (RON) but other octane numbers are also used, such as the motor octane number (MON), blending octane number (BON), pump octane number (PON) and anti-knock index (AKI). Different numbers are used in different countries.

have a higher octane number than longer-chain ones and so cracking increases the octane number of a petroleum fraction. Catalytic cracking also increases the octane number of gasoline because it produces more branched-chain alkanes and aromatic compounds.

The hydrocarbon molecules to be cracked are passed through a bed of a zeolite (aluminosilicate) catalyst at about 500 °C under pressure. The reactions involved in catalytic cracking are complex but a representative reaction is:



At the simplest level, cracking will produce an alkane and an alkene because there are not enough hydrogen atoms in the original molecule to produce two alkanes. Various isomerisation reactions can occur during this process to produce branched-chain alkanes, cycloalkanes and aromatic compounds which increase the octane number.

A variation on the above process is **hydrocracking** which involves heating the long-chain hydrocarbons with hydrogen and a catalyst at high temperature and pressure. This converts the long-chain alkanes into shorter-chain alkanes but no alkenes, due to the presence of the hydrogen. Branched alkanes and cycloalkanes are also produced, which increase the octane number of the fuel.

Thermal cracking

Long-chain molecules may also be cracked simply by heating them. This process is known as **thermal cracking** or **steam cracking**. Typically this uses a high temperature (about 900 °C) and sometimes also high pressure to break down long-chain alkanes into shorter-chain alkanes and alkenes. The alkenes have a higher octane number than alkanes but are not desirable in car engines because they can form gums which can clog up the engine – but they are very useful as a chemical feedstock for making polymers, for example.

Catalytic reforming

Catalytic reforming is a chemical process that increases the octane number of a petroleum fraction by increasing the proportion of branched-chain alkanes, cycloalkanes and aromatic compounds. This is achieved by heating the hydrocarbon feedstock to about 500 °C in the presence of a catalyst such as platinum on an alumina support. Many different reactions can occur – some examples are given in Table C.6.



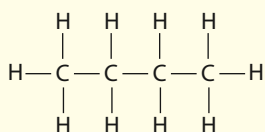
isomerisation	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \begin{array}{cccccc} & \text{H} & \text{CH}_3 & \text{H} & \text{H} & \text{H} \\ & & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & & & & \\ & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \end{array}$ <p style="text-align: center;">hexane 2-methylpentane</p>
cyclisation	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \begin{array}{cccc} & \text{H} & & \text{H} \\ & & & \\ \text{H} & -\text{C} & & \text{C}-\text{H} \\ & & & \\ \text{H} & -\text{C} & & \text{C}-\text{H} \\ & & & \\ & \text{H} & & \text{H} \end{array} + \text{H}_2$ <p style="text-align: center;">hexane cyclohexane</p>
aromatisation	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{C}_6\text{H}_6 + 4\text{H}_2$ <p style="text-align: center;">hexane benzene</p>

Table C.6 Some reactions that can occur in catalytic reforming.

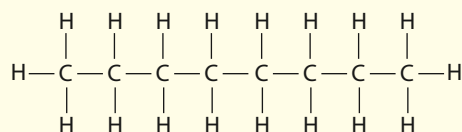
? Test yourself

5 From each pair select the molecule with the higher octane number:

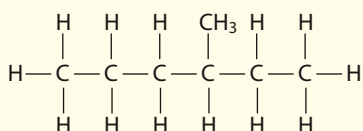
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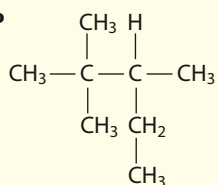
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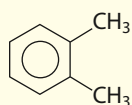
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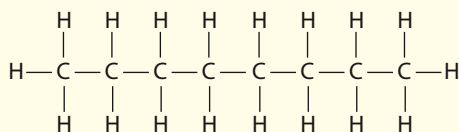
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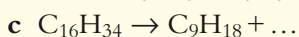
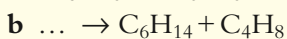
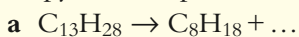
c Q



R



6 Copy and complete the following equations for cracking reactions:



Learning objectives

- Understand what is meant by coal gasification and liquefaction
- Write equations for the processes involved in coal gasification and liquefaction

Exam tip

If asked to write just one equation for the coal gasification reaction

$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$ is probably the most appropriate.

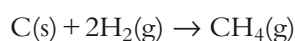
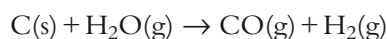
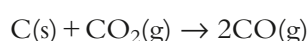
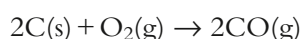
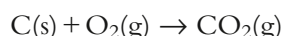


The use of chemical technology can be driven by political factors. Germany used the Fischer–Tropsch process during World War II to produce liquid hydrocarbons to power vehicles; South Africa used the same technology 30 years later when it was largely isolated by trade sanctions during the apartheid era.

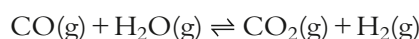
C2.4 Coal gasification and liquefaction

Coal gasification

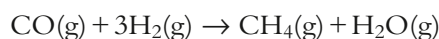
This refers to the process of converting coal (mostly carbon) into a gaseous fuel. The gasification process usually involves conversion of coal into a mixture of carbon monoxide and hydrogen – a mixture known as **syngas** (synthesis gas). There may also be small amounts of methane present. Coal is heated to high temperatures (above 1000 °C) with oxygen and steam; high pressures may also be used. Various reactions occur in the coal gasification process:



Syngas of various compositions (CO:H₂ ratio) is needed for different processes and the **water–gas shift reaction** is used to control this. If syngas is treated with steam, some carbon monoxide reacts with the steam to reduce the carbon monoxide composition relative to H₂:



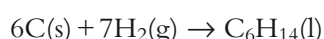
Syngas (which has been purified by removal of sulfur compounds) can be converted into synthetic natural gas (substitute natural gas, SNG) by heating it with more hydrogen:



Coal is more plentiful than natural gas and this reaction can be used to increase supplies of natural gas. The product is a clean-burning fuel (impurities such as sulfur are removed) which is easier to transport.

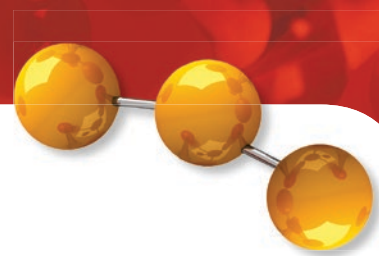
Coal liquefaction

Coal liquefaction refers to the process of converting coal to liquid hydrocarbons. Coal may be liquefied either directly or indirectly. In the direct processes the coal is mixed with a solvent and hydrogen and subjected to high temperature (around 400 °C) and high pressure in the presence of a catalyst (such as ‘red mud’, which is a byproduct of the processing of bauxite for the extraction of aluminium). This can result in reactions such as:

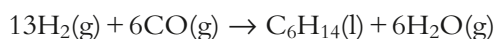


C₆H₁₄ is a liquid at room temperature and pressure.

The indirect process involves the conversion of syngas (mostly CO and H₂) from the gasification process into liquid hydrocarbons using the Fischer–Tropsch process. Different plants use different conditions but a typical set of conditions would be a temperature of about 300 °C, high



pressure and a catalyst (e.g. ruthenium on an alumina support). Alkanes can be formed by reactions such as:



This can be generalised as $(2n+1)\text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$.

C2.5 Carbon footprints

Carbon dioxide production from burning fossil fuels

All fossil fuels contain carbon and when they are burned the carbon is converted into carbon dioxide (and carbon monoxide and soot). Carbon dioxide produced by burning fossil fuels is believed to contribute to climate change and so it is important to be able to compare the amounts of carbon dioxide produced when different fuels are burned.

We can use the enthalpy change of combustion values given in Table C.7 to compare three fossil fuels in terms of the amount of carbon dioxide per gram of fuel burned and per kJ of energy released.

Substance	Enthalpy change of combustion / kJ mol^{-1}
coal – C(s)	–394
natural gas – $\text{CH}_4(\text{g})$	–891
petrol – $\text{C}_8\text{H}_{18}(\text{l})$	–5470

Table C.7 The enthalpy change of combustion of fossil fuels.

The equations for the complete combustion of each of these fuels are:

- $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
- $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
- $\text{C}_8\text{H}_{18}(\text{l}) + \frac{25}{2}\text{O}_2(\text{g}) \rightarrow 8\text{CO}_2(\text{g}) + 9\text{H}_2\text{O}(\text{l})$

We can now calculate the amounts of carbon dioxide produced when one mole of each fuel is burned:

- 1 mol carbon produces 1 mol (44.01 g) CO_2
- 1 mol methane produces 1 mol (44.01 g) CO_2
- 1 mol octane produces 8 mol (352.08 g) CO_2 .

If we divide each value by the molar mass of the fuel burned, we get the mass of CO_2 produced per gram of fuel burned:

- carbon $\frac{44.01}{12.01} = 3.66$ g per gram of fuel burned
- methane $\frac{44.01}{16.05} = 2.74$ g per gram of fuel burned
- octane $\frac{352.08}{114.26} = 3.08$ g per gram of fuel burned

Learning objectives

- Understand what is meant by a carbon footprint
- Calculate how much carbon dioxide is added to the atmosphere when different fuels are burned
- Calculate carbon footprints

We are using a simplified model here to make the calculations easier. We are assuming that coal is made entirely of carbon, that natural gas is pure methane and that petrol is pure octane.

When we are considering energy production, perhaps a more useful comparison is the mass of CO₂ produced per kJ of energy released. This value can be obtained by dividing the mass of CO₂ produced per mole by the enthalpy change of combustion:

- carbon $\frac{44.01}{394} = 0.112$ g of CO₂ per kJ of energy released
- methane $\frac{44.01}{891} = 0.0494$ g of CO₂ per kJ of energy released
- octane $\frac{352.08}{5470} = 0.0644$ g of CO₂ per kJ of energy released

Because coal is composed entirely of carbon it comes out worst in all these calculations.

Carbon footprint

A **carbon footprint** is a measure of the total amount of greenhouse gases (primarily carbon dioxide and methane) emitted as a result of human activities. It is usually expressed as equivalent tonnes of carbon dioxide (e.g. 10 tonne CO₂e). Carbon footprints can be worked out at many different levels – for example by country, region, organisation, household or individual. Your carbon footprint is influenced by many things – major contributions come from transport and electricity usage but what food you eat, whether you buy a newspaper etc. all make a difference.

Contributions to an individual's carbon footprint can be divided into two broad categories – direct production and indirect production. Direct production of carbon dioxide from, say, a car journey is reasonably straightforward to calculate but indirect production from something like eating a frozen pizza bought from a supermarket is much more difficult to quantify.

Worked example

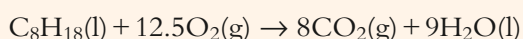
C.1 Work out the carbon footprint for a car journey of 100 km. Assume that the car uses 7 dm³ of fuel for the journey and that the fuel is octane (C₈H₁₈).

The mass of octane burned can be calculated from its density (0.703 g cm⁻³):

$$\begin{aligned}\text{mass} &= \text{density} \times \text{volume} \\ &= 0.703 \times 7000 \\ &= 4921 \text{ g}\end{aligned}$$

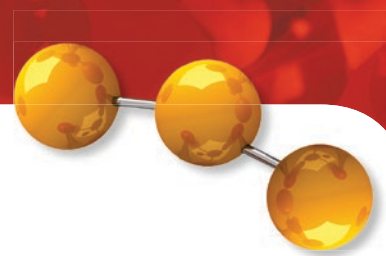
The number of moles of octane is $\frac{4921}{114.26} = 43.07$ mol

The equation for the combustion of octane is:



So $8 \times 43.07 = 345$ mol CO₂ is produced.

The mass of CO₂ produced is $345 \times 44.01 = 15\,200$ g or 15.2 kg



Working out a carbon footprint from using electricity is more complicated because it depends on how the electricity is generated. The carbon footprint from watching television for one hour a day for a year can be estimated by making some assumptions.

The power rating of a typical modern TV set is about 100W, so the approximate annual energy use is $0.10 \text{ kW} \times 365 \text{ h}$ or about 36.5 kWh

To see how much CO_2 this corresponds to, we have to consider what proportion of the electricity in a country is generated from coal (producing a lot of CO_2), natural gas, nuclear energy, renewable sources etc. and the CO_2 emissions associated with each of these methods of generation. A reasonable estimate of CO_2 equivalents per kWh for the US would be about 700 g CO_2e .

So the carbon footprint associated with watching television for one hour a day for a year could be about 36.5×700 , i.e. 26 000 g – or 26 kg of CO_2e .

This calculation considers only the energy associated with using the television and does not take into account the carbon footprint associated with production of the television, its delivery and installation, its disposal etc.

This depends on the size and the type of the television.

The kilowatt-hour is a unit of energy often used for electricity usage.

Nature of science

The problem of dwindling fossil fuel resources is one that transcends any particular science – scientists and technologists from many different disciplines will have to work together to try to solve some of the problems that we will be facing very soon. The problems are, however, not just scientific and scientists will also have to collaborate with politicians, economists, environmental agencies etc. to plan for a world without fossil fuels.

? Test yourself

- 7 Calculate the mass of CO_2 produced per gram of fuel burned and per kJ of energy released when each of the following fuels is burned:
- a ethanol:
enthalpy change of combustion = $-1367 \text{ kJ mol}^{-1}$
 - b hexane:
enthalpy change of combustion = $-4163 \text{ kJ mol}^{-1}$
- 8 Work out the carbon footprint for each of the following car journeys (assume that the fuel is octane, C_8H_{18} , with a density of 0.703 g cm^{-3}):
- a 250 km in a car that uses 8.00 dm^3 of fuel per 100 km.
 - b from New York to Chicago (1145 km) in a car that averages 10.00 dm^3 of fuel per 100 km.

C3 Nuclear fusion and fission

This section deals with nuclear reactions – nuclear reactions are very different to the chemical reactions that we have met so far.

Nuclear reactions involve changes in the nuclei of atoms. In these changes, nuclei may:

- give off particles (radiation)
- absorb other particles (such as neutrons)
- split into smaller nuclei (nuclear fission)
- join together to form larger nuclei (nuclear fusion).

During a nuclear reaction, an atom of a particular element may become an atom of a different element.

Contrast this with chemical reactions – these involve valence (outer-shell) electrons. These may be transferred, as in redox reactions or the formation of ions, or shared, as in the formation of covalent bonds. But no chemical reaction involves an atom becoming a different one.

Learning objectives

- Understand that light nuclei can undergo nuclear fusion reactions because this increases the binding energy per nucleon
- Understand that heavy nuclei can undergo nuclear fission reactions because this increases the binding energy per nucleon

C3.1 Nuclear binding energy

The particles in a nucleus (**nucleons**) are held together by very strong forces and energy is released when protons and neutrons come together to form the nucleus. The nuclear **binding energy** is the energy required to break apart the nucleus into protons and neutrons again. The binding energy is not something that the nucleus ‘has’ – it is the energy released when the nucleus is formed or that required to break it apart again. If the binding energy for a nucleus is divided by the total number of nucleons we get the average binding energy per nucleon which is a measure of the stability of the nucleus.

The greater the binding energy per nucleon, the more stable the nucleus.

Figure C.6 shows a graph of binding energy per nucleon against nucleon number (mass number).

The most stable nuclei have mass numbers around 60 (shaded in pink in Figure C.6) – these have the highest binding energy per nucleon. The most stable nuclei are ^{56}Fe and ^{62}Ni . The arrows on the graph in Figure C.6 indicate the type of nuclear processes that are likely to occur.

Heavier nuclei (to the right of the shaded region in Figure C.6) can undergo fission reactions, in which they split up into smaller nuclei, which increase the binding energy per nucleon.

Lighter nuclei (to the left of the shaded region in Figure C.6) can undergo fusion reactions, in which they join together to form heavier nuclei, giving a higher binding energy per nucleon.

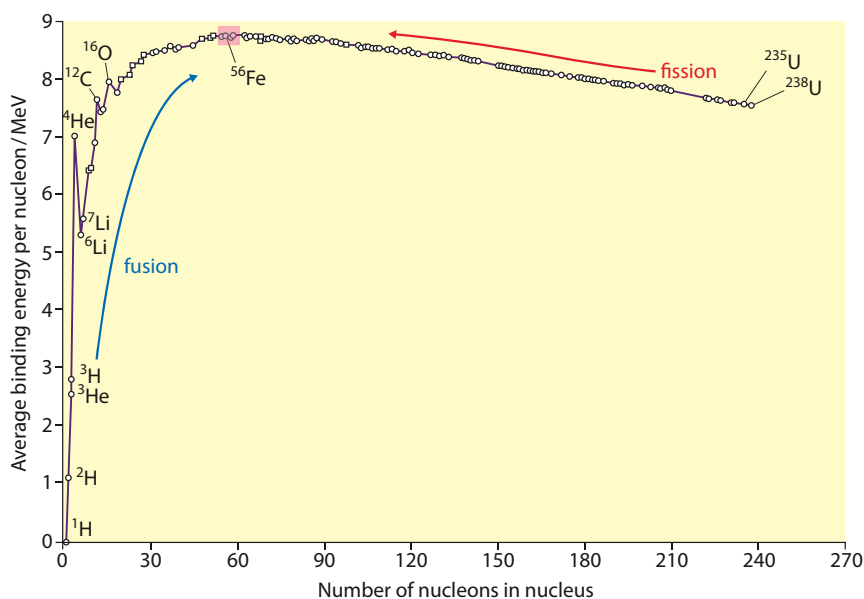
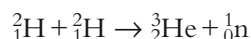


Figure C.6 Average binding energy per nucleon varies with the total number of nucleons.

C3.2 Nuclear fusion

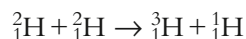
Nuclear fusion is the joining together of smaller nuclei to make a larger one.

A typical fusion reaction is the joining of two deuterium nuclei to form a helium nucleus:



It can be seen from Figure C.6 that the average binding energy per nucleon is greater for ${}^3\text{He}$ than for ${}^2\text{H}$ and that therefore energy is released in this process (in the form of kinetic energy of the particles, which will manifest itself as heat). Note that the mass numbers and atomic numbers must balance in these equations.

Another possible fusion reaction involving deuterium is:



Although ${}^1\text{H}$ has a lower binding energy per nucleon than ${}^2\text{H}$, ${}^3\text{H}$ has a significantly higher binding energy per nucleon and so, overall, there is an increase in the binding energy per nucleon and energy is released.

Nuclear fusion is seen as a potential energy source of the future. It has many advantages over nuclear fission (discussed below) and the burning of fossil fuels:

- It has the potential to produce vast amounts of energy – 1 g of deuterium has the potential to release hundreds of thousands of times the amount of energy released by burning 1 g of coal.
- It does not produce greenhouse gases (but greenhouse gases may result from the production of deuterium etc.).
- It does not produce radioactive waste.

Learning objectives

- Write equations for nuclear fusion reactions
- Understand nuclear fusion reactions in terms of binding energy per nucleon
- Understand that nuclear fusion is potentially a very important energy source
- Understand that absorption spectra can be used to analyse the elements present in stars
- Understand how an absorption spectrum is formed

${}^1_0\text{n}$ represents a neutron.

Nuclear fusion reactions occur in our Sun and therefore nuclear fusion reactions could be regarded as the ultimate source of all energy on Earth.

- The fuel (deuterium) is abundant – its natural abundance is about 0.015%, which corresponds to about 2×10^{16} kg of deuterium in the world's oceans.
- Deuterium is relatively cheap although several factors must be considered here – for example, its production by electrolysis requires a large input of energy.

There is, however, one major disadvantage of nuclear fusion – there is not one working nuclear fusion power plant. No one has yet managed to produce and contain a sustained nuclear fusion reaction that generates more energy than needs to be put in to produce the extremely high temperatures required.

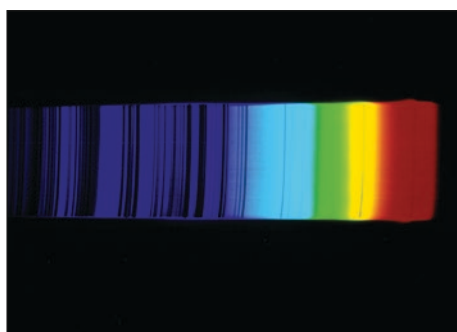


Figure C.7 Solar spectrum showing absorption lines.

When an electron returns to a lower energy level, light is given out – because this is emitted in all directions, very little reaches the observer and so this frequency is essentially missing from the spectrum.

Atomic absorption spectra

Nuclear fusion reactions occur in stars such as our Sun. The Sun emits a continuous spectrum in the visible region but some frequencies are seen to be missing from the spectrum when it is analysed using a spectroscope (Figure C.7).

The dark lines, often called Fraunhofer lines, arise because electromagnetic radiation is absorbed by cooler gases in the outer atmosphere of the Sun. Energy, in the form of certain frequencies of electromagnetic radiation, is absorbed to promote electrons from lower energy levels to higher ones (Figure C.8) in atoms. This frequency of light will therefore be missing from the spectrum as observed by someone on Earth.

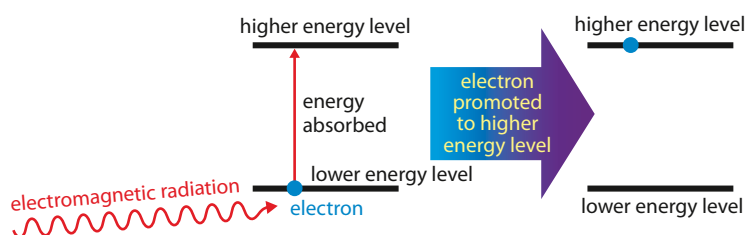


Figure C.8 Absorption of electromagnetic radiation by an atom.

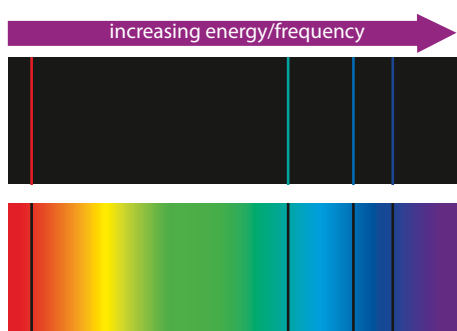


Figure C.9 The relationship between the emission (top) and absorption (bottom) spectra of hydrogen.

An absorption spectrum can also be generated in the laboratory by passing white light (all frequencies) through a sample of gas and analysing the light emerging using a spectroscope.

Each element has a characteristic absorption spectrum – the absorption spectrum of hydrogen is completely different to the absorption spectrum of helium, which is completely different to the absorption spectrum of sodium etc. The dark lines in an absorption spectrum have the same frequency as the lines in the atomic emission spectrum of an element (Figure C.9). Each line in the emission spectrum is caused by an electron falling from a higher atomic energy level to a lower one, whereas each line in the absorption spectrum corresponds to the energy absorbed when an electron is promoted from a lower to a higher energy level. Because the energy levels in the atom are the same, the lines occur at the same frequency in emission and absorption spectra.

The lines in the emission spectrum of hydrogen shown in Figure C.9 are caused by electrons falling from a higher energy level to level 2, whereas the dark lines in the absorption spectrum are caused by energy being absorbed to promote electrons from level 2 to a higher energy level.

The absorption spectrum of helium is much more difficult to analyse than that of hydrogen. The simple model of atomic energy levels can no longer be applied due to repulsion between the two electrons meaning that many different energy states exist.

The elements present in stars can be determined from analysis of the absorption lines in their spectra. The presence of an absorption at a particular frequency, which also corresponds to a line in the emission spectrum of an element, indicates the presence of that element (Figure C.10).

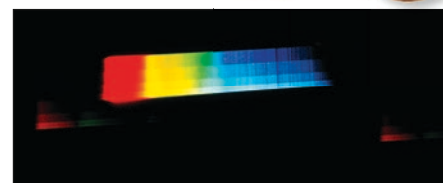


Figure C.10 The spectrum of the star Arcturus showing absorption lines.

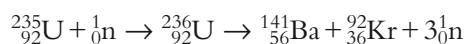
C3.3 Nuclear fission

Nuclear fission

Nuclear fission is the breakdown of a larger nucleus into two smaller fragments of comparable masses.

The average binding energy per nucleon of the daughter nuclei (products of the reaction) is higher than that of the parent nucleus, therefore energy is released in the fission process.

The main fuel used in nuclear reactors is ^{235}U . When bombarded with neutrons, a ^{235}U nucleus absorbs one neutron to produce the highly unstable ^{236}U , which almost instantaneously (picoseconds) breaks apart into two smaller nuclei and more neutrons. A typical reaction is:



The total numbers of protons and neutrons do not change in this type of reaction and so

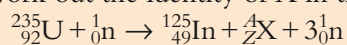
the total mass number and total atomic number on each side must balance.

Learning objectives

- Understand how to write an equation for the fission of uranium-235
- Understand what is meant by critical mass
- Understand that plutonium-239 can be produced in a breeder reactor
- Understand some of the problems associated with nuclear power
- Understand that nuclear waste may contain isotopes with short or long half-lives
- Understand some of the problems associated with the storage and disposal of nuclear waste

Worked example

C.2 Work out the identity of X in the nuclear equation:



The atomic numbers and mass numbers must balance on both sides of the equation.

Atomic number: the total atomic number on the left-hand side is 92, therefore the total atomic number on the right-hand side must also be 92.

$$Z + 49 = 92, \text{ and so } Z = 43$$

From the periodic table we can work out that X is technetium.

Mass number: the total mass number on the left-hand side is $235 + 1 = 236$, therefore the total mass number on the right-hand side must also be 236.

$$125 + A + (3 \times 1) = 236, \text{ and so } A = 108$$

X is technetium-108 or $^{108}_{43}\text{Tc}$.

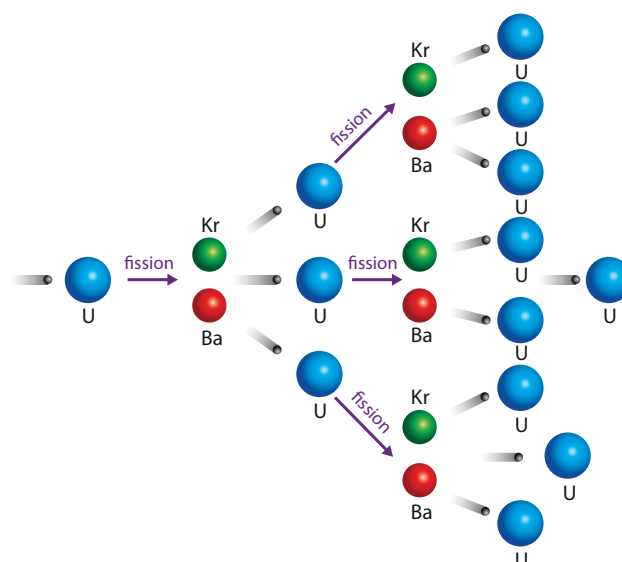


Figure C.11 A nuclear fission chain reaction.

In a nuclear reactor, the neutrons released in the fission process can cause fission of other nuclei, which can result in a chain reaction (Figure C.11). Some of the neutrons produced in a fission reaction will escape from the uranium sample without causing further fission. If all the neutrons escape then a chain reaction will not occur and the sample of uranium is said to be subcritical (Figure C.12a). The mass of uranium needed in order for the reaction to become self-sustaining is called the **critical mass**. For a chain reaction to be self-sustaining, at least one neutron produced in each fission process must go on to cause another fission reaction (Figure C.12b). At the critical mass exactly one neutron from each fission process goes on to cause another fission process.

In a nuclear reactor there must be a sufficient mass of uranium present so that enough neutrons cause fission before escaping from the reactor core. Control rods are inserted between the fuel rods to absorb neutrons in order to keep the average number of neutrons from each fission process that go on to cause further fission at about one. If too many neutrons cause fission the chain reaction could go out of control with potentially catastrophic consequences.

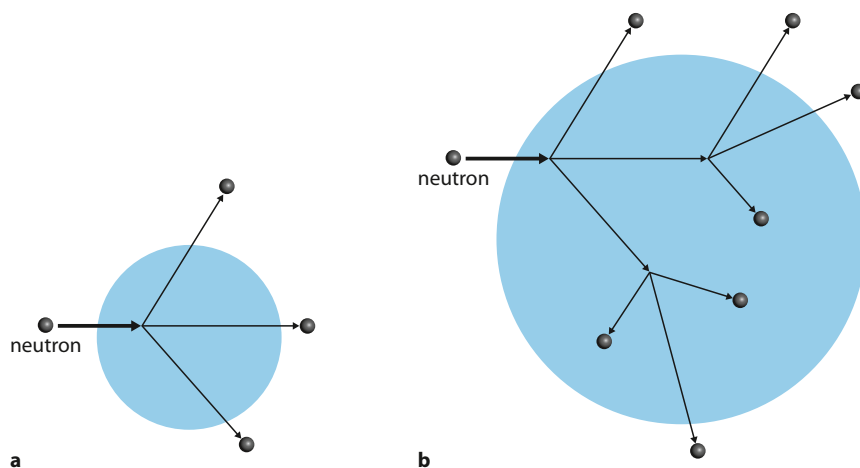
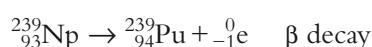
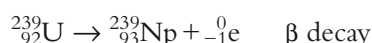


Figure C.12 **a** A subcritical sample of uranium – the neutrons escape before causing further fission; **b** a sample of uranium larger than the critical mass (supercritical) – a self-sustaining chain reaction is produced.

Breeder reactors

The fuel used in a conventional nuclear reactor is uranium enriched with ^{235}U . Naturally occurring uranium contains a very low proportion of ^{235}U (natural abundance 0.72%) – it is mostly ^{238}U , which does not undergo fission. **Breeder reactors** were developed to increase the amount of fissionable nuclear fuel available. ^{235}U undergoes fission most readily with slower-moving neutrons – the neutrons produced in fission processes are slowed down by a moderator so that they are more readily absorbed by ^{235}U nuclei. However, in a breeder reactor there is no moderator and fast-moving neutrons are more readily captured by ^{238}U nuclei which then undergo a series of nuclear reactions to produce ^{239}Pu , a fissionable fuel:



Most breeder reactors use ^{239}Pu as the fissionable fuel – and through the above reactions, starting with uranium-238, they can be designed to produce more fuel than they consume.

Problems associated with using nuclear power

There are many problems associated with the generation of electricity using nuclear fission.

- **Health issues** – there are severe risks associated with exposure to radioactive materials. Exposure to radioactivity can cause radiation poisoning (radiation sickness), cancer and birth defects in children. The workers in nuclear power stations are protected from exposure and the radioactivity level is monitored but escape of radioactive material resulting from an accident poses a severe risk to the health of people living nearby. There have been several examples of nuclear accidents causing a release of radioactive material into the environment – the two most recent are Chernobyl (1986) and Fukushima Daiichi (2011). There is an extensive debate as to how many people died as a result of the Chernobyl disaster and estimates range from hundreds to hundreds of thousands depending on the political/industrial associations of the organisations producing the data.
- **Meltdown** – this is a term usually used to describe accidents in a nuclear reactor. Heat is generated by fission in a nuclear reactor and this is removed from the core by a coolant so that the core remains at a fairly constant temperature. If the nuclear chain reaction is allowed to go out of control or there is a problem with the coolant then the core can overheat. If this is not dealt with, the materials in the core can begin to melt. This can result in radioactive material escaping into the environment. The Chernobyl and Fukushima Daiichi disasters both involved core meltdown.
- **Nuclear weapons** – nuclear reactors, especially breeder reactors, produce ^{239}Pu . Reprocessing of spent fuel from nuclear power stations can produce weapons-grade plutonium. There are severe worries that terrorists could get hold of this and build nuclear weapons. There are hundreds of tonnes of civil-controlled (non-military) plutonium stored around the world – only a few kilograms are needed to make a bomb!

A breeder reactor is a nuclear reactor that produces more fissionable material than it consumes.

β decay involves a neutron in a nucleus becoming a proton and an electron; the electron is ejected from the nucleus.



Breeder reactors have severe reliability problems, use liquid sodium as a coolant (there are dangers associated with this) and are expensive. These reasons, among others, mean that breeder reactors have not generally been a commercial success and many countries have discontinued programs to use them. There are also very great security concerns about the fact that reprocessing of the fuel from breeder reactors can produce large amounts of weapons-grade plutonium.



The plutonium produced by reprocessing is controlled by just a few countries around the world. The UK is believed to have the largest stock of non-military plutonium.

Nuclear waste

Radioactive waste is produced in nuclear power stations, research laboratories, military establishments, industry and hospitals. Numerous radioisotopes are used or produced in various processes and these have half-lives that vary enormously. Some have very short half-lives – ^{131}I , used as a tracer in medicine, has a half-life of just eight days. Others, such as the ^{239}Pu produced in nuclear power stations, have half-lives of thousands of years.

Radioactive waste can be divided into different categories: low-level and high-level. The category ‘intermediate-level’ is also sometimes used. The classification of radioactive waste is important in determining how it can be disposed of and the safety measures that must be used in its transport and handling. The criteria used for the classification of radioactive waste are quite complex and low-level waste is divided into sub-categories (A, B, C and >C) depending on its activity. Generally, low-level waste has lower activity and usually contains isotopes with short half-lives.

Low-level waste

This includes items that have been contaminated with radioactive material or exposed to radioactivity. Examples are gloves, protective clothing, tools, soil, rubble and carcasses of animals that have been treated with radioactive materials. Low-level waste may be stored on site until it has decayed to such an extent that it can be disposed of as ordinary waste (e.g. in landfill sites or released into the sewage system) or shipped to a central site for more specialised disposal. Some low-level waste is incinerated, which reduces its volume considerably and distributes the radioisotopes over a wide area. The ash from incineration is assessed for activity and disposed of appropriately. Low-level waste with higher activity is often just buried underground (‘near-surface’ disposal) – for example, in individual concrete canisters or in concrete-lined vaults. Low-level waste may need to be contained underground for up to 500 years depending on its activity and half-life.

High-level waste

This includes spent fuel rods or other materials resulting from the reprocessing of nuclear fuels. It contains fission products and transuranic (beyond uranium) elements generated in the reactor core. This spent fuel has a high concentration of radioactive isotopes, some of which (such as ^{239}Pu) will remain hazardous to humans and other living things for thousands of years. Spent fuel rods may either be considered as waste and disposed of directly, or reprocessed to extract material to be used as more nuclear fuel. Reprocessing of nuclear fuel produces a highly radioactive liquid waste that can be converted to glass (vitrified) to make storage easier.

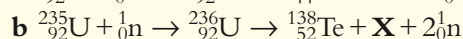
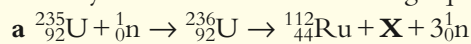
High-level waste is initially stored on site at nuclear power plants in storage pools (cooling ponds). Storage under water is usually for a minimum of nine months but sometimes the spent fuel rods are stored in this way for decades. After sufficient cooling, the fuel rods may be transported to a reprocessing plant, left in the pools or transferred to dry storage casks. These dry casks have very thick walls and are made of steel and concrete. The dry casks are then stored in concrete bunkers. Most spent fuel rods from nuclear power stations in the US are left in cooling ponds or transferred to dry storage awaiting a more permanent method of storage.

Permanent storage of high-level radioactive waste is a major problem and several solutions, such as burying the waste deep underground in stable geological areas, have been suggested. Over thousands of years, however, it is difficult to envisage what processes could occur that might lead to the release of the radioactive material.

? Test yourself

- 9 Write balanced equations for each of the following fission reactions of uranium-235:
- to form caesium-140 and rubidium-93
 - to form molybdenum-105 and tin-129

- 10 Identify X in each of the following equations



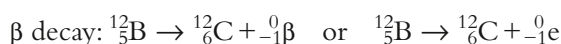
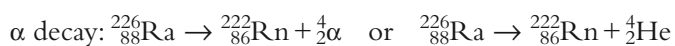
C3.4 Half-life

Radioactive decay involves changes in the nucleus of an atom resulting in particles – and sometimes electromagnetic radiation – being emitted from the nucleus. The two main particles that are emitted are:

- alpha particles, ${}^4_2\alpha$, which are helium nuclei composed of two protons and two neutrons
- beta particles, ${}^0_{-1}\beta$, which are electrons formed when a neutron turns into a proton and an electron.

Emission of γ rays (high-energy electromagnetic radiation) may also accompany radioactive decay.

Examples of radioactive decay processes are:



Radioactive decay is a random process and it is impossible to predict when any one particular nucleus will decay but on average a sample of any radioisotope with a very large number of atoms will decay with constant half-life.

Half-life is the time it takes for the number of radioactive nuclei present in a sample at any given time to fall to half its value.

Half-life ($t_{1/2}$) varies from isotope to isotope – for example the half-life of ${}^{226}\text{Ra}$ is 1600 years but that of ${}^{224}\text{Ra}$ is 3.7 days. Half-life is independent of the ambient conditions (temperature, pressure etc.) and also of the mass of a radioactive sample – the half-life is the same whether 1 g or 1 kg of a particular isotope is present.

Figure C.13 shows a graph of the decay of an isotope with a half-life of 2 s – the number of original nuclei remaining decreases by half every 2 s.

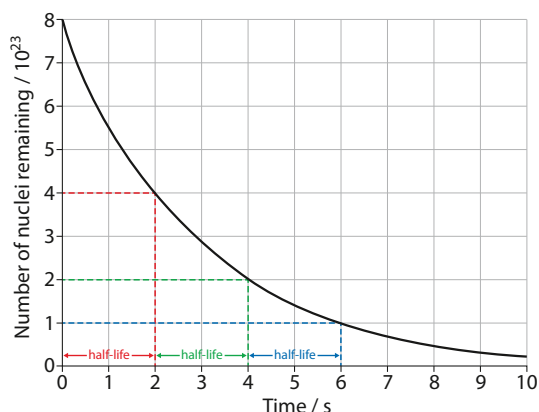
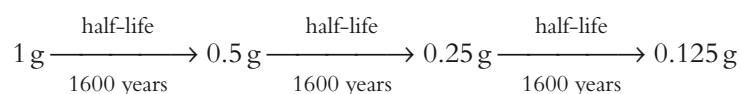


Figure C.13 Decay of a radioisotope with half-life of 2 s – this is exponential decay.

Learning objectives

- Understand what is meant by half-life
- Solve problems involving integral numbers of half-lives

Radium-226 has a half-life of approximately 1600 years. If we start with 1 g of pure ^{226}Ra , after 1600 years there will be 0.5 g left, after a further 1600 years there will be 0.25 g left and after a total of 4800 years (three half-lives) there will be only 0.125 g of radium-226 left:



Half-life can also be expressed in terms of the activity of a sample – this is the number of nuclei that decay per second. The half-life is then the time taken for the activity to drop to half its original value.

Worked examples

C.3 Germanium-71 has a half-life of 11 days. If there were originally 2.00 mg of this isotope present in a sample, calculate the mass remaining after 44 days.

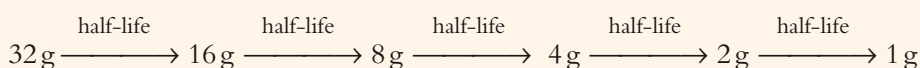
It takes 11 days for the amount to fall by half, therefore there will be 1.00 mg present after 11 days. This will drop to 0.500 mg after another 11 days, 0.250 mg after another 11 days and 0.125 mg after a further 11 days:



Therefore the mass of germanium-71 remaining will be 0.125 mg.

C.4 The half-life of uranium-238 is 4.5×10^9 years. Calculate how long it would take 32 g of uranium-238 to decay to 1 g.

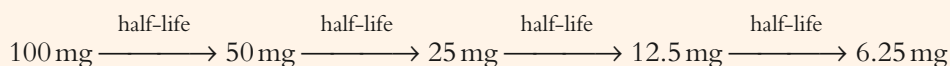
This decay involves five half-lives:



So the total time is $5 \times 4.5 \times 10^9 = 2.3 \times 10^{10}$ years.

C.5 Calculate the half-life of protactinium-233 if it takes 108 days for 100 mg of the element to decay to 6.25 mg.

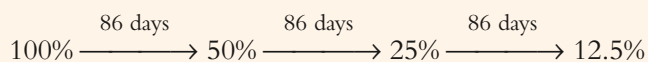
This decay will take four half-lives:



So 108 days is equivalent to 4 half-lives. 1 half-life is therefore $\frac{108}{4} = 27$ days.

C.6 Calculate the time taken for the activity of a sample of rubidium-83 to fall to 12.5% of its original value given that its half-life is 86 days.

The data here are given in terms of activity instead of mass, but the answer is worked out in the same way:



Three half-lives are required for this decay and so the total time is $3 \times 86 = 258$ days.



? Test yourself

- 11 In each of the following questions, calculate the amount remaining from a 100 mg sample of the given radioisotope after the specified time.
- ^{105}Rh has a half-life of 35 h. Calculate the mass remaining after 70 h.
 - ^{209}Po has a half-life of 105 y. Calculate the mass remaining after 420 y.
 - ^{219}Rn has a half-life of 3.96 s. Calculate the mass remaining after 39.6 s.
- 12 Calculate the half-lives of each of the following radioisotopes.
- It takes 180 days for 80 mg of iron-59 to decay to 5 mg.
 - It takes 2.1×10^{12} years for 60 mg of platinum-190 to decay to 7.5 mg.
- 13 Calculate how long each of the following decay processes will take:
- 32 mg of silicon-32 (half-life 160 y) to decay to 1 mg
 - 56 mg of mendelevium-258 (half-life 56 d) to decay to 7 mg.

Nature of science

There are many ethical issues associated with the development of nuclear energy and nuclear weapons. Arguments in favour of nuclear power include the fact that it does not produce greenhouse gases and arguments against focus on the disposal of nuclear waste, safety and the potential to be used in bombs.

The play *Die Physiker* by Friedrich Dürrenmatt provides an interesting treatment of the responsibilities of scientists towards the wider community.

The atomic bombs dropped on Japan in 1945 used fission reactions, the hydrogen bomb also involves a fusion reaction.

C4 Solar energy

Most forms of energy that we use come originally from the Sun – for example, coal is derived from plants that used photosynthesis to store chemical energy and wind power comes from differential heating of the Earth's surface by the Sun. The only form of energy that does not come from the Sun is nuclear – although the uranium was, of course, made in a sun (star) by nuclear fusion reactions. The Sun's energy comes from nuclear fusion reactions that involve the joining together of small nuclei, such as hydrogen, with the release of a great deal of energy.

C4.1 Coloured compounds and photosynthesis

Coloured compounds

Chromophores

In order to absorb electromagnetic radiation in the ultraviolet and visible (UV–Vis) regions of the electromagnetic spectrum, molecules must generally contain a double bond in the form of C=C, C=O or a benzene ring. These groups, which give rise to absorptions in the UV–Vis region, are called **chromophores**.

Learning objectives

- Understand what is meant by a conjugated system
- Understand that molecules with a sufficiently long conjugated system can absorb visible light
- Understand that photosynthesis is the process by which plants turn light energy into visible light
- Write an equation for photosynthesis

A **conjugated system** is a system of alternating single and double bonds in a molecule.

Conjugated systems

The double bonds highlighted in Figure C.14 form a conjugated system but the two double bonds at the ends of the molecule are not part of this system as they are separated from the other double bonds by more than one single bond.

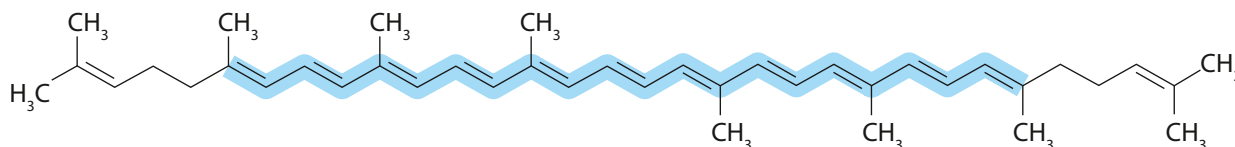


Figure C.14 Lycopene, the red pigment in tomatoes, has 11 conjugated double bonds. Note that not all the C=C units in lycopene are part of the conjugated system.

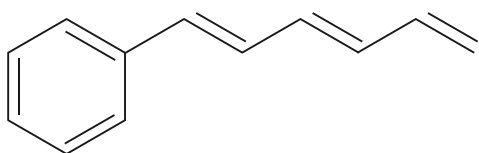


Figure C.15 A molecule with six conjugated double bonds.

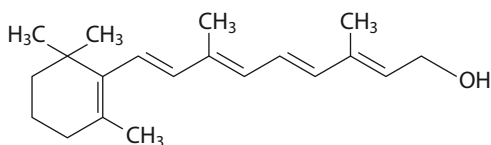


Figure C.16 Retinol has only five conjugated double bonds and absorbs only in the UV region of the electromagnetic spectrum.

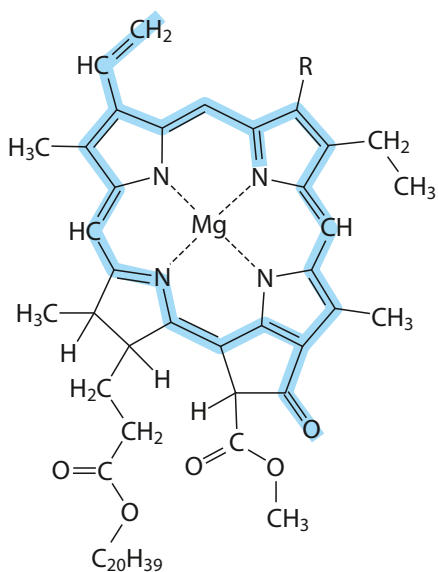


Figure C.17 The basic structures of chlorophyll a (in which R is CH₃) and chlorophyll b (R is CHO) showing the conjugated system. Chlorophyll b has an extra double bond that is part of the conjugated system.

The double bonds must alternate with single bonds for a system to be conjugated – if there are two or more single bonds between the double bonds then the system is not conjugated.

We have already seen that a benzene ring can be represented as a ring with three alternating double and single bonds – so a benzene ring is a conjugated system. The molecule shown in Figure C.15 has six conjugated double bonds.

Absorption of electromagnetic radiation and colour

In order for a compound to be coloured, its molecules must absorb visible light. Visible light is electromagnetic radiation with wavelengths between about 400 and 750 nm, so if a molecule absorbs radiation between these wavelengths it will be coloured. The longer the conjugated system, the longer the wavelength of the radiation absorbed and if a conjugated system involves more than about eight double bonds, the molecules should absorb in the visible region of the spectrum and be coloured.

Lycopene has a system of 11 conjugated double bonds (Figure C.14) and absorbs light in the blue–green part of the visible spectrum, and therefore appears red. Retinol (see Figure C.16), however, only has a system of five conjugated double bonds and therefore does not absorb visible light (it only absorbs ultraviolet radiation) and is colourless.

Chlorophyll a and b have long conjugated systems (highlighted in Figure C.17). They absorb light in the 400–500 nm region and in the 600–700 nm region (Figure C.18). The green light in the middle part of the spectrum is not absorbed, and so chlorophyll appears green.

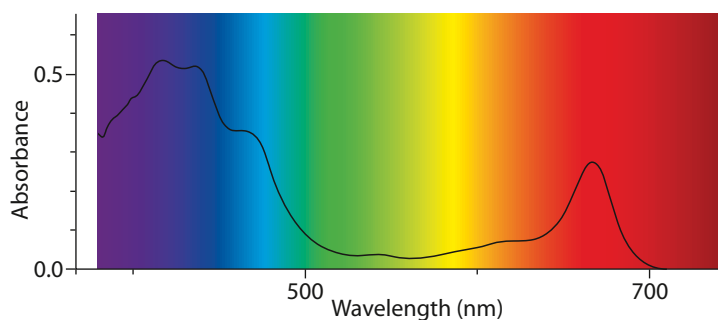
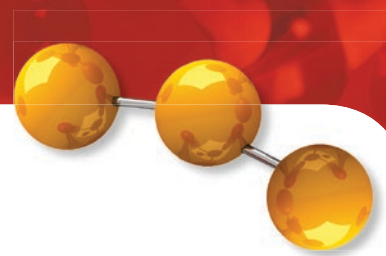


Figure C.18 The visible spectrum of chlorophyll.

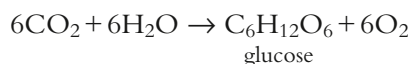


Photosynthesis

The substances needed for photosynthesis are:

- sunlight – the red part of the light is absorbed by plants
- carbon dioxide – from the air
- water – from the air and the ground
- chlorophyll – a green pigment in plants, which absorbs red light.

The exact nature of the reactions which occur is complex but the basic equation is:



The energy absorbed by the chlorophyll is used to drive this process; it is endothermic.

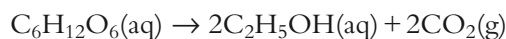
Plants use the glucose produced as an energy source to live and grow (the energy is ultimately released again in the process of respiration, the reverse of the above reaction).

Photosynthesis involves the conversion of light energy from the Sun to chemical energy.

C4.2 Biofuels

Fermentation

The basic reaction that happens during fermentation is the enzyme-catalysed conversion of glucose to ethanol:



Yeast, which contains enzymes, is mixed with a solution of glucose and the reaction mixture kept at a temperature of about 30 °C. Fermentation produces a mixture with an ethanol concentration of about 8–12% and this mixture must be distilled to concentrate the ethanol.

Ethanol produced in this way is a **biofuel** and is mixed with gasoline for use as a fuel in cars. Various blends of ethanol with gasoline are available and, especially in Brazil and the US, flexible-fuel vehicles are available that have been designed to work with all possible mixtures of ethanol and gasoline.

The main producers of ethanol as a fuel by fermentation are Brazil and the US. The main feedstock for fermentation in Brazil is sugar cane, whereas in the US it is corn starch. A disadvantage with corn starch is that it must be pre-treated, which involves heating and mixing with enzymes to produce simple sugars that can undergo fermentation.

Ethanol has an octane number of 111 and so it increases the octane number when added to most fuels.

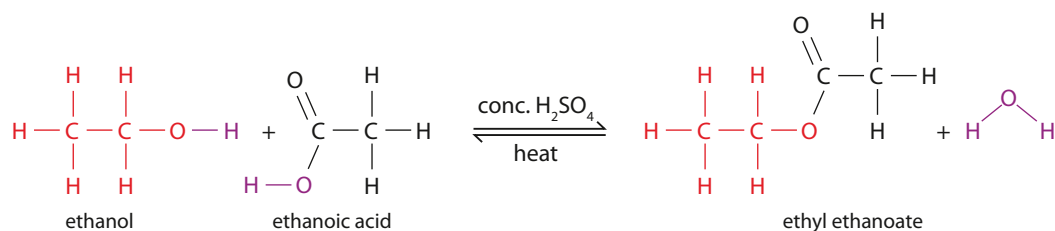
Learning objectives

- Understand that fermentation can be used to produce ethanol for use as a biofuel
- Write an equation for fermentation of glucose
- Understand what is meant by a transesterification reaction
- Write equations for transesterification reactions
- Understand that vegetable oils are too viscous to be used in modern diesel engines
- Understand that biodiesel can be made using a transesterification reaction
- Understand why biodiesel has a lower viscosity than vegetable oils
- Understand some of the advantages and disadvantages of using biofuels

A biofuel is a fuel produced from organic matter obtained from plants, waste material etc.

Transesterification reactions

Esters contain the COOC functional group and are made in the reaction between a carboxylic acid and an alcohol (see Topic 10):



Exam tip

To work out the structure of the new ester formed, the alkyl group of the original ester (on the C-O side) is replaced by the alkyl group of the alcohol that it reacts with.

In a transesterification reaction an ester is reacted with a different alcohol which substitutes for the original one (Figure C.19). This reaction occurs in the presence of a strong acid or base catalyst such as sulfuric acid or sodium hydroxide.

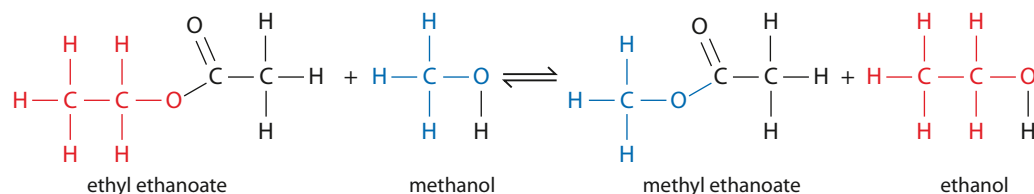
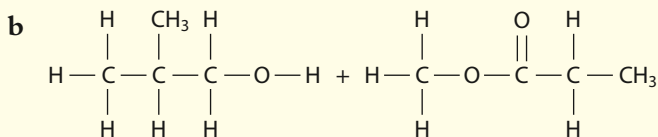
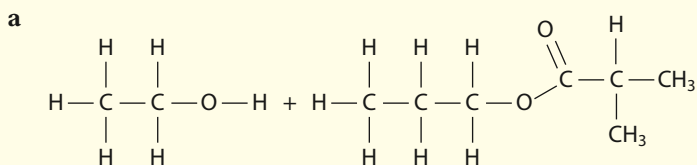


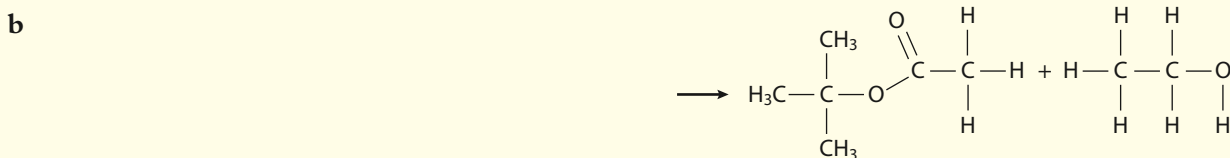
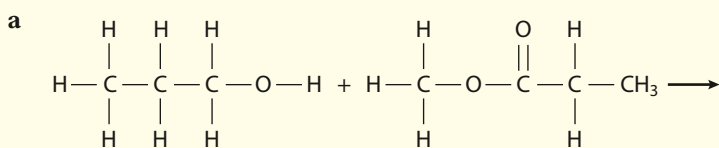
Figure C.19 A transesterification reaction.

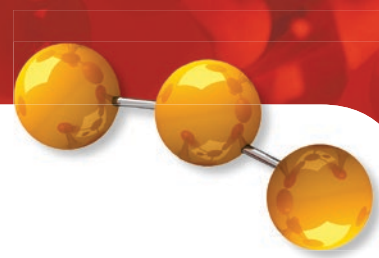
? Test yourself

14 Predict the structure of the ester formed in each of the following transesterification reactions.



15 Copy and complete the equations for these transesterification reactions using structural formulas.





Biodiesel

The specific energy of peanut oil is about $37\,000\text{ kJ kg}^{-1}$, whereas its energy density is about $34\,000\text{ kJ dm}^{-3}$. These values can be compared with those for petrodiesel – approximately $43\,000\text{ kJ kg}^{-1}$ and $36\,000\text{ kJ dm}^{-3}$. The original diesel engine, as designed by Rudolf Diesel, ran on peanut oil and it can be seen that the energy released by burning fats and oils is very similar to that by burning diesel fuel. However, vegetable oils cannot be used directly in modern diesel engines because they are too viscous. There are also other disadvantages such as the fact that they can solidify at lower temperatures.

Biodiesel can be made from plant oils. The structure of a plant oil is shown in Figure C.20. The molecule contains three ester linkages, one of which is highlighted, and is formed when three carboxylic acid molecules (fatty acids) react with propane-1,2,3-triol (glycerol). Because three fatty acid units form ester linkages to propane-1,2,3-triol, these molecules are called **triglycerides** (if two fatty acid molecules were joined it would be a **diglyceride**).

Biodiesel can be made when vegetable oils undergo a transesterification reaction – the fatty acid molecules form an ester linkage to a different alcohol (usually methanol). The reaction is usually carried out in the presence of a strong base – the methanol is first of all reacted with solid sodium hydroxide to form sodium methoxide (CH_3ONa), which is then reacted with the vegetable oil. The overall reaction is shown in Figure C.21.

The biodiesel molecule shown in Figure C.21 belongs to the general class of alkyl esters. If ethanol had been used instead of methanol the product would have been $\text{C}_{17}\text{H}_{33}\text{COOCH}_2\text{CH}_3$.

Because this is a reversible reaction, excess alcohol is used to shift the position of equilibrium towards the products.

Vegetable oils contain a small amount of free fatty acids (more if they have been used for cooking) and these free fatty acids can also be converted to esters when they are reacted with alcohol. When the free

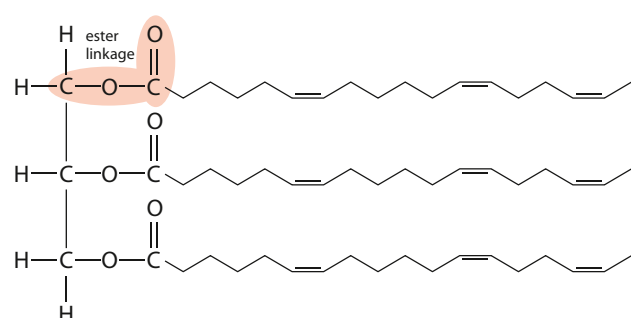


Figure C.20 A vegetable oil.

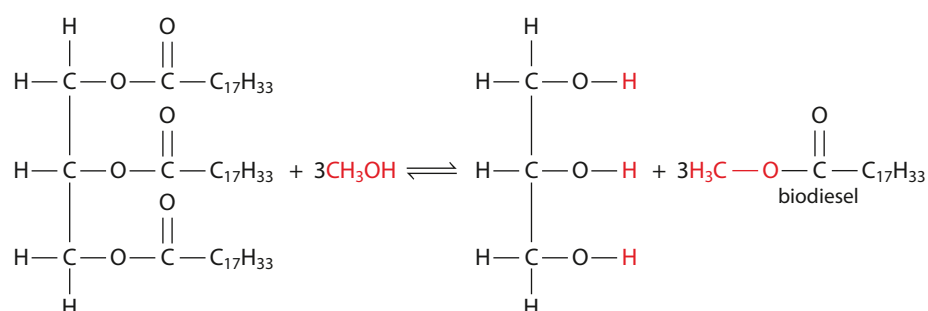


Figure C.21 Biodiesel can be made in a transesterification reaction.

Petrodiesel is diesel fuel obtained from crude oil.

The biodiesel molecule shown in Figure C.21 here is sometimes called a fatty acid methyl ester, FAME.

fatty acid content is very high either some sort of pre-treatment is used to reduce their concentration and/or an acid catalyst is used.

The biodiesel must be separated from the glycerol (the glycerol is denser than the biodiesel and forms a separate layer at the bottom) and then purified before it can be used.

Viscosity is a measure of the resistance of a liquid to flow.

Liquids such as honey have a much higher viscosity than water. The viscosity of biodiesel is significantly lower than that of the original oil and is similar to that of petrodiesel. Viscosity depends, among other things, on the strength of intermolecular forces. Biodiesel molecules have much lower relative molecular masses than the oil molecules from which they were made and therefore have weaker London forces between molecules. Because the forces between biodiesel molecules are weaker they have less resistance to flow and a lower viscosity. The lengths of the hydrocarbon chains in biodiesel and petrodiesel are very similar and therefore the London forces between chains will be similar, and so will their viscosities.

Advantages and disadvantages of biofuels

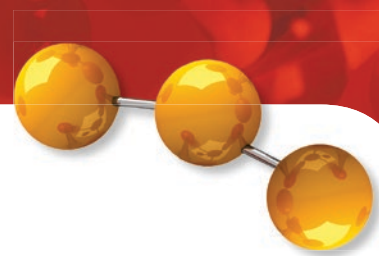
One of the main advantages of using biofuels over fuels derived from petroleum is that biofuels are renewable, whereas fuels from petroleum are non-renewable. An advantage of using biofuels for a country such as Brazil is that they can be produced locally and so there is less reliance on expensive oil imports from other countries. Biofuels can also be produced from waste materials, e.g. biogas from manure or landfill sites or biodiesel from waste oil.

Comparing specific properties of biodiesel fuels and petrodiesel fuels:

- biodiesel is biodegradable and so there is less environmental impact from spillages
- biodiesel contains no sulfur so there are no sulfur dioxide emissions when it is burned – however, use of biodiesel can result in slightly higher emissions of NO_x
- biodiesel is more expensive than petrodiesel
- biodiesel has a lower specific energy than petrodiesel
- biodiesel is a better lubricant than petrodiesel and so can reduce engine wear.

Biofuels are sometimes described as being carbon-neutral in that the carbon atoms in the biofuel originally came from carbon dioxide in the atmosphere and these are replaced when the fuel is burned, so there is no net change in the number of carbon dioxide molecules in the atmosphere. However, the situation is more complicated than this and how environmentally friendly a biofuel such as ethanol is depends on several factors. At first sight it would appear to be carbon-neutral in that the six molecules of carbon dioxide released during the fermentation process and the combustion of ethanol balance exactly with the six molecules of carbon dioxide that were removed from the atmosphere when glucose was formed by photosynthesis. However, several other processes that produce carbon dioxide must be considered:

- the agricultural machinery used to work the land where the corn/sugar cane is grown



- the production of fertilisers for use on the farms
- the transportation of corn/sugar cane
- the processing of corn starch to produce simple sugars
- distillation and so on.

All these processes require energy and, assuming that most of this comes originally from burning fossil fuels, ethanol is far from carbon-neutral. The debate is on-going as to whether some biofuels actually have a *larger* carbon footprint than fuels derived from petroleum. There is also some debate in the US as to whether more energy must be put in to make ethanol from corn than is obtained from it.

Growing biofuel crops requires large areas of land and in a world where there are still severe problems with famine, there are ethical implications in using vast areas of land to grow a foodstuff to be converted into a fuel for vehicles. The use of corn for fuel production has also led to an increase in the cost of this commodity.

Nature of science

It is essential that scientific discoveries that can make a significant difference to society are properly explained to and understood by the public. A basic scientific education is important for all so that they can make sense of headlines such as ‘Brit boffins make petrol from air and water’ – variations on which appeared in many newspapers in the UK in 2012.

C5 Environmental impact – global warming

The greenhouse effect

This is an important mechanism for maintaining the Earth’s temperature at a reasonable level. Without some sort of greenhouse effect the Earth would be too cold to maintain life as we know it.

Some of the short-wavelength solar radiation (visible light) from the Sun that reaches the Earth is reflected back into space, and the rest passes through the atmosphere to reach the Earth’s surface. The surface absorbs some of this radiation and heats up. The warmed surface radiates longer-wavelength infrared radiation. Part of this radiation is absorbed by the greenhouse gases, such as carbon dioxide, in the atmosphere. Some of the radiation absorbed by the greenhouse gases is then re-radiated back to Earth.

The overall effect is that the heat is ‘trapped’ by the gases in the atmosphere (Figure C.22). The natural equilibrium between incoming and outgoing radiation maintains the Earth’s mean temperature at about 15 °C.

If the amount of greenhouse gases in the atmosphere increases then more infrared radiation will be absorbed and re-radiated back to Earth and the global temperature should increase.

Learning objectives

- Understand how the greenhouse effect works
- Understand the mechanism by which greenhouse gases absorb infrared radiation
- Describe the sources of greenhouse gases and the contribution of different gases to global warming
- Understand the evidence for a relationship between increased levels of greenhouse gases and increased global temperature
- Discuss approaches to controlling carbon dioxide emissions
- Explain what is meant by global dimming
- Understand that the carbon dioxide in the atmosphere is in equilibrium with the dissolved carbon dioxide in the oceans
- Understand that increased levels of carbon dioxide in the atmosphere can result in ocean acidification

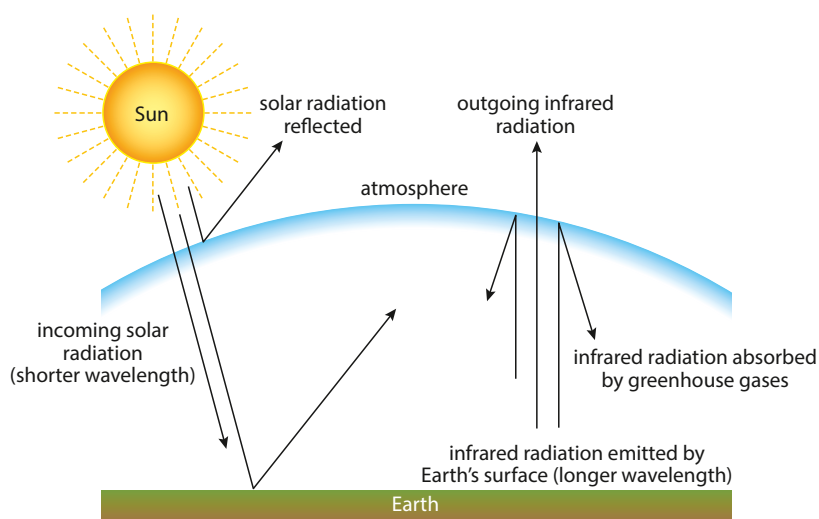


Figure C.22 The greenhouse effect.

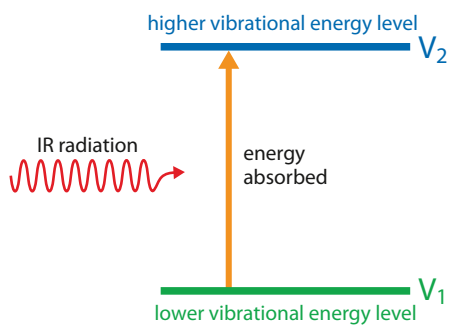


Figure C.23 Molecules can absorb IR radiation to promote them from a lower to a higher vibrational energy level.

The mechanism by which infrared radiation is absorbed by greenhouse gases

Even at absolute zero, atoms in molecules are vibrating relative to each other. Just as the electrons in an atom or molecule can exist only in certain energy levels (the energy of an electron is quantised) the vibrational energy of a molecule is quantised. This means that the vibrational energy of a molecule can take only certain allowed values and not just any value.

For instance, a molecule might be able to exist in either the level with vibrational energy V_1 or that with V_2 (Figure C.23). The molecule can absorb certain frequencies of infrared radiation to move it from a lower vibrational energy level to a higher one.

When molecules of greenhouse gases, such as carbon dioxide in the atmosphere, absorb infrared radiation to promote them to higher vibrational energy levels, they vibrate more energetically. As they move back down to a lower vibrational energy level, the 'extra' energy is given out again. This energy is given out in all directions and so some infrared radiation will be radiated back to Earth.

Diatomic molecules

For a molecule to be able to absorb infrared (IR) radiation, there must be a change in bond polarity (more precisely, dipole moment) when it vibrates. Polar molecules constitute a dipole – two charges separated from each other (see Topic 4, page 130 in the Coursebook).

The size of the dipole moment depends on the magnitude of the partial charges and on the distance between them. The longer the distance between the charges, the higher the dipole moment. So as an H–Cl molecule vibrates, the dipole moment increases and decreases (Figure C.24).

This means that a hydrogen chloride molecule is able to absorb IR radiation and we say that it is *IR-active*.

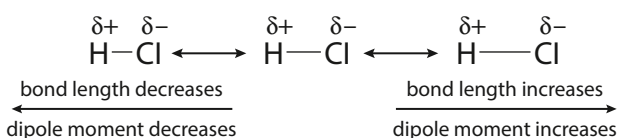
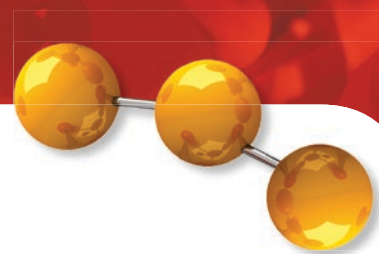


Figure C.24 The vibration of an HCl molecule.

The vibrations of a molecule are often likened to two masses joined by a spring.

If infrared radiation is passed through a sample of hydrogen chloride, radiation of wavenumber approximately 2900 cm^{-1} is absorbed. However, oxygen molecules, O_2 , and nitrogen molecules, N_2 , which are the major gases in the Earth's atmosphere, cannot absorb infrared radiation because these molecules are non-polar and their molecular vibrations do not involve a change in dipole moment. O_2 and N_2 are said to be IR-inactive.



A diatomic molecule can absorb infrared radiation only if it is polar.

Triatomic molecules

Triatomic molecules are more complicated than diatomic ones because they can vibrate in different ways. There are two main types of vibrational mode – *stretching* (bond lengths change) and *bending* (bond angles change).

Such molecules can stretch in two different ways – either both bond lengths can increase and decrease together (symmetric stretch) or one gets shorter as the other gets longer (asymmetric stretch). The vibrational modes for a bent triatomic molecule, such as water, are shown in Figure C.25.

The vibrational modes may also be shown as illustrated in Figure C.26. Only vibrational modes that involve a change in dipole moment are IR-active. For polar molecules such as H_2O , all three vibrational modes are IR-active because they all involve changes in the dipole moment. Water molecules therefore absorb infrared radiation at three distinct frequencies, corresponding to the energy to excite the molecule to a higher vibrational energy level for each vibrational mode.

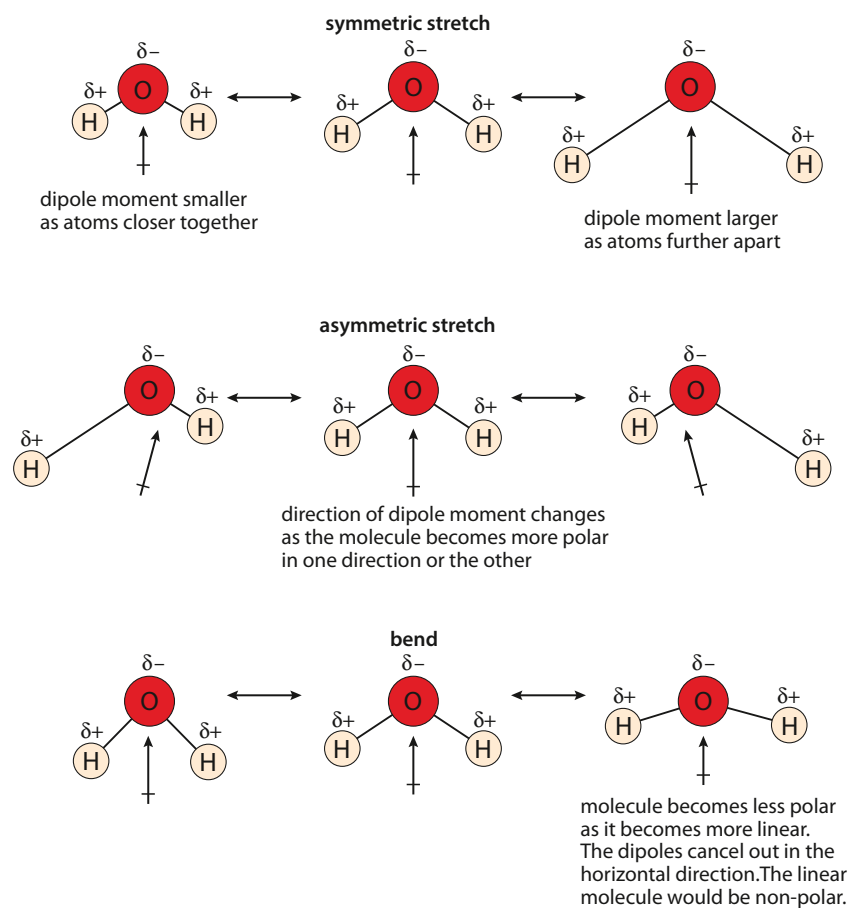


Figure C.25 Vibrational modes of water showing how the dipole changes – all types of vibration are occurring at the same time.

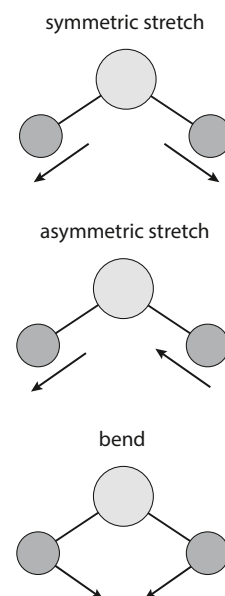


Figure C.26 The types of vibrational mode in a bent triatomic molecule. The central atom can be regarded as fixed in position.

There are actually four different vibrational modes for CO₂ but two are degenerate – they have the same energy.

The vibrational modes of carbon dioxide

Carbon dioxide is a linear non-polar molecule (Figure C.27a). There are three different types of vibrational mode (Figure C.27b) but only two of them (the asymmetric stretch and bend) involve a change in dipole moment and are IR-active. The symmetric stretch is IR-inactive because the molecule remains non-polar when it vibrates in this way (Figure C.27c). Carbon dioxide, therefore, only absorbs infrared radiation at two distinct frequencies.

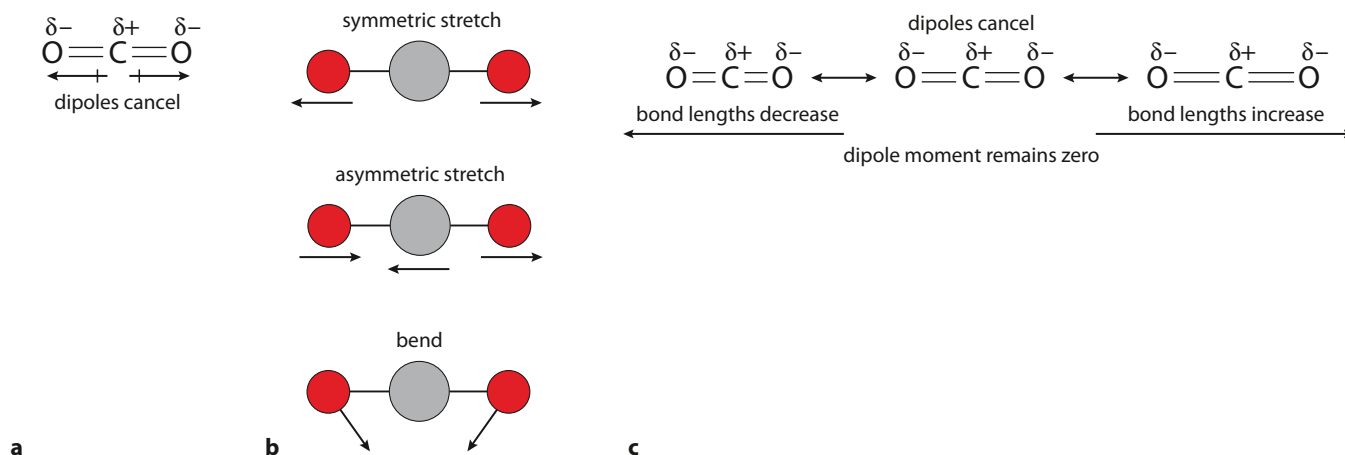


Figure C.27 a The non-polar CO₂ molecule; b the three vibrational modes; c the symmetric stretch which is IR-inactive.

The vibrational modes of methane

The vibrational modes of methane are considerably more complicated – there are four distinct vibrational modes, two of which are IR-active (Figure C.28). Methane is a non-polar molecule and it can be seen that the symmetric stretch, where all four hydrogen atoms move in and out together, involves no change in dipole moment.

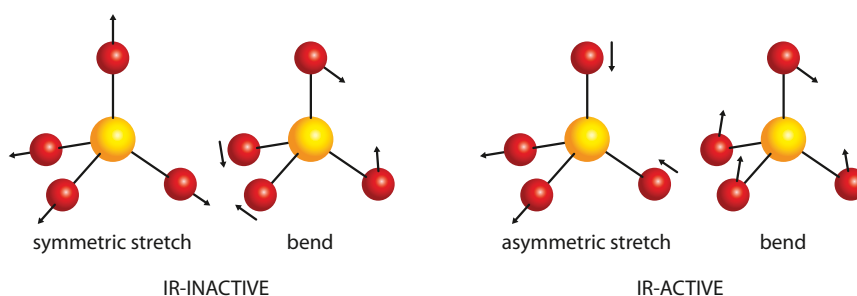


Figure C.28 The vibrational modes of methane.

Extension

Although ozone, O₃, would appear to be a non-polar molecule that does not absorb infrared radiation, an uneven charge distribution in the molecule means that certain vibrational modes are IR-active.

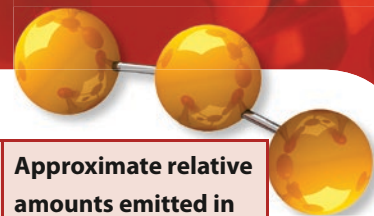
If stretching and bending modes cause a change in dipole moment then a molecule will absorb infrared radiation.



Test yourself

16 Which of the following molecules will absorb infrared radiation?

O₂ HCN HF H₂ CO CO₂ H₂S N₂ CFCI₃ N₂O



Gas	Source	Heat-trapping effectiveness	Approximate relative amounts emitted in US per year
H ₂ O	evaporation from oceans and lakes on the Earth's surface	0.1	
CO ₂	combustion of carbon fuels and biomass*	1	100
CH ₄	anaerobic decay of organic material agriculture: rice fields, marshes, animals (enteric fermentation in the stomachs of ruminant animals such as cows)	26	9.6
N ₂ O	agricultural soil management (fertilisers), nitric acid production	216	5.4
CFCs	refrigerants, propellants, foaming agents, solvents	13 000–23 000	

Table C.8 The main greenhouse gases, their sources and relative heat-trapping ability.

*When considering factors that contribute CO₂ to the atmosphere, we should also consider the effects of removing the mechanisms that reduce the amount of CO₂ in the atmosphere. For instance, if areas of forest are cleared this can increase CO₂ levels in the atmosphere in two ways – first, CO₂ is not being removed by the process of photosynthesis and second, if the wood is burned then CO₂ is produced.

The sources and relative effects of the main greenhouse gases

The main greenhouse gases, their sources and relative heat-trapping ability are shown in Table C.8.

The contribution of a particular greenhouse gas to global warming depends on several factors – its ability to absorb infrared radiation, its abundance in the atmosphere, its atmospheric lifetime and the wavelength range in which it absorbs infrared radiation.

The potential for a particular gas to cause global warming can be described in terms of its global-warming potential. The potential for 1 kg of some gases to cause global warming over a particular time period (e.g. 20 years) is compared to that of 1 kg of CO₂ in Table C.9.

The contribution of each of the anthropogenic gases to global warming between 1980 and 1990 is shown in Table C.10. Methane has a much higher global-warming potential than carbon dioxide, for equal masses, but is produced in much smaller amounts.

Carbon dioxide has a greater influence on global warming than some of the other gases from anthropogenic sources because, even though it does not absorb as much infrared radiation, it is produced in greater amounts.

Water vapour is another important greenhouse gas and most scientists would regard it as the most important greenhouse gas because it is present in the atmosphere at a much higher concentration than other greenhouse gases. However, the amount of water vapour in the atmosphere is only directly influenced to a small extent by human activities.

If the Earth gets hotter through the release of other greenhouse gases, this will increase the evaporation of water and so further increase the amount of water vapour in the atmosphere.

The effect of water vapour on global temperatures is difficult to predict – evaporation of water causes cooling of the Earth's surface (just as evaporation of sweat from your skin causes cooling of your body), but an increase in water vapour in the atmosphere will increase its effect as a greenhouse gas. In addition to this, an increase in water vapour will result in the formation of more clouds which reflect more sunlight back into space and so cause cooling.

Gas	Global-warming potential (20 years)
CO ₂	1
CH ₄	72
N ₂ O	289
CFC-11	3800

Table C.9 The global-warming potential of various gases over 20 years. This compares how effective equal masses of gases are at causing global warming, relative to carbon dioxide.

Gas	Contribution to global warming / %
CO ₂	55
CH ₄	15
N ₂ O	6
CFCs	24

Table C.10 The contribution of anthropogenic gases to global warming between 1980 and 1990.

'Anthropogenic' means that it has been produced by human activities.

The influence of increasing amounts of greenhouse gases on global temperatures

In the 10 000-year period up to 1750, the CO_2 concentration in the atmosphere remained fairly constant at around 280 ppm – this had risen to 379 ppm by 2005. Similarly, CH_4 and N_2O abundances in the atmosphere have increased since the Industrial Revolution.

In the 100 years up to 2005, global temperatures increased by about 0.7°C and in the past 30 years temperatures are estimated to have increased by about 0.2°C per decade. Although there is general agreement that global temperatures are increasing *and* the level of greenhouse gases in the atmosphere is also increasing, the difficulty is to prove a causal link between the two. Most scientists do believe that anthropogenic greenhouse gases are causing global warming and climate change, but there is no universal agreement. Other reasons put forward for the increase in global temperatures include increased solar activity and the effect of volcanic eruptions.

The Intergovernmental Panel on Climate Change (IPCC) stated in its 2007 report: ‘Most of the observed increase in global average temperatures since the mid-20th century is *very likely* due to the observed increase in anthropogenic greenhouse gas concentrations. It is *likely* that there has been significant anthropogenic warming over the past 50 years averaged over each continent (except Antarctica)’.

Evidence of a causal link between increases in the concentrations of greenhouse gases in the atmosphere and global warming can be obtained from complex computer models. These models assume a link between the two variables and are tested against data from the past – if there is good agreement between what is predicted by the models and the trends actually observed, they can be used to make predictions about the effect of future changes on the climate. If there is *then* good agreement between the predictions made by these models (which assume a link between increases in global temperatures and increased levels of greenhouse gases) and future trends, this would strengthen the evidence for a causal link between the two factors.

The effects of climate change

It is difficult to predict the effects of climate change on our planet but some suggested consequences are given here.

- As the Earth’s temperature rises, oceanic water expands – increased sea levels could submerge low-lying areas and many islands. Large populations live in some of these areas. Since 1993, sea levels have been rising at an average rate of more than 3 mm y^{-1} . Only estimates of future rises can be made based on complex models but these predict sea-level rises of up to about 0.5 m during the next 100 years.
- Polar ice caps could melt (Figure C.29) (the melting of floating ice (North Pole) does not cause sea levels to rise).
- Glaciers and snow/ice cover on land could melt – this does increase sea levels.
- The occurrence of extreme weather events such as floods, droughts and heatwaves could increase.
- The amount and distribution of precipitation (rain and snow) could change.



The IPCC is an intergovernmental body that works under the auspices of the United Nations and has 195 countries as members. It reviews and assesses scientific data about climate change in order to provide governments and people around the world with a clearer understanding of the current state of research on climate change and its potential impact. The IPCC does not itself carry out scientific research but thousands of scientists from around the world contribute to it on a voluntary basis.



Figure C.29 Melting sea ice could cause problems for wildlife.

- A warming climate may mean that commercial crops can no longer be produced where they grow now. This could be a massive problem in grain-producing areas that currently produce a large amount of food.
- The distribution of pests and disease-carrying insects could change – e.g. changes in the distribution of the mosquito population could alter the regions where malaria is a danger.

Control of carbon dioxide emissions

The biggest sources of carbon dioxide production in the US are electricity generation, transportation and industry. There are two main approaches to controlling carbon dioxide emissions – reducing the amount of carbon dioxide produced, or capturing and storing the carbon dioxide produced so it is not released to the atmosphere. The effect of deforestation on carbon dioxide levels in the atmosphere should also be considered.

Reducing the amount of carbon dioxide produced

Again there are two approaches – use ways of generating electricity and heat that release less carbon dioxide into the atmosphere, or use less electricity/heat/fossil fuels.

The amount of carbon dioxide produced when electricity is generated can be reduced by switching from using coal-fired power stations to natural gas or, especially, nuclear power. Coal produces the most carbon dioxide per kWh of electricity generated. Also, increased amounts of renewable energy sources such as hydroelectric power, solar energy and wind power could be used.

Wood-burning power stations could reduce emissions because burning the wood simply replaces the carbon dioxide that was removed when the trees grew. How close to carbon-neutral this is depends on various factors such as how far the wood must be transported etc. before being burned. Trees must also be replanted after they are harvested because deforestation reduces the amount of carbon dioxide removed from the atmosphere.

The amount of heat/electricity/fossil fuels we need can be reduced in many ways, for example:

- Design more fuel-efficient buildings by using more insulation and/or active and passive solar heating.
- Turn off lights when not needed and do not leave electrical devices on standby.
- Design electrical devices that use less electricity such as energy-efficient light bulbs and more energy-efficient refrigerators.
- Develop vehicles that are more fuel-efficient. The European Union has introduced legislation that attempts to reduce the average carbon dioxide emissions from all new vehicles produced from 2015 to less than 130 g km^{-1} . This should then be reduced to 95 g km^{-1} by 2020.
- Develop the use of hybrid, fuel cell and electric vehicles. However, the carbon footprint of electric vehicles and those using hydrogen fuel cells depends on how the electricity used to power them is generated and how the hydrogen is produced.
- Encourage the use of public transport, cycling etc.



The effect of global warming on global food production is difficult to estimate but, depending on the extent of the temperature change, it could actually result in an overall increase in the potential for global food production.



The Kyoto Protocol is an international treaty signed in 1997 which attempted to set binding targets for reduction of carbon dioxide emissions by developed countries. The protocol was accepted and ratified by the governments in many countries but some, such as the US and Canada, subsequently withdrew. The Kyoto Protocol was due to expire in 2012 but at a conference in Doha, Qatar it was extended to 2020. However, further withdrawal of countries and the non-inclusion of China means that the treaty only covers countries responsible for less than 20% of the carbon dioxide produced globally.

Carbon capture and storage

Various schemes have been proposed to capture carbon dioxide from the flue gases of power stations, before it can be released into the atmosphere, and storing it in some way – this is called carbon dioxide capture and sequestration, or carbon capture and storage (CCS). Some processes that are already in operation involve capturing the carbon dioxide from power station emissions, transporting it through pipelines and storing it underground, where it is trapped. The carbon dioxide can also be used in enhanced oil recovery which involves pumping carbon dioxide underground to force more oil out of an oil well (carbon dioxide can also mix with the oil to reduce its viscosity). Some of the carbon dioxide does return to the surface with the oil but this is reused and not released to the atmosphere.

Other proposed schemes for CCS include reacting carbon dioxide with minerals underground to form insoluble carbonates. The downside to all these processes is that they will require energy and cost money. However, if there is a net decrease in the amount of carbon dioxide released to the atmosphere it could be worth it.

Deforestation

Deforestation refers to the action of cutting down trees to clear areas of land (Figure C.30), usually so that they can be used for agricultural purposes. Deforestation is a major contributor to carbon dioxide emissions and it has been estimated that this could be responsible for up to 17% of global anthropogenic carbon dioxide emissions. Trees remove carbon dioxide from the atmosphere as they grow, but when they are cut down there are two effects – not only does this removal of carbon dioxide stop, but also the carbon dioxide that they removed is returned to the atmosphere when they are burned or left to rot.



Figure C.30 Deforestation in Indonesia.

Global dimming

Global dimming refers to the decrease in the amount of electromagnetic radiation from the Sun that reaches the surface of the Earth due to the presence of particulates in the atmosphere. These small particles reflect sunlight back into space and therefore cause cooling of the Earth.

Particulates are solid or liquid particles in the air – the term for such particles suspended in a gas is ‘aerosol’. Anthropogenic sources of particulate matter include:

- smoke/soot from incomplete combustion of wood, coal, petrol and diesel
- fly ash – contains soot and metal oxides from fossil fuels burning in furnaces
- dust from mechanical activity, demolition, metal-working etc.

Natural sources of particulate matter include pollen, dust, smoke/soot from forest fires and sea spray. The eruption of volcanoes results in large amounts of dust and sulfur dioxide entering the atmosphere. The sulfur dioxide causes the formation of tiny droplets of sulfuric acid in the upper atmosphere – a sulfate aerosol, which is very good at reflecting sunlight.

Not only can particulates reflect sunlight back into space but they can also have an indirect effect in that they can change the make-up of clouds. Water droplets form around particulates and this reduces the size of water droplets as clouds form. Clouds also cause global dimming by reflecting

sunlight back into space but the polluted clouds, with smaller water droplets, reflect more sunlight.

Ocean acidification

Increasing levels of carbon dioxide in the atmosphere resulting from human activity are making the oceans more acidic. Carbon dioxide is slightly soluble in water and an equilibrium is set up between carbon dioxide in the atmosphere and aqueous carbon dioxide in the oceans:

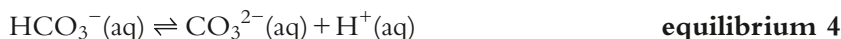
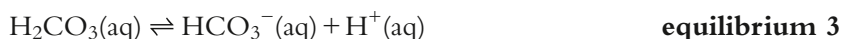


This is called a heterogeneous equilibrium because it involves substances in two different physical states. As the amount of carbon dioxide in the atmosphere increases, this will shift the position of the above equilibrium to the right – therefore there will be more carbon dioxide dissolved in the oceans.

The dissolved CO_2 reacts with water to form carbonic acid:



Carbonic acid is a weak diprotic acid and can dissociate:



As more carbon dioxide dissolves, the position of equilibrium 2 shifts to the right, which increases the concentration of H_2CO_3 ; this causes the position of equilibrium 3 to shift to the right and therefore increases the concentration of the $\text{H}^+(\text{aq})$ ions and hence the acidity of the water.

'Ocean acidification' is the reduction of the pH of the oceans over an extended period of time through the increased uptake of carbon dioxide from the atmosphere. Some scientists believe that the pH of the oceans could fall by up to 0.4 units by the end of this century.

There are many possible consequences associated with ocean acidification such as possible effects on the ability of corals, shellfish, phytoplankton etc. to make calcium carbonate shells and skeletons, a decrease in the metabolic rate and activity of jumbo squid and so on.

Nature of science

The ideas of cause and effect are very important in science. There is a definite correlation between the level of carbon dioxide in the atmosphere and global temperature but it is very difficult to prove that increases in anthropogenic carbon dioxide cause increases in global temperature. There have, for instance, been wide variations in the Earth's temperature in the fairly recent past, for example the 'Medieval warm period and the 'little ice age'. Scientists understand the mechanism by which an increased level of carbon dioxide could cause global warming but this still does not prove a link because planet Earth is an extremely complex system and there are many variables that must be considered. Computer modelling, which uses complex mathematical equations and many approximations, assumptions and simplifications, is an important research tool in the search for more evidence.



The issues concerning man-made climate change are very complex – how do we make decisions about this? To what extent are our decisions based on our trust in the knowledge and understanding of experts in the field, our own understanding or emotion? Is there a tendency to just align ourselves with an organisation (or individual) which has similar views to our own and then oppose all other views? To what extent are our opinions objective? How much information do we need to make a decision – do we need to examine all the primary data? What if we are not capable of understanding the primary data or it is not available?

? Test yourself

- 17 Give the names of **three** greenhouse gases produced by human activity.
- 18 State whether each of the following statements is true or false:
- Methane causes global dimming.
 - Increased levels of carbon dioxide in the atmosphere cause the pH of the oceans to increase.
 - More carbon dioxide than methane is produced each year by human activities.
 - Deforestation probably contributes to climate change.

C6 Electrochemistry, rechargeable batteries and fuel cells (HL)

C6.1 Batteries and fuel cells

Batteries

A battery is a portable electrochemical device that produces electricity – it is made up of one or more voltaic cells connected in series.

The term ‘electrochemical cell’ can refer to either voltaic (Galvanic) cells or electrolytic cells.

Voltaic cells

We have already met voltaic cells in Topic 9. Figure C.31 shows a simple voltaic cell – in general, a cell consists of two different electrodes dipping into an electrolyte.

Cells involve chemical reactions (redox reactions) in which the negative electrode releases electrons as it reacts (is oxidised) while the positive electrode gains electrons (is reduced). A cell ‘runs out’ when at least one of the chemicals involved in these reactions has been used up.

The voltage of a cell depends primarily on the materials used to make the cell.

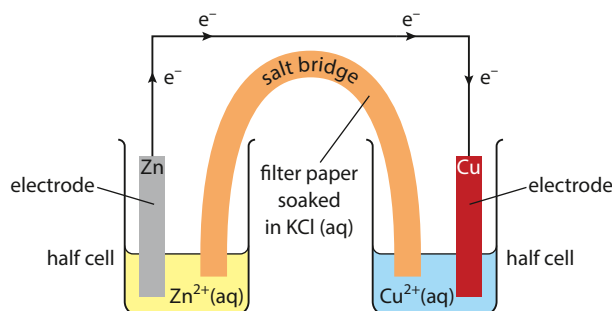


Figure C.31 A typical voltaic cell.

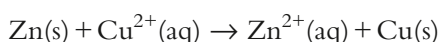
Learning objectives

- Understand that the voltage of a voltaic cell depends on the materials from which it is made
- Understand that the total amount of electrical energy (work) that can be obtained from a cell depends on the quantities of substances used in the cell
- Understand the internal resistance of a voltaic cell in terms of the diffusion of ions
- Distinguish between primary cells, secondary cells and fuel cells
- Understand how fuel cells work
- Write equations for the reactions at the electrodes when fuel cells operate with acidic and alkaline electrolytes
- Understand that microbial fuel cells (MFCs) represent a possible sustainable energy source using organic matter in waste water
- Calculate the thermodynamic efficiency of fuel cells
- Understand the reactions at the anode and cathode in rechargeable batteries
- Discuss the advantages of different types of cells in terms of size, mass and voltage
- Compare fuel cells with rechargeable batteries

If the zinc in the cell in Figure C.31 is replaced by magnesium, the voltage of the cell will increase because magnesium has a more negative standard electrode potential than zinc. The nature and concentration of the electrolyte can also affect the voltage.

The total amount of electrical energy (work) that can be obtained from a cell depends on the quantities of substances used in the cell.

In the cell in Figure C.31 the overall reaction that occurs is:



Zinc metal and copper ions are used up and so if more of these are used initially a greater total amount of energy will be available from the cell.

All voltaic cells have an internal resistance which limits the maximum current that can be obtained from the cell. Current is the rate of flow of charge and the internal resistance arises because of the finite amount of time that it takes for ions to diffuse to the electrodes in the cell. In the cell in Figure C.32 electrons are transferred to Cu^{2+} ions at the copper electrode. Once copper ions at the electrodes have been reduced to copper, more copper ions must diffuse in to replace them – this takes a certain amount of time and therefore limits the number of electrons that can be removed from the electrode per second, and hence the current.

Different types of cells

Primary cells cannot usually be recharged using mains electricity – the reaction in the cell is non-reversible.

Primary cells are a very expensive source of electrical energy compared to mains electricity but are used because of their convenience and portability. Examples of primary cells include zinc–carbon cells/batteries, often used in torches etc., and alkaline cells/batteries.

A secondary cell is one that can be recharged using mains electricity and is often called a rechargeable battery. The chemical reactions in a rechargeable battery are reversible and can be reversed by connecting them to an electricity supply.

Secondary cells include the lead–acid battery used in car engines and lithium-ion batteries used in laptops etc.

A fuel cell differs from other cells in that it uses a continuous supply of reactants from an external source.

Fuel cells use the reaction between a fuel (such as hydrogen or methanol) and an oxidising agent (e.g. oxygen) to produce electrical energy directly. Hydrogen fuel cells are used in, for instance, hydrogen-powered buses (Figure C.33) and were used in the space shuttle.

All cells involve the conversion of chemical energy to electrical energy.

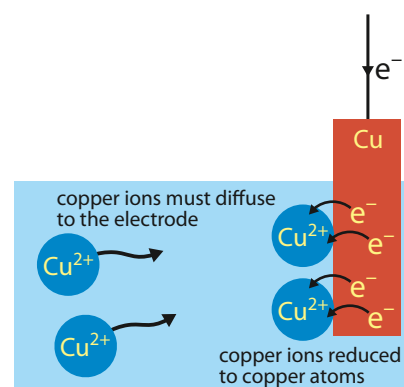


Figure C.32 The time it takes for diffusion of ions in the electrolyte causes internal resistance.



Figure C.33 A London bus powered by hydrogen fuel cells.

Fuel cells

A fuel cell is a specialised type of electrochemical cell in which a fuel and an oxidising agent react in the presence of an electrolyte to produce electrical energy. In the hydrogen–oxygen fuel cell, hydrogen reacts with oxygen to produce water and electricity.

Figure C.34 shows an alkaline hydrogen–oxygen fuel cell with a potassium hydroxide electrolyte. Electrodes are typically made of carbon and incorporate a metal catalyst such as nickel.

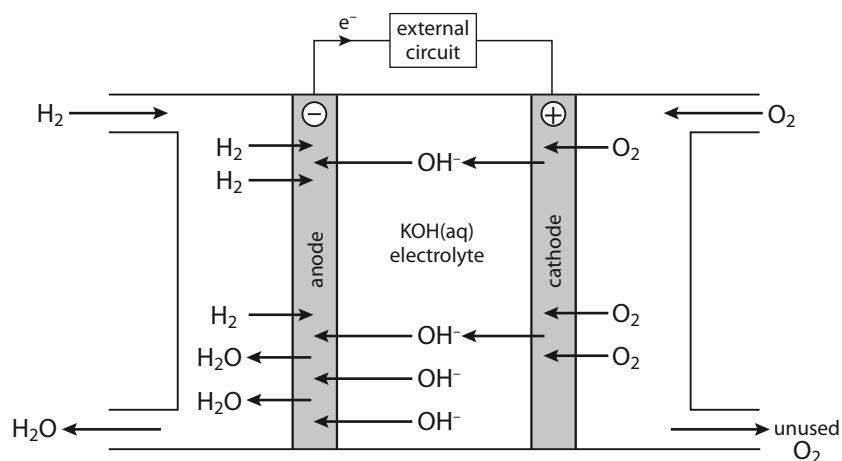
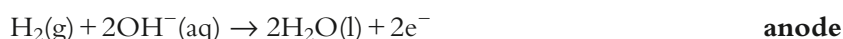


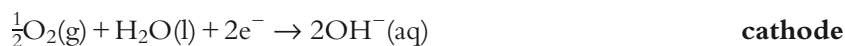
Figure C.34 An alkaline hydrogen–oxygen fuel cell with a potassium hydroxide electrolyte.

The two electrodes are separated by a porous matrix saturated with an electrolyte which may be either an alkaline or an acidic solution. In the case of an alkaline electrolyte, typically a solution of potassium hydroxide (KOH) is used.

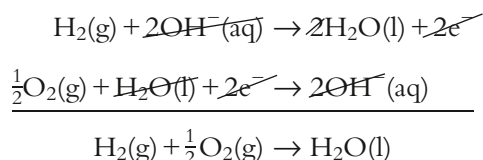
At the anode, hydrogen undergoes oxidation when it reacts with hydroxide ions (OH^-) to form water:



Electrons are released in this oxidation process and flow around the external circuit to the cathode. At the cathode, oxygen undergoes reduction when it reacts with water and gains electrons from the electrode:

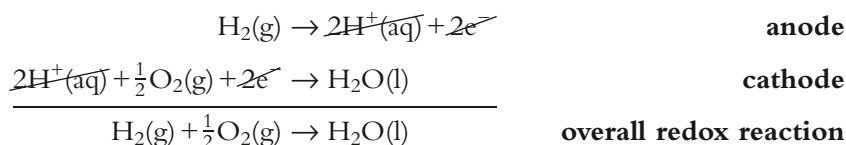


If these reactions are added together and common terms cancelled we get:



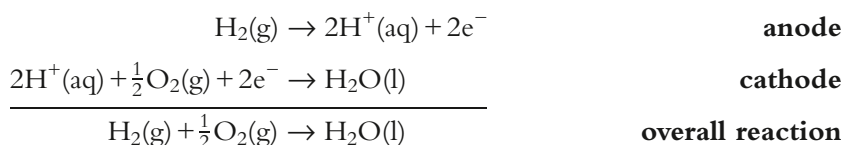
A fuel cell involves a reaction equivalent to a combustion reaction, but releases electrical energy rather than heat energy. The separation of the oxidation and reduction reactions permits the flow of electrons and the generation of an electric current.

In an acidic fuel cell the alkaline electrolyte is replaced by an acidic solution, commonly phosphoric acid. The reactions occurring at the anode and cathode in an acidic fuel cell are different:



Proton exchange membrane (PEM) fuel cells

This type of fuel cell is the one that is increasingly finding use in hydrogen-powered vehicles. Hydrogen passes through a porous carbon anode (Figure C.35) that contains a platinum catalyst and is oxidised to form hydrogen ions (protons) and electrons (which travel through the external circuit). The hydrogen ions travel through the PEM to the cathode (containing a platinum catalyst) where they combine with oxygen molecules and electrons to form water. The reactions that occur are the same as in the phosphoric acid fuel cell:



The fuel cells described above rely on external sources of a fuel and an oxidising agent, which are depleted during use and require constant replenishing. They are therefore very different from primary cells that contain stored chemical energy within them. Once a primary cell runs out it must be disposed of, but a hydrogen fuel cell will never run out as long as more hydrogen and oxygen are supplied.

In a hydrogen–oxygen fuel cell in a vehicle, the hydrogen must be stored on board in some way and the oxygen may come from purified air or an oxygen tank. Hydrogen–oxygen fuel cells do not produce any pollution because the only products are water, electricity and a small amount of heat. However, the production of hydrogen from the electrolysis of water, for example, must be considered when assessing the overall environmental impact of fuel-cell use.

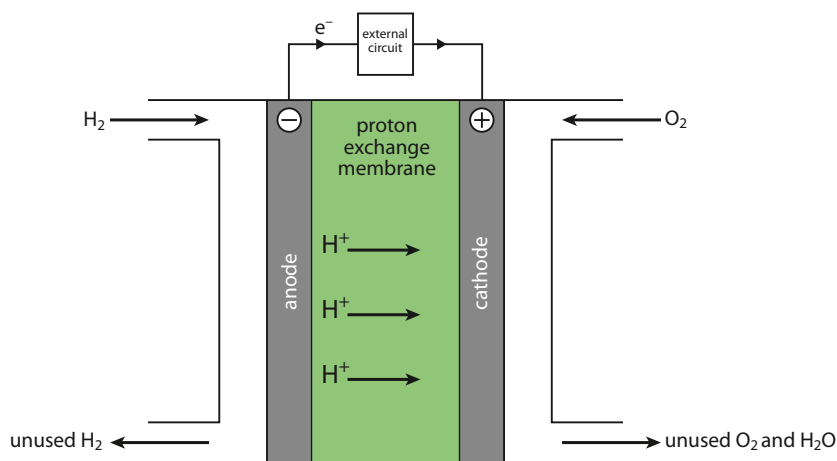


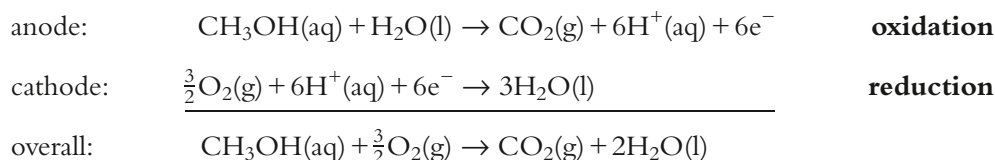
Figure C.35 A PEM fuel cell.

A proton exchange membrane (PEM) is sometimes called a polymer electrolyte membrane.

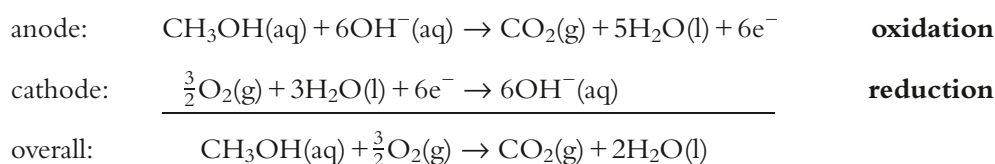
Because of the use of platinum catalysts and precision engineering, hydrogen–oxygen fuel cells are currently very expensive to make.

Methanol fuel cells

One disadvantage of using hydrogen fuel cells is the difficulty of storing hydrogen fuel (a gas) and one solution to this problem is to use a liquid fuel, such as methanol. A direct methanol fuel cell works in a similar way to the PEM fuel cell described above. The anode contains a platinum–ruthenium catalyst, the catalyst at the cathode is platinum and there is a PEM between the electrodes. Methanol solution and oxygen are fed into the fuel cell, and the equations for the reactions are:



A methanol fuel cell can also be constructed using an alkaline electrolyte and the reactions are:



Again, the overall reaction is equivalent to a combustion reaction.

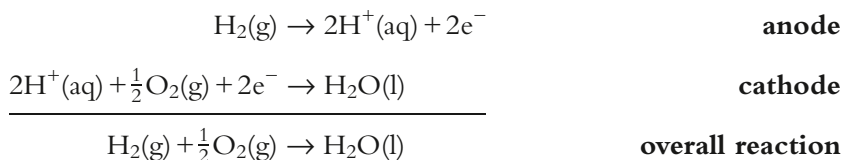
Direct methanol fuel cells are being developed for use in laptop computers and mobile phones. The fuel cell is built into the device and a methanol cartridge is plugged in to provide the fuel. When the fuel has been used up the cartridge is disposed of and replaced by a new one. The use of this sort of technology allows laptops and phones to be used well away from the electricity grid and has many potential military and civilian applications.

Reformed methanol fuel cells

In this type of fuel cell, the methanol is first reformed to hydrogen and carbon dioxide:



The hydrogen is then used as the fuel for the fuel cell. The reactions that occur are the same as in the PEM fuel cell:



Microbial fuel cells

In an MFC, bacteria attach themselves to the anode and when they oxidise organic matter present in, say, waste water, they produce carbon dioxide, protons (H^+ ions) and electrons – the electrons produced are transferred from the bacteria to the electrode. The reactions in the anode chamber (Figure C.36) occur in the absence of oxygen (anaerobic conditions).

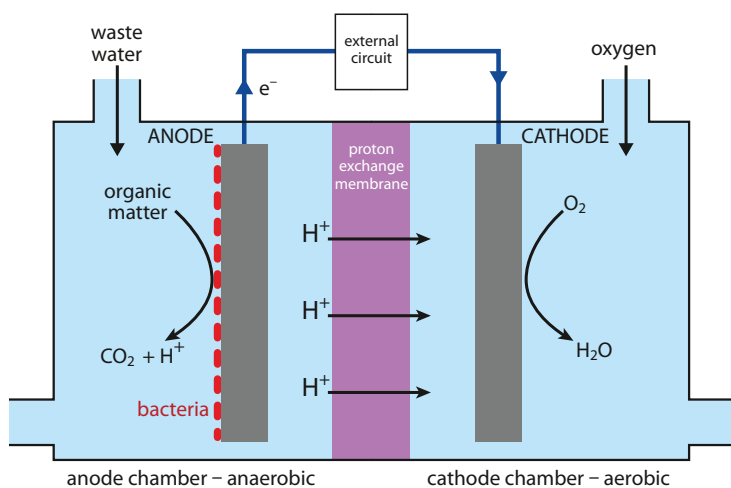
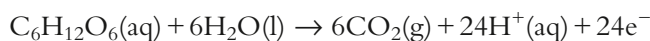
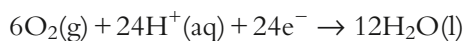


Figure C.36 A microbial fuel cell.

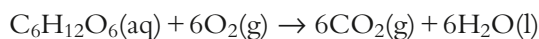
For instance, the oxidation of a carbohydrate such as glucose can be represented as:



The electrons travel through the external circuit to the cathode, while the protons pass through a PEM to the cathode compartment, where they combine with oxygen and electrons to form water.



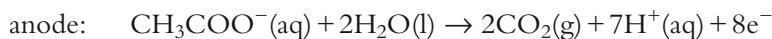
The overall reaction is:



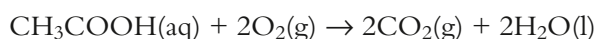
which is equivalent to the combustion of glucose.

The microbial fuel cell represents a possible sustainable source of electrical energy, produced from the oxidation of carbohydrates and other substrates in waste water. They provide two functions – they oxidise the organic matter in waste water, which is one of the important stages in the treatment of waste water, and they generate electricity at the same time.

Geobacter bacteria such as *Geobacter sulfurreducens* are used in some fuel cells to reduce ethanoate ions, CH_3COO^- , under anaerobic conditions. The reactions occurring in the anode and cathode chambers can be represented by:



The actual reactions occurring are substantially more complicated than this. The overall reaction is equivalent to the complete combustion of ethanoic acid:



Thermodynamic efficiency of fuel cells

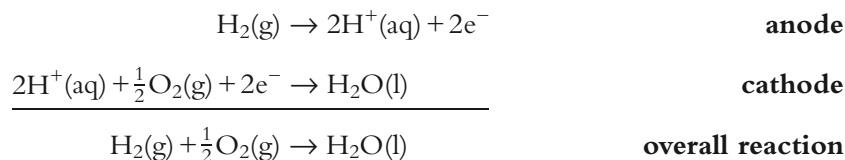
The thermodynamic efficiency of a fuel cell can be calculated using the free energy change for the cell reaction and the enthalpy change for the equivalent combustion reaction.

$$\text{Thermodynamic efficiency} = \frac{\Delta G}{\Delta H}$$

The change in free energy represents the maximum amount of work that can be obtained from a cell and, as shown in Topic 9, can be calculated from:

$$\Delta G^{\ominus} = -nFE^{\ominus}$$

Consider the PEM fuel cell reactions:



The maximum voltage for this cell is 1.23 V and two electrons are transferred, so ΔG^{\ominus} can be worked out from:

$$\begin{aligned} \Delta G^{\ominus} &= -nFE^{\ominus} \\ &= -2 \times 96\,500 \times 1.23 \\ &= -237\,000 \text{ J mol}^{-1} \text{ or } -237 \text{ kJ mol}^{-1} \end{aligned}$$

The amount of heat energy given out in the combustion of one mole of hydrogen is simply the standard enthalpy change of combustion of hydrogen (or the standard enthalpy change of formation of water), which is -286 kJ mol^{-1} .

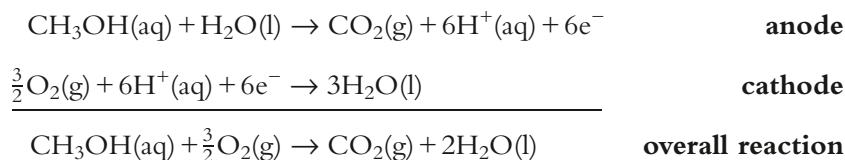
The thermodynamic efficiency is calculated from:

$$\frac{\Delta G}{\Delta H} = \frac{237}{286} = 0.829$$

This can be multiplied by 100 to give a percentage efficiency of 82.9%.

This is the maximum possible efficiency of the fuel cell under these conditions. It is not 100% because of entropy – some energy is unavailable to do work because the reaction involves a decrease in entropy. Energy is needed to cause the redistribution of the available energy among the various energy states of the products – the energy is less spread out or more concentrated in the products.

We can carry out a similar calculation for the direct methanol fuel cell.



The maximum voltage is 1.21 V and six electrons are transferred so:

$$\begin{aligned} \Delta G^{\ominus} &= -nFE^{\ominus} \\ &= -6 \times 96\,500 \times 1.21 \\ &= -701\,000 \text{ J mol}^{-1} \text{ or } -701 \text{ kJ mol}^{-1} \end{aligned}$$

The enthalpy change of combustion of methanol is -726 kJ mol^{-1} and:

$$\frac{\Delta G}{\Delta H} = \frac{701}{726} = 0.965 \text{ or } 96.5\%$$

The value for the enthalpy change of combustion of liquid methanol has been used here.



This value is higher than the previous one because the reaction involves a smaller decrease in entropy (smaller change in the number of moles of gas). If a fuel cell reaction involves an increase in entropy, the theoretical efficiency of the fuel cell will be greater than 1. The values here represent the maximum possible efficiency and operating efficiency is significantly lower than these values.

Rechargeable batteries

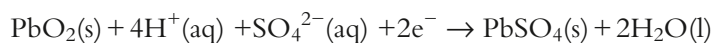
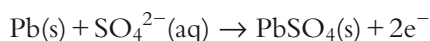
Rechargeable batteries, or secondary cells, are a portable type of electrochemical cell that generates a current via electrically reversible reactions.

Lead–acid battery

One of the oldest forms of rechargeable cell is the lead–acid battery, still used in the majority of car engines. The lead–acid battery consists of lead anodes and cathodes made from lead covered with a layer of lead(IV) oxide (PbO_2) in a concentrated sulfuric acid electrolyte.

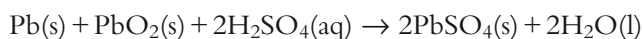
A typical car battery is made up of six electrical cells in series and provides a potential difference of about 12 V. As the battery discharges, lead at the anode is oxidised, releasing electrons, while the lead(IV) oxide at the cathode is reduced. The product of both reactions is solid lead(II) sulfate, which accumulates on the electrodes within the battery.

During discharge:

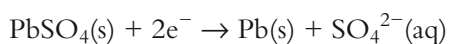


overall reaction

This can also be written as:



When a battery loses its charge, the lead(II) sulfate can be converted back to lead and lead(IV) oxide by applying an external electrical source – the chemical reactions above are reversed. For example, the reaction that occurs at the electrode attached to the negative side of the charging supply (cathode) is:



Lead–acid storage batteries are quite large and heavy and are unsuitable for uses where they have to be carried around.

Nickel–cadmium battery

NiCad batteries are often seen as the classic small rechargeable ones (sizes AAA to D) used for powering small electronic devices such as clocks, calculators, remote controls and toys. They typically generate smaller voltages than lead–acid batteries – around 1.2 V. NiCad batteries use a nickel oxide hydroxide [$\text{NiO}(\text{OH})$] cathode and a metallic cadmium anode separated by a potassium hydroxide electrolyte.

Lead–acid cells are also used as emergency sources of power (standby power). This is vital in places like hospitals – the emergency power cuts in if the mains electricity supply fails. They are also used in theatres, cinemas (and schools) to guarantee emergency lighting at all times.

Exam tip

When the battery is discharging the anode is the negative electrode and the cathode the positive electrode.

anode

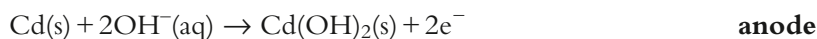
cathode

When a car is in motion, the battery is being charged because it is linked to the car's alternator.

Exam tip

When charging the battery the anode and cathode labels must be changed around – the cathode is the electrode at which reduction occurs. The cathode is thus the electrode attached to the negative side of the electricity supply.

During discharge:



These reactions are reversed when the battery is recharged.

Lithium-ion battery

These batteries are commonly used as rechargeable cells in mobile telephones, laptop computers and high-energy usage portable electronic devices. They can generate higher voltages (around 3–4V) than NiCad batteries. Typically, the anode is made of carbon with lithium atoms inserted in the lattice, and the cathode is a metal oxide such as manganese(IV) oxide or cobalt(IV) oxide with Li^+ ions inserted in the lattice. The electrolyte is a complex lithium salt such as lithium hexafluorophosphate (LiPF_6) dissolved in an organic solvent (Figure C.37).

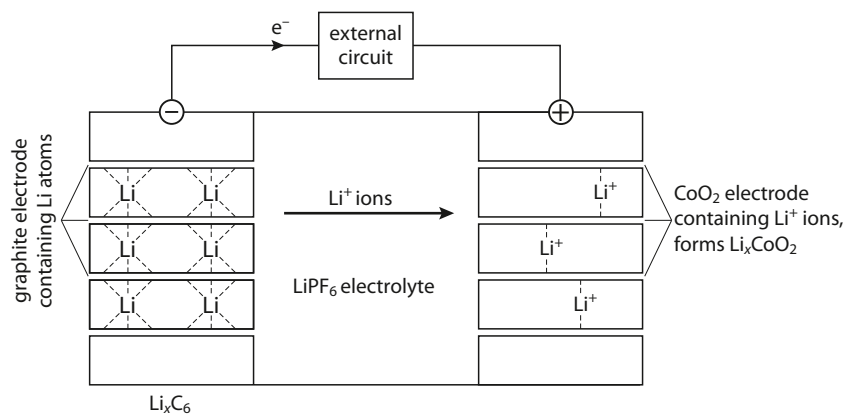


Figure C.37 A lithium-ion battery – lithium ions are exchanged between complexed lithium and graphite electrodes.

During discharge, lithium atoms are oxidised at the negative electrode and electrons are released to the external circuit:



where the equation represents molar quantities reacting and x is a number less than 1.

The lithium ions move through the electrolyte to the cathode, where they become inserted into the lattice of the transition metal oxide:



The overall redox reaction during discharge is:



The net effect of these reactions is that lithium atoms are oxidised at the negative electrode and cobalt ions are reduced at the positive electrode. For every lithium ion present in Li_xCoO_2 , the oxidation number of a cobalt ion must be reduced by 1 from +4 to +3.

The reverse reactions occur during charging, and lithium ions move in the opposite direction.

An Li^+ ion and a Co^{3+} ion together give a charge of 4+ to cancel out the charge on two O^{2-} ions. Therefore if the formula of the species formed at the cathode is $\text{Li}_{0.2}\text{CoO}_2$ what we have present is $(\text{Li}^+)_{0.2}(\text{Co}^{4+})_{0.8}(\text{Co}^{3+})_{0.2}(\text{O}^{2-})_2$.



Both nickel–cadmium and lithium–ion batteries are much smaller and lighter than lead–acid storage batteries and are, therefore, suitable for use in portable devices.

Similarities and differences between fuel cells and rechargeable batteries

Similarities:

- They both generate electrical energy from chemical energy.
- They are both composed of an anode, a cathode and an electrolyte.
- They both generate a current based on the separation of reduction and oxidation reactions and the flow of electrons through an external circuit.

Differences:

- Fuel cells require an external source of chemical energy (fuel), but rechargeable batteries have their chemical energy source within them.
- Fuel cells never run out so long as there is a constant supply of fuel from an external source; rechargeable batteries run out and then have to be recharged by connecting to an electricity supply which reverses the reactions.
- Rechargeable batteries are far cheaper than fuel cells.
- Fuel cells are capable of generating a far greater quantity of electricity than rechargeable batteries because the fuel is supplied constantly.
- Fuel cells are non-polluting – hydrogen fuel cells produce water as the only product; rechargeable batteries may contain toxic metals (Cd, Pb) so are difficult to dispose of.
- Fuel cells can produce drinkable water as a byproduct; there is no byproduct of rechargeable batteries.
- Rechargeable batteries can only be recharged so many times – they have a finite life and must be replaced eventually; fuel cells have much better longevity.

Comparison of different types of cell

Table C.11 compares the various types of cell discussed above in terms of size, mass and voltage of the cells.

Cell type	Size/mass	Voltage
Fuel cells	Can be made in a variety of sizes. Fuel cell stacks used to power buses are quite large and heavy, but small fuel cells have been developed for laptops etc. Some fuel cells have a very high power-to-mass ratio and high power-to-volume ratio.	Typically about 0.6–0.8 V but depends on the type of fuel cell. Used in a stack with multiple fuel cells connected in series.
Lead–acid batteries	Large and heavy – not suitable for portable devices. Low power-to-mass ratio and power-to-volume ratio.	2 V per cell – usually used as a battery with six cells in series
Nickel–cadmium batteries	Small and light – used in a variety of portable devices. Intermediate power-to-mass ratio and power-to-volume ratio.	1.2 V
Lithium-ion batteries	Small and light – used in a variety of portable devices. Produce the greatest amount of power per unit mass or unit volume of the rechargeable batteries.	About 3.7 V – the highest voltage per cell.

Table C.11 A comparison of different types of cell.



Figure C.38 This car is powered by rechargeable batteries.

Much research is being carried out into developing electric vehicles (Figure C.38). These have advantages over gasoline-powered vehicles in that they do not produce carbon dioxide when they are operating – although carbon dioxide might be produced when the charging electricity is generated or when producing hydrogen for a fuel cell.

The two main possibilities for powering vehicles by electricity are to use rechargeable batteries (such as the lithium-ion battery) that can be plugged in and recharged every so often, or to use fuel cells and a hydrogen storage tank which will have to be refilled every so often.

When considering which is the better solution, the two important factors that must be looked at are the mass of the battery/fuel cell and the volume of space it occupies. For fuel cells, the mass/volume occupied by the fuel tank and fuel must also be factored into the calculation – hydrogen must be stored under pressure to reduce its volume and the fuel tank must be reinforced (and so can be quite heavy) to withstand high pressures. There is also safety to consider in the use of hydrogen and other methods of storing hydrogen are being researched.

The energy-to-mass ratio (specific energy) of a fuel cell depends on the type of fuel cell stack but fuel cells used to power vehicles have a higher energy-to-mass ratio than rechargeable batteries which means that the vehicles should be able to travel further for the same mass of a battery/fuel cell + fuel. The advantage of using fuel cells to power vehicles increases with the distance between stops that is required because this can be increased by simply having a larger fuel tank which will not add a large amount of mass (hydrogen is a very light gas). With rechargeable batteries the distance between stops can only be improved by adding extra rechargeable batteries which contribute significantly to the overall mass of the vehicle and take up a lot of space.

The energy density (energy per unit volume) of fuel cells, including the hydrogen tank, is similar to that of lithium-ion batteries – but again, the longer the distance required between stops for refuelling, the greater the advantage of using fuel cells.

? Test yourself

- 19 Write ionic half-equations for the following reactions:
 - a the reaction that occurs at the electrode attached to the negative side of a power supply when a lead–acid battery is charged
 - b the reaction that occurs at the electrode attached to the positive side of a power supply when a NiCad battery is charged.
- 20 Write an overall equation for the reaction that occurs when a lithium-ion cell is charged.

C6.2 The effect of concentration on electrode potentials

The Nernst equation

In Topic 9 we used standard electrode potentials to calculate standard cell potentials. Standard conditions for these measurements are taken as solutions of concentration 1 mol dm^{-3} and gases at a pressure of 100 kPa (1 bar). The **Nernst equation** can be used to calculate the electrode potentials of half-cells or cells under non-standard conditions:

$$E = E^\ominus - \left(\frac{RT}{nF} \right) \ln Q$$

where

E is the electrode potential

E^\ominus is the standard electrode potential

R is the gas constant, $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$

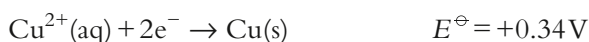
T is the temperature in kelvin

n is the number of electrons transferred

F is the Faraday constant, $96\,500 \text{ C mol}^{-1}$

Q is the reaction quotient (introduced in Topic 7)

Consider the reduction of copper(II) ions:



We can work out the electrode potential when the concentration of copper ions is 0.10 mol dm^{-3} and the temperature is 298 K as follows:

$$\text{The reaction quotient is } Q = \frac{[\text{Cu}(\text{s})]}{[\text{Cu}^{2+}(\text{aq})]}$$

In a heterogeneous reaction, the concentration of a pure solid (or pure liquid) is taken as 1 so we have:

$$\begin{aligned} Q &= \frac{1}{[\text{Cu}^{2+}(\text{aq})]} \\ &= \frac{1}{0.10} \\ &= 10 \end{aligned}$$

The number of electrons transferred is 2 and so we have:

$$\begin{aligned} E &= E^\ominus - \left(\frac{RT}{nF} \right) \ln Q \\ &= +0.34 - \left(\frac{8.31 \times 298}{2 \times 96\,500} \right) \ln 10 \\ &= +0.31 \text{ V} \end{aligned}$$

It can be seen from this that changing the concentration does not have much effect on an electrode potential, unless the change in concentration is very large.

There are two approaches to working out a cell potential under non-standard conditions and this is best illustrated with a worked example.

Learning objectives

- Understand how the Nernst equation can be used to calculate electrode potentials under non-standard conditions
- Understand how concentration cells work
- Solve problems involving the Nernst equation

Exam tip

A temperature is not actually included in the definition of standard conditions but where one is not specified it can be taken as 298 K .

Exam tip

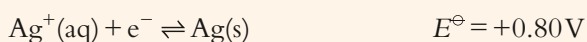
You can use ideas similar to Le Chatelier's principle to work out whether your answer is sensible or not. If we regard $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$ as an equilibrium system, decreasing the concentration of $\text{Cu}^{2+}(\text{aq})$ will shift the position of the equilibrium to the left, and so the forward reaction becomes less favourable and the value of the electrode potential becomes less positive.

Worked examples

C.7 Calculate the cell potential of the $\text{Zn(s)}|\text{Zn}^{2+}(\text{aq})||\text{Ag}^+(\text{aq})|\text{Ag(s)}$ cell at 25°C when the concentration of $\text{Zn}^{2+}(\text{aq})$ is 0.200 mol dm^{-3} and that of $\text{Ag}^+(\text{aq})$ is 0.100 mol dm^{-3} .

The first approach to this is to work out each individual cell potential under the non-standard conditions and then combine them.

The standard electrode potentials are:



Ag⁺/Ag half-cell

The reaction quotient is $Q = \frac{[\text{Ag(s)}]}{[\text{Ag}^+(\text{aq})]}$

In a heterogeneous reaction the concentration of a solid is taken as 1 so we have:

$$\begin{aligned} Q &= \frac{1}{[\text{Ag}^+(\text{aq})]} \\ &= \frac{1}{0.100} \\ &= 10.0 \end{aligned}$$

The number of electrons transferred is 1 and so we have:

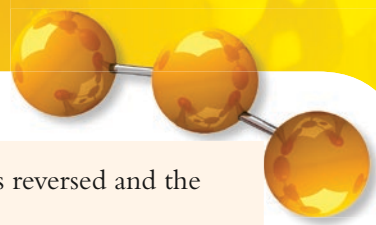
$$\begin{aligned} E &= E^\ominus - \left(\frac{RT}{nF}\right) \ln Q \\ E &= 0.80 - \left(\frac{8.31 \times 298}{1 \times 96\,500}\right) \ln 10.0 \\ &= 0.74\text{ V} \end{aligned}$$

Zn²⁺/Zn half-cell

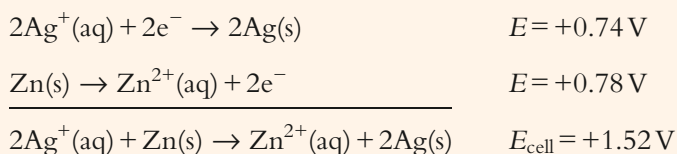
$$\begin{aligned} Q &= \frac{1}{[\text{Zn}^{2+}(\text{aq})]} \\ &= \frac{1}{0.200} \\ &= 5.00 \end{aligned}$$

The number of electrons transferred is 2 and so we have:

$$\begin{aligned} E &= E^\ominus - \left(\frac{RT}{nF}\right) \ln Q \\ &= -0.76 - \left(\frac{8.31 \times 298}{2 \times 96\,500}\right) \ln 5.00 \\ &= -0.78\text{ V} \end{aligned}$$

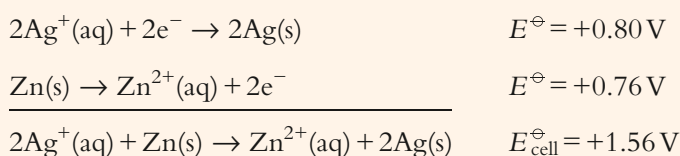


In order to combine the half equations to give the overall cell reaction the $\text{Zn}^{2+}|\text{Zn}$ half-cell is reversed and the $\text{Ag}^+|\text{Ag}$ half-cell reaction is multiplied by 2 to balance out the electrons:



Remember, from Topic 9, that cell potentials are not multiplied by anything when they are combined to give the cell potential.

An alternative approach is to work out the standard cell potential first and then use the Nernst equation to work out the cell potential under non-standard conditions.



The reaction quotient is worked out in the same way as an equilibrium constant and so the concentrations are raised to the powers of the coefficients in the equation. Concentrations of solids are taken as 1.

$$\begin{aligned} Q &= \frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Ag}^+(\text{aq})]^2} \\ &= \frac{0.200}{0.100^2} \\ &= 20.0 \end{aligned}$$

The number of electrons transferred is 2 and so we have:

$$\begin{aligned} E &= E^\ominus - \left(\frac{RT}{nF}\right) \ln Q \\ &= +1.56 - \left(\frac{8.31 \times 298}{2 \times 96500}\right) \ln 20.0 \\ &= 1.52 \text{ V} \end{aligned}$$

C.8 Work out the electrode potential of the $\text{Cr}_2\text{O}_7^{2-}(\text{aq})|\text{Cr}^{3+}(\text{aq})$ half-cell at 298 K given that the concentration of $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ is $0.0200 \text{ mol dm}^{-3}$, that of Cr^{3+} is $0.0600 \text{ mol dm}^{-3}$ and the pH is 3.00.

The half-cell reaction is $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$ and $E^\ominus = 1.33 \text{ V}$.

A pH of 3.00 corresponds to $[\text{H}^+(\text{aq})] = 10^{-3.00} \text{ mol dm}^{-3}$

$\text{H}_2\text{O}(\text{l})$ is a pure liquid and its concentration is taken as 1 in the expression for Q :

$$\begin{aligned} Q &= \frac{[\text{Cr}^{3+}(\text{aq})]^2}{[\text{Cr}_2\text{O}_7^{2-}(\text{aq})][\text{H}^+(\text{aq})]^{14}} \\ &= \frac{0.0600^2}{0.0200 \times (10^{-3})^{14}} \\ &= 1.80 \times 10^{41} \end{aligned}$$

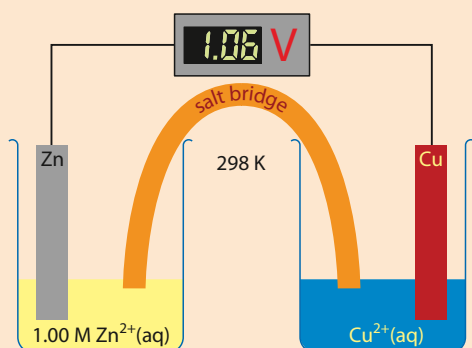
The number of electrons transferred is 6 and so we have:

$$\begin{aligned}
 E &= E^\ominus - \left(\frac{RT}{nF} \right) \ln Q \\
 &= 1.33 - \left(\frac{8.31 \times 298}{6 \times 96\,500} \right) \ln(1.80 \times 10^{41}) \\
 &= 0.924 \text{ V}
 \end{aligned}$$

The Nernst equation can also be used to work out solution concentrations.

Worked example

C.9 A voltaic cell is set up as show in the diagram. The concentration of $\text{Zn}^{2+}(\text{aq})$ is 1.00 mol dm^{-3} but that of $\text{Cu}^{2+}(\text{aq})$ is unknown. The cell potential is 1.06 V – calculate the concentration of the copper(II) solution.



The overall reaction is $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$.

The standard cell potential can be worked out from the standard electrode potentials to be 1.10 V .

The number of electrons transferred is 2 and so we have:

$$\begin{aligned}
 E &= E^\ominus - \left(\frac{RT}{nF} \right) \ln Q \\
 1.06 &= 1.10 - \left(\frac{8.31 \times 298}{2 \times 96\,500} \right) \ln Q
 \end{aligned}$$

Rearranging this gives:

$$\ln Q = (1.10 - 1.06) \times \frac{2 \times 96\,500}{8.31 \times 298} = 3.12$$

To extract Q from this we need to raise both sides as powers of e :

$$Q = e^{3.12} = 22.6$$

Concentrations of solids are taken as 1. So:

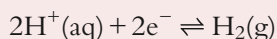
$$Q = \frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]}$$

$$[\text{Cu}^{2+}(\text{aq})] = \frac{[\text{Zn}^{2+}(\text{aq})]}{Q}$$

$$= \frac{1}{22.6} = 0.0443 \text{ mol dm}^{-3}$$

Equilibrium constants expressed in terms of partial pressures have not been covered anywhere else in the course, so it is extremely unlikely that you will get any questions involving this.

In a mixture of gases, the partial pressure of one of the component gases is the pressure that gas would exert if it were in the container by itself. This is its contribution to the total pressure of the mixture. Partial pressures are calculated relative to a standard state of 1 bar (100 kPa) and are inserted into the expression for the reaction quotient (Topic 7, page 287 in the Coursebook). So, if the partial pressure of hydrogen gas in a mixture is 80 kPa, this is equivalent to 0.8 bar. Consider the half-equation:



The standard electrode potential is 0.00 V but if the partial pressure of hydrogen is 0.800 bar, the temperature is 298 K and the concentration of H^+ ions is $0.100 \text{ mol dm}^{-3}$ we get:

$$\begin{aligned} Q &= \frac{P_{\text{H}_2}}{[\text{H}^+(\text{aq})]^2} \\ &= \frac{0.800}{0.100^2} \\ &= 80.0 \end{aligned}$$

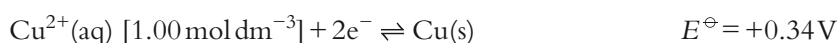
The number of electrons transferred is 2 and so we have:

$$\begin{aligned} E &= E^\ominus - \left(\frac{RT}{nF} \right) \ln Q \\ &= 0.00 - \left(\frac{8.31 \times 298}{2 \times 96\,500} \right) \ln 80 \\ &= -0.0562 \text{ V} \end{aligned}$$

Concentration cells

From the Nernst equation, we can see that an electrode potential depends on the concentration of the electrolyte and therefore it should be possible to set up a cell with two half-cells using the same chemicals but with different concentrations of electrolyte (Figure C.39). This is called a **concentration cell**.

The standard electrode potential for $\text{Cu}^{2+}(\text{aq})|\text{Cu}(\text{s})$ is 0.34 V and we saw earlier (page 53) that the electrode potential is 0.31 V when the concentration of $\text{Cu}^{2+}(\text{aq})$ is $0.100 \text{ mol dm}^{-3}$ and so we have:



and

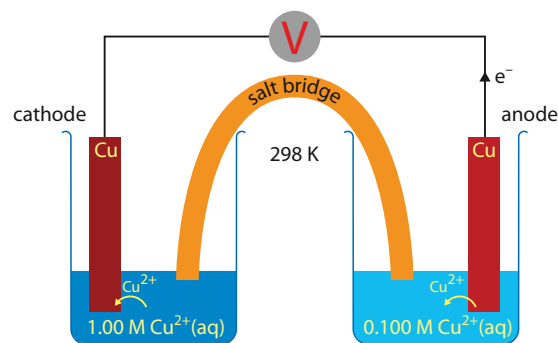
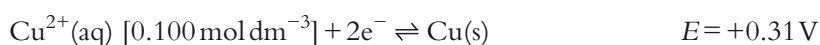
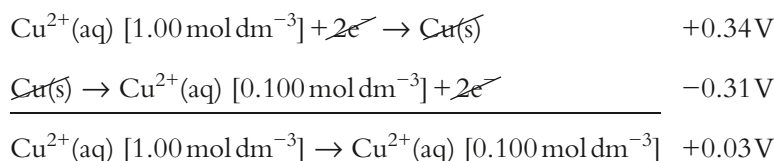


Figure C.39 A concentration cell.

A positive cell potential indicates a spontaneous change and so the half-equation involving the more negative (less positive) electrode potential is reversed to give the overall equation:



So, Cu^{2+} ions are reduced to copper in the left-hand half-cell and copper is oxidised to Cu^{2+} ions in the right-hand half-cell. Overall the reaction is equivalent to the concentration of Cu^{2+} ions in the left-hand half-cell decreasing and that in the right-hand half-cell increasing until they reach equilibrium – when the concentrations are equal and there is no overall cell potential.

The cell potential could also have been worked out directly from the Nernst equation. The standard electrode potential for the overall reaction is 0.00V because there are the same species on both sides and, under standard conditions, the concentration of both would be 1.00 mol dm^{-3} so there would be no reaction.

The reaction quotient for the reaction is given by:

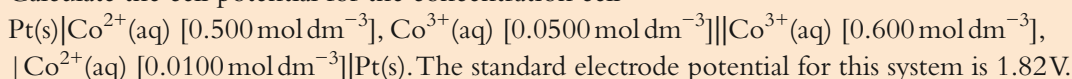
$$Q = \frac{0.100}{1.00} = 0.100$$

The number of electrons transferred is 2 and so we have:

$$\begin{aligned} E &= E^{\ominus} - \left(\frac{RT}{nF} \right) \ln Q \\ &= 0.00 - \left(\frac{8.31 \times 298}{2 \times 96500} \right) \ln 0.100 \\ &= 0.0300\text{V} \end{aligned}$$

Worked example

C.10 Calculate the cell potential for the concentration cell



First of all write down the reduction half-equations:



$$Q = \frac{[\text{Co}^{2+}(\text{aq})]}{[\text{Co}^{3+}(\text{aq})]} \text{ for both reactions and } n = 1.$$

The electrode potential of each is then calculated using the Nernst equation.

$$\text{For reaction 1, } Q = \frac{0.500}{0.0500} = 10.0$$

$$\begin{aligned}
 E &= E^\ominus - \left(\frac{RT}{nF} \right) \ln Q \\
 &= 1.82 - \left(\frac{8.31 \times 298}{1 \times 96\,500} \right) \ln 10.0 \\
 &= 1.76 \text{ V}
 \end{aligned}$$

For reaction 2, $Q = \frac{0.0100}{0.600} = 0.0167$

$$\begin{aligned}
 E &= E^\ominus - \left(\frac{RT}{nF} \right) \ln Q \\
 &= 1.82 - \left(\frac{8.31 \times 298}{1 \times 96\,500} \right) \ln 0.0167 \\
 &= 1.93 \text{ V}
 \end{aligned}$$

For $\text{Co}^{3+}(\text{aq}) [0.0500 \text{ mol dm}^{-3}] + \text{e}^- \rightleftharpoons \text{Co}^{2+}(\text{aq}) [0.500 \text{ mol dm}^{-3}]$ $E = 1.76 \text{ V}$

For $\text{Co}^{3+}(\text{aq}) [0.600 \text{ mol dm}^{-3}] + \text{e}^- \rightleftharpoons \text{Co}^{2+}(\text{aq}) [0.0100 \text{ mol dm}^{-3}]$ $E = 1.93 \text{ V}$

The half-equation with the more negative (less positive) electrode potential is reversed so the cell potential is given by:

$$E_{\text{cell}} = -1.76 + 1.93 = 0.17 \text{ V}$$

Nature of science

Research into batteries is one of those fields where the distinction between science and technology is blurred. Developments in science and technology often go hand-in-hand and the development of better batteries has allowed the design and use of more and more sophisticated electronic devices and changed society.

Advances in science and technology have often been associated with environmental problems. Batteries can contain heavy metals and should be recycled rather than dumped in landfill sites, which can lead to pollution of soil and water with heavy metals. Many countries have laws governing the recycling of batteries.

? Test yourself

- 21 Calculate the electrode potential for each of the following half-cells at 298 K. Standard electrode potentials are given in the table.

Half-cell	E^\ominus / V
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s})$	-0.13
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Co}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Co}^{2+}(\text{aq})$	+1.82
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Cr}(\text{s})$	-0.74
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.34

- a $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s})$ when the concentration of $\text{Pb}^{2+}(\text{aq})$ is $0.0500 \text{ mol dm}^{-3}$
- b $\text{Ag}^+(\text{aq})|\text{Ag}(\text{s})$ when the concentration of $\text{Ag}^+(\text{aq})$ is $0.0100 \text{ mol dm}^{-3}$
- c $\text{Fe}^{3+}(\text{aq})|\text{Fe}^{2+}(\text{aq})$ when the concentration of $\text{Fe}^{3+}(\text{aq})$ is $0.0800 \text{ mol dm}^{-3}$ and that of $\text{Fe}^{2+}(\text{aq})$ is $0.0200 \text{ mol dm}^{-3}$
- d $\text{Co}^{3+}(\text{aq})|\text{Co}^{2+}(\text{aq})$ when the concentration of $\text{Co}^{3+}(\text{aq})$ is $0.600 \text{ mol dm}^{-3}$ and that of $\text{Co}^{2+}(\text{aq})$ is $0.600 \text{ mol dm}^{-3}$
- e $\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Cr}(\text{s})$ when the concentration of $\text{Cr}^{3+}(\text{aq})$ is $0.0200 \text{ mol dm}^{-3}$
- 22 Calculate the electrode potential for:
 $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) \quad E^\ominus = 1.51 \text{ V}$
 under the following conditions – the temperature is 298 K in each case.
- a $[\text{MnO}_4^-(\text{aq})] = 0.0200 \text{ mol dm}^{-3}$, $[\text{Mn}^{2+}(\text{aq})] = 0.0500 \text{ mol dm}^{-3}$, $\text{pH} = 3.50$
- b $[\text{MnO}_4^-(\text{aq})] = 0.00100 \text{ mol dm}^{-3}$, $[\text{Mn}^{2+}(\text{aq})] = 0.00200 \text{ mol dm}^{-3}$, $\text{pH} = 2.00$
- c $[\text{MnO}_4^-(\text{aq})] = 0.100 \text{ mol dm}^{-3}$, $[\text{Mn}^{2+}(\text{aq})] = 0.0800 \text{ mol dm}^{-3}$, $\text{pH} = 1.70$
- 23 Calculate the cell potentials for each of the following voltaic cells under the stated conditions and 298 K. You will also need to use the values given in the table in question 21.
- a $\text{Cu}(\text{s}) + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$, where $[\text{Ag}^+(\text{aq})] = 0.0100 \text{ mol dm}^{-3}$ and $[\text{Cu}^{2+}(\text{aq})] = 0.0200 \text{ mol dm}^{-3}$
- b $\text{Co}^{3+}(\text{aq}) + \text{Ag}(\text{s}) \rightarrow \text{Co}^{2+}(\text{aq}) + \text{Ag}^+(\text{aq})$, where $[\text{Co}^{3+}(\text{aq})] = 0.300 \text{ mol dm}^{-3}$, $[\text{Co}^{2+}(\text{aq})] = 0.500 \text{ mol dm}^{-3}$ and $[\text{Ag}^+(\text{aq})] = 0.100 \text{ mol dm}^{-3}$
- c $2\text{Cr}(\text{s}) + 3\text{Pb}^{2+}(\text{aq}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{Pb}(\text{s})$, where $[\text{Pb}^{2+}(\text{aq})] = 0.0100 \text{ mol dm}^{-3}$ and $[\text{Cr}^{3+}(\text{aq})] = 0.0500 \text{ mol dm}^{-3}$
- 24 Calculate the cell potential for each of the following concentration cells at 298 K. Use the data in the table in question 21.
- a $\text{Ag}(\text{s})|\text{Ag}^+(\text{aq})[0.100 \text{ mol dm}^{-3}]||\text{Ag}^+(\text{aq})[1.00 \text{ mol dm}^{-3}]|\text{Ag}(\text{s})$
- b $\text{Cr}(\text{s})|\text{Cr}^{3+}(\text{aq})[0.0200 \text{ mol dm}^{-3}]||\text{Cr}^{3+}(\text{aq})[1.00 \text{ mol dm}^{-3}]|\text{Cr}(\text{s})$
- c $\text{Cu}(\text{s})|\text{Cu}^{2+}(\text{aq})[0.0100 \text{ mol dm}^{-3}]||\text{Cu}^{2+}(\text{aq})[0.300 \text{ mol dm}^{-3}]|\text{Cu}(\text{s})$
- d $\text{Pt}(\text{s})|\text{Fe}^{2+}(\text{aq})[0.800 \text{ mol dm}^{-3}], \text{Fe}^{3+}(\text{aq})[0.200 \text{ mol dm}^{-3}]||\text{Fe}^{3+}(\text{aq})[0.180 \text{ mol dm}^{-3}], \text{Fe}^{2+}(\text{aq})[0.0200 \text{ mol dm}^{-3}]|\text{Pt}(\text{s})$

C7 Nuclear fusion and nuclear fission (HL)

C7.1 Nuclear binding energy

When protons and neutrons come together to form a nucleus, the total mass of the nucleus is less than the mass of the protons and neutrons from which it was made. This difference in mass is called the mass defect (Δm).

Mass defect (Δm) is the difference between the mass of a nucleus and the sum of the masses of the individual nucleons.

This mass is converted to energy when the nucleus is formed according to Einstein's equation:

$$E = mc^2$$

where E is energy (in J), m is the mass (in kg) and c is the speed of light ($3.00 \times 10^8 \text{ ms}^{-1}$).

The nuclear binding energy (ΔE) is the energy required to break apart a nucleus into individual protons and neutrons.

The binding energy is not something that the nucleus 'has' – it is the energy released when the nucleus is formed, or that is required to break it apart again. If the binding energy for a nucleus is divided by the total number of nucleons we get the average binding energy per nucleon, which is a measure of the stability of the nucleus.

The mass of subatomic particles is often expressed in terms of the **unified atomic mass unit** (u), which is $\frac{1}{12}$ of the mass of a carbon-12 atom. The mass of one mole of carbon-12 atoms is 0.01200 kg and, therefore, the mass of a carbon atom can be worked out by dividing this by Avogadro's constant:

$$\frac{0.01200}{6.02 \times 10^{23}} = 1.99 \times 10^{-26} \text{ kg}$$

The mass equivalent to 1 u is $\frac{1}{12}$ of this:

$$\frac{1}{12} \times 1.99 \times 10^{-26} = 1.66 \times 10^{-27} \text{ kg}$$

Therefore 1 u is equivalent to 1.66×10^{-27} kg. We will use this value in all later work.

The masses of protons, neutrons and electrons are given in Table C.12.

Particle	Mass	Mass
proton	$1.672622 \times 10^{-27} \text{ kg}$	1.007276 u
neutron	$1.674927 \times 10^{-27} \text{ kg}$	1.008665 u
electron	$9.109383 \times 10^{-31} \text{ kg}$	0.0005486 u

Table C.12 Masses of subatomic particles.

Learning objectives

- Understand what is meant by the terms mass defect and nuclear binding energy
- Calculate the mass defect and nuclear binding energy of a nucleus
- Calculate the energy released in fission and fusion reactions

The binding energy could also be defined in terms of the energy released when the nucleons come together to form a particular nucleus.

IUPAC gives the value of 1 u as $1.6605402 \times 10^{-27} \text{ kg}$.

A mass defect can be worked out as follows, using a helium isotope as an example. The mass of a ${}^4_2\text{He}$ atom is 4.002 60 u. If we subtract the mass of the two electrons we get the mass of the nucleus:

$$\text{mass of the nucleus} = 4.002\,60 - (2 \times 0.000\,548\,6) = 4.001\,502\,8\text{ u}$$

This nucleus is made up of two protons and two neutrons. The mass defect is the difference between the mass of the nucleus and the masses of the individual nucleons:

$$\begin{aligned}\Delta m &= (2 \times 1.007\,276) + (2 \times 1.008\,665) - 4.001\,508 \\ &= 0.030\,374\text{ u}\end{aligned}$$

This can be converted to kilograms by multiplying by 1.66×10^{-27} :

$$\begin{aligned}\text{mass defect} &= 0.030\,374 \times (1.66 \times 10^{-27}) \\ &= 5.04 \times 10^{-29}\text{ kg}\end{aligned}$$

This mass is converted into energy when the nucleus is formed and so the binding energy can be worked out using the equation $E=mc^2$:

$$\Delta E = (5.04 \times 10^{-29}) \times (3.00 \times 10^8)^2 = 4.54 \times 10^{-12}\text{ J}$$

This represents the energy required to break apart an ${}^4_2\text{He}$ nucleus into its individual nucleons, or the energy released when the nucleus is formed from the individual nucleons. This may not seem very much but when we work it out for one mole of helium, we get:

$$(4.54 \times 10^{-12}) \times (6.02 \times 10^{23}) = 2.73 \times 10^{12}\text{ J mol}^{-1}, \text{ or } 2.73 \times 10^9\text{ kJ mol}^{-1}$$

This can be compared to the amount of energy released when one mole of carbon is burned, which is 394 kJ mol^{-1} .

The binding energy per nucleon can be worked out by dividing the binding energy by the number of nucleons, four in this case:

$$\text{binding energy per nucleon} = \frac{4.54 \times 10^{-12}}{4} = 1.14 \times 10^{-12}\text{ J}$$

These energies are often expressed in more convenient units such as MeV (megaelectronvolts), where 1 MeV is $1.602 \times 10^{-13}\text{ J}$.

$$\text{binding energy per nucleon for } {}^4_2\text{He} = \frac{1.14 \times 10^{-12}}{1.602 \times 10^{-13}} = 7.12\text{ MeV}$$

Exam tip

The mass must be in kilograms in this equation.

If more figures are carried through on the calculator, the values for binding energy per nucleon come out as $1.13 \times 10^{-12}\text{ J}$ and 7.08 MeV .

? Test yourself

- 25 Calculate the mass defect (in u), the binding energy (in J) and the binding energy per nucleon (in MeV) for each of the following nuclei:
- ${}^{10}\text{B}$ (mass 10.012 937 u)
 - ${}^{23}\text{Na}$ (mass 22.989 770 u)
 - ${}^{56}\text{Fe}$ (mass 55.934 942 u)
 - ${}^{239}\text{Pu}$ (mass 239.052 157 u)

Calculating the energy released in fission and fusion reactions

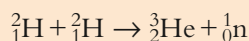
Use the values given in Table C.13 when working through the worked examples that follow.

Atom	Mass / u
^1_1H	1.007 825
^2_1H	2.014 102
^3_1H	3.016 049
^3_2He	3.016 029
^4_2He	4.002 60
$^{141}_{56}\text{Ba}$	140.914 411
$^{92}_{36}\text{Kr}$	91.926 156
$^{235}_{92}\text{U}$	235.043 923

Table C.13 The masses of some atoms in unified atomic mass units.

Worked examples

C.11 Given the atomic masses in Table C.13 and the mass of a neutron given in Table C.12, calculate the energy released in kJ mol^{-1} in the fusion reaction:



The change in mass (Δm) is calculated by finding the difference between the mass of reactants and the mass of the products:

$$\text{total mass of reactants} = 2 \times 2.014\ 102 = 4.028\ 204\ \text{u}$$

$$\text{total mass of products} = 3.016\ 029 + 1.008\ 665 = 4.024\ 694\ \text{u}$$

It can be seen that the total mass of the products is less than the total mass of the reactants:

$$\Delta m = 4.024\ 694 - 4.028\ 204 = -0.00351\ \text{u}$$

The mass change can be converted to kg by multiplying by 1.66×10^{-27} :

$$\Delta m = 0.00351 \times (1.66 \times 10^{-27}) = 5.83 \times 10^{-30}\ \text{kg}$$

This mass is converted to energy when the fusion reaction occurs.

The energy released is worked out by using the Einstein equation:

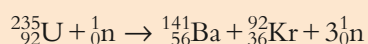
$$\begin{aligned} E &= mc^2 \\ &= (5.83 \times 10^{-30}) \times (3.00 \times 10^8)^2 \\ &= 5.25 \times 10^{-13}\ \text{J} \end{aligned}$$

The energy released per mole is:

$$\begin{aligned} E &= (5.25 \times 10^{-13}) \times (6.02 \times 10^{23}) \\ &= 3.16 \times 10^{11}\ \text{J mol}^{-1} \text{ or } 3.16 \times 10^8\ \text{kJ mol}^{-1} \end{aligned}$$

This is the energy released when two moles of deuterium atoms undergo fusion to form ^3He and it is more than a million times the amount of energy released when one mole of H_2 , which contains the same number of atoms, is burned.

C.12 Given the atomic masses in Table C.13 and the mass of a neutron in Table C.12, calculate the energy released in kJ mol^{-1} in the fission reaction:



This calculation is very similar to the previous one. The change in mass is calculated by working out the difference between the mass of reactants and the mass of the products:

$$\text{total mass of reactants} = 235.043\,923 + 1.008\,665 = 236.052\,588 \text{ u}$$

$$\text{total mass of products} = 140.914\,411 + 91.926\,156 + (3 \times 1.008\,665) = 235.866\,562 \text{ u}$$

$$\Delta m = 235.866\,562 - 236.052\,588$$

$$= -0.186\,026 \text{ u}$$

The mass change can be converted to kg by multiplying by 1.66×10^{-27} :

$$\text{mass change} = 0.186\,026 \times 1.66 \times 10^{-27}$$

$$= 3.09 \times 10^{-28} \text{ kg}$$

This mass is converted into energy in the fission reaction and the energy released is worked out using the Einstein equation:

$$E = mc^2$$

$$= (3.09 \times 10^{-28}) \times (3.00 \times 10^8)^2$$

$$= 2.78 \times 10^{-11} \text{ J}$$

The energy released per mole is:

$$E = (2.78 \times 10^{-11}) \times (6.02 \times 10^{23})$$

$$= 1.67 \times 10^{13} \text{ J mol}^{-1}, \text{ or } 1.67 \times 10^{10} \text{ kJ mol}^{-1}$$

From this we could work out that the energy released when 1 g of uranium-235 undergoes fission is

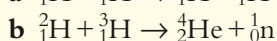
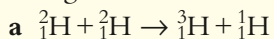
$$\frac{1.67}{235} \times 10^{10} = 7.11 \times 10^7 \text{ kJ g}^{-1}. \text{ This can be compared}$$

with the specific energy of octane, which is only 47.9 kJ g^{-1} .

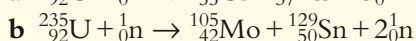
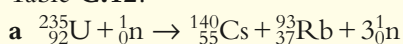
The electrons have been included in all of the calculations above but the calculations are sometimes carried out just using the masses of nuclei (obtained by subtracting the total mass of the electrons from the mass of the atom). However, since there is the same number of electrons on both sides of the equation, their masses will cancel out and make no difference to the overall calculation.

? Test yourself

26 Using the data in Table C.13 calculate the energy released (in kJ mol^{-1}) in each of these fusion reactions:



27 Calculate the energy released (in kJ mol^{-1}) in each of the following fission reactions using the data in the table below and the mass of a neutron given in Table C.12.



Atom	Mass / u
${}^{140}\text{Cs}$	139.91728
${}^{93}\text{Rb}$	92.92204
${}^{105}\text{Mo}$	104.9170
${}^{129}\text{Sn}$	128.9135
${}^{235}\text{U}$	235.043923

C7.2 Half-life

Radioactive decay is a first-order process, so the rate of decay is proportional to the number of undecayed nuclei remaining. We normally discuss the rate of decay in terms of the activity (A), which is the number of nuclei which decay per second, and so we can write a rate equation for radioactive decay as:

$$A = \lambda N$$

where λ is the decay constant and N is the number of undecayed nuclei present. The unit of activity is the becquerel (Bq), which is equivalent to 1 disintegration (decay) per second.

This can be compared to a first-order rate equation for a chemical reaction:

$$\text{rate} = k[X]$$

as described in Topic 6. It can be seen that the decay constant is equivalent to a rate constant.

Integration of the rate equation for radioactive decay in calculus form produces the equation:

$$N = N_0 e^{-\lambda t}$$

where N_0 is the initial number of undecayed nuclei present and N is the number of undecayed nuclei present at time t .

Further mathematical manipulation produces an equation that relates the decay constant to the half-life:

$$\lambda = \frac{\ln 2}{t_{\frac{1}{2}}}$$

It can be seen from this equation that, like the first-order rate constant, the units of the decay constant are time^{-1} . If the activity is measured in becquerels then the decay constant should have units of s^{-1} .

Learning objectives

- Understand that radioactive decay is a first order process
- Use the relationship between the decay constant and half-life
- Solve problems involving non-integral numbers of half-lives

The rate equation for radioactive decay using calculus notation is:

$$\frac{dN}{dt} = -\lambda N$$

This equation could also be written in the form

$$\ln\left(\frac{N}{N_0}\right) = -\lambda t$$

Worked examples

C.13 The half-life of rutherfordium-104 is 65 s. Calculate the decay constant and the percentage of a 1.00 μg sample remaining after 3.00 minutes.

$$\begin{aligned}\lambda &= \frac{\ln 2}{t_{\frac{1}{2}}} \\ &= \frac{0.693}{65} = 0.011 \text{ s}^{-1}\end{aligned}$$

This answer has been rounded to two significant figures but more figures have been carried through for further calculations.

Next we need to use $N = N_0 e^{-\lambda t}$. Both λ and t must be in the same units of time – so if λ is in s^{-1} , t must be in seconds. 3.00 minutes is 180 s.

We are trying to find the ratio $\frac{N}{N_0}$, and we have:

$$\frac{N}{N_0} = e^{-\lambda t} = e^{-0.011 \times 180} = 0.147$$

This is multiplied by 100 to get a percentage and so about 15% remains undecayed after 3.00 minutes.

C.14 Given that the activity of a 1.00 μg sample of nitrogen-13 is $5.35 \times 10^{13} \text{ Bq}$, calculate the half-life and the mass left after 45 minutes. The mass of a nitrogen-13 atom is $2.16 \times 10^{-23} \text{ g}$.

The number of nitrogen-13 atoms in 1.00 μg is:

$$\frac{1.00 \times 10^{-6}}{2.16 \times 10^{-23}} \text{ i.e. } 4.63 \times 10^{16} \text{ atoms}$$

$A = \lambda N$ so:

$$\begin{aligned} \lambda &= \frac{A}{N} \\ &= \frac{5.35 \times 10^{13}}{4.63 \times 10^{16}} = 1.16 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} t_{\frac{1}{2}} &= \frac{\ln 2}{\lambda} \\ &= \frac{0.693}{1.16 \times 10^{-3}} = 600 \text{ s} \end{aligned}$$

To calculate the mass left after 45 minutes we use:

$$N = N_0 e^{-\lambda t} \text{ in the form } \frac{N}{N_0} = e^{-\lambda t}$$

The decay constant is in units of s^{-1} so we must convert the time to seconds:

$$t = 45 \times 60 = 2700 \text{ s}$$

$$\begin{aligned} \frac{N}{N_0} &= e^{-\lambda t} \\ &= e^{-1.16 \times 10^{-3} \times 2700} \\ &= 0.0442 \end{aligned}$$

This is the proportion of the sample *undecayed* after 45 minutes, so the mass of nitrogen-13 left at the end is 0.0442 times the original mass:

$$\begin{aligned} \text{mass} &= 0.0442 \times 1.00 \\ &= 0.0442 \mu\text{g, or } 4.42 \times 10^{-8} \text{ g} \end{aligned}$$

It is important to be consistent with units in these questions. The decay constant in the above example could also have been written as 0.0693 min^{-1} . This is just 60 times the decay constant given.

Using the decay constant in this form means that time can be used in minutes. Substituting in $\frac{N}{N_0} = e^{-\lambda t}$ we get:

$$\frac{N}{N_0} = e^{-0.0693 \times 45}, \text{ which gives the same answer as above.}$$

C.15 1.00 kg of a particular rock was believed to contain 0.120 g of potassium-40 when it was originally formed. Analysis of the rock has determined that it now contains 0.0500 g of potassium-40. Calculate the age of the rock given that the half-life of potassium-40 is 1.25×10^9 years.

We will need to use $\frac{N}{N_0} = e^{-\lambda t}$ and so must first work out the decay constant:

$$\begin{aligned}\lambda &= \frac{\ln 2}{t_{\frac{1}{2}}} \\ &= \frac{0.693}{1.25 \times 10^9} \\ &= 5.54 \times 10^{-10} \text{ y}^{-1}\end{aligned}$$

We can use mass instead of number of atoms in the following equation because any conversion factor will simply cancel out in the ratio.

$$\begin{aligned}\frac{N}{N_0} &= e^{-\lambda t} \\ \frac{0.0500}{0.120} &= e^{-5.54 \times 10^{-10} t}\end{aligned}$$

So $e^{-5.54 \times 10^{-10} t} = 0.4167$

Taking the natural log of both sides:

$$-5.54 \times 10^{-10} t = \ln 0.4167$$

$$-5.54 \times 10^{-10} t = -0.875$$

So $t = \frac{0.875}{5.54 \times 10^{-10}}$

$$= 1.58 \times 10^9 \text{ y}$$

The decay constant was expressed in y^{-1} so the time will come out in years.

Exam tip

$\frac{N}{N_0} = e^{-\lambda t}$ can be used more conveniently in the form $\ln\left(\frac{N}{N_0}\right) = -\lambda t$, which makes the mathematical manipulation simpler in this type of problem.

Exam tip

As a final check we can consider if this answer seems reasonable. The half-life of potassium-40 is 1.25×10^9 years, therefore 0.120 g should decay to 0.0600 g in this time. We are trying to find the time that it takes to decay to 0.0500 g and therefore would expect it to be slightly longer than one half-life, which our answer is.

? Test yourself

28 Calculate the decay constant in each of the following cases:

- a** the half-life of nobelium-259 is 58 minutes
- b** the half-life of rubidium-83 is 86.2 days
- c** the half-life of neodymium-144 is 2.1×10^{15} years

29 Assuming that you start in each case with $5.00 \mu\text{g}$ of the isotopes in question **28**, calculate how long it will take for the amount of the isotope to fall to $1.00 \mu\text{g}$.

30 Calculate what percentage of the stated isotope is left after the stated time.

- a** carbon-14 (half-life 5730 years) after 10 000 years
- b** iodine-131 (half-life 8.04 days) after 3 weeks

31 Given that activity of a $2.00 \mu\text{g}$ sample of osmium-191 is $3.27 \times 10^9 \text{ Bq}$, calculate the half-life and the mass left after 6 weeks. The mass of an osmium-191 atom is $3.19 \times 10^{-22} \text{ g}$.

Learning objectives

- Understand that the rate of effusion of a gas is inversely proportional to the square root of its molar mass
- Understand Graham's law of effusion in terms of the kinetic theory
- Solve problems involving Graham's law of effusion
- Understand the different methods of uranium enrichment
- Describe the different physical properties of UO_2 and UF_6 in terms of structure and bonding

Graham's law is often stated in terms of the density of the gas – the rate of effusion is inversely proportional to the density. The density of a gas is proportional to its relative molecular mass at a particular temperature and pressure.

Basically what we are saying here is that, because average kinetic energy is the same for all gases at the same temperature, heavier molecules move more slowly and therefore will leave the container more slowly.

C7.3 Enrichment of uranium

Graham's law of effusion

Effusion is the process by which a gas escapes through a very small hole in a container (Figure C.40).

Graham's law: the rate of effusion of a gas is inversely proportional to the relative molecular mass of the gas.

The origin of Graham's law can be explained in terms of the kinetic theory. The average kinetic energy of the particles in a gas is proportional to the absolute temperature:

$$KE \propto T$$

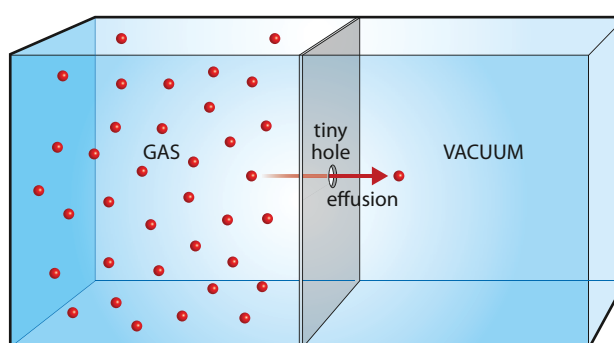


Figure C.40 Gas molecules escape through a very small hole in the container.

The average kinetic energy is given by $\frac{1}{2}m\bar{v}^2$, where m is the mass of a molecule and \bar{v}^2 represents the mean square speed – the average of the squared speeds.

$$\text{So } \frac{1}{2}m\bar{v}^2 \propto T$$

$$\text{and } \bar{v}^2 \propto \frac{T}{m}$$

So at a constant temperature $\bar{v} \propto 1/\sqrt{m}$, where \bar{v} is the root mean square speed which is very similar to the average speed of the molecules in the sample of gas.

How quickly a gas effuses through a small hole will depend on how often gas molecules 'hit' the hole, and this depends on the speed of the gas molecules. From this we can deduce that the rate of effusion is inversely proportional to the square root of the mass of a molecule – in other words, inversely proportional to the square root of the molar mass of the gas.

For two different gases in a container, Graham's law of effusion can be stated in the form:

$$\frac{\text{rate of effusion of gas 1}}{\text{rate of effusion of gas 2}} = \frac{\sqrt{\text{molar mass of gas 2}}}{\sqrt{\text{molar mass of gas 1}}}$$

$$\frac{\text{rate}_1}{\text{rate}_2} = \sqrt{\frac{M_2}{M_1}}$$

This assumes that if the gases are in the same container they will be at the same temperature and pressure.

Worked examples

C.16 Equal numbers of moles of carbon dioxide and oxygen are put in a container containing a small hole in its wall. What is the ratio of the rate of effusion of carbon dioxide to that of oxygen? After one hour will there be more moles of carbon dioxide or of oxygen in the container?

Molar mass of $\text{CO}_2 = 44.01 \text{ g mol}^{-1}$; molar mass of $\text{O}_2 = 32.00 \text{ g mol}^{-1}$

$$\begin{aligned}\frac{\text{rate of effusion of CO}_2}{\text{rate of effusion of O}_2} &= \frac{\sqrt{(\text{molar mass of O}_2)}}{\sqrt{(\text{molar mass of CO}_2)}} \\ &= \frac{\sqrt{32.00}}{\sqrt{44.01}} \\ &= 0.853\end{aligned}$$

This means that oxygen effuses 1.173 times ($\frac{1}{0.853}$) more quickly than carbon dioxide and, because there were equal numbers of molecules present originally, after one hour more moles of carbon dioxide will be in the container.

C.17 A gas, X, effuses through a small hole at the rate of $1.20 \text{ cm}^3 \text{ h}^{-1}$. Under the same conditions of temperature and pressure, nitrogen gas effuses through the same hole at the rate of $1.54 \text{ cm}^3 \text{ h}^{-1}$. Calculate the molar mass of X.

Molar mass of $\text{N}_2 = 28.02 \text{ g mol}^{-1}$

$$\frac{\text{rate of effusion of N}_2}{\text{rate of effusion of X}} = \frac{\sqrt{(\text{molar mass of X})}}{\sqrt{(\text{molar mass of N}_2)}}$$

$$\frac{1.54}{1.20} = \frac{\sqrt{M_x}}{\sqrt{28.02}}$$

$$\text{So } \sqrt{M_x} = \frac{\sqrt{28.02} \times 1.54}{1.20}$$

$$\text{and } M_x = 46.1 \text{ g mol}^{-1}$$

C.18 A container of volume 1.00 dm^3 contains 0.0200 mol of oxygen and 0.0200 mol of helium.

The rate of effusion of oxygen through a very small hole in the container wall is $5.60 \times 10^{-5} \text{ mol h}^{-1}$. Calculate the rate of effusion of helium and the number of moles of each gas present in the container after 48 hours.

Molar mass of $\text{He} = 4.00 \text{ g mol}^{-1}$; molar mass of $\text{O}_2 = 32.00 \text{ g mol}^{-1}$

$$\begin{aligned}\frac{\text{rate of effusion of He}}{\text{rate of effusion of O}_2} &= \frac{\sqrt{(\text{molar mass of O}_2)}}{\sqrt{(\text{molar mass of He})}} \\ &= \frac{\sqrt{32.00}}{\sqrt{4.00}} \\ &= 2.83\end{aligned}$$

So helium effuses 2.83 times as quickly as oxygen. The rate of effusion of helium is $2.83 \times 5.60 \times 10^{-5} \text{ mol h}^{-1}$, or $1.58 \times 10^{-4} \text{ mol h}^{-1}$.

The amount of oxygen that will effuse in 48 hours is $48 \times 5.60 \times 10^{-5} = 2.69 \times 10^{-3} \text{ mol}$

The amount of oxygen remaining in the container will be $0.0200 - 2.69 \times 10^{-3} = 0.0173 \text{ mol}$

The amount of helium that will effuse in 48 hours is $48 \times 1.58 \times 10^{-4} = 7.60 \times 10^{-3} \text{ mol}$

The amount of helium remaining in the container will be $0.0200 - 7.60 \times 10^{-3} = 0.0124 \text{ mol}$

? Test yourself

- 32 Calculate the relative rates of effusion of the gas pairs below:
- helium (He) and sulfur dioxide (SO₂)
 - ethene (C₂H₄) and propane (C₃H₈)
 - hydrogen (H₂) and methane (CH₄)
- 33 Calculate the molar mass of the unknown gas in each case:
- nitrogen effuses at 1.07 times the rate of gas Y
 - gas Q effuses at 1.30 times the rate of carbon dioxide
 - helium effuses at 2.60 times the rate of gas Z
- 34 Mixtures of two gases are put into three different containers so that each container contains 5.00×10^{-3} mol of the gases listed below. In each case, the rate of effusion of one of the gases is given. Calculate the number of moles of each gas present after 24 hours:
- methane (rate of effusion 4.80×10^{-5} mol h⁻¹) and helium
 - carbon monoxide (rate of effusion 3.60×10^{-5} mol h⁻¹) and carbon dioxide
 - fluorine (rate of effusion 6.00×10^{-5} mol h⁻¹) and chlorine (assume no reaction between the gases under these conditions)

Enrichment requires large amounts of electricity and contributes significantly to the cost of nuclear power. Depending on how the electricity for the enrichment plant is generated, it can also make a significant difference to the carbon footprint of nuclear power generation.

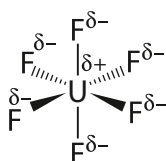


Figure C.41 The structure of UF₆.

The molecules are essentially spherical with a small area of contact between adjacent molecules and the fluorine atoms are not very polarisable – so the London forces between molecules are much weaker than in, for instance, a linear hydrocarbon of similar relative molecular mass.

Uranium enrichment

There are two main naturally occurring isotopes of uranium – uranium-235 and uranium-238. The isotope that undergoes fission in a nuclear reactor is uranium-235, but the problem is that the natural abundance of this isotope is only 0.72%. The proportion of uranium-235 present in a sample, therefore, generally has to be increased before it can be used in a nuclear reactor. The process by which this is done is called **enrichment**.

Different reactors require uranium that has been enriched to different extents but most require the fuel to be enriched to contain at least 3% uranium-235. Nuclear weapons require uranium that has been enriched to contain at least 90% uranium-235.

There are two main techniques for uranium enrichment: **gaseous diffusion** and **gas centrifugation**. Before enrichment can occur, the uranium must be converted into a volatile form – uranium hexafluoride, UF₆. This is made from uranium ore in a series of steps. UF₆ exists in the gaseous state during the enrichment process and both enrichment techniques rely on the difference in mass between gaseous ²³⁵UF₆ and ²³⁸UF₆ molecules.

Properties of UF₆ and UO₂

Uranium(VI) fluoride (uranium hexafluoride, UF₆) is a white crystalline solid that sublimates at 64 °C. It consists of UF₆ octahedral molecules in the solid and gaseous states (Figure C.41). There are covalent bonds between the uranium atom and the fluorine atoms, and London forces between the molecules in the solid state.

Because fluorine is much more electronegative than uranium, all the bonds are very polar. However, the symmetry of the molecule means that the dipoles cancel so the molecule is non-polar overall. There are therefore relatively weak forces (London forces) between the molecules and UF₆ sublimates at a relatively low temperature.

Uranium(IV) oxide (uranium dioxide, UO₂) is a dark-brown, crystalline ionic solid that melts at over 2800 °C. The solid consists of U⁴⁺ ions and O²⁻ ions with very strong electrostatic forces between the ions which require a lot of energy to break.



Gaseous diffusion

In gaseous diffusion, the UF_6 is forced at high pressure through a container with walls made of a semi-permeable membrane (Figure C.42). Because $^{235}\text{UF}_6$ has a slightly lower relative molecular mass, it effuses slightly faster through the membrane and the stream of gas becomes slightly enriched with uranium-235.

The rate of effusion of $^{235}\text{UF}_6$ is only 1.004 times that of $^{238}\text{UF}_6$ because the molar masses are so similar. This means that this process must be repeated several hundred times to achieve an enrichment of even a few percent.

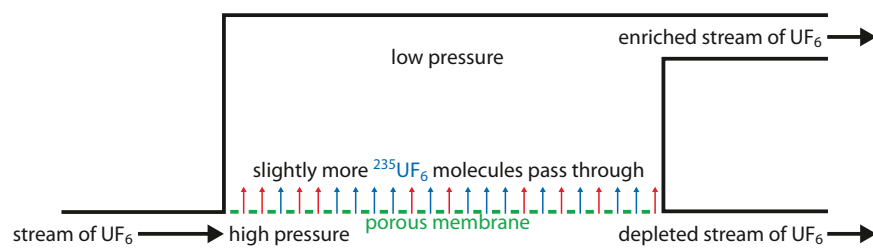


Figure C.42 Enrichment by gaseous diffusion.

Gas centrifugation

In gas centrifugation, the UF_6 molecules are fed into a cylinder (Figure C.43) which is rotated at high speed so that the slightly heavier $^{238}\text{UF}_6$ molecules move more towards the outside. The gas at the centre of the cylinder is slightly richer in the lighter $^{235}\text{UF}_6$ molecules. The slightly enriched stream then passes to the next centrifuge. As with diffusion, this must be repeated many times to achieve significant enrichment. Commercial plants operate large numbers of centrifuges in series and parallel.

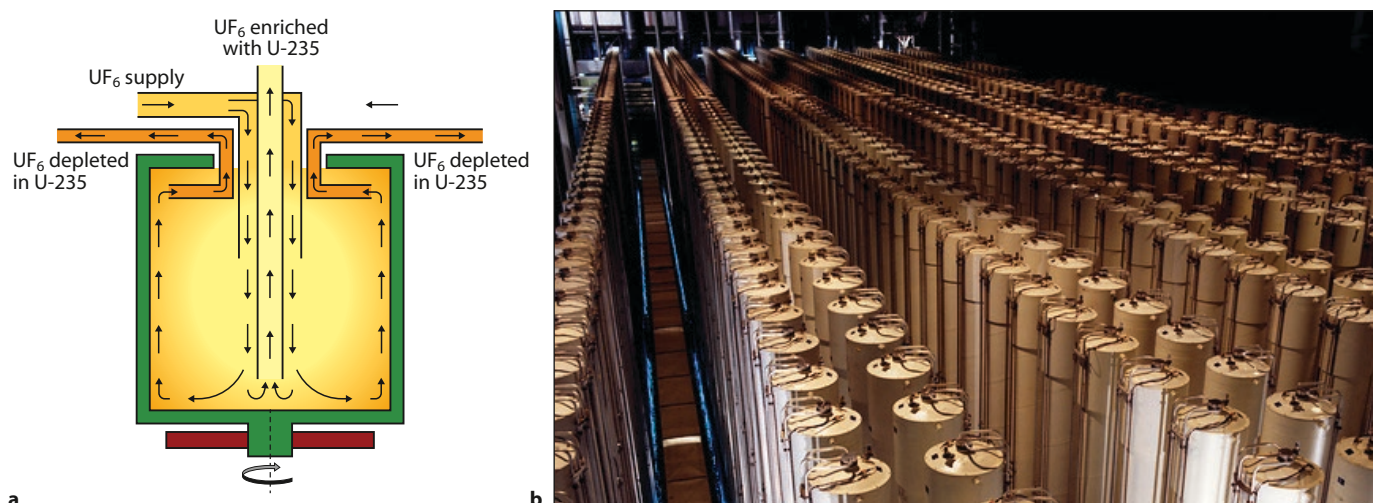


Figure C.43 a A gas centrifuge; b overhead view of rows of centrifuge units at the enrichment plant in Piketon, Ohio, USA.

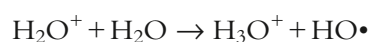
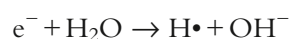
Learning objectives

- Understand that ionising radiation can cause damage to cells

C7.4 The dangers of radioactivity

The fuels used in nuclear reactors and the contents of nuclear waste are radioactive. They contain isotopes that undergo radioactive decay by the emission of alpha particles, beta particles and/or gamma rays (there are other forms of radioactive decay). These forms of radiation are called **ionising radiation** because they cause the formation of ions (by ejection of electrons) when they interact with matter.

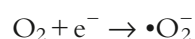
Ionising radiation can damage human cells and the main effect comes from damage caused to DNA. The ionising radiation can either interact directly with DNA, causing ionisation and a change of structure, or there can be indirect effects due to the formation of free radicals from other species, such as water. The most common substance in our body is water and when ionising radiation interacts with this the water molecules can become ionised. The ions and electrons generated can go on to react further to produce free radicals such as the hydroxyl radical (HO•):



The last of these reactions could also be written $\text{H}_2\text{O}^+ \rightarrow \text{H}^+ + \text{HO}\cdot$.

Of the free radicals generated in these processes, the hydroxyl radical is probably the most dangerous. When it interacts with DNA it can set off a series of reactions that results in damage to the DNA. Free radicals can also cause damage to proteins (enzymes) and lipids in cells.

Other free radicals, such as the superoxide ion, can also be formed. This ion can be formed by the reaction of oxygen with an electron (liberated during an ionisation process):



The superoxide ion can be converted into hydroxyl radicals in cells – see Option A.

Nature of science

There have been many large-scale collaborative projects in the history of science and one of the most (in)famous is the Manhattan project, which resulted in the development of the first atomic bombs. At its peak it employed well over 100 000 workers. Two different bombs (one using uranium and the other plutonium) were developed and dropped on Hiroshima and Nagasaki in August 1945. There are many estimates as to how many people died as a result of this, and most are well over 100 000.

C8 Photovoltaic and dye-sensitised solar cells (HL)

C8.1 The effect of conjugation on the wavelength of light absorbed by molecules

Electromagnetic radiation in the visible–ultraviolet region of the spectrum is absorbed to promote an electron from a low energy level (molecular orbital) in a molecule to a higher energy level (molecular orbital). The wavelength at which the maximum amount of radiation is absorbed is called λ_{\max} . We have already met (page 27) the idea that double bonds (chromophores) are needed if electromagnetic radiation is to be absorbed by a molecule and that a conjugated system is a system of alternating single and double bonds. We can see from Figure C.44 that electrons are delocalised in a conjugated system because p orbitals can overlap along the whole chain.

It can be seen from Table C.14 that:

the longer the conjugated chain (delocalised system), the longer the wavelength of radiation absorbed by a molecule.

As the conjugated system gets longer, the energy gap between the lower molecular orbital that the electron is promoted from and the higher molecular orbital that it is promoted to gets smaller (Figure C.45).

If the conjugated system is long enough, light in the visible region of the spectrum will be absorbed and the compound will be coloured.

Molecule	No. of conjugated double bonds	λ_{\max} / nm
$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C} = \text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	1	162
$\begin{array}{c} \text{H} & \text{H} & & \text{H} \\ & & & \\ \text{C} = \text{C} & - & \text{C} = \text{C} \\ & & & \\ \text{H} & & \text{H} & \text{H} \end{array}$	2	217
$\begin{array}{c} \text{CH}_3 & \text{H} & & \text{H} & & \text{H} \\ & & & & & \\ \text{C} = \text{C} & - & \text{C} = \text{C} & - & \text{C} = \text{C} \\ & & & & & \\ \text{H} & & \text{H} & & \text{H} & \text{CH}_3 \end{array}$	3	275
$\begin{array}{c} \text{CH}_3 & \text{H} & & \text{H} & & \text{H} \\ & & & & & \\ \text{C} = \text{C} & - & \text{C} = \text{C} & - & \text{C} = \text{C} & - & \text{C} = \text{C} \\ & & & & & & \\ \text{H} & & \text{H} & & \text{H} & & \text{CH}_3 \end{array}$	4	310

Table C.14 The effect of conjugation on the wavelength of electromagnetic radiation absorbed.

Learning objectives

- Understand that molecules with longer conjugated systems absorb longer wavelength electromagnetic radiation

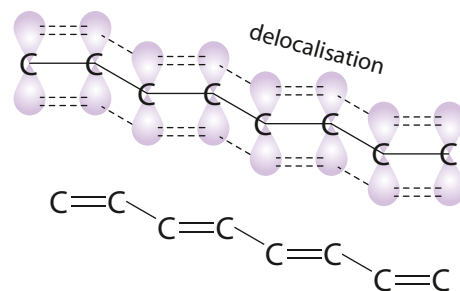


Figure C.44 Delocalised electrons and overlapping p orbitals in a conjugated system.

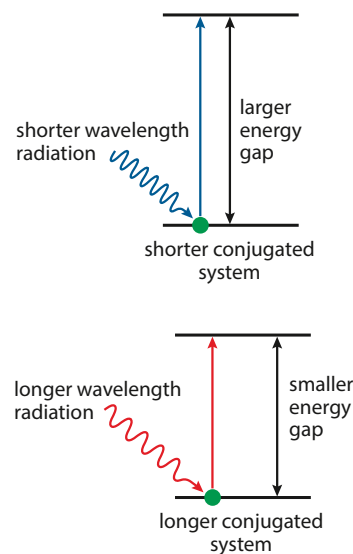
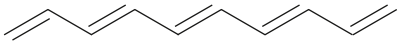
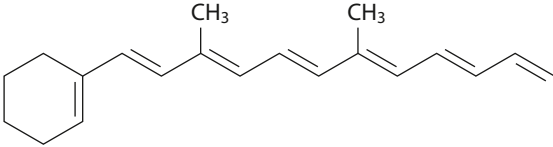
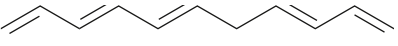
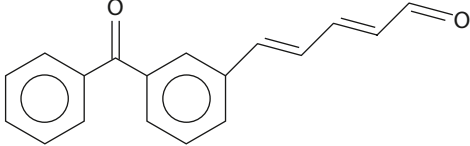


Figure C.45 As the conjugated system gets longer the energy difference between energy levels in a molecule gets smaller.

? Test yourself

35 Arrange the following molecules in order of the wavelength of ultraviolet–visible radiation that they absorb (shortest first):

	hexa-1,4-diene	
I	II	III
	buta-1,3-diene	
IV	V	VI

Learning objectives

- Understand that the electrical conductivity of a metal decreases with increasing temperature, but that of a semiconductor increases
- Understand that the conductivity of silicon can be increased by doping
- Understand how a photovoltaic cell works
- Understand how a dye-sensitised solar cell works
- Understand that the efficiency of a dye-sensitised solar cell can be increased by using TiO₂ nanoparticles
- Discuss some of the advantages of a dye-sensitised solar cell compared to a silicon-based photovoltaic cell

C8.2 Solar cells

Semiconductors

Materials can be divided into three classes according to their electrical conductivity – **metals**, **semiconductors** and **insulators**. Metals are very good conductors of electricity; insulators, to all extents and purposes, do not conduct electricity; and semiconductors have intermediate electrical conductivity.

The electrical conductivity of solids can be described in terms of band theory. The outer orbitals of the atoms making up a solid overlap to form valence and conduction bands of orbitals (Figure C.46).

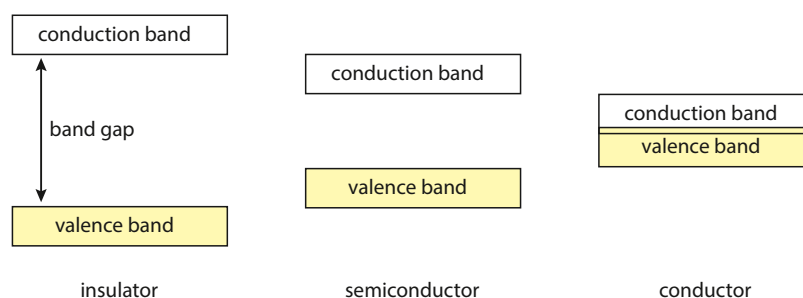


Figure C.46 Valence and conduction bands for different types of materials.

These bands consist of a very large number of orbitals that are closely spaced in energy (Figure C.47).

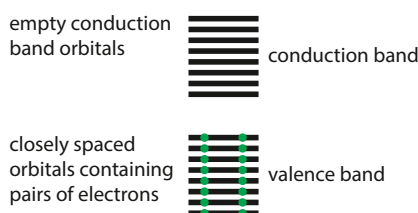


Figure C.47 Electrons in bands.

In insulators and semiconductors at absolute zero, the valence band containing the outer shell electrons of the solid is full, whereas the conduction band is empty. Because the valence band is full, there is nowhere for the electrons to move and neither insulators nor semiconductors conduct electricity at absolute zero. However, the band gap in a semiconductor such as silicon is sufficiently small that as the temperature is raised some electrons are promoted to the conduction band and become free to move. Therefore the electrical conductivity of semiconductors increases as the temperature increases. The promotion of electrons from the valence band also creates 'holes' in this band that other electrons can move into and this also contributes to the electrical conductivity (Figure C.48). A hole is regarded as a positive charge carrier – if an electron has been removed, what is left has a positive charge.

In an insulator, the energy gap between valence and conduction bands is large and at normal temperatures electrons cannot jump to the higher level. In a metal, the conduction and valence bands overlap and the metal is a good conductor of electricity because many electrons are free to move.

Metals conduct electricity well because the delocalised electrons are free to move throughout the structure. Resistance in metals arises because these electrons collide with the positive ions in the lattice (Figure C.49). As the temperature increases, the metal ions vibrate more and so there is essentially a larger cross-section for the electrons to collide with and the electrical conductivity decreases (resistance increases).

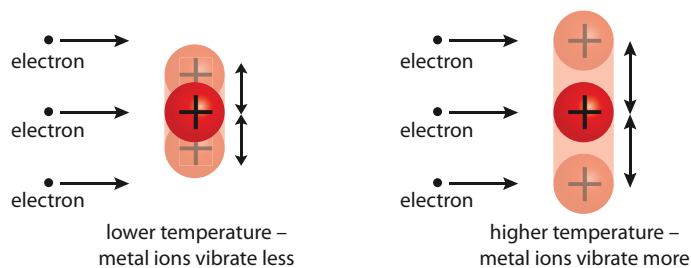


Figure C.49 Metal ions vibrate less at lower temperatures and the electrons are better able to pass through the structure.

The electrical conductivity of a semiconductor increases as temperature increases – but that of a metal decreases as temperature increases.

There is a general correlation between the electrical conductivity of metals and semiconductors and their ionisation energies. Generally, metals have the lowest ionisation energies in any period and therefore hold on to their outer electrons least strongly. This means that metals ionise fairly readily to generate free electrons. Semiconductors such as silicon have higher ionisation energies than metals and so their outer electrons are held more strongly – they will not readily ionise to form free electrons.

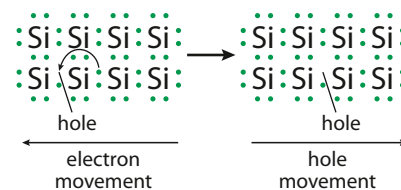


Figure C.48 The movement of a negatively charged electron in one direction is equivalent to the movement of a positively charged hole in the opposite direction.

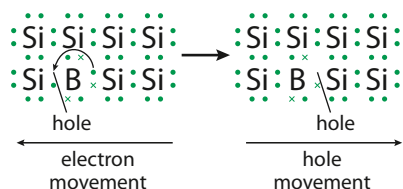


Figure C.50 The movement of holes in p-type semiconductors.

Doping of silicon

The electrical conductivity of silicon can be increased by incorporating atoms of group 13 or group 15 elements as impurities into the lattice – this process is called **doping**.

Inclusion of a small proportion of a group 13 element such as boron, aluminium or gallium into the silicon structure creates a p-type semiconductor (where ‘p’ stands for positive). These group 13 atoms supply only three electrons to the valence band instead of four (as supplied by Si), and therefore there is a hole in the valence band. The introduction of extra gaps in the valence band increases the electrical conductivity of the silicon. Because the main charge carriers are **positively** charged holes, this is now called a p-type semiconductor (Figure C.50).

Incorporation of a group 15 element (e.g. phosphorus, arsenic or antimony) into a silicon lattice also increases the electrical conductivity of the semiconductor, but this time by providing extra electrons. These atoms have five valence electrons, of which four are used in forming covalent bonds and go into the valence band – but the fifth is promoted to the conduction band easily. Because the current is carried by **negatively** charged electrons, the material is described as an n-type semiconductor.

The interaction of sunlight with silicon

We have seen above that electrons can be promoted from the valence band to the conduction band of a semiconductor by thermal energy. Photons of light with wavelengths shorter than about 1100 nm also have sufficient energy to cause electrons to be promoted from the valence band to the conduction band resulting in an increase in the electrical conductivity of silicon. This effect is used in photovoltaic cells (solar cells).

In photovoltaic cells, such as the solar cells found in calculators and other small electronic devices, a p-type semiconductor and an n-type semiconductor are joined together. When these two (both neutral) are joined, electrons move from the n-type to the p-type semiconductor, where they combine with some holes and leave behind positively charged ions. Holes move from the p-type to the n-type semiconductor and combine with the additional electrons, leaving behind negative charge. So, there is a build up of charge at the p–n junction that prevents any further movement of charge across the junction (Figure C.51).

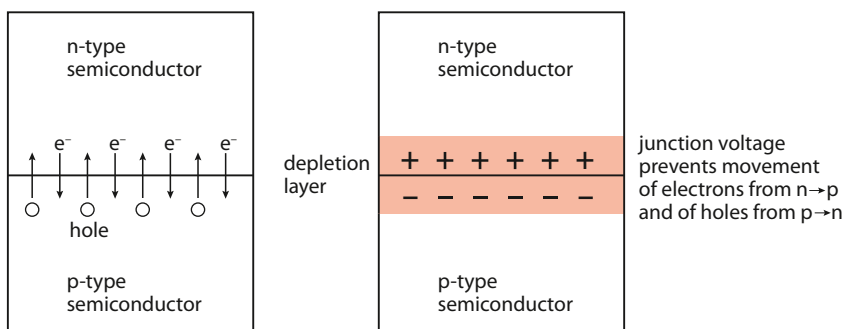


Figure C.51 The build up of charge at a p–n junction produces a layer that prevents further movement of charge across the junction.

Visible light has wavelengths between 400 and 750 nm.

When light hits the n-type semiconductor, electrons are promoted to the conduction band. These electrons are not able to flow from the n-type to the p-type directly, because the voltage at the p–n junction prevents this. They must therefore travel from the n-type to the p-type through the external circuit, and this can be used to power an electrical device (Figure C.52).

? Test yourself

- 36 When silicon is doped with the following atoms, would n-type or p-type semiconductors be produced?
- a Al b In c As d Sb

Dye-sensitised solar cells

During photosynthesis, light is absorbed by chlorophyll to promote electrons to higher energy levels. These electrons are then passed on via an electron transport chain (as series of redox reactions) to a low-energy electron acceptor. In the process the energy of the excited electrons is converted to chemical energy.

A dye-sensitised solar cell (DSSC or DSC) imitates the way in which a plant harnesses solar energy. The process is described in more detail below but the basic principle is that a photon of light is absorbed by a dye molecule to promote an electron to a higher energy level. The electron is passed to ('injected into') the conduction band of titanium oxide semiconductor particles and can then flow through the external circuit to the cathode. The basic idea is the conversion of light energy to electrical energy via an intermediary. Whereas in a photovoltaic cell the absorption of a photon of light causes the movement of electrons directly, in a DSSC the processes of absorption of photons and movement of electrons are separated.

Figure C.53 shows a simple diagram of a DSSC as developed originally by Michael Grätzel and co-workers.

Light passes through a glass cover with a conducting coating and causes electrons in the dye-sensitiser (D) to be promoted to a higher energy level.

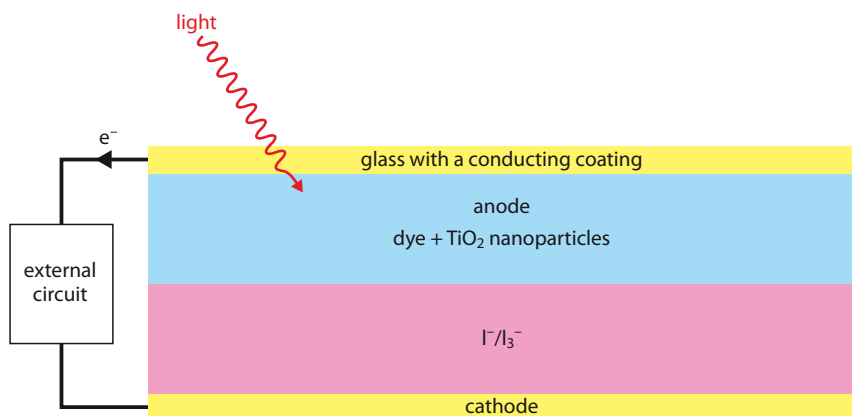
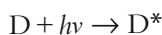


Figure C.53 A dye-sensitised solar cell.

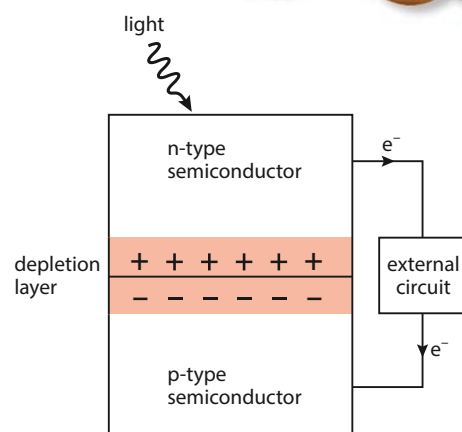
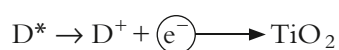


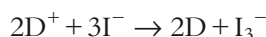
Figure C.52 How a photovoltaic cell can produce a current.

$h\nu$ represents energy from the light.

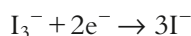
These electrons are then transferred to the conduction band of the TiO_2 nanoparticles:



The sensitiser has been oxidised and is reduced back to its original state by electrons from the I^- ions in the electrolyte:



The electrons at high energy in the conduction band of the TiO_2 flow through the external circuit to the cathode where they reduce the I_3^- ions back to I^- :



To increase the amount of light absorbed in the DSSC, porous TiO_2 nanoparticles coated with the light-absorbing dye are used – this gives an extremely large surface area. Which regions of the electromagnetic spectrum are absorbed depends on the particular dye used – for instance, a black dye gives good absorption over the entire visible spectrum.

DSSCs are still very much in the development stage but the cells produced so far have shown efficiencies similar to those of many traditional silicon-based photovoltaic cells. Several advantages over traditional silicon photovoltaic cells have been suggested:

- DSSCs are likely to be cheaper to manufacture than silicon photovoltaic cells because most of the materials involved are reasonably abundant and inexpensive.
- DSSCs are less sensitive to temperature changes than silicon photovoltaic cells – solar cells get hot in direct sunlight! The efficiency of a silicon photovoltaic cell falls with increasing temperature, whereas a DSSC is hardly affected at all.
- DSSCs can work better in low light conditions than silicon photovoltaic cells – e.g. cloudy conditions. In a silicon photovoltaic cell, electrons promoted to the conduction band by absorption of photons can simply fall back down and recombine with the holes generated at the same time, which results in no current flowing. In low light conditions the rate of recombination is likely to be significant compared to the rate of ejection of electrons. In a DSSC, no hole is generated, just an extra electron in the conduction band of the semiconductor material, and so this cannot happen.

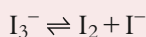
Nature of science

Solar cells in their current form were first developed in the 1950s and their principal use in the 1960s was to power satellites.

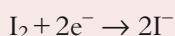
It is often important in science to have knowledge and understanding beyond one individual science and a knowledge of photosynthesis from biology provided the inspiration for scientists to develop DSSCs.

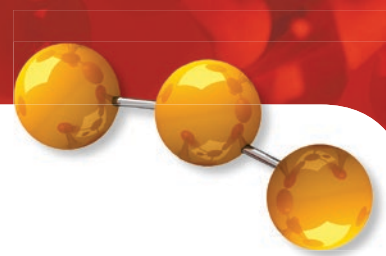
Scientists continue to make advances in the field of renewable energy – but there must also be a drive from governments and the general public to provide funding and to use the new technology. Science can only take us so far, it cannot solve all problems – scientists can develop new solar cells but they cannot make people use them. Everyone has to become more aware of their environment and the problems that we will all face in the very near future.

I_3^- is in equilibrium with I_2 and I^- in solution:



The reduction of I_3^- is thus equivalent to the reduction of molecular iodine:

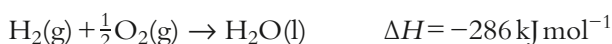




Exam-style questions

- 1 Renewable and non-renewable energy sources are essential in modern society.
- a Explain the difference between renewable and non-renewable energy sources. [2]
 - b State **one** advantage and **one** disadvantage of using solar energy to generate electricity. [2]
 - c Hydrogen–oxygen fuel cells can be used to provide power for electric vehicles. Hydrogen is stored in tanks in the vehicles and a continuous supply of hydrogen must be fed into the cell to produce electricity.

In a hydrogen–oxygen fuel cell, the reaction that occurs is equivalent to the combustion of hydrogen:



- i 10.0 mol of hydrogen were fed into a hydrogen fuel cell and 1500 kJ of electrical energy was obtained. Calculate the efficiency of the fuel cell. [2]
 - ii The density of methanol (CH_3OH) at 298 K is 0.79 g cm^{-3} and the enthalpy change of combustion is -726 kJ mol^{-1} . Calculate the energy density of methanol. [3]
 - iii The specific energy of hydrogen is more than six times the specific energy of methanol, but some scientists believe that methanol might be a more useful fuel for powering electric vehicles than hydrogen. Explain why this might be the case. [2]
- 2 It is estimated that there are over 1 billion cars in the world and the majority of these use petrol/gasoline as fuel.
- a Explain the process by which gasoline is obtained from crude oil. [4]
 - b Octane numbers are often stated on petrol pumps in petrol stations.
 - i State what is meant by the octane number of a fuel. [1]
 - ii Explain how cracking can be used to improve the octane number of fuels. [3]
 - c Transport contributes a great deal to an individual's carbon footprint.
 - i Use the data below to calculate the carbon footprint per person for an aeroplane journey from London to New York. [3]

distance from London to New York	5570 km
fuel consumption of aircraft	$14.0 \text{ dm}^3 \text{ km}^{-1}$
number of passengers + crew	500
carbon dioxide produced per dm^3 of fuel consumed	2.00 kg

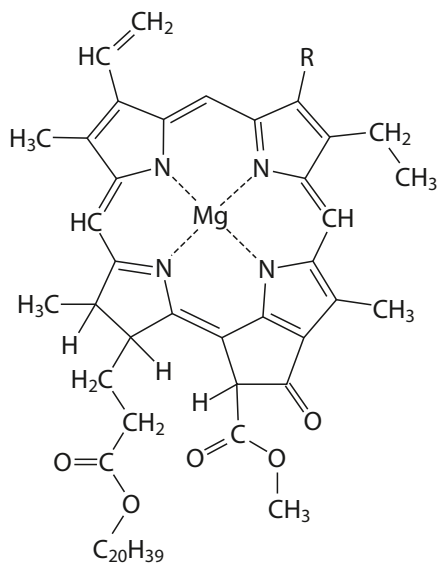
- ii The Ferrari 458 Italia has a fuel consumption of approximately 13.0 dm^3 per 100 km. Calculate the carbon footprint per person for two people travelling 5570 km in a Ferrari 458. Assume that the fuel has the same molecular formula as octane (C_8H_{18}) and a density of 0.700 g cm^{-3} . [5]
- 3 Uranium-235 is an important fuel for nuclear reactors. In a nuclear reactor the uranium-235 undergoes nuclear fission.
- a Explain what is meant by 'nuclear fission'. [1]
 - b Explain in terms of nuclear binding energy why uranium-235 undergoes fission rather than fusion reactions. [2]
 - c A possible reaction that uranium-235 can undergo is:
$${}_{92}^{235}\text{U} + {}_0^1\text{n} \rightarrow {}_{92}^{236}\text{U} \rightarrow {}_{51}^{135}\text{Sb} + {}_{41}^{99}\text{Nb} + \dots {}_0^1\text{n}$$

Calculate the number of neutrons produced in this reaction. [1]

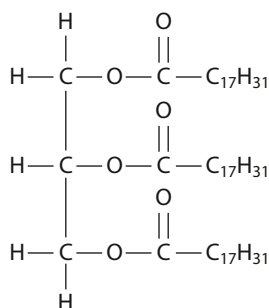
- d Antimony-135 is radioactive with a half-life of 1.7 s.
- State what is meant by 'half-life'. [1]
 - Calculate what percentage of a sample of this isotope would remain after 6.8 s. [2]
- e State **three** problems associated with generating electricity using nuclear power. [3]

4 Biofuels such as ethanol and biodiesel are becoming increasingly important as fuels for motor vehicles. The energy stored in biofuels and fuels derived from petroleum originally came from the Sun.

- a Chlorophyll is the green pigment in plants. The structure of chlorophyll is shown below. Explain what feature of the chlorophyll molecule allows it to absorb visible light. [1]

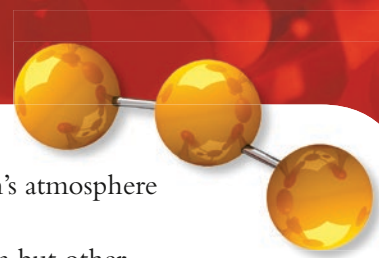


- b Light energy from the Sun is converted into chemical energy in photosynthesis. Write a balanced equation for photosynthesis. [1]
- c The structure of one of the triglycerides in sunflower oil is shown below.



This can be converted to biodiesel in a transesterification reaction with ethanol in the presence of a base catalyst.

- Write an equation for the reaction. [2]
 - Explain why the biodiesel formed in **c i** is less viscous than sunflower oil. [2]
- d Explain **one** advantage and **one** disadvantage of using liquid biofuels, such as ethanol and biodiesel, as opposed to liquid fuels derived from petroleum. [2]



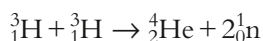
- 5 a The greenhouse effect is a natural phenomenon. It occurs as a result of the way the Earth's atmosphere interacts with radiation from and to space.
- i Explain why certain gases, such as CO_2 and CH_4 , are able to absorb infrared radiation but other gases, such as N_2 and O_2 , are not. [3]
 - ii Explain how the greenhouse effect warms the Earth. [4]
 - iii Explain why human activity may be increasing the effect of the natural greenhouse effect and state **one** consequence of this. [3]
- b Explain how both of the following statements can be true. [2]
- I Carbon dioxide is the most important greenhouse gas.
 - II Methane is a much more important greenhouse gas than carbon dioxide.
- c Explain what is meant by 'global dimming'. [2]

- HL** 6 Batteries are portable sources of electricity that have become increasingly important as we rely more and more on portable electronic devices.
- a Explain in what way a bigger battery may be better than a smaller one of the same type. [1]
- b A nickel–cadmium battery is a type of rechargeable battery often used instead of primary cells in devices such as portable radios.
- i Explain the difference between a primary cell and a rechargeable cell. [2]
 - ii Write equations for the reactions that occur at the anode and cathode when a nickel–cadmium battery is discharged and state which involves oxidation and which reduction. [3]
- c Fuels cells and rechargeable batteries have both been considered as the power source for electric vehicles. Explain why lead–acid batteries are not suitable as the main power source for an electric vehicle. [1]
- d A student carried out an experiment to measure standard electrode potentials by comparing various half-cells to a reference electrode. She obtained the value 0.32 V for the electrode potential of the $\text{Cu}^{2+}(\text{aq})|\text{Cu}(\text{s})$ half-cell. She looked up some literature values and found that the accepted value for this standard electrode potential is 0.34 V. In the conclusion to her experiment, she stated, '*my value is different to the literature value because the electrode potential varies with concentration and temperature, and therefore because the temperature in the room where I carried out the experiment was 19°C and the concentration of copper sulfate I used was 0.800 mol dm⁻³ this explains any difference between my value and the literature value.*' Comment on this statement and carry out a calculation to back up your explanation. [4]

- HL** 7 Nuclear fusion has the potential to produce vast amounts of energy.
- a State what is meant by the terms 'mass defect' and 'nuclear binding energy'. [2]
- b Explain why ^1H has a nuclear binding energy of zero. [1]
- c Tritium (^3H) is an isotope of hydrogen. Given the data in the table, calculate:
- i the mass of a tritium nucleus in unified atomic mass units [1]
 - ii the mass defect in kg [2]
 - iii the nuclear binding energy per nucleon of a tritium nucleus in J. [2]

Particle	Mass / u
proton	1.007 276
neutron	1.008 665
electron	0.000 548 6
tritium atom	3.016 05
helium atom	4.002 60

d A possible fusion reaction is:



Calculate the energy released in this fusion reaction in kJ mol^{-1} .

[4]

e Tritium is radioactive with a half-life of 12.26 years. Calculate how much remains from a $100.0\ \mu\text{g}$ sample of tritium after 20.00 years.

[3]

f Hydrogen is a diatomic molecule and there are various combinations of the three isotopes of hydrogen that can join together to form diatomic molecules. The masses and names of the isotopes are shown in the table below:

Isotope		Mass / u
hydrogen (protium)	${}^1\text{H}$	1.007 825
deuterium	${}^2\text{H}$	2.014 102
tritium	${}^3\text{H}$	3.016 049

i Explain the composition of the molecule that will effuse through a small hole most slowly and that which will effuse most quickly.

[2]

ii Calculate the ratio of the rates of effusion of these two gases under the same conditions.

[2]

HL 8 a Some molecules absorb electromagnetic radiation in the UV–Vis region of the spectrum.

i Draw the structures of penta-1,3-diene and penta-1,4-diene.

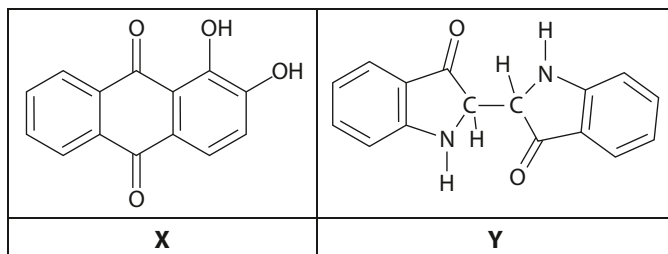
[2]

ii Predict and explain which of penta-1,3-diene and penta-1,4-diene will absorb the longer wavelength of UV radiation.

[3]

iii One of the molecules shown below is coloured. Identify the coloured compound and explain why it is coloured.

[4]



b Silicon is used in photovoltaic cells. Explain how sunlight interacts with pure silicon to enhance its electrical conductivity.

[2]

c DSSCs are an exciting new development in solar cell technology that could replace silicon-based photovoltaic cells in many applications. Explain how a DSSC, as originally designed by Grätzel, works.

[4]