24 Option C Energy

ESSENTIAL IDEAS

- Societies around the world are completely dependent on energy resources.
- The quantity of energy is conserved in any conversion but the quality is degraded.
- The energy of fossil fuels originates from solar energy which has been stored by chemical processes over time. These abundant resources are non-renewable but provide large amounts of energy due to the nature of chemical bonds in hydrocarbons.
- The fusion of hydrogen nuclei in the Sun is the source of much of the energy needed for life on Earth. There are many technological challenges in replicating this process on Earth but it would offer a rich source of energy. Fission involves the splitting of a large unstable nucleus into smaller stable nuclei.
- Visible light can be absorbed by molecules that have a conjugated structure with an extended system of alternating single and multiple bonds. Solar energy can be converted to chemical energy in photosynthesis.
- Gases in the atmosphere that are produced by human activities are changing the climate as they are upsetting the balance between radiation entering and leaving the atmosphere.

Additional higher level (AHL)

- Chemical energy from redox reactions can be used as a portable source of electrical energy.
- Large quantities of energy can be obtained from small quantities of matter.
- When solar energy is converted to electrical energy the light must be absorbed and charges must be separated. In a photovoltaic cell both of these processes occur in the silicon semiconductor, whereas these processes occur in separate locations in a dye-sensitized solar cell (DSSC).

24.1 Energy sources *– societies are completely dependent on energy resources. The quantity of energy is conserved in any conversion but the quality is degraded*

Nature of Science

The quality of energy

In this chapter we will discover that the kinetic and potential energy changes at the molecular level that we have studied in chemistry have profound implications for our world.

The first law of thermodynamics (see Chapter 5) states that *energy cannot be created or destroyed – it can only change form.* This implies then that all the energy we need already exists in nature. So why are we concerned about energy crises or energy shortages? Why can we not just extract the energy we need from our surroundings?

The key concept here is one of 'quality'. Although the quantity of energy is constant, the quality of that energy varies. The idea of the 'quality' of energy was first analysed by William Thomson (later Lord Kelvin) in 1851. He proposed the concept of the 'availability' of energy: that is, energy that we can actually utilize to do work. This idea was highly significant at the time, as the Industrial Revolution was in progress and steam engines were causing major changes to society – what we would today call a disruptive technology.

During this topic we will explore different types of 'high-quality' or 'available' energy. These sources, whether they are plants, fossil fuels or atomic nuclei, all have potential energy 'locked up' in them – they have the potential to provide us with useful work.

■ What is an energy source?

You know from your studies of enthalpy in Chapter 5 that all chemical substances have energy associated with them – potential energy is stored in chemical bonds and intermolecular forces, and during chemical reactions energy may be released to the surroundings (exothermic reactions) or absorbed by the substances (endothermic reactions).

However, not all exothermic reactions are used as a source of energy for heating, lighting, electricity generation, transport and so on. Historically, substances have been adopted as energy sources for a variety of reasons.

What are these factors that lead to certain chemical substances and their reactions being used as sources of energy? Four factors will be discussed here: availability, energy density, pollution and renewability.

Availability

In many parts of the world, availability of the fuel is the most important factor. About half the world's population burns solid fuels that are easily obtainable locally: wood, coal or dried dung. In richer countries, natural gas (methane), liquid hydrocarbons and electricity are more prevalent, but these energy sources require more infrastructures to bring them to the population. Liquefied natural gas (e.g. propane or butane) can be piped into homes or provided in pressurized bottles. Liquid hydrocarbons are provided at filling stations by the roadside for easy replenishment of motor vehicle fuel tanks. Electricity is provided by a power grid, which typically extends across the entire country via overhead or underground cables. However, the electricity is not a source of energy in itself – it must be generated.

The question of availability is also connected to cost. Some sources of fossil fuels have been extractable using known technology but to do so has not been economically worthwhile, as other sources have been plentiful and relatively cheap to extract. However, as fossil fuels start to decrease, other extraction methods have started to be employed. For example, hydraulic fracturing ('fracking') is a controversial method used in parts of the USA.

Energy density or specific energy

In Chapter 5 the combustion of hydrocarbons in terms of the enthalpy change involved in burning 1 mole of the fuel was discussed. In real-life applications it is more useful to consider the energy that can be provided by the combustion of a certain mass or volume of the fuel, as this will influence the ease of transport of the fuel.

There are two ways of conveniently expressing the quantity of energy in a fuel: energy density and specific energy.

- *Energy density:* the energy released from the fuel, per unit volume of fuel consumed. Usually expressed in megajoules (MJ) per cubic decimetre (dm^3) or litre, $MJ\,dm^{-3}$.
- *Specific energy:* the energy released from the fuel, per unit of mass of fuel consumed. Usually expressed in megajoules (MJ) per kilogram (kg), $MJ\,kg^{-1}$.

Some approximate energy densities and specific energies are summarized in Table 24.1.

Table 24.1 Energy densities and specific energies of some common energy sources

Energy source	Energy density/$MJ\,dm^{-3}$	Specific energy/$MJ\,kg^{-1}$
Liquefied petroleum gas (LPG) – propane	26	46
Gasoline (petrol)	36	46
Kerosene	34	43
Coal		24
Wood		16
Lithium-ion battery	0.9–2.2	0.7
Uranium-235 (nuclear fission)		80 000 000
Deuterium-tritium (nuclear fusion)		330 000 000 (theoretical)

Nuclear fuels clearly have the highest energy densities, but they have enormous infrastructure requirements (discussed in Section 24.3). Fossil fuels have lots of energy stored within them, which can be easily and conveniently released on an industrial scale in power stations, or on a smaller scale in homes or vehicles. Compare these to lithium-ion batteries, as used in laptop computers and mobile phones and a small number of automobiles. These represent the cutting-edge of battery technology, but their energy densities are nowhere near those of fossil fuels – it can be seen that carrying a relatively small mass of fuel will give a motor vehicle or aeroplane a very long range, far in excess of that achievable using a battery for energy storage.

How can energy densities and specific energies be calculated?

To calculate the energy density or specific energy we can use the enthalpy of combustion, the molar mass of the fuel and the density of the fuel. If the fuel is a mixture of compounds (e.g. kerosene, which is a mixture of hydrocarbons with chain lengths around 6–16 carbon atoms) then the composition must also be known.

Worked examples

Example 1: specific energy

Octane is a major component of gasoline. Calculate the specific energy of octane.

Necessary data: $\Delta H^{\ominus}_{c}$: $-5530\,\text{kJ}\,\text{mol}^{-1}$; molar mass: $114.23\,\text{g}\,\text{mol}^{-1}$

1 mole of octane releases 5530 kJ when burnt, and this is 114.23 grams, so 1.00 g would release:

$$\frac{5530\,\text{kJ}}{114.23\,\text{g}} = 48.4\,\text{kJ}\,\text{g}^{-1}$$

Converting kJ to MJ involves dividing by 1000, but dividing by kg instead of g would involve multiplying by 1000, so the answer remains $48.4\,\text{MJ}\,\text{kg}^{-1}$.

Example 2: energy density

Ethanol can be obtained from plant matter by fermentation and is increasingly used as a liquid fuel in applications similar to gasoline (petrol). Calculate the energy density of ethanol.

Necessary data: $\Delta H^{\ominus}_{c}$: $-1371\,\text{kJ}\,\text{mol}^{-1}$; density: $0.785\,\text{g}\,\text{cm}^{-3}$; molar mass: $46.07\,\text{g}\,\text{mol}^{-1}$

1 mole of ethanol releases 1371 kJ when burnt, and this is 46.07 g, so 1.00 g would release:

$$\frac{1371\,\text{kJ}\,\text{mol}^{-1}}{46.07\,\text{g}\,\text{mol}^{-1}\,\text{kJ/g}}$$

1.00 g of ethanol is $1.00/0.785\,\text{cm}^3$ ethanol, so the energy released by $1.00\,\text{cm}^3$ is:

$$\frac{1371\,\text{kJ}\,\text{mol}^{-1} \times 0.785\,\text{g}\,\text{cm}^{-3}}{46.07\,\text{g}\,\text{mol}^{-1}} = 23.4\,\text{kJ}\,\text{cm}^{-3}$$

Converting kJ to MJ involves dividing by 1000, but dividing by m^3 instead of cm^3 would involve multiplying by 1000, so the answer remains $23.4\,\text{MJ}\,\text{dm}^{-3}$.

1 Calculate the specific energy and the energy density of liquefied propane (LPG).
Necessary data: $\Delta H^{\ominus}_{c}$: $-2202\,\text{kJ}\,\text{mol}^{-1}$; density: $0.493\,\text{g}\,\text{cm}^{-3}$; molar mass: $44.10\,\text{g}\,\text{mol}^{-1}$

The importance of energy density or specific energy in fuel choice

Fossil fuels such as gasoline and kerosene have a high specific energy, meaning that a comparatively small mass of fuel is needed for a given energy content. Fossil fuels remain the fuel of choice for most transport applications as they offer very long ranges. A modern car with a high-technology gasoline or diesel engine can travel around 800 miles (1290 km) on a tank of fuel, which far exceeds the range of the few electric cars on the market. In addition, the infrastructure for refuelling already exists.

Fossil fuels are used for air travel because airliners must carry their own fuel, so the maximum energy for the minimum mass is needed. (A Boeing 747's maximum take-off weight is about 330 tonnes, of which over a third is fuel!)

The energy density of the fuel itself does not tell the whole story. Different fuels require different amounts of energy to produce them. This may involve harvesting (in the case of biofuels like ethanol), drilling, refining and cleaning up pollution. When these factors are taken into account we arrive at a figure called the **embodied energy**, which must be subtracted from the energy content of the fuel if we are to have an accurate idea of the amount of energy obtained from that fuel.

Pollution

For the large proportion of people around the world who rely on solid fuels, the biggest pollution concern is that of particulates. When solid fuels are burnt, frequently there is an inadequate supply of oxygen, meaning that some of the carbon in the fuel is released as tiny particles of soot, or 'black carbon'. The US Environmental Protection Agency states that clean air should contain fewer than 15 micrograms of particles per cubic metre. An open fire can produce 300 times as much. Among the 3 billion people worldwide who rely on such fires, respiratory illnesses are a major cause of death.

In richer countries, great efforts were made to decrease localized pollution during the 20th century. Electronic management of vehicle engines, and catalytic converters in the exhaust, mean that motor vehicles release a fraction of the black carbon and carbon monoxide they released 30 years ago, which means that smog is far less common in cities in the USA and Europe. However, in rapidly growing economies such as China and India, pollution from motor vehicles remains a huge problem, with respiratory illnesses alarmingly prevalent in large traffic-congested cities.

The massive reduction in carbon, carbon monoxide and other sources of exhaust pollution, such as nitrogen oxides, achieved by mandating the use of catalytic converters, led many to believe that the problem of vehicle pollution was largely solved. However, it is impossible to use hydrocarbon fuels without releasing carbon dioxide, which is a greenhouse gas.

Current thinking on motor vehicle pollution is that, as well as cleaning the exhaust emissions by chemical means, it is increasingly important to improve the fuel economy of engines, to minimize the emission of carbon dioxide.

Energy efficiency

Proponents of electric vehicles suggest that they offer a greener alternative to gasoline or diesel, because the vehicles themselves produce no pollution. The vehicle is plugged into the power grid overnight and then can be used for commuting the next day. The average round-trip commute in the US is 32 miles (51 km) which is comfortably within the range of the few electric vehicles currently available.

However, the energy to charge the batteries must be obtained from somewhere. A proportion of the electricity supply may have come from renewable sources such as hydroelectric or wind power, but most is likely to have come from fossil fuel sources. Critics of electric vehicles argue that they just move the pollution somewhere else, at the cost of the convenience of a conventional hydrocarbon-fuelled vehicle.

Manufacturers of electric vehicles claim that the energy from the fossil fuels is more efficiently transferred to the vehicle by burning the fuel in a large, highly optimized industrial power station, and providing this energy to a vehicle via the power grid rather than burning the fuel in the vehicle itself.

A series of simple efficiency calculations can be used for a first comparison:

$$\text{efficiency of an energy transfer} = \frac{\text{useful output energy}}{\text{useful input energy}} \times 100\%$$

In the case of a typical petrol engine, the efficiency of the engine is approximately 18–20 per cent, meaning that only 20 per cent of the chemical potential energy available in the fuel is converted to kinetic energy moving the vehicle. Most of the rest of the energy is released as thermal energy, because of mechanical friction between the moving parts of the vehicle and heat losses from the engine block.

The electric motors used to move electric vehicles have an efficiency of around 95 per cent.

The lithium-ion batteries used in modern electric vehicles have a charge-discharge efficiency of around 85 per cent, meaning that 85 per cent of the energy transferred to the battery is usefully recovered and can be used to drive the motors.

What is the efficiency of the fossil fuel power station used to generate the electricity? For coal and oil-fired stations, the figure varies between 30 per cent and 49 per cent. We will use a middle value of 40 per cent for our calculation.

We can imagine we begin with 100 J of energy from the fuel and determine how much useful energy remains when it reaches the wheels of the vehicle.

Overall efficiency = efficiency of power station × efficiency of battery × efficiency of motor

$$\frac{40}{100} \times \frac{85}{100} \times \frac{95}{100} \times 100\% = 32\%$$

This overall efficiency exceeds that of a typical gasoline engine, meaning that, in theory, the electric car is a more efficient use of resources than the gasoline car.

The *theoretical* efficiency of a gasoline engine is higher than 18–20 per cent – it is about 37 per cent. This is determined by thermodynamic principles and cannot be bettered. In theory, would a highly efficient gasoline engine be preferable? Actually no, because the gasoline used for vehicle engine has a very large 'embodied energy'. The extraction and refining of the gasoline uses energy equivalent to 1.4 times the actual energy content of the gasoline itself. Coal and oil used in fossil fuel power stations require far less refining.

Worked example

Energy efficiency – a sample calculation:

A car carries 50 litres of gasoline. How much energy is stored in this volume of gasoline? Assuming the car's engine is 18 per cent efficient, how much energy is actually available to propel the car?

Energy density of gasoline: $36\,\text{MJ}\,\text{dm}^{-3}$

Total energy in fuel = energy density × volume of fuel

$$36\,\text{MJ}\,\text{dm}^{-3} \times 50\,\text{dm}^{3} = 1800\,\text{MJ}$$

Efficiency of engine = 18%

So energy available for car = 18/100 × 1800 = 320 MJ (to 2 significant figures)

2 A coal-fired power station consumes 500 tonnes of coal per hour. How much energy is stored in this mass of coal? Assuming the power station is 40 per cent efficient, what is the output of the station per hour? What is the output in watts (joules per second)? Specific energy of coal: $24\,\text{MJ}\,\text{kg}^{-1}$.

Renewability

Renewable energy sources are those that are naturally replenished on a time scale useful to humans.

Non-renewable energy sources are finite, so once they have been used up they will no longer be available to us.

Non-renewables

Non-renewable energy is basically synonymous with fossil fuels. Coal, oil and natural gas will eventually run out, and so alternative energy sources are being sought. In addition, the carbon dioxide, and resultant global warming, produced by fossil fuels has led to great interest in alternative sources of energy.

The realization that fossil fuels will run out led to the concept of 'peak oil'. Peak oil refers to the point at which production of liquid hydrocarbons is at a maximum, before going into decline owing to decreasing availability of such fuels. Peak oil was first predicted to occur in the late 1960s, but discoveries of new oil deposits keep pushing it back. The International Energy Agency says that production of 'conventional' crude oil peaked in 2006, but 'unconventional' sources of liquids have kept production at high levels. Unconventional sources refers to processes such as coal-to-liquid conversion, gas-to-liquid conversion and the extraction of oil from 'tar sands' – loose sand saturated with very heavy hydrocarbons, which require heating and dilution with lighter hydrocarbons to extract them. If unconventional sources are included, then peak oil may still be in the future, but not too far ahead. Some estimates place it in about 2020.

Renewables

Renewable energy sources are often referred to as 'alternative' energy or 'green' energy.

The International Energy Agency defines renewable sources as follows: '*Renewable energy is derived from natural processes that are replenished constantly. In its various forms, it derives directly from the Sun, or from heat generated deep within the Earth. Included in the definition is electricity and heat generated from solar, wind, ocean, hydropower, biomass, geothermal resources, and biofuels and hydrogen derived from renewable resources.*'

In contrast to non-renewable sources, renewables are highly dispersed over the Earth, meaning they should be equally available to everyone, in varying proportions. Non-renewables, in the form of fossil fuels, tend to be concentrated in certain countries or regions, meaning that some countries have become very wealthy on the basis of an accident of geography.

The advantages and disadvantages of energy sources

Table 24.2 summarizes the advantages and disadvantages of energy sources.

Source	Where does it come from?	Renewable or non-renewable?	Advantages	Disadvantages
Coal	Fossilized plants found in seams between layers of rock in the Earth Mostly comprised of carbon with some inorganic impurities such as sulfur Mined by drilling shafts into the Earth	Non-renewable	Cheap to extract High specific energy Energy is easily released – simply burn it Large infrastructure already exists for transport and burning Coal reserves will last much longer than oil reserves – still several hundred years remaining	Releases carbon dioxide when burnt – a greenhouse gas Sulfur impurities release sulfur dioxide when burnt, which leads to acid rain – factory emissions must be scrubbed to remove this Coal mining is a dirty and dangerous activity
Oil	Fossilized animal remains in liquid form, found soaked into layers of porous rock in the Earth; a layer of non-permeable rock above the oil reservoir prevents it from escaping Pipes are sunk into the Earth to release the oil and it is pumped to the surface	Non-renewable	Cheap to extract High specific energy Energy is easily released – simply burn it Large infrastructure already exists for transport and burning Incredibly versatile – different crude oil fractions have various physical properties making them suitable for many different fuel applications Also a chemical feedstock for plastics industry and pharmaceutical industry	Releases carbon dioxide when burnt – a greenhouse gas Will run out quite soon – conventional reserves may have already peaked

■ **Table 24.2** Advantages and disadvantages of energy sources

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Natural gas	Usually associated with crude oil. Natural gas consists of lighter molecules (mostly methane, CH_4) which are gaseous at surface pressure and temperature Pipes are sunk into the Earth to release the oil and it is pumped to the surface	Non-renewable	Cheap to extract High specific energy Energy is easily released – simply burn it Large infrastructure already exists for transport and burning Can be piped directly into homes	Releases carbon dioxide when burnt – a greenhouse gas. Will run out quite soon
Nuclear	Uranium is mined and refined Nuclear 'chain reaction' involving fission of uranium nuclei generates large amounts of heat Heat used to generate steam which can then generate electricity via turbines	Non-renewable	Uranium is cheap to mine Enormous specific energy Fission process itself generates no carbon dioxide or other greenhouse gases	Uranium reserves are finite, although some reactor types can regenerate nuclear fuel Nuclear waste is highly toxic, long-lasting and difficult to dispose of safely Danger of weapons proliferation
Wind	Wind turns turbines that generate electricity	Renewable	In order to produce a useful amount of electricity large numbers of turbines are placed together in a 'wind farm'	Some people object to wind farms on the grounds that the noise and appearance spoils the landscape The wind does not always blow – wind farms are more effective in some regions than others
Solar	Sunlight falls on a solar panel which captures its energy and converts it into electricity	Renewable	In theory, solar power could offer infinite supplies of energy, especially in very hot, sunny countries	Currently, solar panels are inefficient and too costly to be adopted widely, but technology is improving
Tidal/wave	Energy from water moving back and forth is captured by underwater turbines and used to generate electricity (Figure 24.1)	Renewable	Countries with long coastlines could potentially benefit from tidal or wave power	Only suitable for countries with long coastlines Infrastructure is costly and technology is undeveloped Tidal or wave generators need to be very robust and reliable to resist conditions at sea
Hydroelectric power (HEP)	Flow of water from high ground towards oceans is used to generate electricity. A river is dammed, and the flow of water through the dam is used to turn turbines (Figure 24.2)	Renewable	In suitable geographical locations, HEP offers a clean, cheap electricity supply	Limited to mountainous areas Building dams often requires flooding of surrounding areas which may displace populations and lead to loss of biodiversity Dammed rivers also lead to build-up of silt and affects the river ecosystem
Biofuels	Plant or animal material is used to make a liquid or gaseous fuel Biodiesel is an oil extracted from plants such as palm trees Ethanol can be made from corn (maize), sugar cane or the inedible cellulose from grasses or plant waste Biogas is made by fermenting plant or animal waste	Renewable	In theory, biofuels are 'carbon neutral' – the carbon that is released when they are burnt is the same carbon that they absorbed during photosynthesis Liquid biofuels allow existing fuel infrastructure and technology to be retained as they are a direct replacement for fossil fuels	Only renewable if plants are replanted In some countries (e.g. Malaysia), tropical rainforest has been replaced with palm oil plantations, leading to loss of biodiversity Some methods of extraction of biofuels are very energy inefficient Economic demand for biofuels leads to countries displacing food crops. This could lead to lack of food for population
Wood/ charcoal	Trees can be felled and burnt for energy Slowly roasting wood in the absence of oxygen drives off water and organic matter and turns wood into charcoal, which has a higher energy density	Renewable	Wood is widely available to most of the Earth's population and is a convenient source of energy for cooking and heating	Wood is only renewable if trees are replanted Often, wood is burnt in highly inefficient open fires and stoves, with enormous amounts of dangerous particulate emissions
Geothermal	Water is pumped into the Earth where the natural heat turns it into steam. The steam can be used directly for heating or used to generate electricity	Renewable	Geothermal energy is most practical in regions where there is a lot of volcanic activity such as Iceland and New Zealand. In these countries it has the potential to provide unlimited clean energy	Infrastructure can be difficult to engineer and is costly

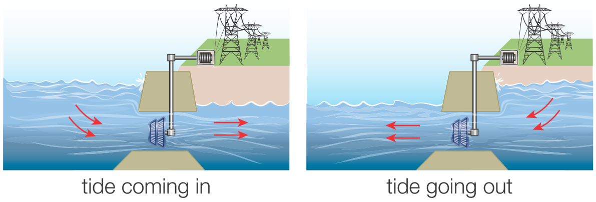


Figure 24.1 Tidal power captures the energy of tidal water moving backwards and forwards. This tidal electricity generation works as the tide comes in and again when it goes out. The turbines are driven by the power of the sea in both directions

Figure 24.2 The Hoover Dam, on the Colorado River, USA, generates about 2000 MW from its hydroelectric turbines

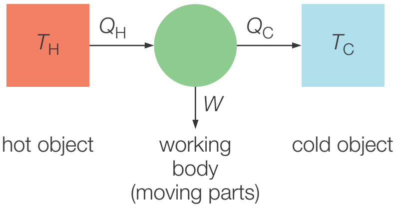


Figure 24.3 Carnot's heat engine. The thermal energy flows (Q_H, Q_C) from the hot body (T_H) to the cold body (T_C) via the working body (the circle). This working body does useful work (W) on the surroundings

The quality of energy and available work

During his analysis of energy 'quality' in the 1850s, William Thomson studied the steam engine. He recognized that the kinetic energy within the hot steam led to its expanding against a piston, driving the engine.

The steam engine, in very basic terms, is a heat engine. The flow of heat from one region to another produces useful work. Nicolas Leonard Sadi Carnot proposed the heat engine concept in 1824 (Figure 24.3).

After use, however, all the components of the engine are at thermal equilibrium and there is no longer any useful work to be extracted. However, the total energy has been conserved.

So, to use Thomson's terminology, the availability of the energy has been lost. During the workings of the steam energy, the quality of the energy has been degraded. The driving force of the engine is the transfer of heat from a region of highly concentrated, highly useful energy (the fuel) to the surroundings.

International cooperation in energy provision

Two international agencies exist to monitor and coordinate the provision of energy for different nations:

- The International Energy Agency (IEA) is an autonomous organization based in Paris, whose goal is to ensure reliable, affordable and clean energy for its 28 member countries and beyond.
- The International Renewable Energy Agency (IRENA), based in Abu Dhabi, seeks to promote increased adoption and sustainable use of renewable energy sources.

The IEA was established in the wake of the 1970s oil crisis, in an attempt to ensure that supplies of oil worldwide remained steady and were not subject to periodic 'shocks' that could cripple the world economy. The IEA maintains a stock of oil that can be released at times of crisis to prevent oil supply disruptions. The IEA is an autonomous organization, not under the control of any particular government, so the intention is that countries are less able to use oil supply as a 'weapon' against other countries. However, the IEA is criticized for two main reasons. Firstly, several very large and powerful countries are not members, including India, China and Russia. Secondly, critics claim that the IEA is too heavily influenced by the more powerful members, such as the USA, which has affected its responses to big issues such as 'peak oil' and climate change.

Although one of the stated aims of the IEA is to consider environmental factors surrounding energy, IRENA was founded in 2009 with the goal of becoming the main driver for increased adoption of renewables worldwide. In particular, it aims to help countries share expertise around the provision of infrastructure for renewables and setting up regulatory frameworks. IRENA also has its critics: when it was announced that it would be based in Abu Dhabi, critics pointed to the enormous carbon footprint of the United Arab Emirates and suggested that the country was a poor role model for renewables adoption. Despite this, over 100 states have joined IRENA, and China has announced its intention to join in the near future.

ToK Link

Factors affecting research priorities

'*I have no doubt that we will be successful in harnessing the Sun's energy. If sunbeams were weapons of war we would have had solar energy centuries ago*' (Lord George Porter). In what ways might social, political, cultural and religious factors affect the types of research that are financed and undertaken, or rejected?

Lord Porter's quote suggests that sociopolitical factors (war being an extreme example) can be catalysts for technological developments. Money is spent on acquiring knowledge for many reasons – social, political, cultural or ideological. This was certainly the case in the development of atomic energy in the 20th century. According to the Brookings Institute, the USA invested about 20 million dollars developing atomic bombs, the expense being justified in terms of beating the Germans to it. After the war, the USA wanted to stay ahead of the Soviet Union, so continued to invest heavily in atomic research. Images of the tragedies at Hiroshima and Nagasaki caused a backlash against this enormous and dangerous source of power, and so the USA tried to improve the image of nuclear power by promoting it as a clean source of energy – 'Atoms for Peace'. For a while it was thought that civilian nuclear power generation would result in electricity becoming 'too cheap to meter' and a new golden age of practically unlimited energy would commence. It never happened – plentiful fossil fuels and the difficulties of waste disposal and heavily publicized accidents meant that the nuclear industry soon became moribund. This led the *Economist* to describe nuclear power as 'the dream that failed' in 2012.

The Cold War in the latter half of the 20th century led to other politically driven projects. The Apollo space programme in the USA cost 25 billion dollars. Although it is sometimes claimed that many useful inventions arose from the space programme, many believe that the ultimate reason for the rapid development of the moon rocket, and the enormous costs associated with it, was competition with the Soviet Union. This might be seen as an attempt to demonstrate the superiority of one political ideology over another.

Sometimes economic and social factors are important. In the early 20th century, when the automobile industry was starting out, electric cars were more prevalent than gasoline cars. What factors led to gasoline winning the edge, leading to the colossal growth in oil industry infrastructure and power through the century? Economic factors were important: the discovery of crude oil reserves all over the world brought the price of gasoline down. As countries developed better road networks, the limited range of electrics became a problem. This led to a cycle of infrastructure development – more roads led to more cars (and mostly gasoline cars, to take advantage of the range available), which led to more roads to accommodate the cars.

There were also social factors at work. In the 20th century the automobile became synonymous with freedom, progress and opportunity as the automobile makers successfully made having a car seem necessary to a fulfilling life. The process is now repeating itself in China and India as they develop.

ToK Link

Ethics of energy generation

There are many ethical issues raised by energy generation and its consequent contributions to pollution and climate change. What is the influence of political pressure on different areas of knowledge?

The European Group on Ethics in Science and New Technologies (EGE) is a committee of the European Commission in Brussels, which attempts to explore the ethical issues surrounding energy production. They propose that international regulatory policies should take into account three main elements: societal impact, economic impact and environmental impact. The committee tries to apply the principle of justice to ensure that all EU citizens have access to energy, that the EU maintains a secure energy supply, and that the policies implemented are sustainable. At times these different considerations come into conflict, so it is the job of politicians to find a balance between them. Different political parties in different countries may disagree with the balance proposed; for example, some feel that sustained economic growth should override all other concerns. Others feel that we have a moral obligation to future generations to protect our environment.

At present, renewable energy sources have yet to match fossil fuels in terms of low cost and ease of production so governments offer funds to promote investment. Governments have to justify this expenditure and the funding is subject to political pressure. Some countries, such as Germany, have very active 'green' movements with a great deal of political influence. In other countries large energy companies are able to exercise their influence to ensure that energy policies continue to favour fossil fuels.

24.2 Fossil fuels – *the energy of fossil fuels originates from solar energy which has been stored by chemical processes over time. These abundant resources are non-renewable but provide large amounts of energy due to the nature of chemical bonds in hydrocarbons*

Nature of Science

The importance of fossil fuels in science

Large-scale fossil fuel use is a relatively recent development. Underground coal mining was developed in the late 18th century, and oil drilling began in earnest in the 19th century.

The industrialization of the world was driven by fossil fuels. Coal led to steam engines, which led to steam ships and mass manufacturing in factories. Factories drove urbanization and steam ships drove migration. As oil gradually overtook coal, motor vehicles and aircraft were developed, which led to further migration, mass travel and globalization, and cities grew outwards, with suburban zones for those who could afford cars.

This progress was driven by science and technology, as scientists around the world invented and developed more efficient ways to utilize fossil fuels for transport and power generation.

However, the existence of fossil fuels has also provided the scientific community with an enormous range of chemicals to draw upon in other applications. Before the mid-19th century, those drugs that existed were usually extracted from plants. In 1869, the first synthetic drug, chloral hydrate (a sedative) was introduced, leading to the multi-billion-dollar pharmaceutical industry today. Petroleum by-products are also used in manufacture of dyes and plastics.

In short, fossil fuels have provided both a 'means' to scientific progress, as they have provided raw materials for many scientific fields, as well as an 'end' as scientists have reacted to demand for fossil fuels to develop more and more efficient ways to use them.

What are fossil fuels?

Fossil fuels are fuels that were formed by the anaerobic decay of biological material from prehistoric times that was buried and acted upon by bacteria over millions of years.

Fossil fuels are rich stores of energy, because they are stores of solar energy, which drove the photosynthetic processes in prehistoric plants. Photosynthesis takes carbon dioxide from the atmosphere and converts it into more complex molecules, starting with glucose. The plants then use some of the glucose to form structural molecules (cellulose). Plant matter therefore contains carbon along with hydrogen and oxygen. In addition, protein molecules found in biological systems contain nitrogen and sulfur in significant quantities.

Photosynthesis is an endothermic process – it requires an energy input to drive the reaction. This energy input from the Sun becomes 'locked up' within the biological molecules present in the plants. Animals eat the plants and the energy passes into them (where it is used to provide energy for the life of the organism). When the plant or animal dies, much of the energy may stay 'locked up' in the remains.

Over geological time, prehistoric plant and animal matter is compressed and becomes highly concentrated. This means that fossil fuels have energy highly concentrated within them, which can be released by combustion.

The three major categories of fossil fuels are coal, crude oil (petroleum) and natural gas.

Coal

Coal is currently the most plentiful of the fossil fuels. It originated as prehistoric forests, which were flooded, buried and then gradually compressed by layer upon layer of soil.

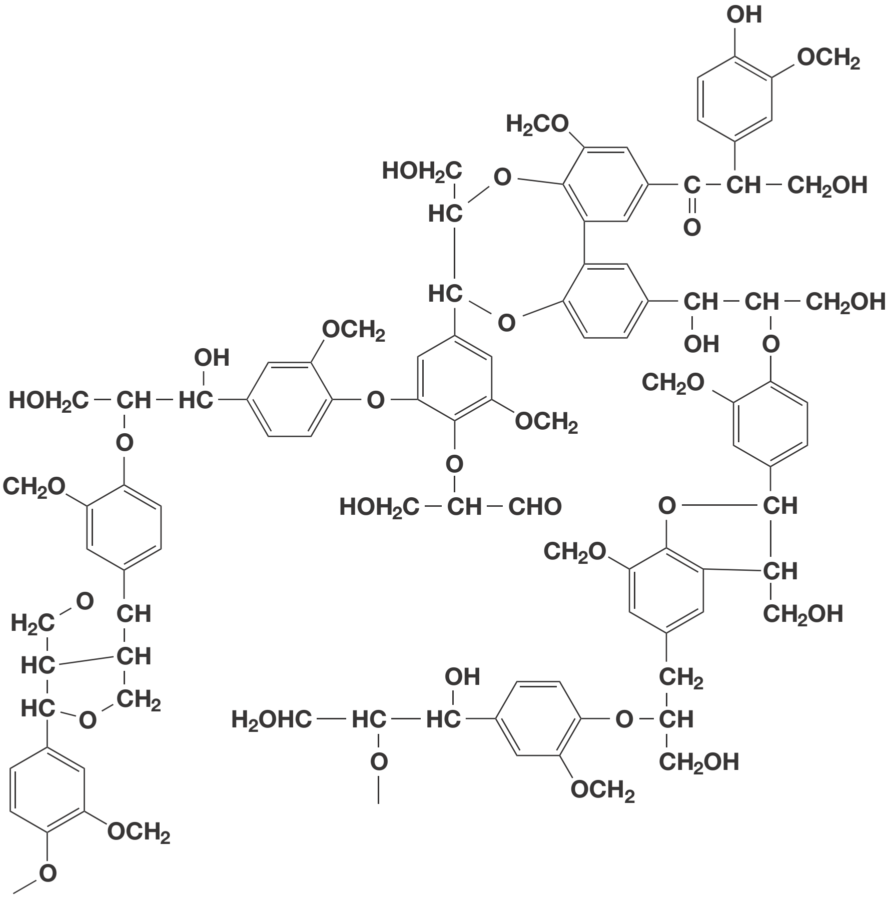
Most dead plant material decomposes where it falls. However, when large quantities of plant matter are buried and isolated from oxygen, it is acted upon by anaerobic bacteria which gradually reduce the biological molecules until a substance consisting mostly of carbon results.

Not all coal is the same, however; different types of coal reflect different stages in the decomposition process:

Peat still contains significant amounts of other chemical elements – the decay process is incomplete. In particular, peat contains quite a lot of water, and the carbon is still found combined with other chemical elements such as hydrogen, oxygen and sulfur.

Lignite (sometimes called 'brown coal') is only about 25–35 per cent carbon and contains a high percentage of water – up to 60 per cent. However, the biological molecules have started to polymerize forming a substance called lignin, characterized by large numbers of benzene rings (Figure 24.4).

Figure 24.4 Lignin



Bituminous coal ('black coal') is a sedimentary rock containing 60–80 per cent carbon but with hydrogen, sulfur and oxygen still present. In particular, the rock is saturated with tar-like hydrocarbon molecules called 'bitumen'. When heated, bituminous coal releases hydrocarbon vapours.

Anthracite coal is the hardest form of coal and the closest to pure carbon. When bituminous coal is subjected to intense heat and pressure beneath the Earth, most of the hydrogen, oxygen and sulfur are driven off, leaving a hard, glossy rock containing 92–98 per cent carbon. Anthracite does not release hydrocarbons when heated.

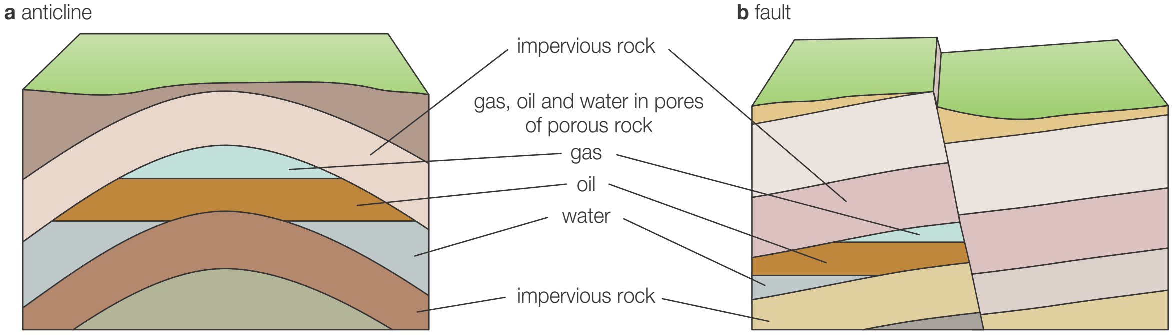
As the carbon content of the coal increases through the formation processes, the energy density of the coal also increases. Although anthracite coal is the most desirable form in terms of the energy density, other forms of coal are often used, mostly because they are plentiful and cheap in local situations. For example, peat is an economically important fuel in Ireland.

Crude oil and natural gas

The term *petroleum* comes from the Latin *petra,* meaning rock, and *oleum*, meaning oil. Some definitions of petroleum include both crude (unprocessed) oil as it is retrieved from the rock, and the products of refining. The 'petroleum industry' is usually taken to include both the oil and gas industries.

Crude oil remains one of the most important raw materials in the world today. It is a complex mixture of hydrocarbons and supplies us with fuels for a range of transport types and for electricity generation. In addition it is an important chemical feedstock for the production of important organic polymers, pharmaceuticals, dyes and solvents.

Crude oil was formed over geological periods of time (that is, millions of years) from the remains of marine animals and plants. These creatures died and were sedimented at the bottom of the oceans, where they became trapped under layers of rock. Under these conditions of high temperature and high pressure, this matter decayed in the presence of bacteria and the absence of oxygen to form crude oil (petroleum) and natural gas. It is a limited resource and eventually reserves will be so depleted that chemists will need to consider other sources of carbon, both as a fuel and as a chemical feedstock. Indeed, the balance of these two uses is an issue if we are to conserve this non-renewable resource for as long as possible.



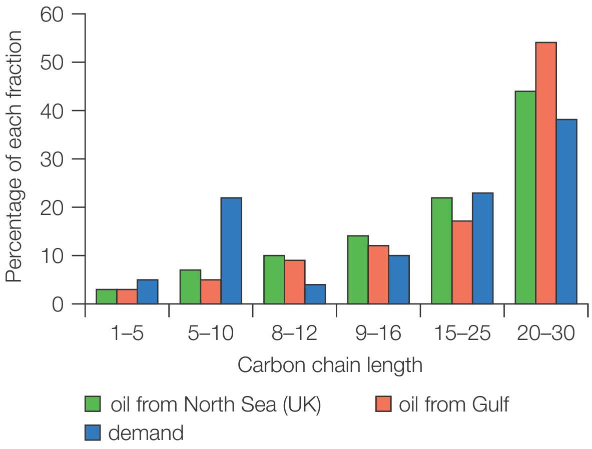
■ **Figure 24.5** Crude oil is found in underground reservoirs in certain geological situations. It permeates the rock in these reservoirs and is usually found in association with natural gas

Crude oil varies greatly in appearance depending on its composition. It is usually black or dark brown. In the underground reservoirs it is usually found in association with natural gas, which forms a gas cap over the crude oil (Figure 24.5). Crude oil may also be found in a semi-solid form mixed with sand and water, as in the Athabasca Oil Sands in Canada, where it is usually referred to as crude bitumen. Venezuela also has large amounts of crude oil in the Orinoco Oil Sands. These oil sands resources are called unconventional crude oil to distinguish them from oil which can be extracted using traditional oil well methods.

The proportion of hydrocarbons in the crude oil (petroleum) mixture differs between oil fields, with samples varying in the balance between the lighter, more profitable fractions and the heavier oils and bitumen fractions. The distribution of the different fractions in the oil from a particular field may well not match the local or international demand and so post-distillation methods of chemically modifying the initial fractions are economically important.

Figure 24.6 shows the distribution of crude oil fractions from North Sea oil and oil from the Persian Gulf, compared to demand for fractions in the UK.

Hydrocarbon chains with five to ten carbon atoms are in high demand as these are used for motor vehicle fuels (gasoline). The supply of these fractions is much lower than the demand. For longer, heavier fractions, supply outweighs demand. However, these longer-chain molecules can be 'cracked' to form shorter chains.



■ **Figure 24.6** Supply and demand of crude oil fractions

Fractional distillation

Properties of hydrocarbons

The various hydrocarbons in crude oil have different properties depending on their molecular structures.

Short-chain molecules (those with small numbers of carbon atoms) have low boiling points, because they have small formula masses and relatively few electrons in each molecule. The instantaneous dipoles generated during molecular vibrations are quite weak, as are the induced diploes in neighbouring molecules, so the dispersion forces are also weak. Short-chain molecules (one to four carbons) are actually gases at room temperature.

Low-boiling-point hydrocarbons are more volatile, meaning that they release more vapour into the surrounding air. When the surrounding air is saturated with fuel vapour the fuel ignites easily.

As the carbon chains get longer, the formula masses increase, along with the number of electrons in the molecules. In addition, the contact area between adjacent molecules in the liquid will also increase. This leads to stronger dispersion forces and higher boiling points. When the boiling point is higher, the volatility is lower. There is less vapour in the air surrounding the fuel, and the fuel is more difficult to ignite.

Stronger dispersion forces also mean that longer hydrocarbon molecules are more viscous (less 'runny').

Separating the compounds in crude oil

Crude oil is a mixture of hundreds of different hydrocarbons, all with slightly different properties. Some are heavy, thick, viscous liquids with a high energy density but are difficult to ignite. Others pour easily and are easily ignited but have less energy stored within them. These different hydrocarbons with different properties find different uses.

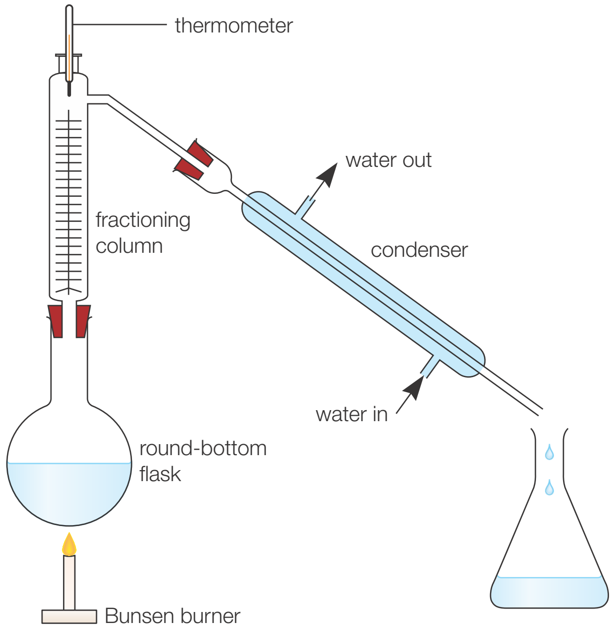


Figure 24.7 Apparatus for fractional distillation of crude oil in a school laboratory

The first step in oil refining involves separating the different hydrocarbons according to their boiling points. It would be impractical to separate every single compound, but it is possible to separate the crude oil into broad groups of similar compounds called fractions.

This process of separating out the oil by boiling point is called **fractional distillation**.

You may have seen a sample of crude oil heated to separate it into its components in the school laboratory (Figure 24.7). As the mixture of compounds increases in temperature, the components will reach their boiling points one by one. They become vapour and can then be condensed into separate containers.

Industrial fractional distillation turns this process on its head. Instead of gradually raising the temperature of the oil mixture and boiling off each fraction, the crude oil is heated to a high temperature so that almost all the compounds within it become vapour. This vapour is injected into the base of a vessel called the **fractionating column**.

The vapours rise up the column. As they get further from the heat source at the base of the column, the temperature falls. Gradually, each fraction condenses out of the vapour mixture. Heavy fractions with high boiling points condense first, close to the bottom of the column. As the column is ascended, successively lighter, shorter chain fractions condense. At the top of the column some very short-chain molecules are still in the vapour phase and are collected as refinery gas. Figure 24.8 summarizes the different fractions from crude oil and their uses.

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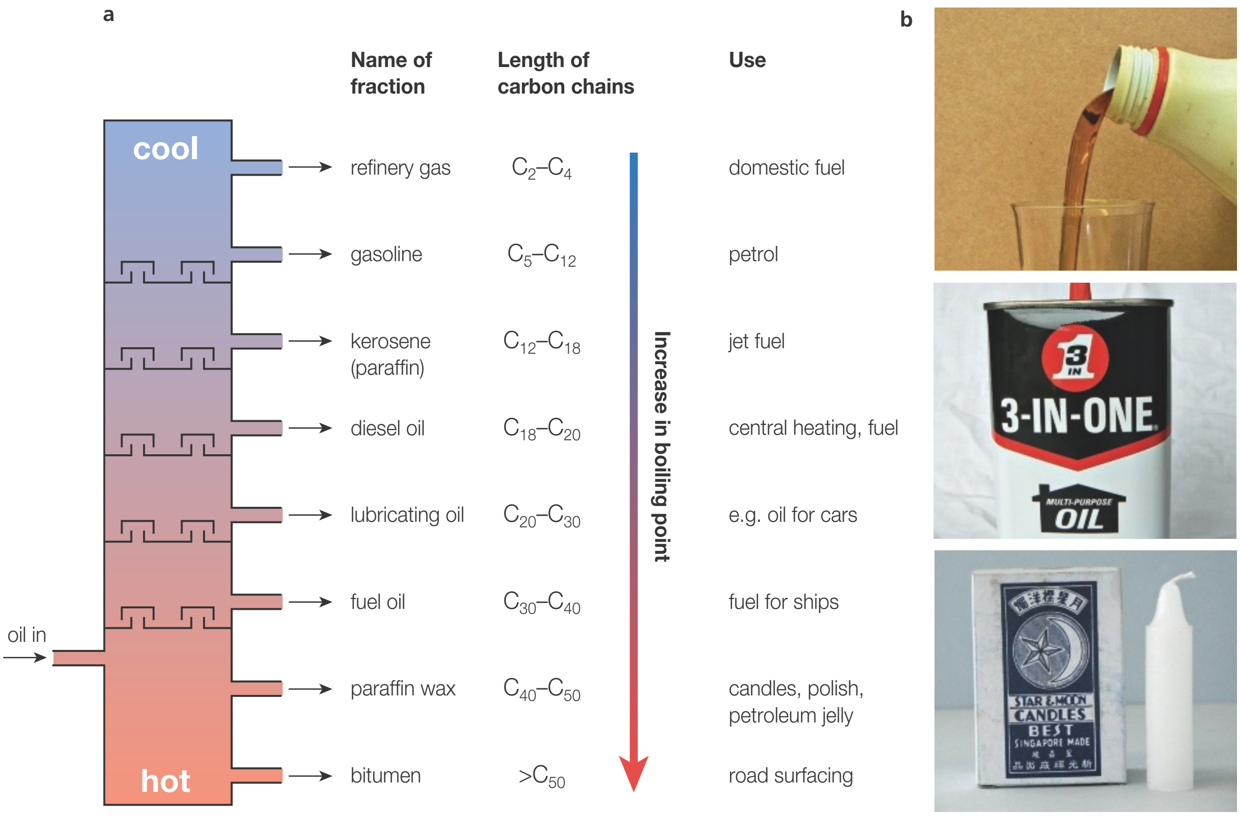

Figure 24.8 a The fractions obtained industrially from crude oil using a fractionating tower; **b** some examples of useful components

The importance of branched-chain alkanes in gasoline

In the internal combustion engine, hydrocarbon fuels are mixed with air, injected into a cylinder and ignited with a spark. The resultant explosion forces a piston to move. The movement of a series of pistons is converted to the rotation of a crankshaft, which in turn drives the wheels of the vehicle.

If we consider a molecule of octane (a component of petrol, or gasoline), we can see that for complete combustion to occur, with full oxidation of every atom of carbon and hydrogen, we require 12.5 moles of oxygen for each mole of octane:

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

This equates to a mass ratio (mass of air : mass of fuel) of approximately 15 : 1. (Remember that only 20 per cent of the air is oxygen.)

If the air : fuel ratio is lower than this, the mixture is said to be 'rich' and the amount of oxygen is insufficient for complete combustion. This will result in the formation of some carbon monoxide. In this example only 10 moles of oxygen is available for each mole of octane:

$$C_8H_{18}(l) + 10O_2(g) \rightarrow 3CO_2(g) + 5CO(g) + 9H_2O(l)$$

A rich mixture may also lead to the emission of unburned hydrocarbon molecules (called 'volatile organic compounds' or VOCs) from the exhaust.

If the air : fuel ratio is increased, the mixture is said to be 'lean'. A lean mixture will not produce carbon monoxide. A disadvantage of a lean mixture is that the mixture may 'pre-ignite' while under compression. Pre-ignition means that the rapid compression of the fuel–air mixture in the cylinder leads to some of the fuel igniting before the spark, causing a sudden pressure increase in the cylinder. This causes a metallic 'knocking' sound. This inefficient combustion actually increases the proportion of unburnt hydrocarbons in the exhaust gases.

It is advantageous to blend the hydrocarbons in the fuel to minimize the chances of knocking. This means that the fuel–air mixture can be as lean as possible, reducing fuel consumption and decreasing the chances of VOCs, carbon monoxide and soot being emitted by the vehicle. Also, high-performance engines in luxury or sports cars often have very high compression ratios, which makes pre-ignition likely with poor quality fuels.

It is known that branched-chain hydrocarbons resist pre-ignition better than straight-chain hydrocarbons. The measure of resistance to pre-ignition is called the **octane number**.

The effect of chain branching on the octane number

Octane number is the measure of a fuel's tendency to resist pre-ignition. Octane number is measured on a scale of 0–100, where 100 refers to 2,2,4-trimethylpentane (historically called *iso*-octane – a highly branched molecule), and 0 refers to heptane (a straight-chain molecule). Figure 24.9 shows these two compounds.

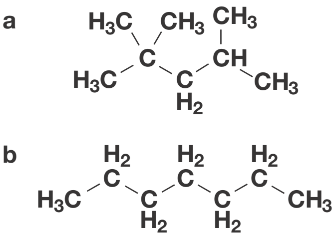

Figure 24.9 a 2,2,4-trimethylpentane: octane number 100; **b** heptane: octane number 0

The octane number of a fuel blend is measured by comparing it to these two benchmarks. This is done by measuring the compression that the fuel sample can withstand before igniting.

The octane number can be increased by adding branched-chain alkanes to the mixture. Arenes (aromatic compounds, those with benzene rings) also increase the octane number.

Gasoline direct from the fractionating column has a large proportion of straight-chain hydrocarbons in it, giving an octane number of around 70, which is not good enough to be sold as motor fuel. Further stages of refining must take place, and these stages cost energy and money.

Cracking and reforming

As we have seen, the supply of hydrocarbon fractions rarely matches demand for those fractions. Typically, the larger fractions are more plentiful, whereas the highest demand is for the gasoline fraction, with carbon chain lengths ranging from around five to ten carbon atoms.

An obvious solution to this problem is to break down the larger molecules into smaller ones. This process is called catalytic cracking. The heavier fractions are heated and passed over a catalyst, which 'cracks' them into shorter chains.

Fractional distillation is a physical process, relying on boiling the crude oil and then condensing its component compounds. Intermolecular forces are overcome but no chemical bonds are broken. Catalytic cracking, by contrast, is a chemical reaction – a form of thermal decomposition. Longer-chain molecules have their covalent bonds broken to split the longer molecules into shorter ones.

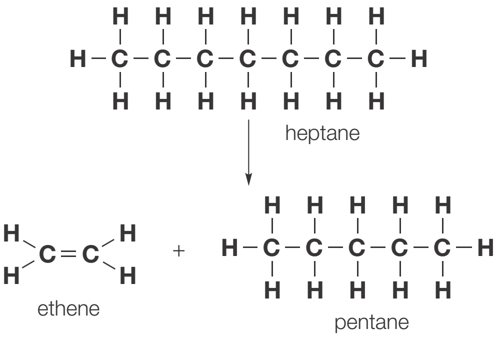

Figure 24.10 Cracking a long saturated hydrocarbon molecule

The original alkane, having the general formula C_nH_{2n+2}, usually results in two products: a shorter alkane (also C_nH_{2n+2}, and an alkene, C_nH_{2n}). It is not possible to crack an alkane into two shorter alkanes – there are not enough hydrogen atoms present.

For example:

$$\underset{\text{heptane}}{C_7H_{16}} \rightarrow \underset{\text{pentane}}{C_5H_{12}} + \underset{\text{ethene}}{C_2H_4}$$

The reaction shown in Figure 24.10 is a straightforward example starting from a relatively short alkane to illustrate the type of reaction being discussed. Note that the alkene splits off the end of the molecule. The process is not a highly specific one. Ethene is not always the alkene product; it is possible to obtain propene and butene as products that are useful in their own right. In certain circumstances hydrogen can also break off the end of the alkane molecule. Some more complex examples of possible reactions are:

$$\underset{\text{hexadecane}}{C_{16}H_{34}} \rightarrow \underset{\text{undecane}}{C_{11}H_{24}} + \underset{\text{ethene}}{C_2H_4} + \underset{\text{propene}}{C_3H_6}$$

$$\underset{\text{dodecane}}{C_{12}H_{26}} \rightarrow \underset{\text{octane}}{C_8H_{18}} + \underset{\text{butene}}{C_4H_8}$$

$$\underset{\text{decane}}{C_{10}H_{22}} \rightarrow \underset{\text{octane}}{C_8H_{18}} + \underset{\text{ethene}}{C_2H_4}$$

Different types of cracking processes have different applications. Some are more useful for producing large quantities of alkenes, which can then be used to make plastics. Other kinds are used predominantly in fuel production, as they produce large proportions of branched products. The different types of cracking are summarized below:

- *Thermal cracking* is carried out by heating the very long-chain alkanes found in the heavy fractions to temperatures of 800–850 °C at pressures of up to 70 atmospheres, and then cooling the mixture rapidly. Under such conditions, a free radical mechanism occurs and a mixture of products is produced that includes shorter-chain alkanes, alkenes and coke (an impure form of carbon). Ethene is a favoured product as it is the key starting material for the preparation of other chemicals such as poly(ethene) and ethanol.
- *Steam cracking* is a different form of thermal cracking. The initial reaction mixture of ethane, butane and alkanes up to eight carbon atoms long is preheated, vaporized and mixed with steam at 1250–1400 °C. The steam dilutes the feedstock and the reaction produces a higher yield of ethene and other short-chain alkenes. The addition of steam also reduces the amount of coke produced, which otherwise produces an unwanted lining in the reaction vessel.
- *Catalytic cracking* uses a catalyst in the cracking process to allow the reaction to occur at lower temperatures, around 500 °C, and gives a higher degree of specificity to the process by controlling the steps involved in the mechanism. The reactions are complicated and involve an ionic (carbocation) mechanism. The carbocations are produced and then undergo a rearrangement reaction on the catalyst surface. Large and intermediate-sized alkanes are passed over a mixed alumina (Al_2O_3) and silica (SiO_2) catalyst, which is in powdered form to increase its surface area. **Zeolites** (see below), naturally occurring minerals containing aluminium, silicon and oxygen, are also very good catalysts for this process as their crystal structures contain an extensive network which offers the hydrocarbons a large surface area for reaction. Catalytic cracking produces a mixture of alkanes, alkenes and molecules containing the benzene ring (arenes). A high proportion of branched alkanes is produced which can then be blended into petrol to increase the octane number. Some carbon is, however, formed during the process and this can coat the catalyst and stop it working. The catalyst must be cleaned or regenerated regularly by steam jets followed by heating, otherwise it becomes coated in carbon.
- *Hydrocracking* occurs when the feedstock is mixed with hydrogen at a pressure of about 80 atmospheres and cracked over a platinum or silica/alumina catalyst. This gives a high yield of branched alkanes, cyclic alkanes and aromatic compounds for use in unleaded petrol (gasoline). The presence of hydrogen ensures that no alkenes are produced in this type of cracking.

Petrol produced by cracking longer hydrocarbons will tend to have reasonably high octane numbers because the cracking method chosen (usually catalytic cracking or hydrocracking) will produce lots of branched molecules.

However, it is also necessary to utilize the so-called 'straight-run' gasoline produced in the fractionating column. The octane number of straight-run gasoline can be increased by subjecting it to a series of **reforming** processes that will increase the proportion of branched and aromatic compounds in the mixture.

Zeolites

The term zeolite is derived from the Greek words *zeo,* meaning to boil, and *lithos,* meaning stone. Zeolites release large amounts of steam when heated. A zeolite has a three-dimensional structure in which the silicon, aluminium and oxygen atoms form a framework of tunnels and cavities into which small molecules, such as water, can fit. Many occur naturally as minerals and are extensively mined in many parts of the world. Others are synthetic and are made commercially for specific uses. Because of their unique porous properties, zeolites are used in a variety of applications with a global market of several million tonnes per year. Major uses are in catalytic cracking, ion-exchange (water softening and purification) and the separation and removal of gases and solvents.

Reforming

In reforming processes, alkane molecules are rearranged to form branched or cyclic molecules.

Isomerization is a process in which straight-chain molecules, such as butane, are converted into their branched isomer(s), 2-methylpropane in this case. The process involves heating the alkanes in the presence of an aluminium chloride catalyst. The straight chains break apart and then re-join as branched chains. The resulting mixture consists of branched chains and straight chains in equilibrium. The equilibrium mixture can then be passed over another form of zeolite catalyst which acts like a molecular 'sieve'. Branched chains are separated from straight chains. The branched chains are used as fuel additives, and the straight chains can be returned to the reaction vessel (Figure 24.11).

Cyclization and **aromatization** are processes in which cycloalkanes and aromatic hydrocarbons are made from the straight-chain C_6–C_{10} alkanes in the naphtha fraction from distillation. The naphtha vapour is heated to 500°C and passed over a platinum catalyst on an aluminium oxide support. In a typical reaction under these conditions, hexane could be converted into cyclohexane initially, and then into benzene, for instance (Figure 24.12).

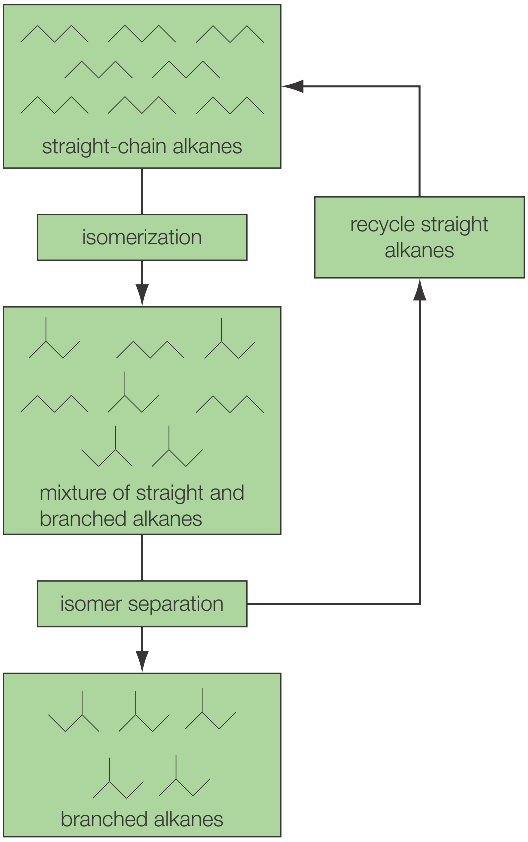

Figure 24.11 Isomerization

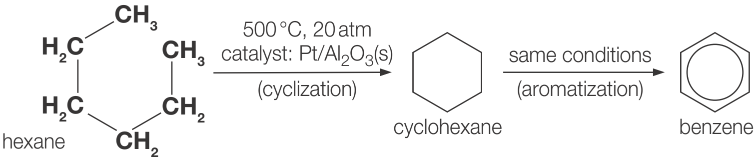

Figure 24.12 The cyclization and aromatization of hexane through to benzene via cyclohexane

The reforming and cracking reactions of hydrocarbons and explanation of how these processes improve the octane number

Table 24.3 summarizes the products and primary advantages of the various cracking and reforming reactions.

Table 24.3 Advantages and main products of different cracking and reforming processes

Reaction	Main products	Primary advantage(s) of this reaction
Thermal cracking	Shorter-chain alkanes Very small alkenes such as ethene	Supply of long-chain hydrocarbons outweighs demand – process produces more shorter-chain alkanes Ethene is important for plastics manufacture
Steam cracking	Mostly short-chain alkenes such as ethene Some hydrogen	High yield of short-chain alkenes for plastics manufacture Less coke produced, which clogs up the reaction vessel
Catalytic cracking	Branched alkanes, alkenes and arenes	Highly specific catalysts can be used which direct the reaction towards certain products, such as branched alkanes, which are used to increase the octane number of gasoline
Hydrocracking	Branched alkanes and arenes	Branched alkanes and arenes are used to increase the octane number of gasoline No alkenes produced
Isomerization	Branched alkanes	'Straight-run' gasoline contains relatively few branched alkanes and octane number is low. Isomerization increases the proportion of branched alkanes
Cyclization and aromatization	Cyclic hydrocarbons and arenes	Unbranched hydrocarbons with low octane number are converted to arenes with a much higher octane number

Worked example

Write balanced equations to illustrate an example of:

a thermal cracking

b steam cracking

c catalytic cracking.

a Thermal cracking

Thermal cracking starts with relatively long-chain hydrocarbons (up to C_{20}) and cracks them to shorter alkanes suitable for use in gasoline (such as C_8). Short-chain alkenes such as ethene and propene are also produced. A suitable equation might be:

$$\begin{array}{ccccccc} C_{18}H_{38} & \rightarrow & C_8H_{18} & + & 2C_3H_6 & + & 2C_2H_4 \\ \text{octadecane} & & \text{octane} & & \text{propene} & & \text{ethene} \end{array}$$

Ensure that the total number of carbons and hydrogens is conserved on each side of the equation. Note that at least one product is an alkane and the others are alkenes.

b Steam cracking

Steam cracking uses shorter-chain alkanes (up to C_8) and cracks them to form mostly short-chain alkenes such as ethene. Some hydrogen may be formed. A suitable equation might be:

$$\begin{array}{ccccc} C_8H_{18} & \rightarrow & 4C_2H_4 & + & H_2 \\ \text{octane} & & \text{ethene} & & \text{hydrogen} \end{array}$$

Again, the numbers of carbon and hydrogen are conserved. No alkanes are formed here but the presence of hydrogen allows the hydrogen number to be conserved.

c Catalytic cracking

Catalytic cracking in industry is highly specific, with catalysts chosen carefully to give the required mixture of branched alkanes. The feedstock for catalytic cracking is intermediate-length carbon chains from the naphtha fraction (around C_{15}).

$$\begin{array}{ccccccc} C_{16}H_{34} & \rightarrow & C_7H_{16} & + & C_7H_{14} & + & C_2H_4 \\ \text{Hexadecane} & & \text{heptane} & & \text{heptene} & & \text{ethene} \end{array}$$

Note that in this example, the products are likely to be branched isomers of heptane and heptene rather than straight chains

Write a structural equation showing how heptane could be cyclized and aromatized to form methyl benzene, and state the conditions necessary for this conversion.

Comparison with Figure 24.12 suggests that heptane, although a seven-carbon chain, might cyclize to a six-membered ring with a methyl branch. This cyclic hydrocarbon will then aromatize to a benzene ring with a methyl branch – methyl benzene.

3 Suggest equations for the following processes:

- **a** Steam cracking of decane ($C_{10}H_{22}$) forming ethene and hydrogen.
- **b** Thermal cracking of eicosane ($C_{20}H_{42}$) to octane plus short-chain alkenes.

Additional Perspective

The mechanisms of cracking

Thermal cracking

Homolytic carbon–carbon bond fission produces alkyl radicals near the end of the chain. These alkyl radicals tend to split apart two carbon atoms along the chain, producing an ethene molecule and leaving a new alkyl radical with two fewer carbon atoms (Figure 24.13). This can then undergo further splitting, or a hydrogen atom can be transferred from another radical, if two radicals were to collide and react.

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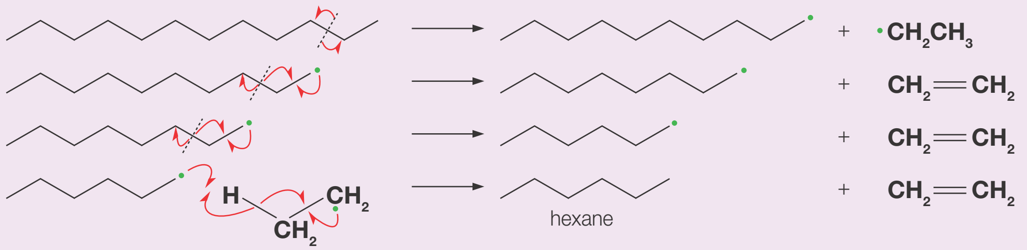
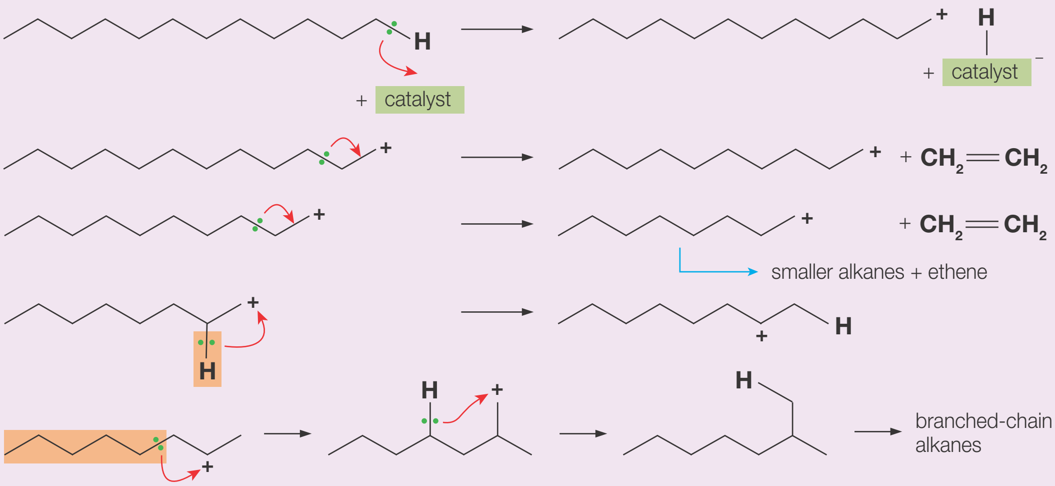
Figure 24.13 The free radical mechanism of thermal cracking



Catalytic cracking

The transfer of a hydrogen atom to the surface of the catalyst produces a carbocation. In a similar way to the free radicals formed during thermal cracking, carbon–carbon bond fission occurs at the next-but-one bond to the electron deficient positive carbon, producing a molecule of ethene and an alkyl carbocation with two fewer carbon atoms (Figure 24.14). The shift of a hydrogen atom from a carbon atom in the centre of the chain to the carbon of the primary carbocation produces a more stable secondary carbocation. Further rearrangements produce branched-chain alkanes. Rearrangement reactions are another fundamental type of organic reaction, in addition to substitution, elimination and addition.

Figure 24.14 The carbocation mechanism of catalytic cracking



Octane number ratings in different countries

When you visit a petrol station, you will often find a range of numbers quoted on the fuel pumps, telling you the octane ratings of different types of fuel. There are three main octane number standards worldwide:

- *RON or Research Octane Number:* An engine is run at 600 rpm and different compression levels, and the fuel is compared to 2,2,4-trimethylpentane and heptane. An octane number of 92 means that the fuel has the same tendency to pre-ignite as a mixture of 92 per cent 2,2,4-trimethylpentane and 8 per cent heptane.
- *MON or Motor Octane Number:* The fuel is tested at higher engine speeds, and with a variety of ignition (spark) timings, to give a better indication of how the fuel performs under driving conditions. Typically the MON is 8–10 points lower than the RON.
- *PON or Pump Octane Number (sometimes called AKI or Anti-Knock Index):* In the USA, Canada, Brazil, Mexico and some other countries, the number displayed on the fuel pump is the average of the RON and the MON (PON = (RON + MON)/2).

In most countries, oil companies market different grades of gasoline. These are often termed 'regular' and 'super' or 'premium' gasoline. The octane numbers of regular and super vary from country to country, depending on the quality of fuel available and the costs the market will bear.

In the UK, regular fuel is 95RON and super is 97RON. Some companies also market 99RON fuel at a higher price for high-performance cars.

In the USA, the PON/AKI standard is used. Regular is usually 85AKI (about 90RON). In some areas 94AKI (about 98RON) is available.

Countries whose populations drive mostly cheap, economical vehicles with low-compression engines typically offer predominantly low-octane fuels. For example, in India fuel ratings range from 89 to 91RON, and in Indonesia regular fuel is only 88RON. Conversely, in Hong Kong, where luxury vehicles are commonplace, consumers rejected 95RON fuel and now only 98RON is offered there.

In some countries, such as Brazil, gasoline fuel is mixed with ethanol (a biofuel). Originally this was for economic reasons – sugar, the raw material for ethanol manufacture, is cheap and plentiful in Brazil. In recent years other countries, such as the USA and Sweden, have adopted ethanol–gasoline mixtures for environmental and political reasons as they try to lower their dependence on imported oil. Biofuels are covered in detail in section 24.4.

Liquid fuels from coal

Coal is the most plentiful of the fossil fuels, but it has the disadvantage that the energy within it is most efficiently extracted in large-scale power plants.

Liquid fuels have the enormous advantage that they can be carried by vehicles and aircraft and used *in situ*. Gaseous fuels are easily piped to homes and used directly for heating and cooking.

The chemistry of converting coal into liquid fuels that can use the existing infrastructure designed for natural gas, gasoline, diesel, kerosene and so on has been widely investigated and implemented.

Coal gasification

The production of gaseous fuels from coal pre-dates the industrial production and domestic use of natural gas.

'Coal gas' is a mixture of carbon monoxide and hydrogen (both of which are combustible gases) formed by the reaction of coal with steam:

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$

Coal gas (sometimes called town gas) was widely used in the USA and the UK before the adoption of natural gas in the 1940s and 1950s.

Fossil fuel use in different countries

Hong Kong does not have natural gas resources, so it remains dependent on town gas manufactured from other fossil fuels. Some countries use coal gas (a mixture of carbon monoxide and hydrogen only, produced by combining coal with steam). Hong Kong uses a gas obtained from naphtha.

Until 1960, Hong Kong used coal gas. Then the change was made for a number of reasons. At that time, before the rise in the price of oil in 1973, oil was cheaper than coal. There was also the greater convenience of transporting and storing naphtha. Pollution from the combustion of naphtha is less than pollution from coal.

Naphtha consists of alkanes with 7–14 carbon atoms. Vaporized naphtha is passed with steam over a hot nickel catalyst. The products are hydrogen, carbon monoxide and other products.

naphtha + steam → carbon monoxide + hydrogen

Taking naphtha as $C_{10}H_{22}$, an example equation for the production of town gas is:

$$C_{10}H_{22}(l) + 10H_2O(g) \rightarrow 10CO(g) + 21H_2(g)$$

Substances added to town gas are:

- tetrahydrothiophene (THT) – to give town gas an unpleasant smell
- naphtha – to increase the energy density
- air – to increase the density.

It is essential that town gas has an unpleasant smell to allow leaks to be detected quickly. Leaks must be detected because an explosion might result, and also because carbon monoxide is a very poisonous gas.

The Hong Kong and China Gas Company, which supplies town gas to the territory, was founded in 1862 and is one of the oldest companies in Hong Kong.

This example illustrates how the balance of fossil fuel use can be highly specific to a country or territory, and will depend upon factors such as fuel availability, cost, and locally available technology and infrastructure.

Methods of coal liquefaction

Coal is made up mostly of carbon, but there is also hydrogen present. The proportion of hydrogen in the coal depends on the stage of fossilization reached by a particular sample of coal. Lignite contains more hydrogen than anthracite coal.

In any case, the proportion of hydrogen in liquid hydrocarbon fuels is much higher than in coal. Coal liquefaction relies on increasing the hydrogen : carbon ratio in the fuel. This is done in one of two ways:

1. Increase the amount of hydrogen in the coal.
2. Decrease the amount of carbon in the coal.

These processes lead to the formation of a mixture of hydrocarbons.

Direct hydrogenation of coal

Coal is crushed, mixed with a solvent (often heavy fuel oil) and heated in the presence of an iron-based catalyst. Hydrogen is added to the mixture. A mixture of hydrocarbons is formed, according to the following general equation:

$$nC + (n+1)H_2 \rightarrow C_nH_{2n+2}$$

The products are typically heavy hydrocarbons that require significant further refining (cracking, reforming) before they are of use as motor fuels.

Distillation of coal

Some coal types contain large amounts of hydrocarbons, so the liquefaction process involves separating the hydrocarbons from the solid carbon. As discussed above, bituminous coal is saturated with heavy hydrocarbon molecules. Such coals can be heated (a process called destructive distillation, or pyrolysis), which produces a mixture of tar (containing mostly cyclic or aromatic hydrocarbons), heavy oil and a solid residue of mostly carbon.

The tar and heavy oil can be further refined by cracking and reforming in order to make them useful as motor fuels.

Liquid fuels from coal gas

A third approach to coal liquefaction is to use the coal gas produced in the gasification process outlined previously to produce liquid hydrocarbons.

Recall that the products of coal gasification were carbon monoxide and hydrogen. These two products can be re-combined to make hydrocarbons:

$$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$$

The gas mixture is passed over an iron- or cobalt-based catalyst at 150–300 °C and pressures up to several dozen atmospheres.

Coal liquefaction and energy costs

Conversion of coal into liquid fuels by any of the processes outlined above requires a considerable input of energy, because high temperatures and pressures are necessary. Although the resulting liquid fuels are more convenient than coal for transport applications, they represent a very inefficient way of obtaining the maximum useful energy output from coal. Therefore, coal liquefaction is unlikely to present a long-term solution to our liquid fuel energy needs, although it does become economically viable when the cost of crude oil is particularly high or when supply is limited.

Worked example

Octane, C_8H_{18}, and its isomers are important components of gasoline. Deduce equations for the production of octane by:

a direct hydrogenation of coal

b liquefaction of coal gas, carbon monoxide, CO (g).

a The general equation for the production of an alkane containing n carbon atoms via hydrogenation is $nC + (n+1)H_2 \rightarrow C_nH_{2n+2}$ where C represents carbon within the coal.

For octane, $n = 8$, so the equation becomes:

$8C + 9H_2 \rightarrow C_8H_{18}$

b The general equation for the production of an alkane containing n carbon atoms via hydrogenation is:

$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$

For octane, $n = 8$, so the equation becomes:

$17H_2 + 8CO \rightarrow C_8H_{18} + 8H_2O$

Carbon footprints

Concern about the quantity of carbon dioxide entering the atmosphere due to human activities (see Section 24.5) has led to the adoption of a standard measure of the carbon dioxide emissions of particular activities. In simple terms it is a measure of the total carbon dioxide emissions resulting from a given activity, such as owning and using a car for a year, taking a transatlantic flight, or producing a certain output of a product such as computers, newspapers or foodstuffs.

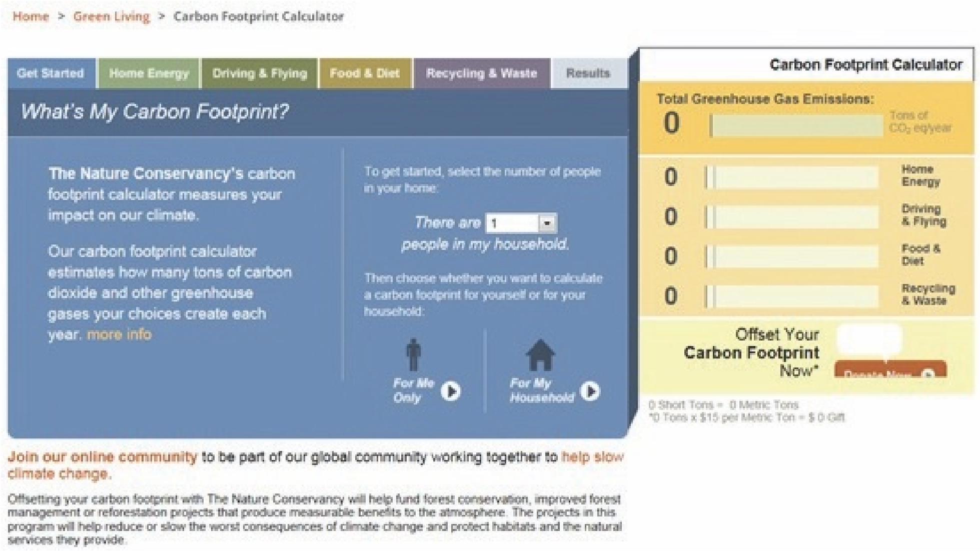
However, most of these activities involve the emission of numerous gases in addition to carbon dioxide, which might also contribute to global warming. For example, methane has a global warming potential approximately 25 times greater than carbon dioxide, for a given mass, so emissions of methane must be multiplied by this factor.

To simplify matters, instead of quoting the emissions of a whole series of greenhouse gases, the global warming potential of each, relevant to carbon dioxide, is factored in and the overall emissions are quoted as 'tonnes of carbon dioxide equivalent', which is abbreviated to CO_2-e. The carbon footprint expressed in this way offers a clear and simple measure of the climate change impact of the activity in question.

In order to calculate the carbon footprint, it is necessary to know the mass of each greenhouse gas emitted by the particular activity and the global warming potential of each. This can be a challenge, because the majority of emissions for many groups or activities actually take place far away from their actual location. For example, if we wished to calculate the carbon footprint of a typical household in the USA, we would need to know the amount and type of fuel consumed to generate their electricity, to fuel their cars, to produce all the goods they buy (food, clothing, cleaning materials and so on), to provide clean water, to remove their waste, and many more contributing factors. Most of these emissions are termed 'indirect' emissions

– the householders are not actually emitting the greenhouse gases themselves. Instead they are responsible for a small share of a much larger emission by a power station, a steelworks, a water treatment plant, and so on. The 'direct' emissions might only include using gas for cooking and heating and gasoline for driving, but even here there are indirect emissions arising from the extraction or refining of the fuels.

Despite the difficulty in estimating the thousands of carbon-emitting processes indirectly linked to everyday activities, carbon-footprint calculators have proliferated on the internet. By entering estimates of the size of your home, the type of car you own, the number of flights taken each year and various other factors, you can receive an estimate of the carbon footprint of your household. Corporations can undertake similar calculations to estimate their environmental impact. Often they will hire a consultancy firm to do the research and produce the final footprint figure. The danger here is that it is very easy to underestimate the carbon footprint by omitting indirect emissions. An example might be a magazine publisher that considers the heating and lighting of their offices and the cars driven by its staff, while ignoring the emissions of the printing firm that produces the final product; or the computer company that considers its own factories and workers, but omits the emissions due to mining the minerals needed to make the microchips and the oil needed to make the plastic casings. There is a marketing advantage in quoting a low carbon-footprint figure, but consumers need to examine the small print carefully to see what has been left out. Table 24.4 displays the typical carbon footprints of some different people, groups and activities. Many websites are available that enable the calculation of a personal carbon footprint (Figure 24.15).



What's My Carbon Footprint?

The Nature Conservancy's carbon footprint calculator measures your impact on our climate.

Our carbon footprint calculator estimates how many tons of carbon dioxide and other greenhouse gases your choices create each year. more info

To get started, select the number of people in your home:

There are 1 people in my household.

Then choose whether you want to calculate a carbon footprint for yourself or for your household:

Total Greenhouse Gas Emissions: 0 Tons of CO_2 eq/year

0	Home Energy
0	Driving & Flying
0	Food & Diet
0	Recycling & Waste

Offset Your Carbon Footprint Now*

0 Short Tons = 0 Metric Tons
*0 Tons x $15 per Metric Ton = $ 0 Gift

Join our online community to be part of our global community working together to help slow climate change.

Offsetting your carbon footprint with The Nature Conservancy will help fund forest conservation, improved forest management or reforestation projects that produce measurable benefits to the atmosphere. The projects in this program will help reduce or slow the worst consequences of climate change and protect habitats and the natural services they provide.

■ **Figure 24.15** An online carbon-footprint calculator from the Nature Conservancy Council

■ **Table 24.4** Some examples of carbon footprints

Person, group or activity	Carbon footprint (tonnes CO_2-e)
USA, average per person per year	19.8
UK, average per person per year	9.2
China, average per person per year	4.2
India, average per person per year	1.1
Google, all activities worldwide per year	1 500 000
Manufacture of one Ford Mondeo sedan	17
Manufacture and use of Apple iPhone over whole product lifecycle	0.075

Carbon calculations: CO_2 and motor vehicles

Most countries charge a road tax on motor vehicles. This is payable to the government and is intended to cover the cost of upkeep of the road network.

Many countries charge more road tax for larger and heavier vehicles, as these are presumed to cause more wear and tear to the roads. However, in 2005 the UK introduced new road tax charges based on carbon emissions. This was an incentive to purchase lower-emitting vehicles.

All new vehicles sold in the UK are given an official CO_2 emissions figure, quoted in grams per kilometre driven (g/km). This figure is obtained by measuring the CO_2 emissions under different driving conditions.

For some vehicles, usually hybrids (those with a supplementary electric motor alongside the gasoline engine) or those with very small engines, the CO_2 emission figure is below 100 g/km. Owners of these vehicles pay no road tax. As the CO_2 emission figure increases, the road tax increases, up to a maximum of £1100 (approximately US$1750) for the most powerful cars, which emit more than 255 g/km.

Worked example

Estimate the carbon footprint (tonnes CO_2-e) of driving a VW Polo BlueMotion with a CO_2 rating of 91 g/km, for 1 year, with a total distance covered of 20 000 km.

$$\text{Total mass of } CO_2 = 91\,\text{g/km} \times 20\,000\,\text{km} = 1\,820\,000\,\text{g}$$

$$1 \text{ tonne } CO_2 = 1000\,\text{kg} = 1\,000\,000\,\text{g}$$

$$\text{So footprint tonnes } CO_2\text{-e} = \frac{1\,820\,000}{1\,000\,000} = 1.82 \text{ tonnes } CO_2\text{-e}$$

4 A car with an average fuel consumption of 7 litres/km covers 10 000 km in one year. Assume the fuel is octane, C_8H_{18}. Calculate the carbon footprint (tonnes CO_2-e). Necessary data: density of octane $0.703\,\text{g cm}^{-3}$, molar mass = $114.23\,\text{g mol}^{-1}$.

Oil spills and international cooperation

Oil spills at sea, whether from oil tanker leaks or drilling accidents, are major sources of ocean pollution. If such an accident occurs in international waters, who is responsible for cleaning it up? Such questions can be sources of enormous social political friction, so international committees exist to mediate such disputes.

In 1989 the International Maritime Organization prepared the International Convention on Oil Pollution Preparedness, Response and Co-operation (OPRC). Signatories to the OPRC are required to make preparations for dealing with pollution incidents and establish rules for ships and oil drilling operations under their jurisdiction. They are also required to provide assistance to other countries where necessary.

Conventions such as these are intended to ensure that there are rapid and efficient responses to pollution incidents without delays caused by political disagreements.

24.3 Nuclear fission and fusion

– the fusion of hydrogen nuclei in the Sun is the source of much of the energy needed for life on Earth. There are many technological challenges in replicating this process on Earth but it would offer a rich source of energy. Fission involves the splitting of a large unstable nucleus into smaller stable nuclei

Nature of Science

The ethics of nuclear research

This section outlines the scientific concepts underpinning the production of useful energy by nuclear processes. The energy densities involved are enormous, meaning that nuclear energy is perhaps the only energy source that can hope to compete with fossil fuels in terms of meeting the world's energy needs.

Chemistry for the IB Diploma, Second Edition © Christopher Talbot, Richard Harwood and Christopher Coates 2015

The debate surrounding nuclear energy raises questions about the ethical nature of science. The main question is sometimes expressed as '*just because we* can *do something, does that mean we should?*'

In the 1940s, the goal of 'splitting the atom' was pursued for essentially militaristic reasons. After the atomic bombing of Japan, many (but by no means all) of the atomic scientists expressed regret that they had participated in the research while giving insufficient attention to the morality of what they were trying to achieve.

In the early part of the Cold War, despite the threat of annihilation, there was an optimism surrounding nuclear energy that was never fully realized. Atomic aircraft, ships and even cars were proposed, and atomic power was to become 'too cheap to meter', but the momentum of weapons development never translated into a peaceful, clean, atomic-powered utopia. Instead, a series of nuclear accidents, and the realities of the costs of nuclear infrastructure, led to disillusionment and nuclear power became less important to the worldwide energy mix than was predicted (currently nuclear power contributes about 12 per cent of worldwide electricity production).

Today, the threat of climate change means that even environmentalists disagree about the desirability of nuclear energy. Some feel that the utilitarian calculus (the cost/benefit analysis of the potential outcomes) leads to the conclusion that nuclear power is a lesser evil. That is, the potential dangers of nuclear energy are far outweighed by the potential benefits, in terms of lowering carbon emissions. Even nuclear risks are not rationally understood, with statistics on the harm caused by fossil fuels (for example, respiratory illness and coal-mining accidents, before even considering the climate-related dangers) exceeding those from the nuclear industry. However, others reject the utilitarian argument, suggesting that we have a duty to future generations not to build a nuclear 'mess' that will be their responsibility to clean up.

Many scientists believe that the capability to lower carbon emissions exists, and that there is an imperative to invest in and develop nuclear power. We *should* do it because we *can*. However, the 'should' involves a value judgement that is not straightforward. The connection between nuclear power and nuclear weapons cannot be ignored, and this, combined with high-profile accidents, means that many people do not trust science to solve this problem.

Nuclear power from fission

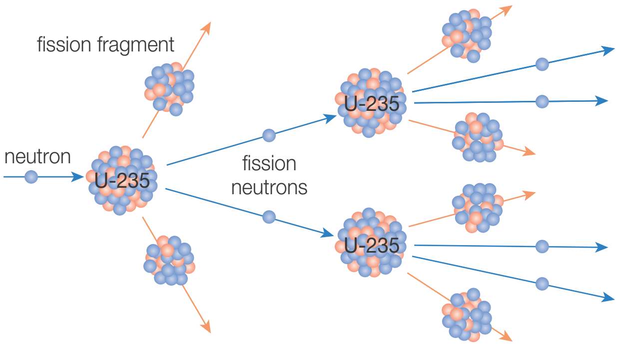
In a nuclear power station, radioactive nuclear fuel (uranium or sometimes plutonium) undergoes a process of nuclear fission. The process generates large amounts of thermal energy that can be used to boil water, producing steam. The pressurized steam can then be used to turn turbines for electricity generation. Naturally occurring uranium is mostly isotope ^{238}U, with a little ^{235}U. For fuel, it is enriched; that is, the proportion of ^{235}U is increased to allow the chain reaction to take place.

Nuclear power accounts for around 12 per cent of worldwide electricity generation, with the USA, France and Japan responsible for over half of this total. These figures looked likely to rise, as some governments seek to lower their dependence on fossil fuels, for environmental and economic reasons. However, the Fukushima Daiichi disaster of March 2011 led some governments, such as Germany's, to re-think their reliance on nuclear power. Some environmentalists see a shift from fossil fuels to more nuclear power as a useful way of cutting carbon emissions, while others see the production of larger quantities of dangerous radioactive waste, and the risk of accidents, as too great a price to pay.

Nuclear reactors

A nuclear reactor contains an array of ceramic uranium oxide rods separated by a so-called moderating material, or moderator, such as graphite. Nuclear fission typically involves the nucleus of a uranium-235 atom breaking apart and releasing slow-moving neutrons. These neutrons move through the uranium, colliding with other nuclei, which in turn causes them to split apart, releasing more neutrons (Figure 24.16). Therefore an ongoing chain reaction occurs. If this reaction is not controlled carefully, it proceeds rapidly, releasing massive amounts of energy. This is the basis of an atomic explosion. However, in a nuclear power station, this cannot happen, firstly because the uranium fuel contains only a small percentage of fissile uranium-235 (being mostly composed of uranium-238, which requires much faster neutrons and is therefore very unlikely to undergo fission), and secondly because the moderator absorbs and slows the neutrons moving through the material, preventing the chain reaction from running out of control.

Figure 24.16
A nuclear chain reaction



Deducing fission equations

Nuclear reactions must be balanced, just like chemical equations. Balancing is done by comparing the mass numbers and the atomic numbers of all the components in the equation. These numbers must be conserved.

$$^{1}_{0}\mathrm{n} + {}^{235}_{92}\mathrm{U} \rightarrow {}^{236}_{92}\mathrm{U}$$

In this first step, the U-235 nucleus (92 protons, 143 neutrons) absorbs an incoming neutron (1 neutron, no proton), becoming U-236 (92 protons, 144 neutrons)

$$^{236}_{92}\mathrm{U} \rightarrow {}^{92}_{36}\mathrm{Kr} + {}^{141}_{56}\mathrm{Ba} + 3{}^{1}_{0}\mathrm{n}$$

Then the U-236 atom decays into two smaller nuclei, krypton-92 (36 protons, 56 neutrons) and barium-141 (56 protons, 85 neutrons). So far this adds up to 141 neutrons, so the remaining three neutrons from the U-236 atom are released. It is these neutrons that can go on to split more U-235 nuclei.

5 The first nuclear reaction ever observed was Ernest Rutherford's transmutation of nitrogen-14 into oxygen using alpha particles in 1917. Protons were produced as a by-product. Write an equation for this reaction and deduce which isotope of oxygen was formed.

Explaining energy changes during fission using binding energies

During the nuclear chain reaction, enormous amounts of energy are released. This energy is released as electromagnetic radiation (mostly gamma rays) and kinetic energy of the fast-moving fission products (in the example above, the krypton and barium nuclei). This heats up the nuclear material.

This energy has to come from somewhere. It is accounted for by comparing the nuclear binding energy of the original nucleus and the fission products.

Nuclear binding energy holds the subatomic particles of the nucleus together. In order to break up a nucleus, energy must be provided. Upon formation of a nucleus, energy will be released. (Compare this with chemical bonds, in which bond breaking is also endothermic, while formation is exothermic.)

In the example cited, the total binding energy of the two lighter elements, krypton and barium, is greater than the binding energy of the uranium nucleus. The amount of energy released when krypton and barium are formed is greater than that needed to split the uranium nucleus.

Why do large nuclei split but small nuclei fuse?

The binding energy depends on the relationships between two forces. The nucleus is held together by the **strong nuclear force**. This force acts over very small distances, and is sufficient to overcome the **electrostatic repulsion** which acts between protons, which repel each other because they all have a positive charge. At the distances involved within the nucleus, the strong nuclear force is about 1000 times as strong as the electrostatic repulsion.

The graph in Figure 24.17 shows that for small nuclei, the binding energy increases with nucleon number. (This graph is also available in the *IB Chemistry data booklet*, Section 36.) This occurs because the strong nuclear force within the nucleus increases as the number of nucleons increases. The electrostatic repulsion increases too, but is less important when there are relatively few protons to repel each other. Overall, small nuclei experience an increase in binding energy as nucleon number increases.

The graph is then approximately horizontal for a while, as the balance between the strong nuclear force and the electrostatic repulsion gives similar binding energies for nuclei of intermediate size.

At very high nucleon numbers, the binding energy starts to fall with increasing numbers of nucleons. The electrostatic repulsion factor starts to outweigh the increase in the strong nuclear force. For each successive nucleon, more repulsion than attraction is experienced, so the binding energy falls.

This explains why there are a limited number of chemical elements. At higher nucleon numbers the nucleus becomes increasingly unstable. For elements higher than $Z = 83$ (83 protons; bismuth), the nuclei are prone to decay, so they are radioactive. Uranium atoms ($Z = 92$) are the largest to occur naturally.

Recall that a nuclear reaction will take place, and release energy, if the binding energy of the products is larger than the binding energy of the reactant particles.

For large nuclei, the binding energy is lower than that of a pair of smaller nuclei, so these large nuclei are prone to fission, and will release energy when they do so.

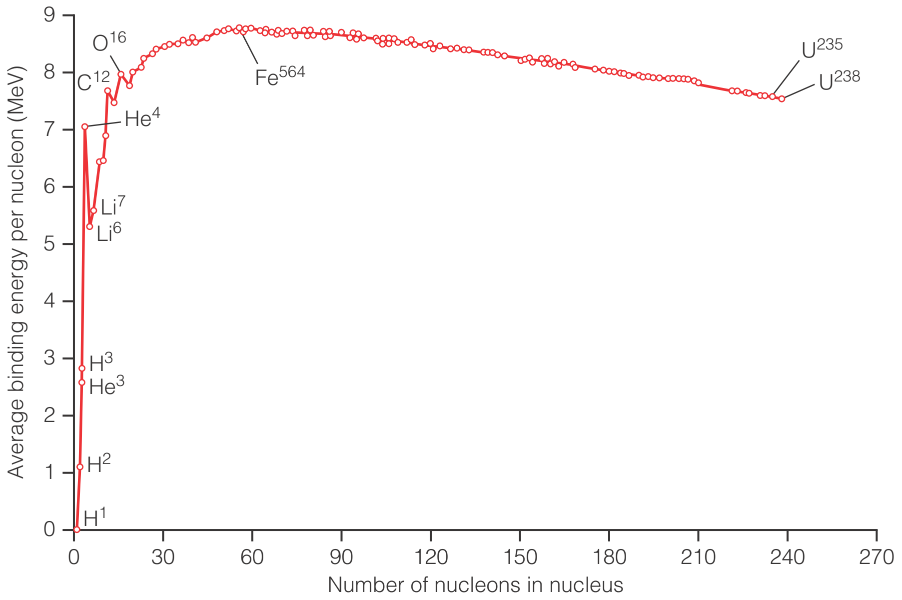
For small nuclei, the binding energy of a larger nucleus (the fusion product) is greater, so when small nuclei fuse together, energy output (binding energy of the product nucleus) is greater than the energy input (binding energy of the two smaller nuclei).

This explains the perhaps counter-intuitive observation that both nuclear fission and nuclear fusion are exothermic processes. Nuclear fission involves very large nuclei splitting into medium-sized products. Nuclear fusion involves very small nuclei combining into products that are still rather small.

The mega electronvolt (MeV) shown on the graph is a unit of energy often used when describing nuclear processes. For a full explanation see Section 24.7.

It should be noted that while most energy diagrams in chemistry have the lowest (most stable) energy state at the bottom of the diagram, this one is an exception. The most stable state is at the top.

Figure 24.17 The binding energy curve



Additional Perspective

The liquid drop model of the nucleus

We now understand that atomic nuclei are held together by the strong nuclear force. Atomic physicists used analogies to attempt to explain the behaviour of nucleons under this force.

George Gamow suggested that the nucleus be thought of as a droplet of incompressible fluid. In the model, each nucleon behaves like a molecule in the liquid, and the strong nuclear force is represented by the intermolecular forces within the liquid drop.

Niels Bohr and John Wheeler developed the model and found that it closely modelled many features of the nucleus (Table 24.5).

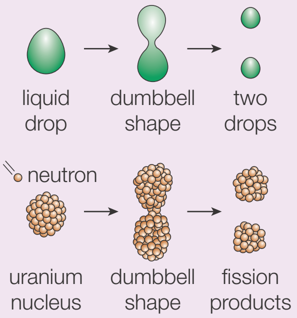
■ **Table 24.5** Similarities between liquid drops and atomic nuclei

Liquid drop	Atomic nucleus
Liquid drops are spherical because there are no intermolecular forces acting on the outside of the outermost molecules in the drop. The spherical shape maximizes the intermolecular forces between the molecules and is the lowest energy configuration	Nuclei are spherical because the spherical shape is the lowest energy configuration, maximizing the number of strong nuclear force interactions
The liquid drop has the same density throughout, which is independent of the size of the drop	The density of the nucleus is independent of the size of the nucleus
Liquid molecules attract one another by dispersion forces but cannot get too close, otherwise repulsive forces (e.g. between the outer electrons of each molecule) start to become important	Nucleons attract one another by the strong nuclear force. However, there are also electrostatic repulsive forces between similarly charged particles (i.e. protons within the nucleus)
Liquid drops reach a maximum size before breaking apart into smaller drops	Nuclei reach a maximum size before breaking apart into smaller nuclei
When they split apart, liquid drops form a dumb-bell shape, which then splits apart at the 'neck' of the dumb-bell, forming two similarly sized fragments (Figure 24.18)	When they split apart, nuclei tend to form similarly sized fragments

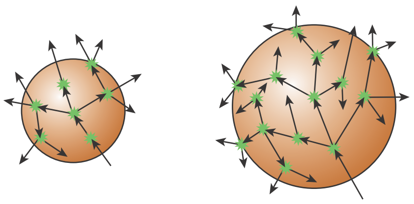
Carl Friedrich von Weizsäcker quantified many of the energy terms outlined above and used his equations to make predictions of nuclear binding energy.

The liquid drop model is not a perfect one. For example, the number of molecules in a liquid drop is far larger than the number of nucleons in a nucleus, and the amount of movement available to a molecule within a drop is much larger than the size of the molecule itself, whereas the amount of movement available to a nucleon is similar to the size of the nucleon itself.

Nonetheless the liquid drop model proved useful when theorizing the contribution to the binding energy from different interactions within the nucleus.



■ **Figure 24.18** Liquid drops and atomic nuclei can be modelled in similar ways



■ **Figure 24.19** The critical mass of fuel is the minimum size necessary to sustain a chain reaction: **a** in a small sphere neutrons can easily escape so the chain reaction does not become self-sustaining; **b** for a sphere with a mass greater than the critical mass the chain reaction is self-sustaining

Sustaining the fission chain reaction

Naturally occurring uranium contains only 0.7 per cent uranium-235, which in most reactors is insufficient to sustain a chain reaction. Uranium for reactors is processed to increase the percentage of uranium-235 to around 4 per cent, a process called 'enrichment'.

In order for the chain reaction to proceed, there must be a sufficient density of neutrons moving through the reactor. If too small a quantity of nuclear fuel is used, too many neutrons 'escape' from the edges of the material. The minimum quantity of nuclear fuel needed to sustain a chain reaction is called the 'critical mass'. Figure 24.19 shows how the size of the mass of fuel is important in sustaining the chain reaction.

For a pure sphere of uranium-235 the critical mass is 52 kg, which represents a sphere of about 17 cm diameter. For much less pure uranium-235, as used in reactors, the critical mass is hundreds of kilograms.

Reactor design

Most nuclear reactors in current service were built from designs originating in the 1960s and 1970s. Most of these are light-water reactors, which use ordinary water as a moderator and coolant. Water pumped through pipes inserted into the nuclear fuel vessel acts as a moderator (to slow down the neutrons, making neutron capture by U-235 nuclei more likely) and a coolant. When it leaves the reactor the water is at a temperature of more than 300°C, but it remains liquid because the pressure in the cooling system is about 150 atmospheres. A heat exchanger is used to transfer this heat to another, unconnected water supply. This new water is boiled to form high-pressure steam that turns turbines.

Concern about global warming has put nuclear power back on the energy agenda in the UK, the USA and many other countries. Japanese companies are working on modular sealed unit reactors that can be quickly manufactured in factories and shipped to the required location, simplifying the setting up of reactors. In South Africa, pebble-bed reactors have been developed which use spheres of uranium oxide combined with graphite. They can be piled together and a chain reaction starts. The energy is transferred from the reactor using an inert gas such as helium. These are solutions to the massive investment required for earlier generations of reactors, most of which had to be subsidized by governments. These simple modular designs are easier to scale up or down according to need. They also address the problem of decommissioning reactors when they reach the end of their useful lives. Traditional reactors accrue enormous costs for dismantling and decontamination.

Breeder reactors

Uranium is not a renewable resource. Although quite plentiful, only a small fraction of naturally occurring uranium is fissile uranium-235, and reserves of uranium ore will eventually run out. When the nuclear fuel is used up, the resultant waste contains more than 90 per cent unreacted uranium-238. The waste is very dangerous, owing to the presence of radioactive actinoid (lower row f-block) elements such as plutonium-239 and neptunium-236. A breeder reactor aims to solve two problems:

1. Traditional light-water reactors use only a small percentage of the uranium in the nuclear fuel – the fissile uranium-235 portion. Can the left-over uranium-238 be utilized?
2. Highly radioactive waste fuel rods must be disposed of safely. Can they instead be employed to useful purpose?

A breeder reactor is designed differently from a commercial light-water reactor, to take advantage of another reaction that occurs in a nuclear reactor.

$${}^{1}_{0}\mathrm{n} + {}^{238}_{92}\mathrm{U} \rightarrow {}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\mathrm{e}$$

In this scheme, a uranium-238 nucleus captures a neutron, and then undergoes two stages of nuclear decay, in which beta particles (electrons – see Dangers of nuclear power, pp. 34–5) are released, leading to conversion into neptunium-239 and then plutonium-239. Plutonium-239 is fissile, unlike uranium-238, so can contribute to the energy output of the reactor.

Although this reaction does occur in ordinary reactors, the plutonium fissions, meaning its abundance in the reactor decreases. However, in a breeder reactor, the plutonium-generating reaction occurs more quickly than the plutonium is used up by fission. This is achieved by using a coolant that is less effective at moderating (slowing down) the neutrons. Fission of uranium-235 is more efficient at low neutron speeds (as in water-cooled and moderated 'ordinary' reactors). Breeder reactors use alternative coolants such as helium gas or liquid sodium.

The breeder reactor, then, is so-called because it 'breeds' nuclear fuel: fissile plutonium-239. More fissile material comes out than went in.

Once the reaction is under way, spent uranium fuel rods, which contain mostly non-fissile uranium-238, along with the highly radioactive plutonium and neptunium products from traditional fission, can be introduced. In the breeder reactor these substances are recycled and fissioned. Hence radioactive waste can be put to use generating energy.

A slightly different reactor design leads to the consumption of the dangerous actinoid waste in fuel rods, so that the waste only contains fission products (such as barium and krypton). These have much shorter half-lives (less than 100 years) meaning the waste is much more easily disposed of. Such reactors are called **burner reactors**.

Problems with breeder reactors

The relatively low cost of uranium ore, combined with the greater cost of breeder reactors, means that they have not been widely adopted despite their advantages. However, as waste stockpiles increase and uranium reserves run low, they have been subject to renewed interest.

Safety considerations are even more important with breeder reactors because the coolants might be hazardous. For example, if hot liquid sodium coolant is exposed to air, it is likely to ignite, leading to a sodium fire.

The other problem with breeder reactors is that they produce plutonium, which is used in building nuclear weapons. A country that proposes to build breeder reactors is likely to come under scrutiny from the International Atomic Energy Agency, which seeks to limit the proliferation (spreading) of nuclear weapons.

Nuclear power from fusion

Nuclear fusion involves smaller nuclei joining together to make larger ones. It is a subject of intense interest and study because in theory fusion reactions can also produce larger amounts of energy per kilogram of fuel than fission reactions.

Solar fusion

The most well-known fusion reaction is that which takes place in the Sun. The Sun is primarily made of hydrogen. Under the intense gravitational pressures and enormous temperatures inside the star, hydrogen nuclei fuse together to make helium nuclei.

In order for this to occur the hydrogen nuclei must be moving fast enough to overcome the electrostatic repulsion between them. To fuse together, two nuclei must approach within 10^{-15} metres of each other, so that the strong nuclear force is able to bind them together.

The most abundant isotope of helium is ${}^{4}_{2}\mathrm{He}$ (helium-4) and the most common isotope of hydrogen is ${}^{1}_{1}\mathrm{H}$. Conservation of mass numbers and atomic numbers makes it clear that the formation of helium does not occur by simple fusion of two ${}^{1}_{1}\mathrm{H}$ nuclei, as this would result in a new nucleus with two protons and no neutrons.

Instead the formation of helium-4 occurs by a multi-step mechanism involving a less common isotope of hydrogen called **deuterium**. Deuterium differs from common hydrogen in that it has one neutron in addition to the usual single proton. The symbol for deuterium is ${}^{2}_{1}\mathrm{H}$ (sometimes written as ${}^{2}_{1}\mathrm{D}$).

Construction of nuclear equations for fusion processes

The following scheme is proposed for the formation of helium-4 in the Sun. The mechanism also involves formation of a positron (symbol ${}^{0}_{1}\mathrm{e}$): a particle with the same mass as an electron, but a positive charge instead of a negative charge. (Physicists refer to the positron as a particle of antimatter, or an antiparticle.)

$$ {}^{1}_{1}\mathrm{H} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{2}_{1}\mathrm{H} + {}^{0}_{1}\mathrm{e} + \nu $$

These products are a deuterium nucleus, a positron and a neutrino (symbol ν (nu), an electrically neutral, almost massless particle). Note that the mass numbers and atomic numbers are conserved in this equation (follow the subscript numbers and superscripts numbers on each side of the arrow).

The deuterium combines with another hydrogen nucleus, with the production of a helium-3 nucleus and gamma radiation:

$$ {}^{2}_{1}\mathrm{H} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{3}_{2}\mathrm{He} + \gamma $$

The two reactions above take place twice, forming two ${}^{3}_{2}\mathrm{He}$ nuclei. In total six ${}^{1}_{1}\mathrm{H}$ nuclei are involved. Then, the two ${}^{3}_{2}\mathrm{He}$ nuclei fuse giving a ${}^{4}_{2}\mathrm{He}$ nucleus and reforming two ${}^{1}_{1}\mathrm{H}$ nuclei.

$$ {}^{3}_{2}\mathrm{He} + {}^{3}_{2}\mathrm{He} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{1}\mathrm{H} + {}^{1}_{1}\mathrm{H} $$

The overall nuclear equation is:

$$4{}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + 2{}^{0}_{1}\mathrm{e} + 2\nu$$

Each of the fusion processes above releases lots of energy, because the binding energy of the fusion product is greater than that of the two colliding nuclei.

The process by which small nuclei 'build up' to form larger nuclei is called **nucleosynthesis** and is the source of all the chemical elements heavier than hydrogen in the universe.

6 An important nucleosynthetic process in stars is the formation of nitrogen from carbon. In this series of reactions, carbon-12 fuses with hydrogen (${}^{1}_{1}\mathrm{H}$) forming nitrogen-13. This then releases a positron to become a new isotope. This new isotope fuses with a further hydrogen nucleus, forming nitrogen-14. Write equations for this series of reactions and deduce the identity of the unknown isotope.

How do we know the composition of stars?

The elements present in the Sun and their abundance were determined by examining the absorption spectra of elements in the laboratory and comparing these spectra with solar radiation.

Absorption spectra

In Chapter 2 we discussed the emission spectrum of hydrogen and observed that electron transitions from higher energy levels to lower energy levels in hydrogen atoms led to the emission of photons with specific wavelengths. These appear as a line-spectrum – a series of bright lines of light against an otherwise dark background.

An absorption spectrum is the opposite of this. If white light is passed through a gaseous sample of atoms at low temperature and pressure, and the emerging light is analysed, the light beam will be found to be missing certain wavelengths of light. This is because the gaseous atoms have absorbed certain wavelengths. Electrons within the sample will have been promoted (or 'excited') to higher energy levels. Again, the wavelengths absorbed will be specific and will correspond to the difference in energy between the energy levels in the sample atoms. Each chemical element has its electron energy levels at slightly different energies, meaning that the wavelengths of light absorbed when electrons are excited will also be slightly different.

The relationship between emission and absorption spectra is shown in Figure 2.40 in Chapter 2.

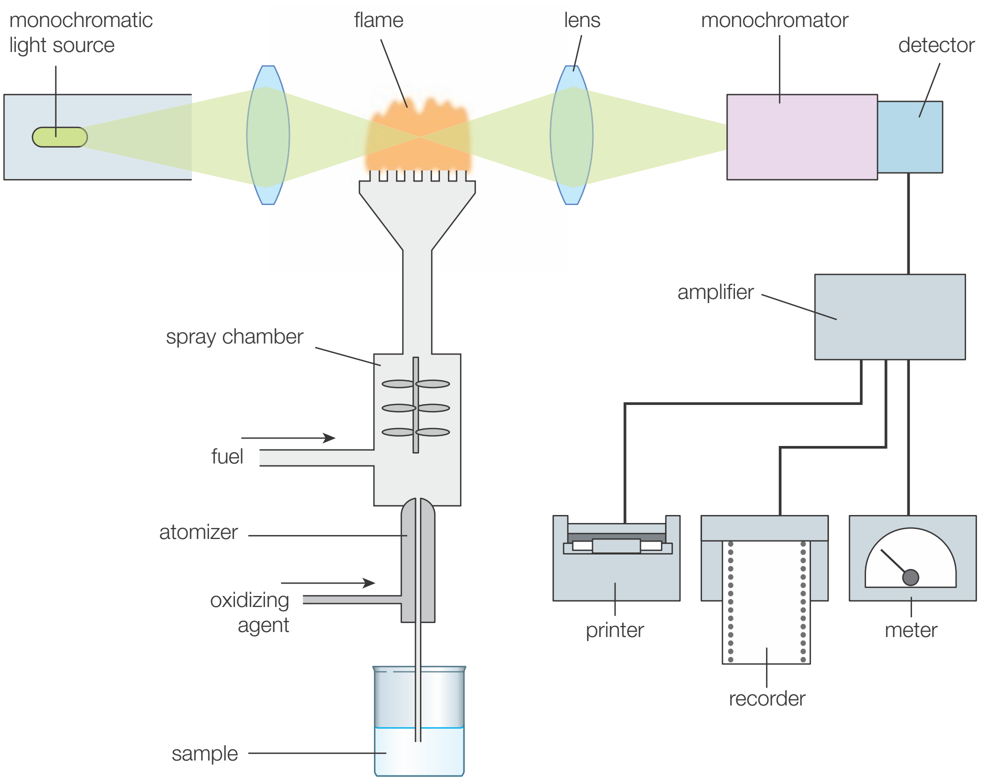
Examining the Sun using absorption spectra

In very simple terms, an atomic absorption spectrometer basically consists of a source of white light (light containing all the visible wavelengths), a means of vapourizing the sample and a detector. Light from the source passes through the sample and is then examined to determine which wavelengths are present and which have been absorbed. Figure 24.20 shows a schematic of a laboratory atomic absorption spectrometer. In the laboratory set-up, a flame is used to vapourize the sample, and a monochromator is used to filter out unwanted frequencies of radiation (those not likely to be absorbed by the sample).

The Sun can be thought of as a gigantic absorption spectrum experiment. The core of the Sun acts as the white light source, generating the full range of visible light wavelengths. As this light moves from the core outwards, it passes through the layers of gas in the outer part of the Sun. As it does so, atoms in this gaseous region will absorb some of the visible light wavelengths. Sunlight that reaches Earth therefore has narrow bands of missing wavelengths, corresponding to the absorption frequencies of the elements in the Sun.

The dark lines in the solar spectrum were discovered by the German optician Joseph von Fraunhofer (1787–1826) and named Fraunhofer lines. By comparing Fraunhofer lines with absorption spectra obtained in the laboratory, scientists were able to identify the presence of hydrogen, oxygen, sodium, magnesium, calcium and iron in the Sun. However, there was absorption at 587.5 nm, which was not present in any elements examined on Earth. Norman Lockyer, a British astronomer, proposed that the line was due to a new element, which he named helium, after Helios, the Greek Sun god. Lockyer is jointly credited with discovering the helium spectral line, along with Jules Janssen, a Frenchman, in 1868. Helium was not identified on Earth until 1895, when it was isolated from the air in small quantities.

Figure 24.20 Schematic diagram of a flame atomic absorption spectrometer



The solar spectrum, and the use of spectral lines to identify atoms present in the Sun, is the basis of our understanding of the fusion reactions occurring in the Sun and our knowledge of its composition (Figure 24.21).

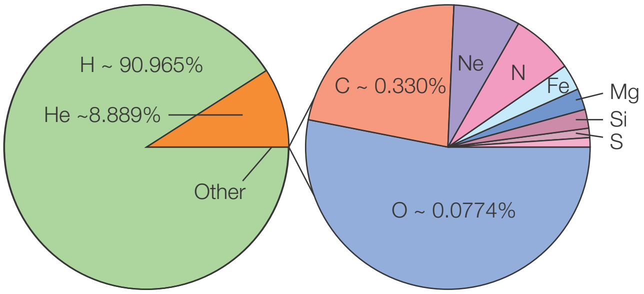


Figure 24.21 The composition of the Sun (data from NASA's planetary factsheet)

Explaining energy levels and absorption lines

As the Sun is mostly made up of hydrogen, the solar spectrum has strong absorptions in the lines corresponding to the hydrogen spectrum. Transitions from the first energy level to higher levels have energies greater than photons in the visible spectrum. This series of lines appears in the ultraviolet.

Transitions from the second energy level ($n = 2$) to the third, fourth, etc. correspond to wavelengths in the visible spectrum. This is called the Balmer series of the absorption spectrum (Figure 24.22). When an electron is excited from $n = 2$ to $n = 3$, light of wavelength 656 nm is absorbed from the white light spectrum, leading to a dark line on the spectrum. The solar absorption spectrum includes other dark lines at 486 nm, 434 nm and 410 nm, which correspond to the $n = 2 \rightarrow 4$, $n = 2 \rightarrow 5$ and $n = 2 \rightarrow 6$ electron transitions, respectively.

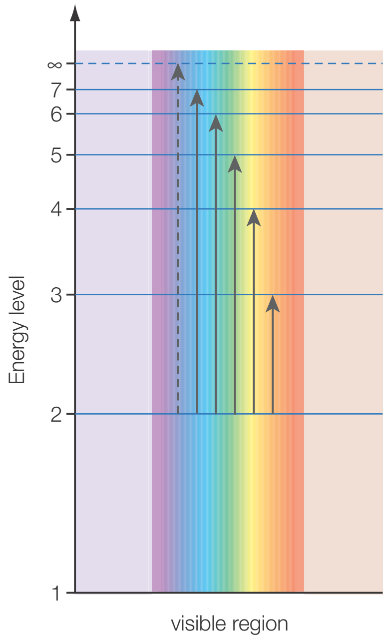


Figure 24.22 The Balmer series

None of these lines corresponds to the strong absorbance (a dark line) observed by Lockyer and Janssen in 1868. Lockyer initially thought that the line must be attributed to hydrogen under unique temperature or pressure conditions, but he eventually concluded that an entirely new element, with differently spaced energy levels, must be responsible. This was helium.

Man-made fusion

The hydrogen bomb

Soon after the invention of the atomic bomb in 1945, the USA began developing an even more powerful weapon: the hydrogen bomb. This weapon uses the fusion of hydrogen to produce massive amounts of energy very quickly, leading to an enormous explosion.

An atomic bomb uses uranium or plutonium and involves a fission reaction. However, the size of an atomic bomb is limited, because when the mass of plutonium or uranium exceeds a certain size, it starts to blow apart before the fission reaction is complete. The smaller pieces of fuel do not then have sufficient mass for the chain reaction. Eventually, a size is reached where adding more uranium or plutonium to the bomb does not lead to an increase in the power of the explosion. By 1952 the USA had developed a fission weapon with an explosive yield equal to 500 000 tonnes (500 kT) of TNT (compared with about 15 kT for the Hiroshima weapon). This bomb used 60 kilograms of uranium-235.

It was theorized that a weapon using a fusion reaction could be much more powerful. In fact there is no theoretical upper limit to the size of the weapon. If more nuclear fuel is added, the fusion reaction will continue, just as the Sun consumes its hydrogen fuel continuously.

In order to generate the enormous temperatures required, a fusion weapon uses a fission bomb to ignite the fusion reaction. When the fission bomb explodes, the energy is channelled into a vessel containing deuterium fuel. A combination of the very high temperature and the compressive force of the intense radiation generated by the fission bomb is enough to start the deuterium nuclei fusing together. A possible fusion reaction is:

$${}^{2}_{1}\mathrm{H} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{3}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n}$$

This process is termed **thermonuclear fusion**, as thermal energy is used to ignite the fusion reaction. Hydrogen bombs are sometimes called thermonuclear weapons.

The most powerful hydrogen bomb tested by the United States ('Castle Bravo', 1954) had an explosive yield of 15 000 000 tonnes (15 megatonnes (Mt), or 1000 Hiroshimas), while the Soviet Union's '*Tsar Bomba*' ('King of Bombs', 1961) reached 50 Mt.

Fusion reactors

Fusion weapons rely on igniting a fusion chain reaction that generates heat quickly, leading to more fusion. A commercial fusion reactor is more difficult to operate, because the fusion reaction must be carefully controlled, producing sufficient heat to maintain fusion, without 'running away' and exploding.

Most commercial attempts at producing a sustainable fusion reaction have used deuterium fuel, or a combination of deuterium and a third hydrogen isotope, called tritium, which is hydrogen with two neutrons: ${}^{3}_{1}\mathrm{H}$.

Deuterium–deuterium fusion is written:

$$ {}^{2}_{1}\mathrm{H} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{3}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} $$

Deuterium–tritium fusion is written:

$$ {}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} $$

Unlike fission reactors, there are no dangerous actinoids produced, so there are no long-term fuel disposal problems. However the reactor vessel itself becomes highly radioactive due to its being bombarded by neutrons.

If they are to fuse, overcoming their mutual electrostatic repulsion, the nuclei must be heated to very high temperatures while containing them in a vessel without contaminating them. At such high temperatures, a vessel made of steel, for example, would release vaporized iron atoms, contaminating the nuclear fuel. Instead the nuclear fuel is suspended and isolated in a magnetic field – a process called **magnetic confinement**.

The confinement vessel is in the shape of a torus (simply described as a 'doughnut shape'). The fuel is accelerated around the 'doughnut' to very high speeds. The particles reach such high temperatures that their electrons are stripped away, resulting in the formation of a 'plasma' of highly charged nuclei. The nuclei have sufficient kinetic energy to collide and fuse, overcoming the electrostatic repulsion.

Although fusion reactions have been achieved in this way, the power consumption of the magnetic confinement and heating the fuel has so far been greater than the energy output from fusion. Further research and development is needed until the energies 'break even' and then an overall production of energy is achieved.

A further difficulty of building a fusion reactor is developing the materials required. A sustained fusion reaction would produce enormous numbers of neutrons. These neutrons would constantly bombard the walls of the vessel, so materials must be used which can maintain their properties under this bombardment.

If these problems can be overcome, nuclear fusion is an attractive prospect, as it produces much less dangerous waste than nuclear fission; and deuterium, although not the most common isotope of hydrogen, is plentiful enough in natural sources of hydrogen (for example, sea water) to offer cheap and abundant fuel almost indefinitely.

Dangers from nuclear power

The dangers of nuclear power arise from two main factors. Firstly, the by-products of nuclear fission are highly radioactive, meaning that they release ionizing radiation. Secondly, many of these substances have long half-lives, meaning that they remain dangerously radioactive for very long periods of time.

Types of radiation

Nuclei decay in order to stabilize their structure. In general, radioactive decay decreases the neutron/proton ratio of the nucleus in question. There are three types of radiation that are emitted from decaying atomic nuclei: alpha, beta and gamma radiation. The types of radiation differ in their ability to ionize atoms in materials with which they come into contact. If ionizing radiation comes into contact with biological systems it can damage genetic material such as DNA. This can lead to mutations, which in turn can lead to cancers or deformities in unborn children.

Alpha radiation

Alpha radiation is the most harmful type, as alpha particles are relatively heavy, meaning they are more likely to ionize nearby atoms. Alpha particles are composed of two protons and two neutrons – they are helium nuclei. The symbol for an alpha particle is ${}^{4}_{2}\mathrm{He}$ or α.

In the equation below, a uranium-238 nucleus decays by ejecting an alpha particle, forming a nucleus of thorium-234. Note that in doing so, the neutron/proton ratio has decreased from 146 : 92 (or 1.59 : 1) to 142 : 90 (1.58 : 1). In the equation the mass numbers and atomic numbers are conserved.

$${}^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}$$

Alpha radiation is highly ionizing, meaning that it is very likely to damage nearby atoms. However, since it interacts so strongly with material it enters, it is very quickly absorbed by atoms in the material. This makes poisoning by alpha radiation relatively unlikely, since clothing or even human skin is able to prevent alpha radiation penetrating the body. However, if alpha-producing material is ingested or inhaled, then serious radiation poisoning results, as the radiation is able to damage soft tissues inside the body.

Beta radiation

Beta radiation consists of high-energy electrons ejected from the nucleus. However, the nucleus does not normally contain electrons! In fact, a neutron transmutes into a proton and an electron, and the electron is ejected. In this way the neutron number falls by one, and the atomic number (proton number) increases by one. The neutron/proton ratio therefore decreases. The symbol for a beta particle is ${}^{0}_{-1}\mathrm{e}$ or β.

In the following nuclear equation, a caesium-137 nucleus decays into a barium-137 nucleus.

$${}^{137}_{55}\mathrm{Cs} \rightarrow {}^{137}_{56}\mathrm{Ba} + {}^{0}_{-1}\mathrm{e}$$

Beta radiation can penetrate clothing and body tissues. Exposure to beta radiation outside the body is potentially harmful, but inhalation and ingestion is more so.

Gamma radiation

Gamma radiation is a form of electromagnetic radiation. Gamma radiation (sometimes referred to as 'gamma rays') is usually released in addition to either alpha or beta decay, since these decay types often leave the nucleus in an energetically 'excited' state. Energy is emitted in the form of gamma radiation, allowing the nucleus to return to the ground state. The symbol for gamma radiation is γ. In the equation below, iodine-131 decays to xenon-131 with emission of beta and gamma radiation.

$${}^{131}_{53}\mathrm{I} \rightarrow {}^{131}_{54}\mathrm{Xe} + {}^{0}_{-1}\mathrm{e} + \gamma$$

Gamma radiation is weakly ionizing but highly penetrating. It is still able to cause damage to DNA but is more likely to pass straight through tissues without interacting with them.

The likelihood of harm from gamma radiation increases with prolonged exposure, and gamma sources are difficult to shield, since they are able to penetrate metal containers and brick walls. Most radioactive waste is placed in deep storage sites, to prevent radiation harming humans, plants or animals (see below). This is mainly because of the risk of prolonged exposure to gamma rays.

The properties of alpha and beta particles and gamma rays are summarized in Table 24.6.

■ **Table 24.6** Summary of properties of alpha, beta and gamma radiation

Radiation	Relative charge	Relative mass	Nature	Penetration	Deflection by electric field
Alpha particles	+2	4	2 protons and 2 neutrons (He^{2+} ion)	Stopped by a few sheets of paper	Low
Beta particles	–1	$\frac{1}{1837}$	Electron	Stopped by a few millimetres of plastic or aluminium	High
Gamma rays	0	0	Electromagnetic radiation of very high frequency	Stopped by a few centimetres of lead	None

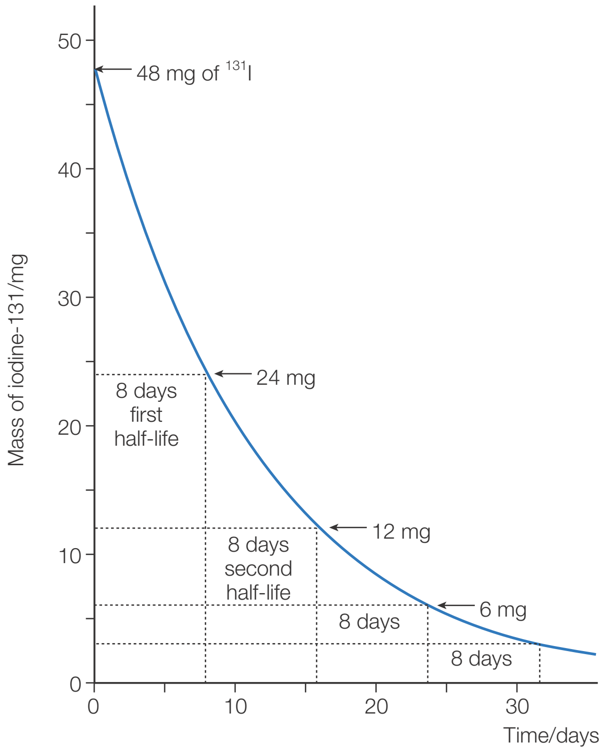


Figure 24.23 Half-life curve for iodine-131

Half-life

The rate at which nuclei undergo radioactive decay varies between chemical elements. Radioactive decay is an exponential process. The rates of radioactive decay are compared using the half-life, which is the time taken for half of the radioactive nuclei to undergo decay.

Each radioisotope has its own unique half-life which is unaffected by temperature or pressure. For example, iodine-131 has a half-life of 8 days. This means that every 8 days the number of radioactive atoms present halves (Figure 24.23).

Waste from nuclear fission contains a mixture of fission products, with nuclei of intermediate size, along with small amounts of actinoids – very heavy elements formed by neutron capture by uranium-238 nuclei. These actinoids, including plutonium and neptunium isotopes, have half-lives of thousands of years. Fission products, such as isotopes of krypton, barium, caesium and strontium, typically have half-lives of less than 100 years. As the radioactive elements in the waste fall into these two distinct categories, at first the radioactivity falls relatively quickly over the first few centuries, as the fission products decay, and then the radioactivity settles to a low but almost constant level for thousands of years. Typically, nuclei with high activity have short half-lives and those with low activity have longer half-lives. Table 24.7 summarizes the half-lives of some isotopes.

Table 24.7 Examples of half-lives of isotopes in nuclear waste

Isotope	Half-life
Fission products	
Iodine-131	8 days
Barium-140	12.7 days
Krypton-85	10.7 years
Strontium-90	28.8 years
Caesium-137	30 years
Actinoids	
Plutonium-239	24 000 years
Plutonium-242	376 000 years
Neptunium- 237	2.2 million years

The presence of actinoids in fission waste creates enormous difficulties for waste disposal. After 100 years the majority of radioactivity from fission products has disappeared, but the presence of actinoids means that the waste is still dangerously radioactive and will be almost indefinitely. Breeder reactors, which can 'burn up' the actinoids in nuclear waste, help solve this problem.

Solution of radioactive decay problems

Half-life calculations

As each half-life elapses, the number of radioactive nuclei in the sample will drop to half of its original value. The amount of radioactive material in the sample after a given time can therefore be calculated.

The equation $N = N_0e^{-\lambda t}$ is given in the *IB Chemistry data booklet*.

N = amount of nuclear material remaining

N_0 = amount of nuclear material present at the beginning

λ = decay constant for the material

t = time elapsed

The equation $t_{\frac{1}{2}} = \frac{\ln 2}{\lambda}$ is also given in the *IB Chemistry data booklet*.
$t_{\frac{1}{2}}$ = half-life
Rearranging the first equation for λ and substituting in the second equation gives:

$$t_{\frac{1}{2}} = t\frac{\ln 2}{\ln\left(\frac{N_0}{N}\right)}$$

Which can also be expressed as $N = N_0\left(\frac{1}{2}\right)^{\textit{no. of half lives}}$

Worked examples

A sample contains 10 g of iodine-131, with a half-life of 8 days. Calculate the mass of iodine-131 remaining in the sample after 24 days.

No of half-lives: $\frac{24}{8} = 3$ half-lives
Mass of ^{131}I in sample after 24 days, $= N = N_0\left(\frac{1}{2}\right)^{\textit{no. of half lives}} = 10 \times (0.5)^3 = 1.25\,\text{g}$

The mass of radioactive carbon-14 in a fossilized mammal bone is 1.16 g. The mass of the same isotope in a recently killed mammal is 18.56 g. The half-life of carbon-14 is 5700 years. How old is the fossilized bone?

Rearranging gives $t = t_{\frac{1}{2}}\frac{\ln\left(\frac{N_0}{N}\right)}{\ln 2} = 5700 \times \frac{\ln\left(\frac{18.56}{1.16}\right)}{\ln 2} = 5700 \times 4.00 = 22\,800$ years

7 Neptunium-237 is an actinoid produced in nuclear reactors. It has a half-life of 2.14 million years. How long will it take for its radioactivity to fall to 10 per cent of its original value?

Discussion of the storage and disposal of nuclear waste

Hazards from radioactive waste

Nuclear accidents or accidental exposure to high-level nuclear waste can result in acute radiation poisoning which results in death within a matter of days. However, the risks of such occurrences are minimized by careful reactor design and regulation of waste disposal. Nonetheless, many people are worried about possible exposure to low levels of radiation over prolonged periods. Such exposure can lead to cancers and birth defects. Concern about the dangers of such exposure leads to local opposition to the siting of nuclear power stations and waste storage facilities.

High-level waste

When the uranium-235 fuel in a reactor is used up, the fuel rods are extremely radioactive. They contain actinoids, such as uranium-234 and plutonium-241 (the f-block on the periodic table consists of actinoids and lanthanoids), which emit alpha particles, and other fission products such as strontium-90 and caesium-137, which emit beta particles and gamma rays, respectively. Much waste also contains plutonium-239, which can be used to make nuclear weapons.

The long half-lives of these materials, combined with their very dangerous levels of radioactivity means that they must be disposed of very carefully. Alpha and beta sources present the most risk when ingested, so it is vital that the materials are well contained and not allowed to enter groundwater.

Some high-level waste is treated by a process called vitrification. The waste is heated in a furnace with broken glass. The resulting liquid glass is poured into steel containers. The glass solidifies into cylinders with the radioactive materials fused into the glass structure, which is fully waterproof. It is thus impossible for the radioactive materials to be washed out if exposed to water.

However, the vitrified waste is still radioactive. It must be stored in places where people are unlikely to accidentally encounter it, and a safe distance from plant and animal life. Much vitrified waste is actually held in temporary storage facilities under guard, but countries such as the USA and Australia are exploring options for burying the waste in very deep bunkers, in isolated areas. The thick surrounding rock will absorb any gamma rays from the waste, minimizing the chances of radiation harming any plant and animal life.

High-level waste such as fuel rods contains radioactive material that, with further processing, could be used as nuclear fuel. Temporary burial allows for the possibility that the waste could be reclaimed in the future when technology makes such reprocessing economically viable.

Low-level waste

The removal of items from nuclear power station sites is carefully controlled. Even materials that have not been near the reactor itself are designated as radioactive waste, and their disposal is monitored. These articles include protective clothing, paper filters and plastic bags. The radioactivity is low level and short lived. Although these materials are classified as radioactive waste as a precautionary measure, they are usually barely more radioactive than normal domestic waste. Such waste is treated in a similar way to municipal solid waste – it is incinerated to reduce its volume and then buried in dedicated landfills.

Medical waste

Radioactive isotopes are used in numerous medical applications. Examples include:

- Use of short half-life substances as medicines or diagnostic tools: iodine-131 is used to treat thyroid cancers, as the thyroid gland absorbs iodine. The radiation is therefore carried to the source of the tumour, killing the cancer cells. The short half-life means that the radiation level falls rapidly, so the rest of the body is not subject to dangerous levels of radiation.
- Use of long half-life substances to generate radiation in machines used for radiotherapy: caesium-137 is used to generate beta radiation, which can be directed in a beam at tumours.
- Long half-life substances such as cobalt-60 and iridium-192 are also used to generate X-rays for radiography.
- Technetium-99m is used as a radioactive tracer. This is a gamma-emitting isotope with a short half-life of only about 1 day. It can be injected into the body and the gamma emission detected by a gamma camera. It is carried by the blood into the organs (for example, the brain, the kidneys or the liver) and can be used to determine blood flow in these regions. Abnormal blood flow might indicate the presence of tumours.

Most radioactive materials used in hospitals have a short half-life which means they are rendered safe by leaving them to decay for some time. Materials used by medical professionals such as clothing and gloves are classified as low-level waste and are disposed of as described above.

Disposal of isotopes from old X-ray or radiotherapy machines is carefully regulated. These materials are buried, as with high-level waste from reactors.

ToK Link

Risk assessment in the nuclear industry

The assessment of risk in the field of nuclear energy presents challenges that illustrate the difficulty of applying a consequentialist (utilitarian) ethical framework.

Under a consequentialist framework, the ethical decision is reached via a 'calculation' of the costs and benefits of an action. When comparing nuclear power with fossil fuels, for example, the difficulty arises when deciding which factors to include in the calculations.

Some commentators suggest that the risks of nuclear power are overemphasized. Even allowing for the victims of prominent nuclear accidents, the number of victims of the fossil fuel industry (for example, coal mining in China or the gas industry in Africa) is far larger. There are also larger-scale externalities to these industries. For nuclear power, these are the risk of accident and the disposal of waste. For fossil fuels, the major issue is climate change. The utilitarian calculation differs depending on what we include: do we just consider the direct impact on human life right now, or do we consider wider implications or possible risks? Should the lives that might be lost in both industries be treated as statistics to be inserted into a formula?

Others resist the utilitarian calculus altogether, and suggest that we should reject nuclear power on principle, as we have a duty not to inflict the waste problem on later generations. Similar arguments could be applied to fossil fuels and climate change, of course.

So how do we decide on the best course of action? There is no simple answer. Various international organizations exist to monitor and police nuclear energy and carbon emissions, but countries are always likely to consider their own interests before those of the wider world. Less economically developed countries want to utilize their fossil fuel resources in order to develop their economies. Other countries might see nuclear energy as a means to ensure their energy security as fossil fuels supplies start to dwindle.

International cooperation in the nuclear industry

The International Atomic Energy Agency (IAEA)

The International Atomic Energy Agency was founded in 1957 with the twin goals of promoting international cooperation in the development of peaceful applications of nuclear energy and policing the proliferation of atomic weapons.

It is essential that international standards exist in nuclear safety, because the harmful effects of a nuclear accident do not respect international borders. After the 1986 accident in Chernobyl, Ukraine, a cloud of radiation led to elevated levels of radioactivity in soil throughout Europe. Subsequently the IAEA performed checks on other countries' nuclear safety standards. A similar process occurred after the Fukushima nuclear accident in 2011.

In the anti-proliferation role, the IAEA is authorized to establish safeguards designed to limit the spread of both nuclear material and information relevant to weapons manufacture.

In both its roles, the IAEA cannot actually prevent sovereign states from contravening international agreements. Instead it aims to work with states to ensure that their own laws regarding nuclear safety meet international standards and that these laws are properly enforced.

International cooperation in particle research

Research into particle physics involves enormously expensive facilities called particle accelerators. The most famous of these is probably the Large Hadron Collider at CERN in Switzerland, which cost around US$ 9 billion, funded by 20 European nations. There are other facilities at Fermilab (near Chicago, USA), SLAC (California, USA) and DESY (Germany).

These facilities offer perhaps the ultimate example of international collaboration in the sciences. Although in one sense they work in competition with one another, their research findings are published in international peer-reviewed journals, and scientists will move from one facility to another to share expertise and gain experience.

Figure 24.24 Architect's rendition of the International Thermonuclear Experimental Reactor in France

The International Thermonuclear Experimental Reactor (ITER)

ITER is an internationally funded project aiming to build a nuclear fusion reactor. Participating countries include India, Japan, China, Russia, South Korea, the USA and as well as the European Union, which hosts the project and is the major funding body.

The reactor is being constructed in the south of France, and will be the largest magnetic confinement fusion reactor in the world (Figure 24.24). The purpose of the reactor is to demonstrate the feasibility of getting more energy out of the fusion reaction than is put in, and to develop containment materials capable of withstanding the intense neutron bombardment of a sustained fusion reaction. It is hoped that the success of ITER will lead to the first commercial fusion reactor.

24.4 Solar energy – *visible light is absorbed by molecules that have a conjugated structure with an extended system of alternating single and multiple bonds, when the electrons within those bonds absorb light energy and are excited to higher energy levels. Solar energy can be converted to chemical energy in photosynthesis*

Nature of Science

Science, technology and public understanding

The field of solar energy can be used to exemplify two important aspects of scientific endeavour.

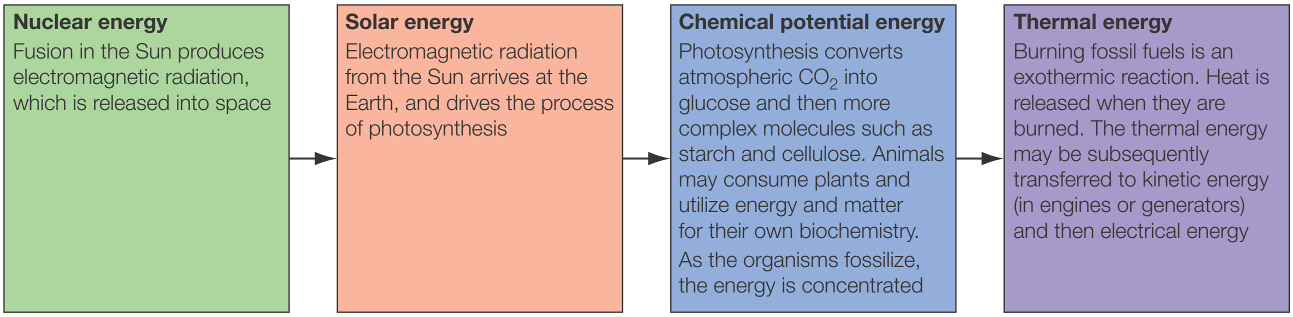
The first is the relationship between science and technology. Frontier research on solar cells is reliant on highly specialized experimental design that proceeds incrementally as the efficiency of such solar cells is measured and evaluated and successful designs carried forwards. In contrast, the technological side is more concerned with how the science will actually be used, and ensuring that it can be applied in cost-effective ways. Real-world solar panels must be as reliable as possible, as cheap as possible and as aesthetically pleasing as possible.

The second is the public understanding of science, and how that understanding is reached. It is widely understood that biofuels are desirable, as they are potentially carbon neutral and therefore offer a solution to climate change. This is a reassuring prospect. This view of biofuels has been heavily promoted by industry and by governments keen to demonstrate action against climate change. This is in contrast to the actual situation, in which the advantages of biofuels must be balanced against the impact on food production and biodiversity. Such a view of solar energy and biofuels cannot be conveyed in a sound bite and is a much more difficult concept to present to the public.

Solar energy

The phrase 'solar energy' probably prompts thoughts of solar panels capturing sunlight as part of a 'green' electricity-generation project. Indeed, research is progressing in this area, and the technology used to convert sunlight into electricity will be studied in Section 24.8.

However, energy that originated in the Sun is already widely used. Fossil fuels can be thought of as concentrated solar energy, as the photosynthetic process that drove the capture of atmospheric carbon into living organisms was powered by sunlight. As the living things decayed, the energy density of the dead organisms increased, until the fossil fuels we use today were produced (Figure 24.25).



Nuclear energy
Fusion in the Sun produces electromagnetic radiation, which is released into space

Solar energy
Electromagnetic radiation from the Sun arrives at the Earth, and drives the process of photosynthesis

Chemical potential energy
Photosynthesis converts atmospheric CO_2 into glucose and then more complex molecules such as starch and cellulose. Animals may consume plants and utilize energy and matter for their own biochemistry.
As the organisms fossilize, the energy is concentrated

Thermal energy
Burning fossil fuels is an exothermic reaction. Heat is released when they are burned. The thermal energy may be subsequently transferred to kinetic energy (in engines or generators) and then electrical energy

Figure 24.25 The historical energy transfers involved in the burning of fossil fuels

Photosynthesis

Fossil fuels are non-renewable, meaning that they will not be replenished within human time scales, as fossilization takes many millennia.

However, plants are still photosynthesizing and converting solar energy into chemical potential energy. Can the chemical energy in plants be efficiently converted into useful fuels?

The biochemical processes in photosynthesis:

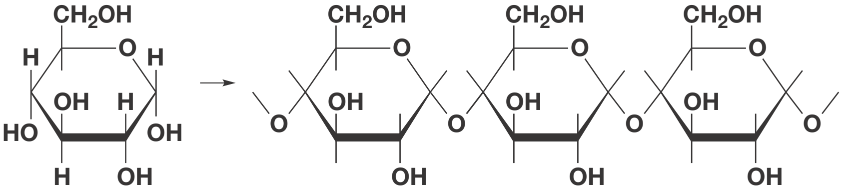
Photosynthesis converts atmospheric carbon dioxide and water vapour into glucose and oxygen:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

Glucose is a carbohydrate – a molecule containing carbon, hydrogen and oxygen, with the general formula $C_n(H_2O)_m$, where n and m are integers, but not necessarily having the same value. For glucose, m and n are both 6: $C_6H_{12}O_6$ can be written $C_6(H_2O)_6$. For sucrose, $C_{12}H_{22}O_{11}$, m is 12 and n is 11: $C_{12}(H_2O)_{11}$.

Plants consume glucose as a source of energy during respiration. Glucose is a monosaccharide molecule that can be polymerized into starch chains via condensation reactions, which the plant uses as an energy store (Figure 24.26).

Figure 24.26 Polymerization of glucose forming starch



Plants also use glucose as a structural ‘building block’: glucose molecules combine together to make cellulose, a tough, fibrous substance, which is used to make cell walls (Figure 24.27).

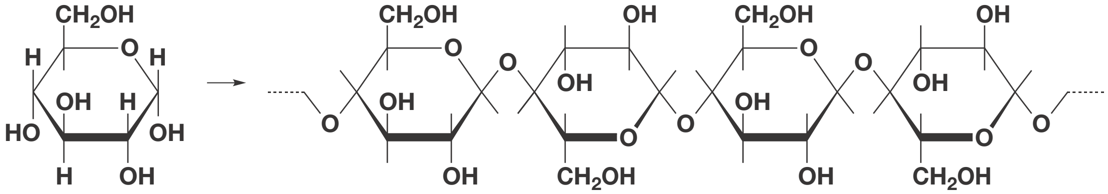


Figure 24.27 Formation of cellulose from glucose

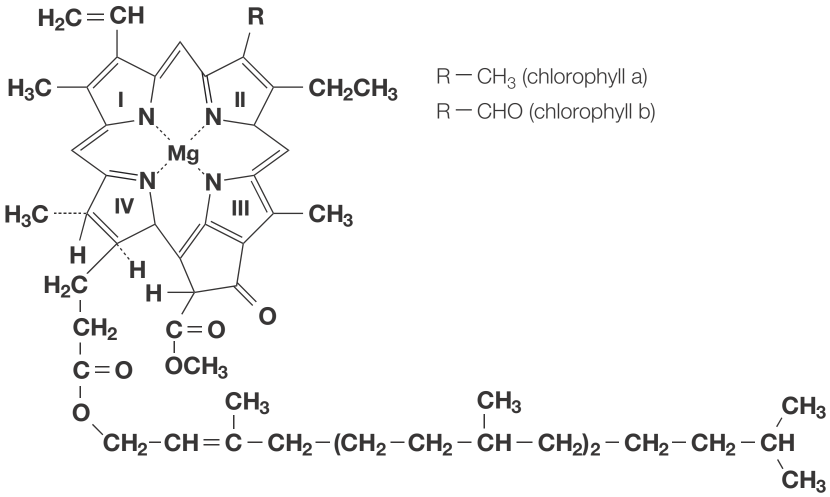
The structures of cellulose and starch are in many ways quite similar. However, they are sufficiently different that enzymes in the digestive systems of living organisms cannot break down both. Close inspection of the two structures reveals that the orientation of the glucose monomers is different in each structure.

Photosynthesis happens inside plant cell structures called chloroplasts, which are disc-shaped organelles (cell organs) adapted for harvesting light energy.

Absorption of light by chlorophyll

Chloroplasts contain a molecule called **chlorophyll**, which is a very efficient absorber of sunlight. Chlorophyll is a **pigment** – a coloured molecule. It is coloured because it absorbs some of the wavelengths present in white light, with the remaining wavelengths being reflected. Chlorophylls absorb light most strongly in the red and violet parts of the visible spectrum. The green part of the spectrum is poorly absorbed, so when white light (which contains the whole visible spectrum) shines on to leaves, the green light is reflected, meaning that the leaves appear green.

Chlorophyll actually exists in two slightly different forms (chlorophyll a and chlorophyll b; Figure 24.28), which absorb slightly different wavelengths. This means that they appear as slightly different shades of green.



R – CH₃ (chlorophyll a)
R – CHO (chlorophyll b)

Figure 24.28 Structure of chlorophyll

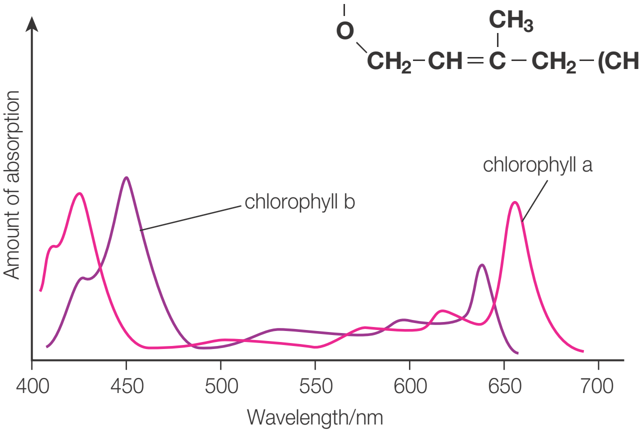


Figure 24.29 Absorption spectra of chlorophylls a and b

Both types of chlorophyll have strong absorption at each end of the spectrum (Figure 24.29). However, chlorophyll a has its largest absorbances around the 430 nm mark which corresponds to the blue–violet region and the 670 nm mark which is in the red region. Chlorophyll b has its strongest absorbances at about 455 nm (blue) and 640 nm (the orange end of the red region). The different proportions of blue, violet, red and orange absorbed leads to us perceiving chlorophyll a as blue–green and chlorophyll b as yellow–green.

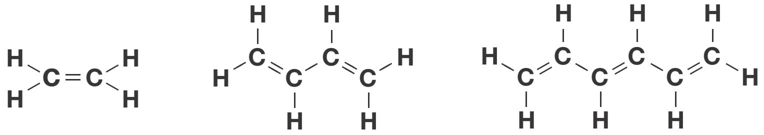
Identification of features of the molecules that allow them to absorb visible light

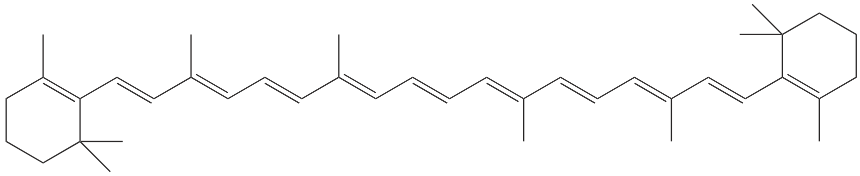
Chlorophylls are members of a family of molecules called **porphyrins**, which feature four **pyrrole** groups (five-member carbon rings containing a nitrogen atom) joined together by alternating carbon–carbon single and double bonds. This structure is called a **tetrapyrrole**. The four nitrogen atoms are held in place in the centre of the molecule, where they are able to bond to metal ions using dative bonds. The porphyrin molecule acts as a polydentate ligand (Chapter 13) forming a complex with the central metal ion. In chlorophyll the central metal ion is an Mg^{2+} ion.

Metal ions complexed by porphyrins feature in a number of biological systems. The iron(II) ion complexed by a heme group in hemoglobin is another example (Section 23.9).

Both forms of chlorophyll feature an extensive system of alternating single and double bonds, within the pyrrole rings and between them via the connecting linkages. Such a system of bonds is called a conjugated system, and it allows for delocalization of the π electrons over large parts of the molecule. Figure 24.30 shows a series of molecules with increasing amounts of conjugation. The chlorophyll porphyrin therefore features π molecular orbitals above and below the plane of the molecule. It is this π system which is responsible for the colour of chlorophyll and other porphyrin pigments.

Figure 24.30 Molecules showing increasing amounts of conjugation


ethene buta-1,3-diene hexa-1,3,5-triene


β-carotene

When light is shone on to an unsaturated organic molecule, one of the π electrons may be excited to a higher energy level called π*. The energy needed to promote the electron to this higher level corresponds to a photon of a specific wavelength. For most π bonded molecules, these photons are in the ultraviolet region, so there is no effect on the visible light region, and the molecule is colourless. However, as more conjugated π bonds are added, the energy of the photons absorbs falls, as the π* levels decrease in energy. This means that the wavelengths absorbed increase until they appear in the visible region. Therefore, molecules with large conjugated systems absorb visible radiation, making them coloured.

Table 24.8 shows some examples of maximum absorption wavelengths (λ_{max}) for a series of organic molecules with increasing amounts of conjugation.

Table 24.8 Maximum absorption wavelength, λ_{max}, for a series of organic molecules

Molecule	λ_{max}/nm	Colour
Ethene	175	Colourless (absorbs in ultraviolet)
Buta-1,3-diene	217	Colourless (absorbs in ultraviolet)
Hexa-1,3,5-triene	258	Colourless (absorbs in ultraviolet)
β-carotene *(11 conjugated C=C bonds)*	approximately 450	Orange (absorbs blue–violet)
Chlorophyll a	approximately 650	Blue–green (absorbs red)

Chlorophyll a and chlorophyll b have different values of λ_{max} because of the slight differences in their structures. Figure 24.28 shows that chlorophyll a has a methyl ($-CH_3$) group attached to the second pyrrole ring, whereas chlorophyll b has an aldehyde group ($-CHO$) in the same position.

This slight difference changes the energy difference between the π energy level and the excited π* level, which changes the wavelengths of light absorbed, changing the colour of the molecule.

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What does chlorophyll do?

Chlorophyll a is the molecule that most green plants use to capture the Sun's energy. Look again at the structure of chlorophyll a. In addition to the porphyrin group discussed above, it has a long hydrocarbon 'tail'. Recall that chlorophyll molecules are found inside cell structures called chloroplasts. These chloroplasts carry many chlorophyll molecules, grouped together.

Imagine the porphyrin part of a chlorophyll a molecule as the 'head'. The porphyrin is planar (flat) so if placed face-on towards the light source it can capture sunlight effectively. The hydrocarbon 'tail' helps to position the porphyrin, like the handle of an umbrella. The hydrocarbon tails are embedded into the chloroplast membranes and hold the porphyrins in place.

A chloroplast contains hundreds of thousands, possibly millions, of chlorophyll molecules embedded in protein scaffolds in its membrane, which 'harvest' light energy. Each chlorophyll a absorbs photons of red light. The energy is channelled along the chloroplast membrane, from chlorophyll to chlorophyll, until it reaches a 'reaction centre' where it powers photosynthesis.

Chlorophyll a fulfils a dual role:

1. It captures photons efficiently, owing to its shape.
2. It uses the energy from the light to initiate the photosynthetic process.

Photosynthesis is a redox reaction, which can be split into two half-reactions as follows:

Step 1: the oxidation of water:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Step 2: the reduction of carbon dioxide to carbohydrate (eventually glucose):

$$4e^- + 4H^+ + CO_2 \rightarrow (CH_2O) + H_2O$$

Addition of the two half-reactions gives:

$$H_2O + CO_2 \rightarrow (CH_2O) + O_2$$

Which generalizes to:

$$nH_2O + nCO_2 \rightarrow (CH_2O)_n + nO_2$$

Each of the two half-reactions requires energy input from sunlight. Chlorophyll molecules in different regions of the chloroplast carry out the two processes.

The presence of chlorophyll b in plants broadens the range of light wavelengths that can be absorbed, so chlorophyll b tends to be present in higher concentration in 'shade-adapted' chloroplasts – those which function better at lower light levels.

8 Photosynthesis involves the reduction of carbon dioxide to glucose. Deduce the oxidation numbers of carbon in carbon dioxide and glucose. Take the oxidation numbers of hydrogen as 1 and oxygen as –2.

Additional Perspective

Photosystems

Chlorophyll molecules act as 'light-harvesters' which provide energy to drive the reduction of carbon dioxide to carbohydrates. This requires the formation of an actual chemical species which will act as the reducing agent. This process occurs in reaction centres called photosystems, of which there are two types, called PSI and PSII. The two systems absorb light of slightly different wavelengths and are linked together by a series of reactions in which PSII transfers electrons to PSI. A PSII complex might contain 100–250 chlorophyll molecules, and there will be hundreds of photosystems on each of hundreds of membranes in each chloroplast, leading to millions of chlorophyll molecules in a chloroplast. Figure 24.31 shows a PSII supercomplex.

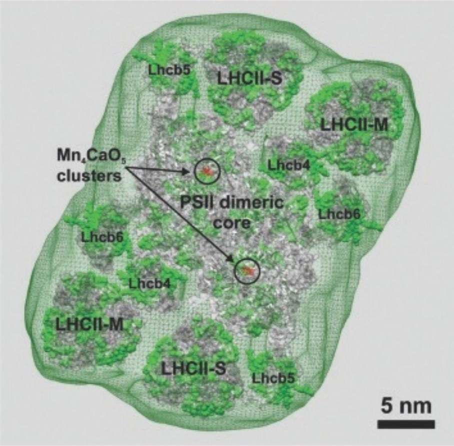


Figure 24.31 An electron micrograph of a PSII supercomplex. In this diagram, the individual chlorophyll molecules (about 220 of them) are shown as green spheres

During the electron transfer processes in the photosystems, water is oxidized to oxygen in PSII and the electrons released are fed into PSI. PSI then takes these electrons and uses them to reduce an electron acceptor molecule, A. The structure of molecule A is not fully known.

The reduced form of molecule A, A^-, is then able to reduce carbon dioxide to glucose elsewhere in the plant. Figure 24.32 shows the action of photosystems I and II.

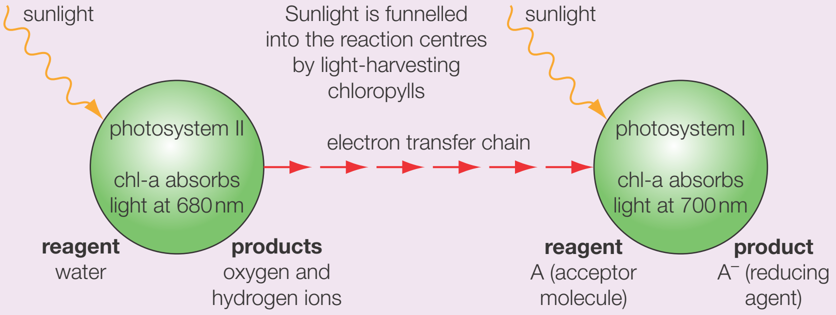


Figure 24.32 Photosystems I and II; chl-a refers to chlorophyll a

Using the stored energy in plants: biofuels

Ethanol

Ethanol (C_2H_5OH) is a biofuel made by fermentation of glucose. It is most widely used in Brazil and the USA, where crops such as corn (maize) and sugar cane are used as the source of glucose.

Fermentation is carried out by single-celled fungi called yeasts, which use an enzyme called **zymase** to convert glucose molecules into ethanol molecules, with production of carbon dioxide:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

The glucose is added to the yeasts in a vessel called a **bioreactor**. The reaction is exothermic, so the temperature must be carefully controlled so that it does not get too hot, denature the enzyme and kill the yeasts.

Fermentation produces a solution of ethanol, along with side products such as aldehydes and other alcohols. The maximum achievable ethanol concentration is limited to about 15 per cent as concentrations higher than this will poison the yeasts.

The mixture is distilled to remove side products and remove the water, increasing the ethanol concentration.

Evaluation of the advantages and disadvantages of the use of ethanol

Advantages of ethanol

- *Lower greenhouse emissions:* ethanol has been enthusiastically adopted in some countries as a means of lowering greenhouse gas emissions. Ethanol does produce carbon dioxide when burned:

  $$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

  However, the carbon in the ethanol was absorbed from the atmosphere by the plants used to make the ethanol, as they grew, so theoretically the ethanol is 'carbon neutral'.
- *Reduced oil use:* ethanol is widely used in Brazil as sugar cane is a large-scale crop there. Since 1976 it has been mandatory to blend ethanol with gasoline, as a way of reducing oil use. Many vehicles sold in Brazil are designated 'flex-fuel', because they can run on a wide range of blends, ranging from almost pure ethanol to almost pure gasoline. In the USA, most new cars sold can run on gasoline containing 10 per cent ethanol, which means that in areas where ethanol is widely available, oil use (and so carbon footprint) per person will decrease.

Disadvantages of ethanol

- *Lower specific energy and potential damage to engines:* ethanol has a lower specific energy than gasoline. Approximately 1.5 litres of ethanol is required to provide the equivalent energy of 1 litre of gasoline. Unlike gasoline, ethanol absorbs moisture from the atmosphere, which can lead to engine corrosion. Blended fuels containing ethanol and gasoline are more prone to causing engine damage than pure gasoline.
- *High embodied energy:* although ethanol is a renewable fuel, as sugar crops can be quickly replenished, ethanol production is criticized for being energy intensive. Ethanol from bioreactors must be distilled which requires large amounts of energy. By some calculations, when the processing is taken into account, use of ethanol does not actually reduce greenhouse gas emissions relative to traditional gasoline.
- *Food versus fuel debate:* when maize (corn) is used as a source of ethanol, as in the USA, critics claim that the price of maize on world markets is forced up, making poorer countries more likely to export their staple food crops and leaving their own populations vulnerable to hunger. However, others argue that the majority of world maize production is used for animal feed, so the impact of maize-based ethanol on human food production is minimal.

Use of gasoline and ethanol mixtures in different countries – the E nomenclature

Most cars in the USA can run on 'E10' – gasoline containing 10 per cent ethanol by volume. In corn-producing regions of the USA, higher proportions of ethanol are common: E85 is widely available.

In Brazil, some vehicles run on 100 per cent ethanol (E100), but an ethanol content of at least 18 per cent (E18) is mandatory for all gasoline vehicles.

In Sweden, flex-fuel vehicles are available which run on a wide range of gasoline–ethanol blends, from pure gasoline (E0) up to E85. Such vehicles rely on electronic engine management systems, which adjust the spark and inlet valve timings according to the fuel composition, to prevent knocking (pre-ignition) in the engine.

Biodiesel

Diesel engines run on a much heavier crude oil fraction than gasoline. Whereas gasoline is composed of hydrocarbons with about eight carbon atoms, diesel fuels contain longer hydrocarbons, typically 14–20 carbon atoms. Diesel is therefore more viscous and less volatile than gasoline.

Ethanol is not a suitable fuel for vehicles with diesel engines because it is less viscous and much more volatile than diesel, so the vehicle's fuel system would need to be extensively modified. Also, ethanol has a much lower energy density than diesel.

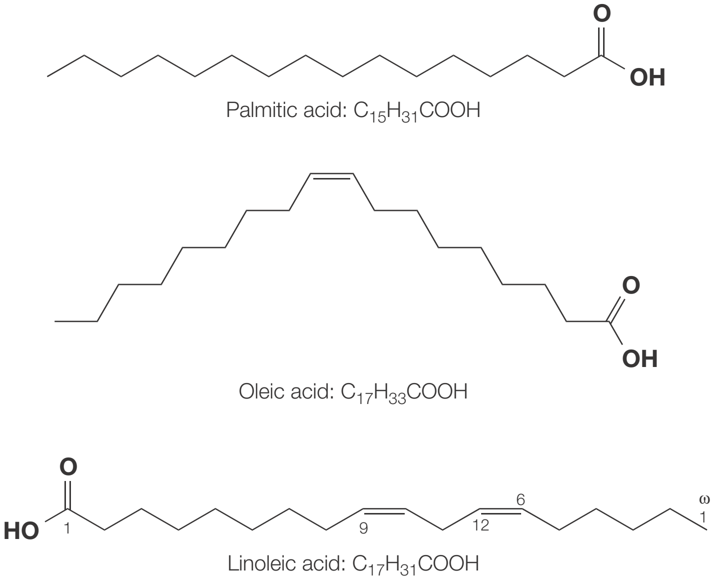
However, there are plant-based fuels that are much closer to diesel in their properties. These fuels are derived from vegetable oils and are commonly called biodiesels.

The structures of vegetable oils

Fats and oils are examples of **lipids**, naturally occurring biochemical molecules found in both plants and animals. In plants, lipids are more often liquids and are called oils. In animals, lipids are more often solid and are called fats.

Lipids are esters of propane-1,2,3-triol (glycerol) and long-chain carboxylic acids called **fatty acids** (Figure 24.33). Glycerol has three hydroxyl groups, each of which performs a condensation reaction with a fatty acid molecule, with a water molecule being eliminated. Figure 24.34 shows an example of the formation of a lipid.

In this example the three fatty acid chains are identical saturated molecules with 18 carbon atoms (octadecanoic acid). Such molecules are called **triglycerides**. However, the three fatty acids may be different from one another and may be unsaturated.



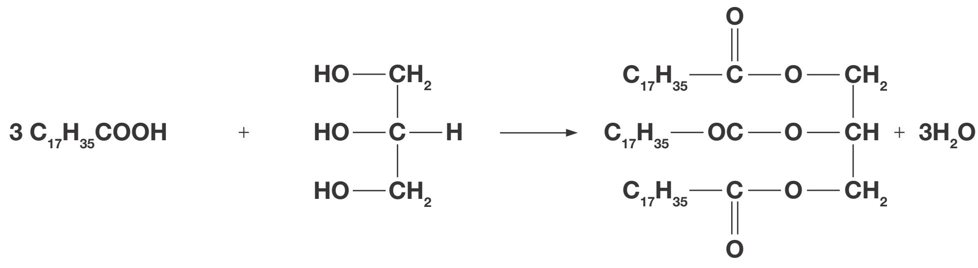
Palmitic acid: $C_{15}H_{31}COOH$

Oleic acid: $C_{17}H_{33}COOH$

Linoleic acid: $C_{17}H_{31}COOH$

Figure 24.33 Some commonly occurring fatty acids

Figure 24.34 The formation of a lipid



octadecanoic acid (stearic acid)

propane-1,2,3-triol (glycerol)

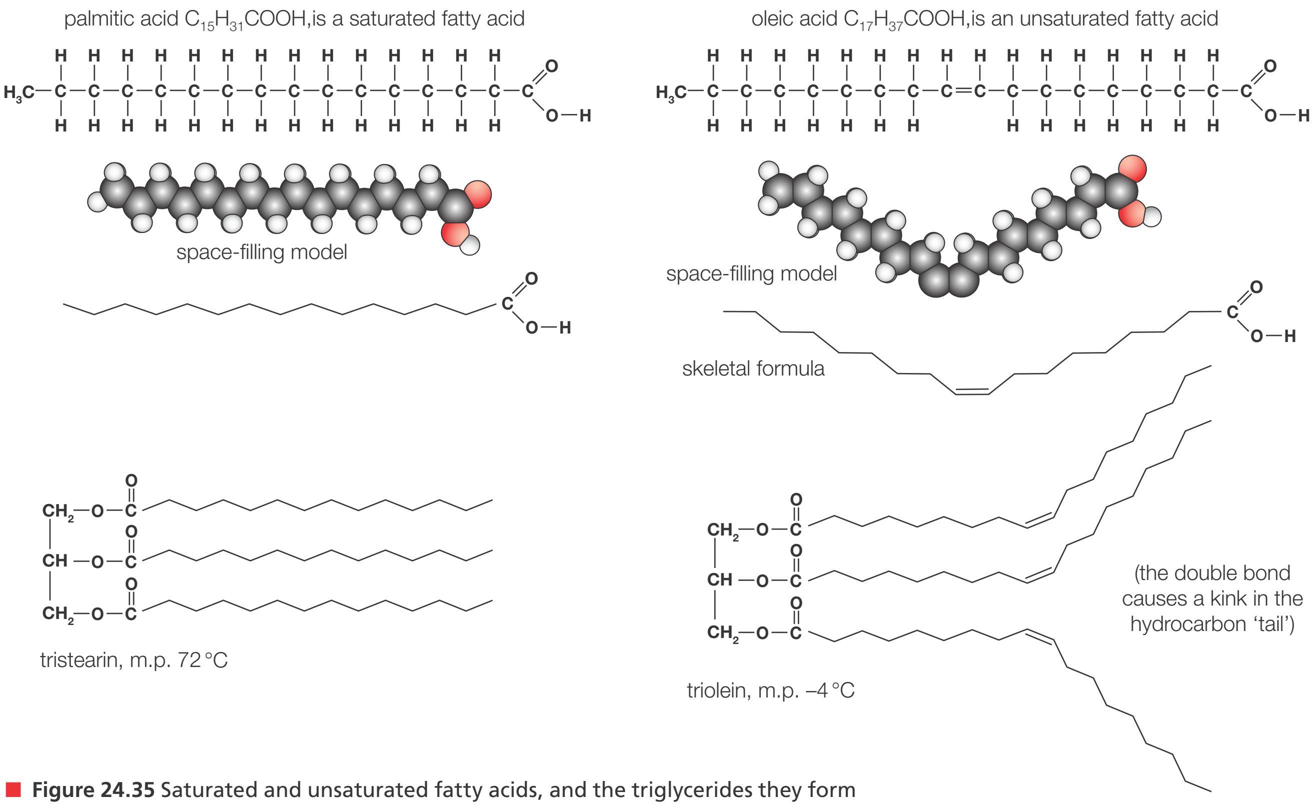
propane-1,2,3-triyl trioctadecanoate (tristearin)

In plant oils, the fatty acids are more commonly mono-unsaturated (with one carbon–carbon double bond) or poly-unsaturated (with several double bonds). Table 24.9 lists some examples.

Table 24.9 Composition of some vegetable oils

Oil	Approximate composition of triglyceride
Olive oil	Up to 80% palmitic acid Up to 20% linoleic acid Up to 20% oleic acid
Canola oil	Approximately 60% oleic acid Approximately 20% linoleic acid Plus others including up to 7% saturated fatty acids
Palm oil	Approximately 44% palmitic acid Approximately 39% oleic acid Approximately 10% linoleic acid Plus others

Lipids with unsaturated fatty acids have lower melting points than those with saturated fatty acids. The presence of the double bond introduces a 'kink' in the carbon chain. The fatty acid chains are less able to lie closely alongside one another, so the dispersion forces are weaker. Lipids with unsaturated fatty acids are therefore likely to be liquid at room temperature. Figure 24.35 illustrates the structures of saturated and unsaturated lipids:



■ **Figure 24.35** Saturated and unsaturated fatty acids, and the triglycerides they form

The properties of vegetable oils

Vegetable oils are extracted by pressing the fruit or the seeds of plants. For example, palm oil is made from the fruit pulp, and canola oil is made from the seeds of rapeseed or field mustard plants. Olive oil is made by pressing whole olives – the fruit of the olive tree.

When extracted, vegetable oils are more viscous, but their energy densities are close to fossil fuel diesel (Table 24.10). Some older diesel engines are able to use untreated vegetable oils directly. This is referred to as straight vegetable oil (SVO). In Germany it is possible to buy a kit to modify the fuel system of a diesel vehicle so that SVO is preheated to lower the viscosity before it enters the engine. A vehicle so modified is able to run on used cooking oil.

■ **Table 24.10** Energy density of fossil fuels compared with plant-derived fuels

Fuel	**Energy density/MJ dm^{-3}**
Gasoline	46
Diesel	43
Sunflower oil	33
Commercial biodiesel	33–35

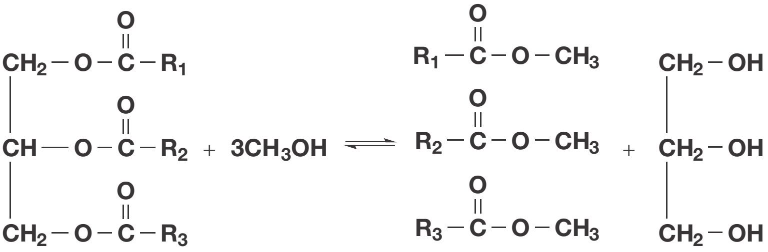
More modern turbocharged diesel engines cannot tolerate the higher viscosity, and so the vegetable oil must be chemically treated to lower the viscosity.

Transesterification of vegetable oils

The high viscosity of vegetable oils arises from their high relative formula masses and the long-chain fatty acid chains present, which leads to strong dispersion forces. To lower the viscosity of the oils, the approach taken is to break up the triglyceride into fatty acid esters and glycerol, by a process called **transesterification**.

Transesterification involves reacting the triglyceride with methanol or ethanol, replacing the glycerol in the esters with alcohol molecules and freeing the glycerol. The products are three methyl or ethyl ester molecules and a glycerol molecule (Figure 24.36).

Figure 24.36 Transesterification of a triglyceride with methanol, producing methyl esters and glycerol



The reaction is catalysed by a strong acid such as sulfuric acid, or a strong base such as potassium hydroxide. Esterification reactions are covered in Chapter 10.

The equation in Figure 24.36 shows that three moles of methanol (or ethanol) should be used for the transesterification process. However, as the reaction is in equilibrium, in commercial manufacture about 6 moles of methanol are provided per 1 mole of triglyceride. By applying Le Châtelier's principle, we see that this has the effect of shifting the equilibrium to the right, which increases the yield of methyl esters. Excess methanol is then recovered and recycled into the reaction vessel.

The transesterification process is often incomplete, meaning that some of the triglycerides are broken down into fatty acids which do not then re-esterify with the added methanol or ethanol. The resultant mixture therefore has some fatty acids present in it.

Deduction of equations for transesterification reactions

If ethanol is used for the transesterification reaction, then ethyl esters will be formed. If methanol is used then methyl esters will be formed.

Worked example

Olive oil is largely composed of triglycerides of palmitic acid, $C_{15}H_{31}COOH$. Deduce the equation for transesterification with methanol of this triglyceride.

The triglyceride can be expressed as $(C_{15}H_{31}COO)_3CH(CH_2)_2$

Three methanol molecules are used in the transesterification process:

$$(C_{15}H_{31}COO)_3CH(CH_2)_2 + 3CH_3OH \rightleftharpoons \underset{\text{methyl palmitate}}{3C_{15}H_{31}COOCH_3} + \underset{\text{glycerol}}{CH_2OHCHOHCH_2OH}$$

Explanation of the reduced viscosity of esters produced with methanol and ethanol

The mixture of substances present after transesterification has broadly similar chemical bonds and functional groups within it as the original vegetable oil, so the energy density of the mixture remains close to fossil fuel diesel. However, the molecules within it are much smaller than the original triglycerides, meaning that the dispersion forces in the mixture are weaker.

9 Deduce the transesterification reaction, using ethanol, of a triglyceride of linoleic acid, $C_{17}H_{31}COOH$.

Evaluation of the advantages and disadvantages of biodiesel

Many of the advantages and disadvantages of ethanol fuel, discussed above, can also be applied to biodiesel. Briefly:

Advantages:

- decreased fossil fuel use
- potential for lower greenhouse emissions, but this is open to question.

Disadvantages:

- lower specific energy than the fossil fuel equivalent
- displacement of food crops by crops grown specifically for fuel
- high embodied energy in biodiesel, because extensive processing is required.

Another particular point of controversy surrounding biodiesel is **loss of biodiversity**. In South-East Asian countries such as Malaysia and Indonesia, large areas of primary tropical rainforest have been logged for timber and then replaced with a monoculture based on palm oil production (Figure 24.37). Palm oil is an extremely important oil for food uses around the world but can also be processed for biodiesel. Palm oil plantations consist of very large areas of land planted with palm trees in continuous rows. Primary rainforests contain an enormous range of trees and other plants, which support a complex ecosystem of insects, birds and mammals. Many of these organisms cannot survive in a palm oil plantation. As plantations grow and rainforests shrink, the numbers of organisms that can be supported will fall. Governments in Indonesia and Malaysia are under pressure from environmental groups to protect regions of primary rainforest in order to prevent widespread extinctions. However, the palm oil industry is hugely important economically. It provides employment not only on plantations but also in associated transport and infrastructure projects to support the industry, and it also provides export income for the countries concerned. The rise of biodiesel as a popular 'green' fuel in economically developed countries is potentially a driver for environmental harm in less developed countries.

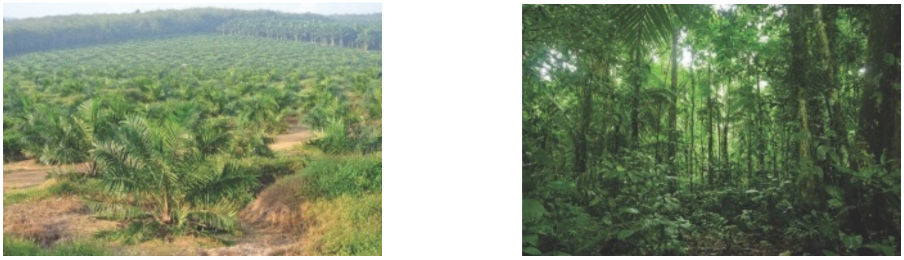


Figure 24.37 a Palm oil plantation in Malaysia; **b** primary rainforest in Borneo, Malaysia

ToK Link

Cold fusion

In 1989, two chemists at the University of Utah made a spectacular announcement: they had achieved nuclear fusion at room temperature. Had this claim proven true, the world might have entered a new era of unlimited clean energy.

Stanley Pons and Martin Fleischmann had devised an experiment involving the electrolysis of heavy water. Heavy water is water in which the hydrogen atoms are replaced with atoms of deuterium. During the electrolysis of water, hydrogen is liberated at the cathode (the negative electrode). However, in Fleischmann and Pons' experiment, the cathode was made of the element palladium, which has an unusual property: palladium is able to absorb hydrogen atoms. The metal absorbs atoms of hydrogen, and the hydrogen atoms fill up spaces in the palladium crystal structure. So effective is this process that a piece of palladium is able to absorb 900 times its own volume of hydrogen. When Fleischmann and Pons connected their apparatus, they reported spikes of intense heat in the apparatus: more energy than was being pumped in by the electrical supply.

The university recognized the implications immediately and encouraged the chemists to announce their findings in a press conference. Fleischmann and Pons speculated that the palladium was packing the deuterium atoms in so tightly that they were fusing together, producing enormous amounts of heat.

Although deuterium is a relatively rare form of hydrogen, there is so much water on Earth that 'cold fusion', as it was dubbed, could solve all the world's energy problems.

What Fleischmann and Pons had not done, however, was remove the inaccuracies in their experiment. The energy spikes were erratic and not reliably reproducible in subsequent experiments. Other research institutions around the world seized on cold fusion and tried to reproduce the results, with little success.

Within weeks of their press conference, Pons and Fleischmann's work had been comprehensively discredited, and the pair were castigated in the scientific press. Today, research in the area of cold fusion is extremely limited as funding institutions are reluctant to associate themselves with such a high-profile failure. This is despite the fact that Fleischmann and Pons' energy spikes have not been fully explained.

Scientific research runs into dead ends like this all the time. Most scientists are able to refine and improve their work, or move on to other projects. Unless results are deliberately falsified, it takes a lot to completely lose a scientific reputation. Why were Fleischmann and Pons treated so harshly? One factor is the way that cold fusion was announced. The normal way of presenting new scientific research is via a peer-reviewed journal. Articles are prepared and are scrutinized by experts in the field, before publication. The cold fusion press conference, although it made an enormous impact, was viewed as arrogant by other researchers – an attempt to circumvent the normal review process. Fleischmann has since claimed that he wanted to publish the research in the normal way, but the university pressured him into the press conference for publicity reasons.

Another problem was that Pons and Fleischmann were reluctant to issue all the technical details of their work. In peer review, a very detailed account of the experiment is provided for the express purpose of allowing others to attempt to replicate the data. This is seen as a necessary part of scientific endeavour. Fleischmann and Pons' approach left them open to further accusations of 'glory-seeking' – as if they wanted all the credit for cold fusion in the future.

The cold fusion affair raises some interesting questions about scientific enquiry:

- Peer review is sometimes criticized as a rather 'closed' way of recording scientific discoveries. In the internet age, some believe that all research findings should be freely available. What might the implications of this be?
- The lack of reproducibility of Fleischmann and Pons' work led to its being discredited. Why do scientists place such great emphasis on reproducibility?

24.5 Environmental impact – global warming – *gases in the atmosphere that are produced by human activities are changing the climate as they are upsetting the balance between radiation entering and leaving the atmosphere*

Nature of Science

Climate science as a transdisciplinary endeavour

The study of global warming and its likely effects is highly transdisciplinary, encompassing aspects of biology, chemistry, physics and geology.

Atmospheric chemists study the composition of the atmosphere. In order to do so they use a combination of direct measurement, laboratory work and computer modelling.

Direct measurement can be carried out by using aircraft to collect samples of the atmosphere or using spectroscopic methods to assess the concentration of different compounds. Laboratory experiments allow the kinetics of atmospheric chemical reactions to be studied. Atmospheric and experimental data can then be used to set the parameters for a computer model which will attempt to predict future changes in the composition of the atmosphere and its interaction with electromagnetic radiation.

Atmospheric physicists study these interactions with electromagnetic radiation, and also use statistics in developing more advanced climate models. The National Aeronautics and Space Administration (NASA) in the USA has some of the most advanced climate models in the world.

Biologists also play a part as they explore the natural processes involved in sustaining carbon dioxide levels, and the impact of global warming on different ecosystems. Geologists employ an understanding of volcanic emissions to the atmosphere.

Experts in all these fields, from countries all over the world, contribute to our understanding of climate change.

Climate treaties

The Intergovernmental Panel on Climate Change (IPCC) was established by the United Nations in 1988. Its purpose is to study anthropogenic (man-made) climate change, its likely impacts and possible solutions.

The IPCC is a collaborative endeavour. A volunteer team of scientists, numbering thousands, assesses the peer-reviewed literature on climate and prepares summary reports which are then reviewed by governments. The IPCC then publishes a summary report that sets out its recommendations based on this broad review of literature.

The IPCC report is used to inform action on global warming. The United Nations Framework Convention on Climate Change (UNFCCC) is an international treaty that draws on the conclusions and recommendations of the IPCC report. The most well-known outcome of the UNFCCC was the Kyoto Protocol of 1997 – a binding agreement to control carbon dioxide emission levels. Kyoto was extended at another conference in Doha, Qatar in 2012.

Although over 190 countries signed up to Kyoto, not all the major carbon-emitting states agreed to be bound by it. The most famous was the USA, which withdrew from Kyoto as a protest against what it saw as insufficient demands upon developing economies such as China.

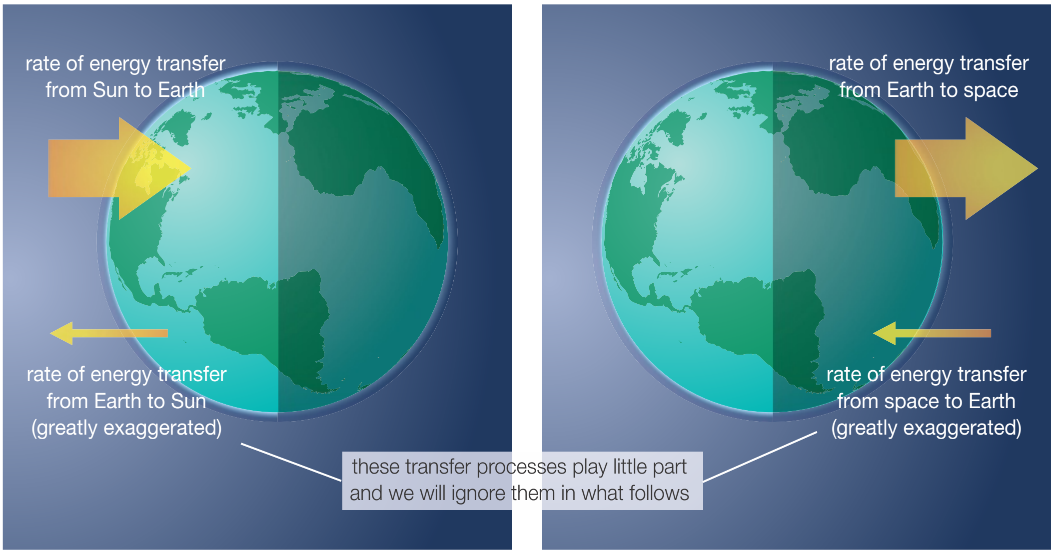
Another major climate treaty is planned for 2020, when the success or failure of Kyoto and Doha will be assessed in detail.

The greenhouse effect

The **greenhouse effect** is often referred to as the cause of the phenomenon of **global warming**, in which the average temperature of the Earth rises, causing various environmental disasters. In fact the greenhouse effect is a necessary mechanism for maintaining the Earth's temperature at a habitable level. However, it is thought that human activity is disrupting the natural equilibrium in the atmosphere, causing warming of the planet.

The average temperature of the troposphere at sea level is 14–15°C, but varies with location (the tropics are hotter than the poles, for instance). This average temperature is maintained because the energy incident on the Earth (coming from the Sun) is balanced by the energy leaving the Earth and escaping into space (Figure 24.38).

Figure 24.38 The greenhouse effect of the Earth's atmosphere



Most of the radiation from the Sun is in the visible region, with some at invisible longer wavelengths close to the visible region (known as near infrared), and a smaller amount at shorter wavelengths close to the visible region (near ultraviolet).

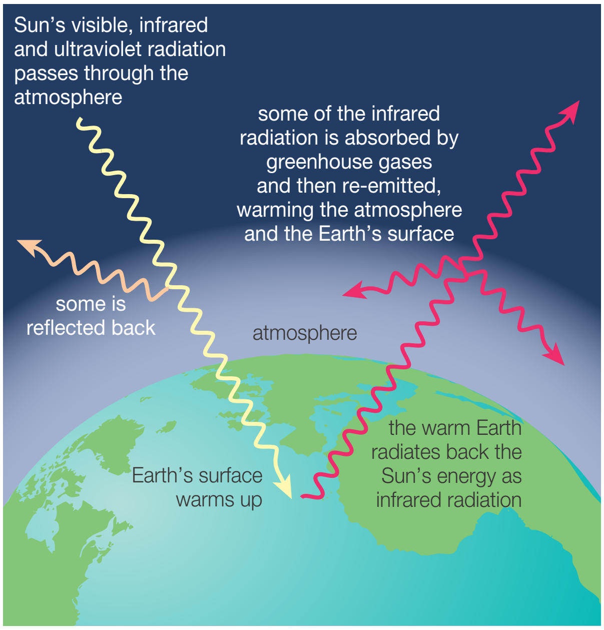
If all this radiation reached the Earth's surface, the average temperature would be intolerably hot. In fact only about 47 per cent of the energy reaches the surface; the remainder is reflected back into space by the atmosphere and clouds, or is absorbed and retained by the atmosphere.

The peak of the incoming radiation has a wavelength in the visible region at around 500 nm. This wavelength is not absorbed to a significant extent by any of the major atmospheric gases (oxygen, nitrogen or argon), or even the less abundant gases (carbon dioxide or water vapour).

This radiation is therefore mostly absorbed by the Earth's surface. This causes the surface temperature to rise. Since energy flows from hotter to colder regions, energy is transferred to the atmosphere, warming it. The atmosphere is hence mostly warmed from below. (This explains why it gets colder as you go higher up in the troposphere.)

The energy that is re-radiated from the surface, and transferred to the atmosphere, is no longer in the visible region. It is in the infrared region, with a much longer wavelength, with a maximum intensity at around 10 000 nm. This change in wavelength occurs because the Earth is radiating at a much lower temperature than the Sun. If all of this energy was allowed to escape into space, the Earth would cool to a temperature around −20 °C. However, these wavelengths, while still not absorbed by nitrogen or oxygen, are strongly absorbed by water vapour and carbon dioxide.

The carbon dioxide and water molecules are able to both emit and absorb infrared radiation. They therefore emit (or re-radiate) the energy they have absorbed from the surface. Some of this energy is re-radiated in the direction of space, and the remainder is radiated back down towards the surface (Figure 24.39).



■ **Figure 24.39** The different types of radiation involved in the greenhouse effect

The temperature at the surface is therefore maintained by a balance between the downward solar radiation and downward infrared radiation from the atmosphere, and the upward radiation of infrared from the surface.

There are other factors to consider. Some energy is carried by water as it vaporizes. It then rises in the atmosphere by convection. The vapour condenses in the cooler upper troposphere, producing clouds, and releasing the energy at this higher altitude. The energy may then escape the Earth in the form of infrared radiation. The atmosphere is therefore heated not only by radiation but also by convection.

Despite these complications, it can be seen that an increase in the concentration of infrared-absorbing gases, carbon dioxide and water vapour, will decrease the amount of energy escaping from the Earth by radiation (by absorbing the energy on its journey upwards) and will increase the amount of energy moving downwards towards the surface (by re-radiating this infrared). The upwards/downwards equilibrium is therefore disturbed, and the surface temperature will rise until the upwards energy flow again equals the downwards flow.

Global dimming

In Section 24.1 it was noted that emission of solid carbon particles from inefficient fossil fuel combustion or from open fires is a major health issue in developing countries. This so-called 'black carbon' emission contributes to high levels of respiratory disease in many parts of the world.

However, despite its public-health implications, the international community has only recently focused much attention on black carbon emissions, because these particulate emissions are responsible for the phenomenon of 'global dimming'.

The presence of particulates in the atmosphere leads to a small percentage of the incoming sunlight being reflected. As much as a 4 per cent reduction in sunlight intensity may be occurring. This leads to a cooling of the planet, as there is less energy reaching the Earth's surface.

Climate scientists are concerned about global dimming because the cooling effect may have masked the effect of greenhouse gases on global warming. If the measures being taken to reduce carbon emissions also lead to a reduction in black carbon, then the lack of a cooling effect may actually lead to an increase in global temperatures.

Using dimming to mitigate climate change

Some scientists have considered using dimming as a means to mitigate global warming. If we cannot successfully reduce carbon dioxide emissions in time to prevent a climate disaster, perhaps we should aim to cut down the amount of sunlight reaching the Earth. This might be achieved by introducing particulates into the stratosphere.

Current research has focused on introducing sulfur dioxide into the stratosphere, which will react with water, generating an aerosol, or fine mist, of sulfuric acid droplets. These would then reflect solar radiation. The process is thought to be reasonably cheap and fast-acting. Although it sounds drastic, it is actually a process that occurs naturally after volcanic eruptions.

However, computer modelling does suggest that there are risks associated with the process. A major issue is that sulfur dioxide can deplete stratospheric ozone, leading to a damaged ozone layer. Other risks include ocean acidification (as sulfuric acid falls from the atmosphere) and drought. Environmentalists point to the unpredictability of the climate, warning that we should not manipulate the climate without a very clear idea of the extent of the outcomes. In addition, some believe that using dimming to mitigate climate change will divert attention from the need to cut down on carbon dioxide emissions.

The history of climate modelling

Jean Baptiste Joseph Fourier (1768–1830) was a French mathematician and physicist who is best known for investigating the Fourier series. The Fourier transform is named in his honour. In 1824 he discovered that the gases in the atmosphere might increase the surface temperature of the Earth, later termed the greenhouse effect (see Figure 24.38). He established the concept of planetary energy balance – that planets obtain energy from a number of sources that cause temperature increase. Fourier recognized that the Earth primarily obtains energy from solar radiation. Later Svante Arrhenius (see Chapter 16) suggested that changes in the levels of carbon dioxide in the atmosphere could alter the surface temperature via the greenhouse effect. He predicted that the emission of carbon dioxide from the burning of fossil fuels would lead to a warmer Earth, but felt that a warmer Earth would be a positive change.

How do the greenhouse gases absorb and emit infrared radiation, and how does this warm the atmosphere?

Absorption and emission in the infrared range of wavelengths occur when molecules vibrate and rotate. Recall that the absorption and emission of ultraviolet radiation occurs when electrons move up and down between fixed energy levels (see Chapter 2). The vibrational and rotational energies of molecules are similarly quantized; that is, a molecule can absorb a photon and move to a higher vibrational energy level. If it falls to a lower energy level, a photon is emitted. These photons have wavelengths in the infrared region.

Absorption and emission of infrared radiation by molecules can only occur if the molecule has an electric dipole. Nitrogen and oxygen, being diatomic molecules, do not have permanent dipoles and create no temporary dipoles when they vibrate. Water absorbs strongly because it is an asymmetric molecule, and also the O–H bonds have a permanent dipole owing to the greater electronegativity of oxygen (see Chapter 3).

Inspection of the carbon dioxide molecule suggests that it has no permanent dipole (see Chapter 4), because the individual C=O bond dipoles cancel out, as the molecule is linear. However, one of the vibrational modes of carbon dioxide is a so-called asymmetrical stretching mode, in which the symmetry of the molecule is disrupted and a temporary dipole formed. Vibrational transitions of carbon dioxide can therefore occur, resulting in emission or absorption in the infrared at a wavenumber of 2360 cm^{-1}. (Wavenumber is related to frequency. For a full discussion see Chapter 11.) Carbon dioxide also has a second vibrational mode corresponding to a bending vibration. This mode absorbs much more weakly at a wavenumber of 670 cm^{-1}. Both vibrational modes can be seen in Figure 24.40.

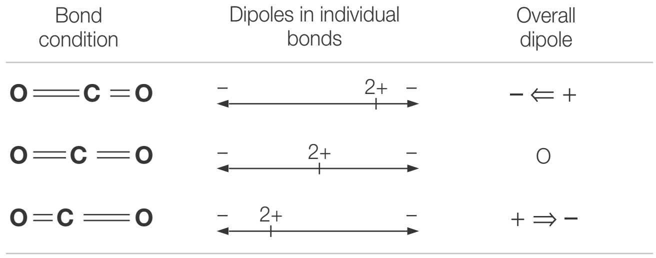


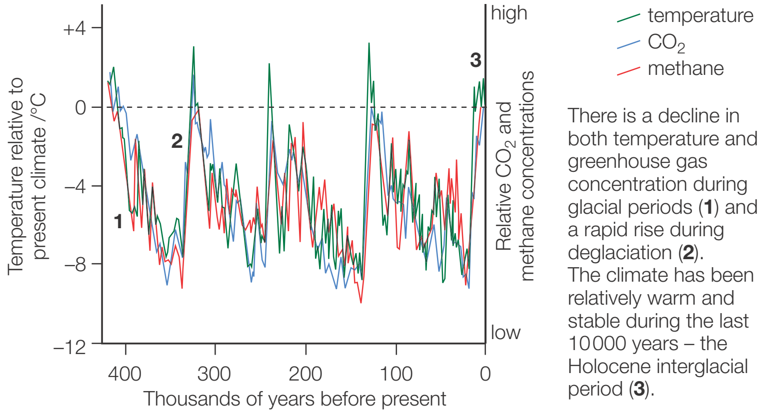
Figure 24.40 A diagram illustrating how the asymmetrical stretch (bending) leads to a change in the dipole moment of carbon dioxide

Both the emission and absorption of infrared are important to the greenhouse action of water and carbon dioxide. Collisions between molecules may ‘excite’ the molecules to higher energy levels. When the molecule ‘relaxes’ to a lower energy level, infrared radiation is emitted. This radiation may move upwards into space, or downwards towards the surface. Conversely, a molecule may absorb infrared radiation. Collisions pass this additional energy to the surrounding gas, warming it.

The evidence for the relationship between the increased concentration of gases and global warming

Evidence for the rise in global temperature came from the Greenland Ice Core Project. Between 1989 and 1992 this group drilled into the polar ice and analysed samples from different depths. The deeper the ice sample, the older the ice. The atmospheric temperature at the time the ice was laid down can be determined by finding the ratio of ^{18}O and ^{16}O atoms in the water molecules of the ice using mass spectrometry (see Chapter 2). Water molecules containing ^{18}O are slightly heavier than those containing ^{16}O, and hence require more energy to vapourize. A lower ratio of $^{18}O/^{16}O$ corresponds to a lower temperature. The project reported that there have been cyclic temperature changes throughout the past 200 000 years, but that the present period of warming has been mostly steady since industrialization in the 19th century (Figure 24.41).

In addition to the temperature studies, measurement of atmospheric carbon dioxide has taken place in isolated areas of Greenland and Hawaii (Figure 24.42), with similar steady increases shown. Comparison of carbon dioxide levels from the 19th century (again, obtained by analysis of ice cores) shows that this increase has continued for 150 years or more.



There is a decline in both temperature and greenhouse gas concentration during glacial periods (**1**) and a rapid rise during deglaciation (**2**). The climate has been relatively warm and stable during the last 10 000 years – the Holocene interglacial period (**3**).

Figure 24.41 The three types of data recovered from the Vostok ice cores over 400 000 years of Earth history

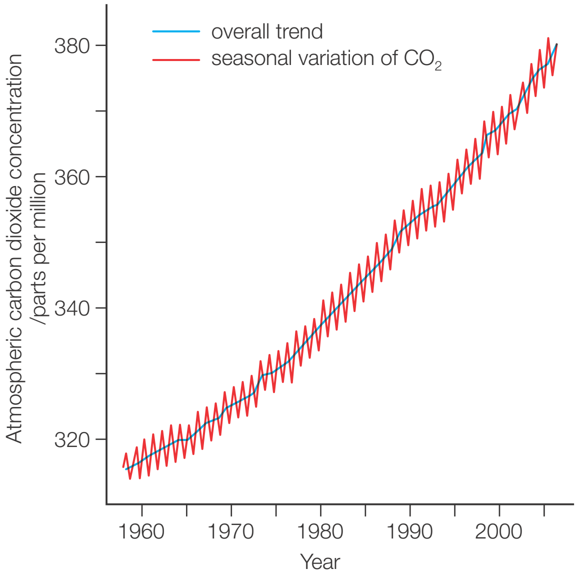


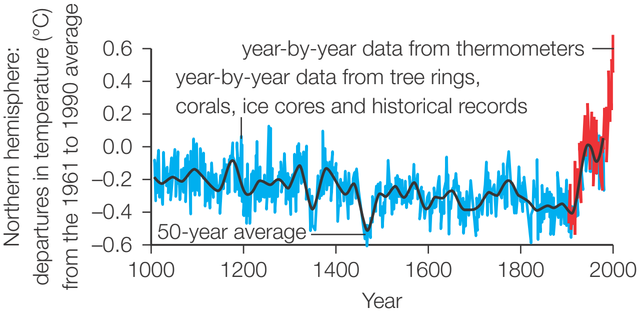
Figure 24.42 Atmospheric carbon dioxide levels recorded at Mauna Loa, Hawaii, 1957–2005

Both carbon dioxide levels and global temperatures have increased. However, has one caused the other? Is there a causal relationship? The IPCC and other scientific organizations believe so.

Nature of Science

Correlation, cause and understanding: the hockey stick controversy

Figure 24.43 shows a graph that first appeared in the IPCC report of 2001. On the graph, temperatures show minimal fluctuation between around 1000 and 1900. This section of the graph is likened to the shaft of a hockey stick. Then, over the past 100 years there is a marked increase in temperature – the blade of the stick. The graph, which summarizes data from many sources including ice cores, tree rings and lake sediments, seems to offer compelling evidence of global warming, outside the normal natural variation. Not only that: the warming coincides with the recent decades of industrialization and the increased carbon emissions that have accompanied it.



■ **Figure 24.43** The 'hockey stick' graph – variations in the Earth's surface temperature

It is widely accepted by scientists that the anthropogenic carbon emissions are the cause of the unprecedented warming.

However, the hockey stick graph is a source of disagreement among scientists, some of whom question the statistical analysis used to estimate the older temperature data. Some scientists and statisticians claim that the hockey stick oversimplifies the message and points to a misleading conclusion. They claim that the true shape of the temperature graph is more nuanced, with a pronounced bulge in the years 1000–1200. They argue that this analysis points to an earlier warm period in medieval times, and so, in theory, the current warming may not be unprecedented. Climate sceptics have seized on this idea, claiming that the current period of warming was matched some 1000 years ago, when there were essentially no anthropogenic carbon emissions to cause it.

However, for scientists keen to alert policymakers and the public to the current climate crisis (as they see it) the 'hockey stick' is convenient 'shorthand' for the temperature trend. Whatever the cause of the medieval warm period, there is sufficient evidence and cause for concern that anthropogenic warming is real and should be acted upon.

The graph shown does illustrate that year-by-year data sometimes reaches large extremes, which are de-emphasized by using the 50-year averages. However, the vast majority of climate scientists do accept that the current period of warming is both warmer and of longer duration than the possible medieval warm period.

ToK Link

Doubt surrounding climate change

The Intergovernmental Panel on Climate Change reported in 2001 'most of the observed increase in globally averaged temperatures since the mid-twentieth century is very likely due to the observed increase in anthropogenic (man-made) greenhouse gas concentrations'.

The national academies of science of all the major industrialized nations, and many others, are explicit in their belief that there is a scientific consensus regarding the existence of global warming, and that it is largely caused by anthropogenic emissions.

Why then is there widespread belief among the public that global warming may be a myth or that the scientific community is divided on the issue?

Some politicians, business leaders, scientists and journalists have claimed that climate scientists have a vested interest in presenting global warming as a forthcoming disaster. The scientists are motivated by a desire to secure funding for their work and have exaggerated the extent of its effects.

However, these same individuals may themselves have vested interests. If global warming is real, and action to mitigate it is urgent, then this will have a detrimental impact on the fossil fuel industry.

Some political parties are quite explicit in their belief that economic growth (involving rampant fossil fuel use) is more important than any environmental concern. However, in the business world, some organizations fund climate research designed to reach conclusions favourable to their interests.

These organizations with a vested interest in continued fossil fuel use, such as oil companies, have been able to exploit the doubt regarding the *extent* of global warming by equating it with doubt regarding the *existence* of global warming. This phenomenon is sometimes referred to as '*manufacturing doubt*'. (Similar techniques were previously used by the tobacco industry, which denied for many years the connection between smoking and chest diseases.) Selective presentation of evidence, such as the idea that the Earth's atmosphere undergoes cyclic variations in temperature, ignores ice core evidence that places current carbon dioxide levels far outside these natural variations.

Scientists do disagree about the likely effects of global warming, as they disagree about the details in other fields, such as evolution by natural selection. However, this is not to say that they reject the existence of anthropogenic climate change.

Another difficulty surrounding the science of global warming is that while it is believed to be occurring, the amount of future warming and the extent of its effects are difficult to predict. Climate modelling involves writing a computer simulation based on certain assumptions and parameters. This is complicated by uncertainty about how changes in one greenhouse gas impact on the concentration of another, for example, and also by unknown feedback effects. For example, the role of clouds in warming is not well understood: clouds add to warming by reflecting radiation back to the Earth and clouds reduce warming by reflecting the Sun's radiation away from the Earth. The uncertain issue here is the net result.

A possible positive feedback effect relates to methane gas locked up in ice in the Siberian tundra. If this ice were to melt, massive amounts of greenhouse-enhancing methane would be released into the atmosphere, accelerating warming further. Similarly, the loss of Arctic ice and glaciers reduces the amount of radiation reflected from the Earth, and increases the area of more absorbing land and sea water, leading to further warming. Some scientists are concerned that a point will be reached at which the greenhouse effect cannot be reversed, and runaway global warming will occur.

The Precautionary Principle (see also Section 24.7) states that if an action has a risk of causing harm to the public or to the environment, then the burden of proof that it is not harmful falls on those taking the action.

The Precautionary Principle is widely accepted and used by scientists. For example, climate scientists claim that there is sufficient consensus that anthropogenic climate change will lead to disaster so that the burden of proof lies with policymakers to prove that continued fossil fuel use is harmless. Fossil fuel proponents dispute this and claim that the burden of proof lies with climate scientists to prove that climate change will definitely lead to harm.

The main greenhouse gases and their contributions to global warming

The contribution of a greenhouse gas to the warming of the atmosphere depends on three factors:

- the abundance of the gas in the atmosphere
- its ability to absorb infrared radiation
- its their lifetime in the atmosphere, before being removed by chemical processes.

The second and third factors are often combined to give a figure called the **global warming potential (GWP)**. Note that this figure must specify the timescale over which it is measured. Some gases are extremely effective at absorbing radiation but are present in the atmosphere for a very short time, minimizing their contribution. Other gases are less effective but are present for many years, so their contribution to global warming is more significant. Carbon dioxide is assigned a GWP of 1 over all time periods. Other gases are assigned a relative value comparing their infrared absorption to that of the same mass of carbon dioxide.

Water vapour, H_2O

Water vapour is the most important greenhouse gas. The GWP of water is sometimes given as 0.1 but is often not calculated because water vapour is constantly cycling through the atmosphere, and its concentration varies according to temperature and location. Typically the percentage of water vapour in the troposphere ranges from 1 per cent to 4 per cent: far greater than any other greenhouse gas. In addition, water absorbs infrared over a broad range of frequencies. Increased atmospheric temperatures lead to more rapid evaporation of the oceans, and a larger capacity of the air to carry water vapour, leading to increased concentration of water in the atmosphere, which may lead to further warming. Estimates of water's contribution to global warming range from 36 per cent to 75 per cent.

Carbon dioxide, CO_2

The percentage of carbon dioxide in the atmosphere is only 0.039 per cent, or about one-thirtieth that of water. However, it is more efficient than water at absorbing infrared radiation (GWP = 1, by definition). Importantly, carbon dioxide absorbs infrared in a 'window' of wavelengths at which water does not absorb. Increases in carbon dioxide concentration therefore upset the equilibrium of absorption and transmission though the atmosphere. Atmospheric concentrations of carbon dioxide are rising for three reasons:

1. Combustion of fossil fuels releases carbon dioxide into the atmosphere.
2. Manufacture of cement and concrete involves the thermal decomposition of calcium carbonate to calcium oxide, releasing carbon dioxide:
   $CaCO_3 \rightarrow CaO + CO_2$

3 Deforestation in the tropics leads to lower rates of photosynthesis, meaning that carbon dioxide is entering the atmosphere more quickly than it is being removed.

Estimates of carbon dioxide's contribution to global warming range from 9 per cent to 26 per cent. The Earth's oceans are warming, making them less able to absorb (dissolve) carbon dioxide emissions.

Methane, CH_4

The concentration of methane in the atmosphere is around 1.7×10^{-4} per cent. However, its GWP (100 years) is 25, meaning it absorbs infrared more much efficiently than carbon dioxide. In fact, methane's GWP (20 years) is 72, meaning that methane is a very powerful greenhouse gas in the short term but is removed from the atmosphere relatively quickly.

Methane is formed when cellulose (plant fibre) decomposes anaerobically by the action of bacteria. Cellulose is a long-chain carbohydrate made from glucose units (represented below as $(CH_2O)_n$).

$$(CH_2O)_n \rightarrow \frac{n}{2} CH_4 + \frac{n}{2} CO_2$$

This reaction occurs on a large scale in the following situations:

1 rice cultivation (paddy fields)
2 fermentation of grass in the stomachs of ruminants (cows), and methane produced from rotting manure; in the European Union around 10 million tonnes annually are produced this way – it is the largest source of methane
3 leaking gas pipelines
4 fermentation of organic material in covered landfills (waste tips).

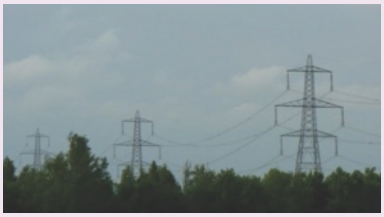
Estimates of methane's contribution to global warming range from 4 per cent to 9 per cent.

Additional Perspective

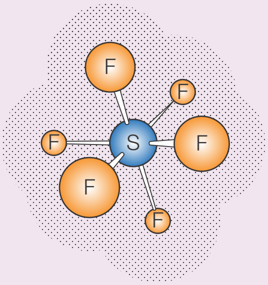
SF6, NOx, CFCs and ozone

Sulfur hexafluoride

Sulfur hexafluoride, SF_6, is a colourless, odourless, non-toxic and flammable gas. It is poorly soluble in water but soluble in non-polar organic solvents. It is prepared by direct synthesis from sulfur and fluorine. Over 8000 tonnes are produced per year. It is used in the electrical industry in circuit breakers on electrical transmission lines (Figure 24.44) and as a contrast agent for ultrasound imaging to improve the visibility of blood vessels. Sulfur hexafluoride is the most potent greenhouse gas with a global warming potential of 22 000 times that of carbon dioxide measured over 100 years. Its ability to strongly absorb infrared radiation is a consequence of the large number of vibrational modes accessible to the molecule due to the cage-like structure in which the sulfur atom is suspended (Figure 24.45). There are no natural sources of sulfur hexafluoride and it is one of six types of greenhouse gases to be regulated by the Kyoto Protocol. The emissions into the atmosphere are small, but it has an atmospheric lifetime of 3200 years.



■ **Figure 24.44** Overhead pylons: potential emitters of SF_6



■ **Figure 24.45** Sulfur hexafluoride molecule, SF_6

Nitrous oxide (nitrogen(I) oxide), N_2O

Nitrous oxide has a GWP (100 years) of 296. It is less efficient at absorbing infrared radiation than carbon dioxide; its high GWP arises from its long residence time in the atmosphere. Its concentration in the atmosphere stands at 0.031 per cent, but this figure is increasing. Despite its low concentration, its high GWP means that it is thought to account for about 5 per cent of global warming effects.

Nitrous oxide is produced naturally by bacteria in the oceans and the soil, and human activity only accounts for about 10–12 per cent of the nitrous oxide

Figure 24.46 A tractor spreading fertilizer

produced each year. However, anthropogenic nitrous oxide is increasing for the following reasons:

- Industrialized agriculture, including the use of nitrogenous fertilizers (Figure 24.46), stimulates soil bacteria to produce more nitrous oxide.
- Industrialized livestock farming and poor handling of animal waste generate nitrous oxide.
- The chemical industry, especially nitric acid and nylon production, generates nitrous oxide.

Chlorofluorocarbons, CFCs

Chlorofluorocarbons (CFCs) are usually encountered in discussions about ozone depletion, but they are also important greenhouse gases. CFC-12, full name dichlorodifluoromethane, CCl_2F_2, has a GWP (100 years) of 8500. This gas was banned in the USA in 1994, but its long residence time in the atmosphere means it will contribute to global warming for centuries to come.

CFCs have been largely replaced as aerosol propellants and refrigerants by **hydrochlorofluorocarbons** (HCFCs) and **hydrofluorocarbons** (HFCs). These gases are less damaging to the ozone layer but still have GWP values much higher than carbon dioxide (for example HFC-23 (trifluoromethane, CHF_3) has a GWP (100 years) of 14 800) and are important contributors to global warming, some sources claiming a 25 per cent contribution.

Ozone, O_3

Ozone formed in the troposphere is a constituent of photochemical smog, and it also acts as a natural greenhouse gas. The production of ground level ozone has risen dramatically since the Industrial Revolution. This ozone is formed by the action of sunlight on hydrocarbons and nitrous oxide from the burning of fossil fuels. This ozone rises in the troposphere and acts as a greenhouse gas. However, ozone in the stratosphere is necessary to filter out harmful cosmic rays.

Effects of greenhouse gases

As the Earth's temperature increases there will be potentially catastrophic effects. However, the scientific community is uncertain as to the extent of these effects. Indeed, the IPCC published a report in 2001 in which they attempted to assess the risks, assigning categories ranging from 'risks to unique or threatened systems' to 'risk of irreversible large-scale and abrupt transitions'.

There is general agreement as to the types of effects that might be expected. These are:

- rising sea levels
- glacier retreat
- acidification of the oceans
- changing patterns of agriculture.

Figure 24.47 The Aletsch glacier in Switzerland

Rising sea levels

As the temperature increases sea levels will rise for two reasons. Firstly, the increased temperature causes accelerated melting of polar ice and glaciers (Figure 24.47). This will deposit more water into the oceans. Note that the floating ice at the Arctic will not cause a sea-level rise on melting, as it already displaces water while it floats. However, melting land-based ice will add to the volume of the oceans. Secondly, as the oceans warm up, the water in them will expand, occupying more volume. The IPCC predicts a sea-level rise of up to 59 cm in the 21st century. However, other climate scientists, such as James Hansen, predict a much larger rise, measured in metres. Some low-lying countries, such as the Maldives, are faced with being almost completely submerged (Figure 24.48).

■ **Figure 24.48** The Maldives. What responsibility do the major carbon-emitting nations have towards this small island country, which is faced with being swamped by rising sea levels?

Glacier retreat

Glaciers undergo a seasonal melting and refreezing cycle as temperatures vary through the year. In the Himalayas glacial melt water is an important source of fresh water, feeding the rivers of South Asia. Increased melting increases erosion and risk of flooding downriver, a particular problem in low-lying countries such as Bangladesh. In addition, the retreating glacier will eventually disappear entirely, meaning that countries in South Asia will lose an important source of fresh water.

Changing patterns of agriculture

In temperate regions (e.g. Europe), yields of grain will most likely increase due to the higher temperature, longer growing season and increased concentration of carbon dioxide available for photosynthesis. However, the increased humidity and rainfall that accompanies the temperature rise may lead to increased incidence of fungal crop diseases and migration of tropical insects to higher latitudes. In addition, the increase in yield of useful crops will be accompanied by increased weed growth, leading to greater use of herbicides. Raised sea levels will reduce land availability both directly, as land becomes submerged, and indirectly, as salt concentrations in groundwater increase, damaging the land's ability to support crops.

At higher latitudes, more land may become available as now-frozen land thaws and becomes workable. However, in tropical regions, temperature increases will lead to now-fertile land becoming desert, with much lower crop yields and erosion of the existing soil.

Worldwide, the possibility of extreme weather increases the likelihood of ruined harvests due to soil erosion, flooding or storms.

Ocean acidification

Carbon dioxide dissolved in the upper part of the oceans and carbon dioxide in the atmosphere exist in dynamic equilibrium:

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

As the concentration of carbon dioxide in the atmosphere rises, the rate of absorption of carbon dioxide in the oceans will increase until a new equilibrium is established in which the concentration of dissolved CO_2 is greater.

The oceans therefore act as a **carbon sink** – a means of storing carbon. Much of the additional carbon entering the atmosphere from human activities ends up in the oceans.

You might think that the 'sink' role of the oceans means that we need not be so concerned about adding carbon to the atmosphere. However, there are two reasons that the oceans are not the answer to climate change.

1. The solubility of carbon dioxide decreases as the temperature rises. As the atmosphere warms, the upper oceans will warm also, lowering their ability to absorb and retain carbon dioxide. A negative feedback loop is set up, in which increasing temperatures will harm the oceans' ability to absorb carbon and minimize the problem.
2. Dissolved carbon dioxide leads to the formation of carbonic acid, which lowers the pH of the oceans. This ocean acidification is one of the environmental effects of global warming that scientists are most concerned about.

pH change in the oceans

As carbon dioxide dissolves in the oceans it forms carbonic acid, H_2CO_3:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \quad [1]$$

Carbonic acid is a weak diprotic acid, which dissociates to form hydrogen carbonate ions (HCO_3^-):

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq) \quad [2]$$

The hydrogen carbonate ion then dissociates (to a smaller extent) to form carbonate ions (CO_3^{2-}):

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq) \qquad [3]$$

Both these reactions generate H_3O^+. As the reactions move to the right the solution becomes more acidic and the pH falls.

An increase in the concentration of dissolved carbon dioxide will lead to an increased concentration of carbonic acid in equilibrium [1]. Increasing the concentration of carbonic acid in equilibrium [2] leads to a shift to the right and therefore more hydrogen carbonate and oxonium (H_3O^+) ions. More hydrogen carbonate ions in equilibrium [3] causes a shift towards more oxonium ions again.

In summary, increased carbon dioxide concentrations in the atmosphere will lead to more carbon dioxide in the oceans and an increase in the oceans' acidity.

Increased acidity may kill sea creatures with calcium carbonate shells, an effect which will then move through the entire food chain. In addition, the larvae or eggs of sea creatures may be unable to survive.

A further effect may be the loss of coral. Coral reefs have formed over millions of years as corals (tiny marine organisms similar to anemones) secrete calcium carbonate. The accumulation of calcium carbonate eventually leads to a massive coastal formation that supports thousands of marine plants and animals. As the pH of the ocean falls, the loss of calcium carbonate may occur more quickly than the corals can replace. The result is a substantial decrease in ocean biodiversity.

Experimental work: modelling the equilibrium between $CO_2(g)$ and $CO_2(aq)$

Commercial soda water ('club soda') contains carbon dioxide dissolved under pressure. If the drink is placed in a sealed container, an equilibrium will be established between dissolved carbon dioxide and gaseous carbon dioxide in the 'head space' above the liquid.

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

Some of this dissolved carbon dioxide will react with water, forming carbonic acid:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

The amount of CO_2 dissolved in the water could therefore be estimated by measuring the pH of the liquid.

Several variables could be investigated:

- *Stirring the solution*: this will increase the rate of diffusion of CO_2 towards the surface of the liquid and will increase the surface area of contact between the liquid and the atmosphere.
- *Raising the temperature of the solution:* this will tend to shift the equilibrium in the endothermic direction. CO_2 dissolving in water is exothermic, so we expect the concentration of dissolved CO_2 to decrease.
- *Adding sodium hydrogencarbonate to the solution:* this increase in hydrogencarbonate ions will influence equilibrium [3] above.
- *Adding dilute hydrochloric acid to the solution:* this will influence equilibria [2] and [3] above.

Approaches towards controlling carbon dioxide emissions

A number of approaches have been proposed to control carbon dioxide emissions in order to limit the progress of global warming.

Increased fuel efficiency

Many countries have introduced fuel efficiency standards in an attempt to reduce the amount of fossil fuels used and decrease carbon dioxide emissions. Government regulations are often based on the average fuel consumption of the various vehicles sold by a particular manufacturer. This encourages the manufacturer to provide a range of vehicles including some very efficient models. However, large powerful cars are still associated with high status, and in many markets larger cars are associated with greater safety, despite statistical evidence to the contrary.

Alternative energy sources (renewables)

Switching to alternative sources of energy such as solar, tidal or wind power is a potential way of lowering carbon dioxide emissions. However, in each case, expensive infrastructure is required, meaning that such sources are unlikely to form more than a small part of the energy mix in the near future. For more information about solar energy and its potential as a major energy source, see Section 24.8.

Carbon-neutral fuels

In theory, biofuels are carbon neutral, meaning that the carbon dioxide released into the atmosphere when they are burnt can be offset by the carbon dioxide absorbed when the plants used to make the fuel were grown.

In practice, such fuels have a large embodied energy, because energy is needed to process the plants and manufacture the fuels. Although biofuels most likely do not achieve carbon-neutral status, blending biofuels with gasoline does offer a way of lowering the net carbon emission per litre of fuel used.

However, another cause of concern for biofuels is that switching to fuel crops might displace food crops and lower biodiversity (see Section 24.4).

Market-based controls

Market-based emission controls seek to offer economic incentives to cut carbon emissions. There are two main models: 'cap-and-trade' and carbon taxation.

In **cap-and-trade** schemes, a cap, or overall limit on emissions, is proposed. Nations or companies that emit less than their assigned limit can sell 'carbon credits' to other nations or companies that might exceed their limits.

The Kyoto Protocol introduced emissions limits for the signatory nations. These nations could buy carbon credits from other, less polluting nations, or they could also win credits by sponsoring carbon-reduction schemes in other countries.

Cap-and-trade schemes only work if countries agree to be bound by them. The USA famously refused to ratify the Kyoto Protocol in protest at what it saw as lenient treatment of developing nations.

In **carbon taxation** schemes, governments decide on appropriate limits to carbon emissions and will tax emitters (e.g. energy companies, car manufacturers) directly in an attempt to force them to take steps to lower emissions. However, this may affect economic growth in the country, and so it is politically unpopular, especially during economic downturns.

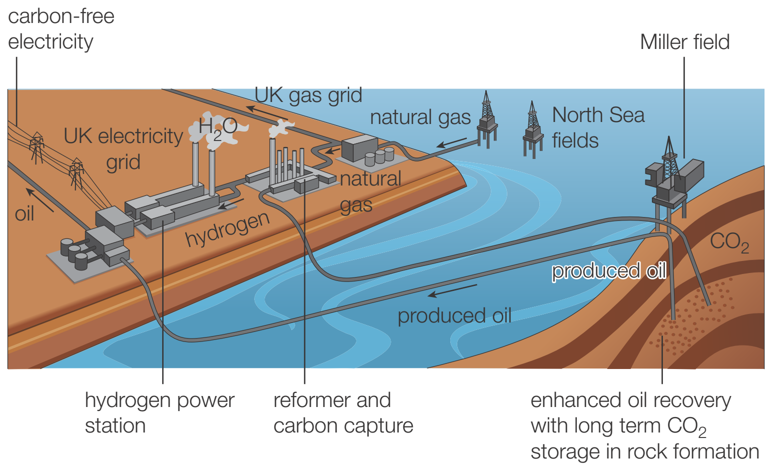


Figure 24.49 Carbon capture and storage

Carbon sequestration (capturing carbon)

One simple way of capturing carbon dioxide is to plant long-lived plants such as trees, which will absorb carbon dioxide as they grow. Eventually these trees will die and the carbon within them will return to the soil and eventually the atmosphere as microorganisms feed on the organic matter and use it for respiration.

Carbon capture and storage (CCS; Figure 24.49) is an approach to reducing global warming based on capturing carbon dioxide from fossil fuel power stations and storing it instead of releasing it into the atmosphere. The carbon dioxide could be pumped into the sea or into underground salt-water deposits and exhausted oil or natural gas fields. However, there are significant energy costs in capturing and compressing carbon dioxide. Carbon dioxide can be chemically removed from the air by the use of sodium hydroxide, but current approaches use zeolites (aluminosilicates) or ion-exchange resins.

24.6 Electrochemistry, rechargeable batteries and fuel cells

– chemical energy from redox reactions can be used as a portable source of electrical energy

Nature of Science

Risk/benefit analyses of batteries and fuel cells

Batteries and fuel cells are sometimes viewed as an essential part of moving us away from fossil fuels towards renewables. Motor vehicles rely on densely stored energy to provide them with adequate range. Fossil fuels have met this need superbly, but with the disadvantage that they produce pollution. If energy can be obtained from solar power, wind power or other renewables, then in theory an effective battery can store this energy, leading to a less polluting vehicle.

However, critics of electric vehicles claim that they are actually more environmentally damaging for three reasons:

1. Batteries contain harmful substances. If the vehicle is in use for 10 years or so, what happens to the batteries after this time?
2. Many of these modern batteries contain rare-earth elements (lanthanoids and actinoids) that must be mined. Mining these rare elements is itself environmentally damaging.
3. Production of the batteries (mining raw materials and manufacturing) uses a lot of energy. This energy must be factored in to the 'embodied' energy of the vehicle.

Car maker Renault released a report in 2011 that claimed that its electric vehicles were less polluting than its conventional petrol vehicles, measured over the whole lifecycle of the car. Although manufacturing the electric car was more polluting, it led to fewer emissions. This was true even if the electricity used to charge the batteries came from coal-fired power stations.

Car makers address point 1 above by undertaking to take the batteries back when the car's useful life is over, so that useful parts can be recycled and toxic substances disposed of appropriately.

Voltaic cells

When a voltaic cell is connected into a circuit it provides the energy for charge to flow around the circuit. The external circuit is the connecting wires and other electrical components, for example an electric motor or light bulb. In this, the flow of charge is electrons and this flow is called an electric current.

A voltaic cell (Chapter 9) has the following components:

- a positive electrode (cathode) that receives electrons from the circuit as the cell discharges and does work – a reduction reaction takes place at this electrode while current is provided to the circuit
- a negative electrode (anode) that donates electrons to the circuit as the cell discharges and does work – an oxidation reaction takes place at this electrode during discharge
- a conducting electrolyte which allows ions to migrate between the two electrodes
- sometimes a porous separator (analogous to a salt bridge) is inserted between the two electrodes to prevent them from making physical contact and causing a short circuit.

As the process continues, the active materials (the chemically reactive materials on the surface of the electrodes that participate in the redox reactions) gradually get used up and the reactions slow down until the battery is no longer able to move electrons around the external circuit. The battery is now described as being 'discharged' or 'flat'.

In this chapter, you will study some real-world applications of electrochemistry and explore ways in which electrochemical cells might contribute to new types of transport in the future.

Power, voltage and current

The power P generated by a battery is measured in watts (W) and is calculated as the product of the voltage V and the current I in amps:

$$P = V \times I$$

However, since $V = I \times R$ (Ohm's law), where R represents the resistance:

$$P = I^2 \times R \text{ and } P = \frac{V^2}{R}$$

Larger batteries (of the same type) deliver more power because, although their voltage is unchanged, the maximum current they can deliver increases proportionally.

The total energy E (in joules) generated by a battery is calculated as the product of the power P in watts and time t in seconds:

$$E = P \times t = V \times I \times t$$

A larger battery, containing more chemicals, will be capable of generating power for a longer period of time.

Many commercial batteries express their total energy content using non-SI units, most commonly kilowatt-hours (kWh). A 100 kWh battery is capable of delivering 1 kW of power for 100 hours.

Internal resistance

The potential difference set up by the chemical reaction in the voltaic cell is responsible for the electromotive force (EMF) that drives the current round the circuit.

If a high-resistance voltmeter is connected to the voltaic cell, no current can flow, and the potential difference measured is the same as the theoretical potential difference delivered by the chemical reaction.

However, if the cell is connected to a load (e.g. a light bulb) then a current will flow. The current flow is affected not only by the resistance of the light bulb, but also by the so-called 'internal resistance' of the cell itself. The current within the voltaic cell consists of ions diffusing to and from the electrodes, and this diffusion takes time. The maximum current delivered by the cell is limited by the rate of this diffusion.

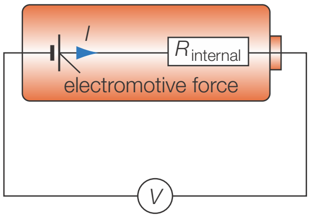


Figure 24.50 Internal resistance

In Figure 24.50 the circuit symbol for the cell (which can be thought of as an 'ideal' or theoretical cell capable of delivering infinite current) is accompanied by a resistor symbol, representing the internal resistance of the cell.

The internal resistance of the cell is affected by the temperature – at higher temperatures the internal resistance falls because the ion mobility increases. As the cell runs down, the build-up of chemical products around the electrodes causes an increase in internal resistance.

Anodes and cathodes

Throughout the following sections bear in mind the formal definitions of the terms anode and cathode.

- **Anode**: the site of **oxidation**. Electrons are lost, so they flow away from the anode.
- **Cathode**: the site of **reduction**. Electrons are gained, so they flow towards the cathode.

Cells and batteries

In Chapter 9 you studied the Daniell cell, which uses copper and zinc electrodes to generate an EMF of approximately 1.1 V. Most applications of cells require larger voltages than this, so a number of cells are connected together in series. An array of voltaic cells connected in series is called a **battery**. The word battery has come to mean any portable device which offers a self-contained source of electricity.

There are three main types of cells or batteries: primary cells, secondary cells, and fuel cells.

Primary cells

Disposable batteries used for household items such as torches, clocks and toys are primary cells. A primary cell contains a chemical mixture that uses an electrochemical reaction to generate an EMF when connected in a circuit When the chemicals have 'run out' the battery is exhausted and is thrown away. Such batteries are referred to as **dry cells** because they use an almost dry paste, rather than a liquid, as the electrolyte. This lowers the chance of toxic chemicals leaking from the battery.

Primary batteries cannot be efficiently recharged because the redox reactions that occur involve the formation of solids or gases. Sometimes these substances tend to build up around an electrode (and increase the internal resistance and as a consequence the voltage drops). However, the battery may ‘recover’ partially as these substances slowly diffuse away.

The alkaline dry cell (e.g. a Duracell or Energizer battery) contains an anode of powdered zinc and a cathode of manganese(IV) oxide. Each of these is mixed to a paste in an electrolyte of potassium hydroxide.

The electrode half-equations are:

Anode: $Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$

Cathode: $2MnO_2(s) + 4H_2O(l) + 2e^- \rightarrow 2Mn(OH)_2(s) + 2OH^-(aq)$

Overall reaction: $Zn(s) + 2MnO_2(s) + 4H_2O(l) \rightarrow Zn(OH)_2(s) + 2Mn(OH)_2(s)$

Under the conditions of the cell, this generates an EMF of 1.5 V.

Alkaline dry cells are cheap and convenient, but they are not useful for large-scale applications such as motor vehicles, as they have a low voltage and cannot be re-used.

Secondary cells

The workings of rechargeable cells

Secondary cells are more commonly known as rechargeable batteries. They differ from primary cells in that once they are exhausted, a current can be passed through them which reverses the chemical reaction and returns the chemical mixture to its initial state. Secondary cells can be used many times and can be thought of as a way of storing electricity, rather than simply generating it.

Three common types of secondary cells are the **lead-acid cell**, the **nickel–cadmium cell** and the **lithium-ion cell**. These have different strengths and weaknesses and find different applications.

Lead-acid cells

Lead-acid cells are very widely used. They are commonly known as car batteries.

■ **Figure 24.51** A car battery

The car battery consists of six cells (shown by the six caps on the example in Figure 24.51). Each cell generates an EMF of approximately 2 V, leading to an overall voltage of 12 V for the battery.

The car battery must be able to generate a very high current for a short period of time, as it is used to drive the starter motor. The starter motor spins the engine to enable the internal combustion reaction to begin. It also generates the ‘spark’ for ignition in a gasoline engine. The car battery is recharged by a generator (called an alternator) attached to the car engine once the car is running.

Each of the six cells consists of an anode of lead–antimony alloy and a lead(IV) oxide cathode. The electrolyte is 6 mol dm^{-3} sulfuric acid (a solution of 38% sulfuric acid by mass).

When the electrochemical reaction is allowed to proceed, generating a current, this is called the ‘discharge’ reaction, as it discharges or ‘runs down’ the battery.

The electrode half-equations for the discharge reaction are:

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

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

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

In this scheme the lead anode is oxidized to lead(II) sulfate, and the lead(IV) oxide cathode is reduced to lead(II) sulfate. Both electrodes are coated with lead(II) sulfate.

However, when a current is passed through the cell, these reactions are reversed. (Imagine the electrochemical reaction running 'downhill' as the cell discharges. When the cell is recharged, the external power source drives it back 'uphill'.)

The half-equations for the 'recharge' reaction are the reverse of the above:

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

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

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

The charging and discharging reactions are summarized in Figure 24.52.

A side reaction that can limit the life of the battery is that the water in which the sulfuric acid is dissolved gets electrolysed to hydrogen and oxygen in the battery. These gases diffuse away, and the fluid level in the battery gradually drops. The battery can be topped up with distilled water by opening each cell in turn via the screw caps.

Some batteries are marketed as 'maintenance-free' batteries without the screw caps. They use anodes of lead–calcium alloy (replacing the antimony) which slows down the electrolysis of water.

Key questions about the lead-acid cell

- **Why is the lead-acid cell able to deliver such a high current?**

  All batteries experience a phenomenon known as 'internal resistance'. The amount of current that can be delivered is limited by the battery's ability to transfer electrons. In most cases, the internal resistance arises from the limited speed at which ions can diffuse through the electrolyte. However, the lead-acid cell benefits from a liquid electrolyte (rather than a paste, like many cells), and the very high conductivity of the sulfuric acid electrolyte.

- **Why is the lead-acid cell able to be recharged?**

  Lead(II) sulfate, which is the product of the discharge reaction at both anode and cathode, is a very insoluble substance. It adheres to the anode and cathode plates. This means that it remains close to the two electrodes, and is able to gain or lose electrons during the recharging process.

- **Why don't car batteries have an infinite lifespan?**

  As well as the possibility of losing water by electrolysis, if the battery is left in its 'run down' state the lead(II) sulfate continues to crystallize on the electrodes. This lowers the surface area of the electrodes, and then the crystals do not fully dissolve during the recharging process.

- **Why does each cell in the lead-acid battery have a voltage of approximately 2V?**

  The reduction and oxidation reactions that occur inside a simple battery each produce a fixed standard electrode potential E° measured as a voltage. The sum of the two electrode potentials is the voltage of the battery.

  For example, the discharge reaction and associated standard electrode potential at the positive electrode of a lead–acid battery is:

  $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^- \qquad E = +1.685\,V$

  The reaction at the negative electrode and associated standard electrode potential is:

  $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l) \qquad E = +0.356\,V$

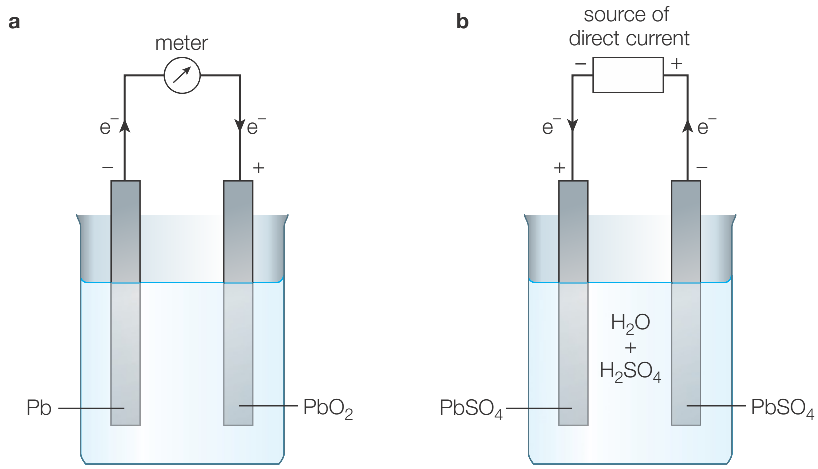
  Adding the two half-equations and cancelling electrons gives the overall cell reaction for the discharge process:

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

  $E_{cell} = +1.685\,V + (+0.356\,V) = 2.041\,V$

  Note that the concentration of the sulfuric acid electrolyte can also affect the voltage of a lead-acid battery – as its concentration decreases, so does the voltage.

Figure 24.52 A lead-acid cell **a** discharging **b** recharging



Experimental work

In a school laboratory, it is possible to make a lead-acid battery and investigate the effect of a number of factors on its ability to hold its charge. Two lead plates are immersed in sulfuric acid. These plates will have a layer of lead(II) oxide on their surfaces. The battery can therefore be formed by connecting it to a power supply that causes the lead(II) oxide on the surface of one electrode to be reduced and the lead(II) oxide on the surface of the other electrode to be oxidized.

The relevant half-equations describing this forming process are:

$$PbO(s) + 2H^+(aq) + 2e^- \rightarrow Pb(s) + H_2O(l)$$

$$PbO(s) + 2H_2O(l) \rightarrow PbO_2(s) + 2H^+(aq) + 2e^-$$

Possible independent variables for investigation

Variables that may affect the ability of the lead-acid storage cell to hold a charge include:

1 surface area of the lead electrodes
2 acid temperature
3 sulfuric acid concentration
4 charging time
5 voltage used during charging
6 charge reversal during charging.

Charge reversal

If the power pack connections are reversed occasionally during the life of the battery it is thought that the surface of the lead electrodes will be roughened, which will increase their surface area. This might increase the useful life of the battery and enable it to retain its charge for longer.

Measurement of dependent variable

After charging, the battery is connected to a bulb. The time that this bulb remains lit is our measure of the ability of the battery to hold its charge. A series of different values of the independent variable can be tried, for example a series of different-sized electrodes (surface area). The time for the bulb to remain lit is measured and compared to the independent variable.

Nickel–cadmium cells

For most applications, the typical 1.5 V alkaline dry cell can be replaced with a similar-looking 1.25 V nickel–cadmium rechargeable cell.

Nickel–cadmium (or Ni–Cad) cells consist of a cadmium anode and a nickel(III) hydroxide cathode. As with the alkaline dry cell, the electrolyte is potassium hydroxide.

The half-equations for the discharge reaction are:

Anode: $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$

Cathode: $2Ni(OH)_3(s) + 2e^- \rightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$

Overall reaction: $Cd(s) + 2Ni(OH)_3(s) \rightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$

Ni–Cad batteries suffer from what is known as the ‘memory effect’. This effect occurs when a battery is partially discharged and then recharged. The Ni–Cad battery ‘remembers’ the lower state and will not fully charge. Ni–Cad batteries should be completely discharged prior to being fully charged. This phenomenon occurs due to the formation of a passive (very unreactive) surface on the electrodes. This increases the internal resistance of the cell and forms a barrier to further cell reactions during the charging process.

Lithium-ion batteries

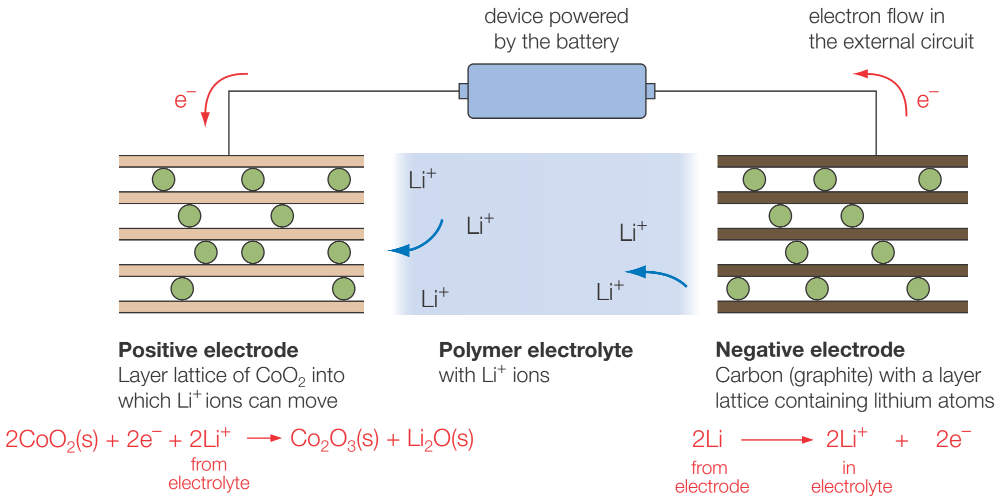
Lithium can be used to make primary cells. It is an attractive option for battery manufacture as it has a very high (very negative) reduction potential, meaning that it is a powerful reducing agent. However, lithium primary cells have certain disadvantages. The main problem arises from the high reactivity of lithium and the generation of potentially explosive hydrogen during the cell reactions. Lithium cells are therefore dangerous if punctured.

However, lithium-ion batteries do not contain any metallic lithium. Instead, they contain lithium ions which migrate between the two electrodes during charge or discharge. These lithium-ion batteries should be viewed as a separate category of battery. They are rechargeable and were introduced for use in mobile phones, video cameras and laptop computers. Lithium-ion batteries are secondary batteries, whereas lithium batteries are primary cells.

Reaction at the anode

The anode is made of graphite, into which lithium atoms are **intercalated** (Figure 24.53). This means that lithium atoms are inserted into the spaces between the graphite layers. During the cell reaction, lithium ions migrate out of the graphite electrode via the electrolyte, while their electrons enter the external circuit.

$$2\text{Li (graphite)} \rightarrow 2\text{Li}^+ \text{ (electrolyte)} + 2\text{e}^-$$



■ **Figure 24.53** Schematic diagram of a lithium-ion polymer battery showing the battery discharging. The electrode processes are reversible so that the battery can be recharged

Reaction at the cathode

The cathode is commonly made of cobalt(IV) oxide, CoO_2, which has a layer structure into which the lithium ions can move from the electrolyte. Electrons from the external circuit enter this lattice and reduce cobalt(IV) to cobalt(III).

$$2\text{CoO}_2\text{(s)} + 2\text{e}^- + 2\text{Li}^+\text{(electrolyte)} \rightarrow \text{Co}_2\text{O}_3\text{(s)} + \text{Li}_2\text{O(s)}$$

During recharging, the lithium ions are driven back though the polymer electrolyte to the graphite anode.

Lithium-ion batteries are much lighter than lead-acid batteries for a given capacity, and they are being used in the latest generation of electric vehicles (Figure 24.54) and new aircraft such as the Boeing 787 Dreamliner.

Lithium-ion batteries must be manufactured to very high standards. If the thin polymer film between the electrodes is damaged the battery can short circuit, leading to overheating and 'thermal runaway', in which the heat produced by the chemical reaction leads to further battery damage and more heat being generated. Lithium-ion batteries can catch fire if not carefully treated, which creates a serious hazard if used in cars or aircraft (Figure 24.55).

■ **Figure 24.54** The Tesla Model S claims a 300 mile range from its 85kWh lithium-ion battery pack

■ **Figure 24.55** The Boeing 787 has experienced a number of fires caused by thermal runaway of its on-board lithium-ion batteries

The advantages of different types of secondary cells

Table 24.11 summarizes the advantages and disadvantages of different types of secondary cells.

■ **Table 24.11** Advantages and disadvantages of different types of secondary cells

	Advantages	Disadvantages
Lead-acid battery	Very well-established technology Ability to deliver high current essential for vehicle applications (starter motor, ignition system) Battery can be recycled and lead re-used	Low power-to-weight ratio (i.e. they are heavy). They are suitable for small, slow electric vehicles such as golf carts but not higher-performance vehicles Not suitable for fast recharging, because it leads to electrolysis of water or break-up of the lead(II) sulfate layer, which shortens battery life Possibility of damage if left 'flat' for too long, owing to crystallization of lead(II) sulfate
Nickel–cadmium battery	High number of charge–discharge cycles possible (thousands) Long storage time – can retain a charge 'on the shelf' for months	Cadmium is highly toxic so batteries must be disposed of carefully Memory effect – if the battery is not discharged fully it 'remembers' the lower-charge state and will not fully charge on subsequent cycles
Lithium-ion battery	High energy density – batteries are light and powerful Minimal memory effect – batteries are more tolerant of incomplete charge–discharge cycles	Manufacturing flaws or battery damage can lead to thermal runaway and the battery catching fire

Fuel cells

A fuel cell converts the chemical energy of a fuel directly into electrical energy. Fuel cells are designed so that the substances to be oxidized and reduced at the electrodes are stored outside the cell and are continually supplied to the electrodes. A fuel cell is therefore a flow battery that continues to operate so long as reactants are introduced.

Explanation of the workings of fuel cells including diagrams and deduction of the relevant half-equations

Hydrogen–oxygen fuel cells

One of the most successful types of fuel cells uses the reaction between hydrogen gas and oxygen gas to form water, and is known as the hydrogen–oxygen fuel cell. A cross-section of a hydrogen–oxygen fuel cell is shown in Figure 24.56. The cell consists of porous carbon electrodes which are impregnated with catalyst (platinum, silver or cobalt(II) oxide). There are two types of hydrogen–oxygen fuel cells – alkaline cells and acidic cells.

- **Alkaline fuel cells:** hydrogen and oxygen gases are bubbled through the electrodes into an electrolyte of concentrated aqueous sodium hydroxide. The fuel cell runs continuously so long as the two gases are supplied at a relatively high temperature and pressure. The electrode reactions are:
  Anode: $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$ (oxidation)
  Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ (reduction)

  Multiplying the first half-equation through by 2, and then adding it to the second gives the overall (redox) reaction:

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

  Note that hydroxide ions (OH^-) are consumed in the oxidation reaction but produced in the reduction reaction, so the pH of the electrolyte remains constant.
- **Acidic fuel cells:** in some fuel cells, an acidic electrolyte is used – the electrode reactions are:

  Anode: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$ (oxidation)
  Cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ (reduction)
  Overall reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ (redox)

  This time, hydrogen ions are released in oxidation but consumed in reduction.

The overall reaction is the same in both types of cell. In these fuel cell reactions the energy released when hydrogen and oxygen combine is transferred as electrical energy, rather than the thermal energy that is transferred when hydrogen burns in oxygen.

Proton-exchange membrane fuel cells

Proton-exchange membrane (PEM) fuel cells are currently in development. These replace the platinum electrodes with a very thin polymer membrane (i.e. a plastic film) into which much smaller amounts of platinum or other catalysts are embedded. The membrane needs to allow protons to flow through it with minimal resistance, while preventing electrons from passing through. It must also be impermeable to the gases entering the cell.

Methanol fuel cells

One disadvantage of hydrogen–oxygen fuel cells is that a supply of hydrogen must be available. Hydrogen is a flammable gas that must be stored under pressure.

An alternative to hydrogen is methanol, which is a liquid at room temperature and pressure and so is far more easily stored and transported. Methanol can be stored in sealed cartridges which have an energy density far higher than hydrogen or even lithium-ion batteries.

Methanol fuel cells rely on the catalytic oxidation of methanol to form carbon dioxide. The electrode reactions are:

Anode: $CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2$ (oxidation)

Cathode: $\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ (reduction)

Overall reaction: $CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 3H_2O$ (redox)

Once again, methanol fuel cells rely on platinum as a catalyst at both electrodes, which contributes to the high cost of these cells.

Although convenient, methanol fuel cells produce carbon dioxide, which is a greenhouse gas, although in small quantities. There may be a risk associated with carrying a laptop computer, for example, powered by a methanol cartridge, as the fuel is flammable and the reaction produces gas that must be allowed to diffuse away.

The use of methanol fuel cells to power military equipment such as satellite communications units and computers is being explored.

The design of the fuel cell

The traditional fuel cell shown in Figure 24.56 shows the hydrogen passing over an anode made of finely divided platinum, which splits the hydrogen into H^+ ions (protons) and electrons. The protons move into the electrolyte (in this case, sodium hydroxide, so a neutralization reaction occurs, forming water). The electrons enter the external circuit. Excess hydrogen gas passes out of the cell and can be re-used.

The platinum cathode similarly catalyses the reaction of oxygen gas and water, forming hydroxide ions. Platinum is a much less effective catalyst for this reaction, which means that superior alternatives are sought.

Fuel cells are very useful as power sources in remote locations – such as spacecraft, remote weather stations, large parks and rural locations – and in certain military applications. Potential household uses include smart phones (with high power consumption due to large displays) and notebook computers where alternating current (AC) charging may not be available for weeks at a time. Fuel cells are used in electric (Figure 24.57) and hybrid vehicles.

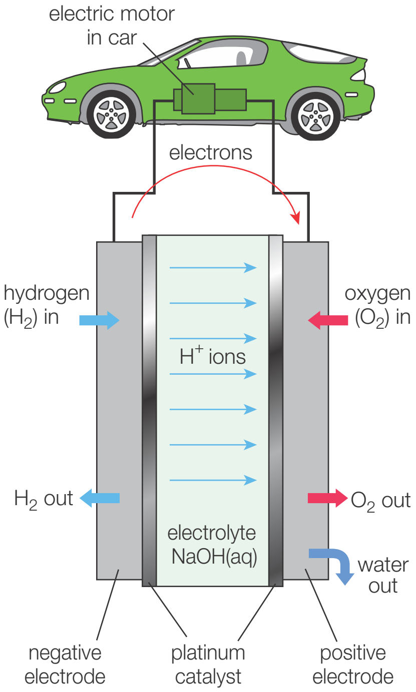


Figure 24.56 A hydrogen–oxygen fuel cell providing power to drive a car

Figure 24.57 A Mercedes–Benz Ecobus uses a hydrogen-based fuel cell

Microbial fuel cells

A microbial fuel cell typically uses waste water containing organic compounds, which are acted upon by bacteria to generate electricity. Instead of using inorganic catalysts such as platinum to enable the redox reactions, the cell taps into the electron transfer chains within the microorganism, using the microbe's biochemical pathways to catalyse the reaction.

Design of a microbial fuel cell

Like a hydrogen–oxygen fuel cell, the microbial fuel cell consists of two compartments separated by a membrane.

At the anode, bacteria consume the organic substrate, generating carbon dioxide, hydrogen ions (protons) and electrons. The electrons enter the external circuit while the protons pass through the membrane (Figure 24.58).

At the cathode, the protons combine with electrons and oxygen, forming water.

One particular reaction that shows promise is the use of *Geobacter sulfurreducens* to oxidize ethanoate ions.

Possible electrode reactions are:

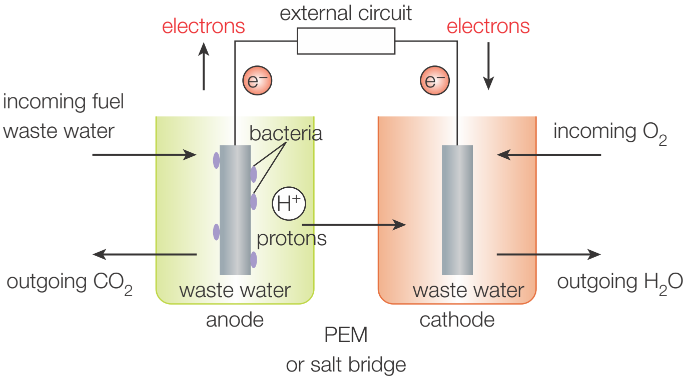
Anode: $CH_3COO^- + H_2O \rightarrow 2CO_2 + 5H^+ + 6e^-$ (oxidation)

Cathode: $\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ (reduction)

Overall reaction: $CH_3COO^- + H^+ + \frac{3}{2}O_2 \rightarrow 2CO_2 + 2H_2O$

Microbial fuel cells offer a number of advantages: they produce useful energy from a waste product, they help to clean up waste water by removing organic pollutants, and they decrease the demand for expensive catalysts such as platinum.

Figure 24.58 Microbial fuel cell



Calculating thermodynamic efficiency (ΔG/ΔH) of a fuel cell

The thermodynamic efficiency of a fuel cell is given by: efficiency $= \frac{\Delta G}{\Delta H} \times 100$ where ΔG is the Gibbs free energy change of the cell reaction and Δ*H* is the enthalpy change of the reaction.

Worked example

Calculate the thermodynamic efficiency of the methanol fuel cell reaction. Use the data in Table 24.12.

$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 3H_2O(l)$$

Substance	Enthalpy of formation/ ΔH_f, kJ mol^{-1}	Gibbs free energy of formation/ ΔG_f, kJ mol^{-1}
$CH_3OH(l)$	–239	–166
$O_2(g)$	0	0
$CO_2(g)$	–394	–394
$H_2O(l)$	–286	–237

Table 24.12 Enthalpy and Gibbs free energy data

Standard Gibbs free energy change is found by:

$$\Delta G^\ominus = \sum \Delta G^\ominus_f(\text{products}) - \sum \Delta G^\ominus_f(\text{reactants}) = [(-394) + (-237 \times 3)] - [-166] = -939\,\text{kJ mol}^{-1}$$

Standard enthalpy change of the cell reaction is found by:

$$\Delta H^\ominus = \sum \Delta H^\ominus_f(\text{products}) - \sum \Delta H^\ominus_f(\text{reactants}) = [(-394) + (-286 \times 3)] - [-239] = -1013\,\text{kJ mol}^{-1}$$

$$\text{Efficiency} = \frac{\Delta G}{\Delta H} \times 100 = \frac{-939}{-1013} \times 100 = 92.7\%$$

What is the significance of the thermodynamic efficiency of the fuel cell?

In the efficiency equation, the standard Gibbs free energy change tells us how much electrical energy can be theoretically generated by this chemical reaction, per mole of methanol.

The standard enthalpy change tells us how much heat can be released when methanol is burnt, per mole.

Why are the two values not the same? The second law of thermodynamics essentially tells us that 'you cannot break even'; in other words, some proportion of the energy released in a chemical process will be released as heat (wasted, for our purposes). You can think of this in terms of entropy (Chapter 15). The methanol combustion equation shows a decrease in the moles of gas, so the degree of disorder in the system falls. The reaction is exothermic though, so it heats up the surroundings, causing an increase in entropy. The Gibbs free energy is the proportion of the energy change that can be usefully employed to do work (in our case, the electrical energy generated by the cell) while still releasing sufficient heat to the surroundings that they warm up enough to offset the decrease in the entropy of the system.

In this example, 92.7 per cent of the energy released by cell reaction can be used to do useful work. The remainder is released as heat.

10 Calculate the thermodynamic efficiency of the hydrogen fuel cell. Use the data in Table 24.13.

Substance	**Enthalpy of formation/ ΔH_f, kJ mol^{-1}**	**Gibbs free energy of formation/ΔG_f, kJ mol^{-1}**
$H_2(g)$	0	0
$O_2(g)$	0	0
$H_2O(l)$	–286	–237

■ **Table 24.13** Enthalpy and Gibbs free energy data

Comparison between primary cells, fuel cells and rechargeable batteries

Table 24.14 offers a comparison between primary cells, fuel cells and rechargeable batteries.

■ **Table 24.14** Advantages of primary cells, fuel cells and rechargeable batteries

	Advantages	**Disadvantages**
Primary cells	Cheap and widely available Small and highly portable Low toxicity compared to most secondary cells Long shelf life	Wasteful – they are used once and thrown away
Fuel cells	Do not require recharging – they can operate continuously as long as new fuel is supplied Fuel cells are well suited to remote locations	Expensive catalysts required (e.g. platinum in methanol fuel cells) Some fuel cells produce carbon dioxide Cannot be used in enclosed spaces due to fire risk Hydrogen fuel cells require a source of hydrogen stored under pressure
Rechargeable batteries (secondary cells)	Highly convenient for use in portable devices Potentially long lifetime with many charge cycles	Often contain toxic substances that can enter the environment if thrown away

Energy from batteries and fuel cells

We have already studied how batteries and fuel cells enable an EMF to be generated from redox reactions. But what determines the value of that EMF? In Chapter 9 you studied electrochemical cells operating under standard conditions, in which metals are suspended in solutions of their own ions, at concentrations of 1 mol dm^{-3} at 298 K.

As we have seen, commercial batteries do not use standard electrolytes or concentrations, so how can EMF be determined?

As a starting point to a discussion of non-standard electrode systems, we will consider the effect of changing electrolyte concentration.

Electrode potentials can only be used to predict the feasibility of a redox reaction under standard conditions. Electrode potentials for oxidizing agents in acidic conditions refer to $1.0\,\text{mol}\,\text{dm}^{-3}$ concentrations of hydrogen ions, H^+ (pH 0), as in the standard hydrogen electrode.

Consider the following reaction:

$$MnO_2(s) + 4H^+(aq) + 2Cl^-(aq) \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l) + Cl_2(g)$$

This reaction can be thought of as the combination of these two half-reactions:

$$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l) \quad E^\ominus = +1.23\,\text{V}$$

$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \quad E^\ominus = +1.36\,\text{V}$$

The reaction as written reverses the second reaction (i.e. chloride ions are oxidized to chlorine gas molecules) so the electrode potential sign is reversed.

$$E^\ominus_{\text{cell}} = 1.23 + (-1.36) = -0.13\,\text{V}$$

Since the cell potential, $E^\ominus_{\text{cell}}$ is negative, this reaction is not spontaneous under standard conditions. However, when *concentrated* hydrochloric acid is heated with manganese(IV) oxide the cell potential becomes positive and the reaction can occur: chlorine gas is evolved.

This happens because the pH conditions are no longer standard ($1\,\text{mol}\,\text{dm}^{-3}$) and neither is the temperature (298 K, 25 °C).

In addition, the loss of chlorine gas shifts the equilibrium to the right, favouring the formation of more chlorine.

In general, for a redox equilibrium:

$$\text{Ox} + ne^- \rightleftharpoons \text{Red}$$

Increasing the concentration of the oxidized species, [Ox], or decreasing the concentration of the reduced species, [Red], will shift the equilibrium to the right, reducing the number of electrons transferred and hence making the cell potential more positive. Similarly, the cell potential will become more negative if the concentration of the oxidized species, [Ox], is decreased or the concentration of the reduced species, [Red], increased. These shifts can be predicted from application of Le Châtelier's principle.

Consider the Daniell cell, consisting of a zinc half-cell connected to a copper half-cell:

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E^\ominus = -0.76\,\text{V}$$

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^\ominus = +0.34\,\text{V}$$

Under standard conditions the cell reaction is:

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

and

$$E^\ominus_{\text{cell}} = +0.34 - (-0.76) = +1.10\,\text{V}$$

Now imagine that we decrease the concentration of Zn^{2+} ions in the zinc half-cell:

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E^\ominus = -0.76\,\text{V}$$

This will shift the half-cell equilibrium to the left, increasing the tendency of the zinc electrode to release electrons, making the electrode potential more negative.

Going back to the expression for $E^{\ominus}_{\text{cell}}$, if we increase the magnitude of the zinc half-cell potential (make it more negative) this will lead to E_{cell} becoming more positive, so the cell will have a larger EMF.

If the concentration of Zn^{2+} ions in the zinc half-cell is increased, the half-cell reaction shifts to the left, decreasing the tendency of zinc atoms to release electrons, and making the electrode potential more positive (less reducing, and hence more oxidizing). A more positive value of E for the zinc system leads to a lower E_{cell}.

The Nernst equation

The Nernst equation allows chemists to calculate the cell potential of non-standard half-cells where the concentrations of ions are not 1 mol dm^{-3}. The mathematical relationship between the electrode potential and the concentration of aqueous ions is called the Nernst equation. It describes the relationship between cell potential and concentration (at constant temperature). It also describes the relationship between cell potential and temperature (at constant concentration).

For the generalized case of a redox system:

$$\text{Ox} + ne^- \rightleftharpoons \text{Red}$$

$$E = E^{\ominus} + \frac{RT}{nF}\ln\frac{[\text{Ox}]}{[\text{Red}]}$$

where R represents the gas constant (8.31 J mol^{-1} K^{-1}), F the Faraday constant (96 485 C mol^{-1}, which is the product of the charge on an electron and the Avogadro constant), T the absolute temperature (in Kelvin, often 298 K) and n the number of electrons transferred.

Solution of problems using the Nernst equation

For a metal/metal ion system:

$$\text{M}^{n+}(\text{aq}) + ne^- \rightleftharpoons \text{M(s)}$$

$$E = E^{\ominus} + \frac{RT}{nF}\ln\frac{[\text{M}^{n+}(\text{aq})]}{[\text{M(s)}]}$$

In these circumstances, the concentration of a solid, [M(s)], is taken as 1.

Worked examples

What is the electrode potential of a half-cell consisting of zinc metal suspended in a 0.01 mol dm^{-3} solution of zinc ions, at 298 K?

$$E = E^{\ominus}_{\text{Zn}} + \frac{RT}{nF}\ln\frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Zn(s)}]}$$

$$E = -0.76 + \frac{8.31 \times 298}{2 \times 96485}\ln\frac{0.0100}{1.00}$$

$$E = -0.76 + (-0.0600) = -0.82\text{V}$$

Note that the E value is more negative when the zinc solution is diluted, as predicted in the qualitative example above.

Note that if $R = 8.31$, $T = 298$ and $F = 96485$, then the equation simplifies to

$$E = E^{\ominus} + \frac{0.0257}{n}\ln\frac{[\text{M}^{n+}(\text{aq})]}{[\text{M(s)}]}$$

Nernst equation applied to a voltaic cell (two half-cells)

In a voltaic cell in which both half-cells have non-standard concentrations, we can combine the Nernst equations for each half-cell to devise a single equation which allows calculation of the cell EMF.

Consider the Daniell cell. The standard EMF is calculated by:

$$E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{Cu}} - E^{\ominus}_{\text{Zn}}$$

Substituting the non-standard equations for the copper and zinc half-cells gives:

$$E_{\text{cell}} = \left(E^{\ominus}_{\text{Cu}} + \frac{RT}{nF}\ln\frac{[\text{Cu}^{2+}(\text{aq})]}{[\text{Cu(s)}]}\right) - \left(E^{\ominus}_{\text{Zn}} + \frac{RT}{nF}\ln\frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Zn(s)}]}\right)$$

Remembering that the concentrations of the solids are both 1, we can simplify this to:

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} + \frac{RT}{nF}\ln\,[\text{Cu}^{2+}(\text{aq})] - \frac{RT}{nF}\ln\,[\text{Zn}^{2+}(\text{aq})]$$

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{nF}\ln\frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]}$$

Or, at 298 K:

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{0.0257}{n}\ln\frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]}$$

Note the *negative* sign between the two terms.

The expression $\frac{\text{Zn}^{2+}(\text{aq})}{\text{Cu}^{2+}(\text{aq})}$ generalizes as the 'reaction quotient', sometimes called 'Q' (see Chapter 7) as the spontaneous reaction here is:

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

A general form of the Nernst equation is therefore:

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{0.0257}{n}\ln Q$$

Worked example

Use the Nernst equation to calculate the cell potential at 298 K of a Daniell cell where the zinc ion concentration is 0.00500 mol dm^{-3} and the copper(II) ion concentration is 1.50 mol dm^{-3}.

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{0.0257}{n}\ln\frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]}$$

$$E_{\text{cell}} = +1.1\,\text{V} - \frac{0.0257}{2}\ln\frac{0.00500}{1.50}$$

$$E_{\text{cell}} = +1.1\,\text{V} - (-0.070\,\text{V})$$

$$E_{\text{cell}} = +1.17\,\text{V}$$

Use the Nernst equation to calculate the cell potential at 298 K of a voltaic cell consisting of a silver electrode suspended in 0.0100 mol dm^{-3} aqueous silver nitrate and a zinc electrode in 1.50 mol dm^{-3} aqueous zinc sulfate.

The cell reaction here is: $\text{Zn(s)} + 2\text{Ag}^{+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag(s)}$

The reaction quotient Q is therefore $\frac{\text{Zn}^{2+}(\text{aq})}{\text{Ag}^{+}(\text{aq})^2}$ (note the Ag^+ concentration raised to second power, because Ag^+ has a coefficient of 2).

Under standard conditions:

$$E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{Ag}} - E^{\ominus}_{\text{Zn}}$$

$$E^{\ominus}_{\text{cell}} = +0.80\,\text{V} - (-0.76\,\text{V}) = +1.56\,\text{V}$$

Under these non-standard conditions:

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{0.0275}{2}\ln\frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Ag}^{+}(\text{aq})]^2}$$

$$E_{\text{cell}} = +1.56\,\text{V} - \frac{0.0275}{2}\ln\frac{150}{0.0100^2}$$

$$E_{\text{cell}} = +1.56\,\text{V} - (0.120\,\text{V})$$

$$E_{\text{cell}} = +1.44\,\text{V}$$

Concentration cells

As the concentration affects the electrode potential of a half-cell, this means that it is possible to generate a cell EMF using two electrodes of the same material, and the same electrolyte, but at different concentrations.

In such cases, the standard electrode potential $E^{\ominus}_{\text{cell}}$ equates to zero, as this would have both electrolytes at 1 mol dm^{-3}. However, when the two concentrations are changed, a measurable EMF is produced.

For concentration cells at 298 K, the Nernst equation takes the form:

$$E = \frac{0.0257}{n} \ln \frac{C_2}{C_1}$$

where C_2 and C_1 represent the concentrations of electrolyte in the half-cells containing the anode and cathode.

Worked example

An example of a concentration cell is a nerve cell. Different concentrations of potassium ions inside and outside the cell can result in the generation of an electrical potential. Estimate this potential if the concentration of potassium ions (K^+) outside the cell is known to be about 20 times that inside the cell.

$$E = \frac{0.0275}{1} \ln \frac{20}{1}$$

$$E = 0.077\ \text{V}$$

11 Use the Nernst equation to calculate the cell potential at 298 K of a voltaic cell consisting of a copper electrode suspended in 0.100 mol dm^{-3} aqueous copper(II) sulfate and an iron electrode suspended in 0.0200 mol dm^{-3} aqueous iron(II) nitrate.

12 Use the Nernst equation to calculate the cell potential at 298 K of a concentration cell consisting of two zinc electrodes – one suspended in a solution of 0.100 mol dm^{-3} zinc sulfate and the other in 0.000500 mol dm^{-3} zinc sulfate.

Experimental work

The Nernst equation offers an excellent source of experimental investigations. A simple Daniell cell (copper/zinc) can be set up in the school laboratory (Figure 24.59) and the effect of changing the concentration of either the copper(II) ion solution or the zinc ion solution can be investigated. Alternatively the temperature of one or both half-cells could be changed using a water bath and the voltage measured.

An alternative investigation might involve a concentration cell, in which two copper or zinc half-cells are connected (with an EMF of zero expected) and the concentration of ions in each half-cell is then varied.

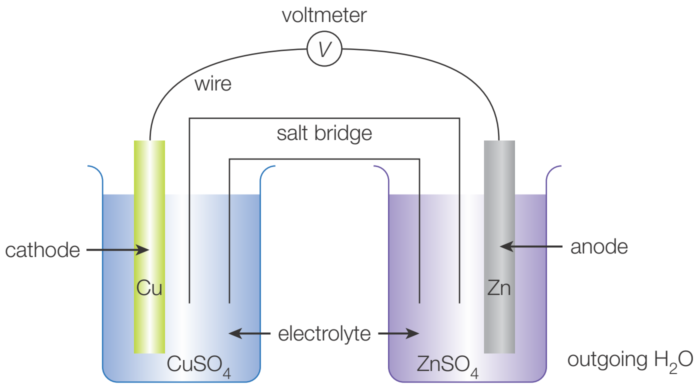


Figure 24.59 A simple Daniell cell. The voltage reading on the voltmeter can be investigated as the concentrations of the copper(II) sulfate or zinc sulfate solutions is changed at constant temperature

Battery disposal

Primary cells contain elements such as zinc and manganese. Secondary cells contain elements such as nickel, cadmium and cobalt. How do we ensure that these substances do not enter the environment?

Responses to this question vary widely around the world. In more economically developed countries, battery recycling and careful disposal has gained more attention recently. The European Union passed a directive in 2009 requiring battery producers to collect and dispose of their products. In the USA, many state laws require that rechargeable batteries are recovered and recycled, owing to their toxicity, although few primary cells are recycled.

Even within the same country, laws vary. For example in Western Australia, all used batteries are required to be encased in concrete so that harmful substances cannot leach out in landfill areas. Queensland has no such requirement.

Laws regulating recycling of lead-acid batteries in rich countries can actually do more harm than good. Manufacturers often export the batteries to less economically developed countries such as Mexico, India and Brazil where environmental and labour laws are less stringent. This may result in lead pollution entering the local environment and lead poisoning of employees and their families.

ToK Link

The language of electricity

You have probably studied electricity during school science using a series of metaphors. Electric current is likened to a flow of water, or traffic on a road; voltage or electromotive force is the ‘push’ given to the charged particles by a power supply; resistance is like the narrowing of a river or a decrease in the lanes of traffic, making it more difficult for current to flow.

These metaphors are helpful because they render the atomic world inside a wire (for instance) as comprehensible, and in many cases the metaphoric explanation does lead to predictable outcomes. For example, a thinner wire (like a narrower road) has a higher resistance.

Upon considering the nature of ‘current’ more carefully we might say that likening it to a fluid is incorrect, when it is actually a series of electrons, moving from valence shell to valence shell of a series of atoms. But even at this point, we are using metaphors such as ‘shells’ to represent the location of electrons, while also assuming that the electron is a discrete particle, when it also exhibits wave-like behaviour.

This example illustrates that it is difficult to eradicate metaphor entirely from scientific discourse. Some philosophers of science express a wish to do so, proposing that scientific theories should be literal and precise. One the other hand, some of the greatest minds in science appreciated the power of metaphor. James Clerk Maxwell used ‘lines of force’ to explain magnetism. Richard Dawkins described genes as ‘selfish’. When advanced scientific theories can in fact only be described accurately using mathematics, a simple metaphor can be incredibly useful.

24.7 Nuclear fusion and nuclear fission *– large quantities of energy can be obtained from small quantities of matter*

Nature of Science

Theory and experiment

The development of our understanding of nuclear processes, and its application in weapons and power generation, demonstrates the interplay between theory and experiment in the sciences.

In 1933, Hungarian physicist Leó Szilárd conceived the possibility of a nuclear chain reaction driven by the recently discovered neutron. However, it was only after failed experiments on various elements by many scientists that he and Enrico Fermi established that uranium was able to sustain a nuclear chain reaction.

Later, during the Manhattan Project, it was established by theoreticians led by Seth Neddermeyer that one way to create the critical mass needed for detonation of a bomb was to compress a mass of plutonium using an explosive shockwave. However, the technical difficulties in creating a symmetrical shockwave that would compress the mass of plutonium evenly and not simply blow it apart were enormous. It required dozens of experimental tests to develop the shaped explosive charges needed to achieve this, as well as theoreticians calculating the shapes of the explosive charges needed.

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A much more modern example is the development of nuclear fusion. We know that nuclear fusion is possible: it takes place in the Sun. However, a self-sustaining fusion reaction on Earth has yet to be achieved. One major technical hurdle is maintaining a 'plasma' of hydrogen nuclei at a temperature high enough that they are able to collide and fuse. In 2012, researchers at the Princeton Plasma Physics Laboratory made a theoretical breakthrough in the understanding of the behaviour of this plasma. They realized that the formation of 'clumps' in the plasma led to it cooling down and collapsing. Experimental physicists now have a basis for further work in establishing how to design reactors to prevent this cooling effect.

Energy from nuclear processes

In Section 24.3 we explored the applications of nuclear fission and fusion. The main point is that these processes are able to generate enormous quantities of energy.

Two major questions that remain to be answered are these:

1. Why is so much energy produced by these processes (nuclear fuels have energy densities hundreds of thousands of times higher than chemical fuels)?
2. How can it be that fission (splitting the nuclei of large atoms) and fusion (combining the nuclei of small atoms) both result in release of energy?

To answer these two questions requires an understanding of the mass–energy relationship proposed by Einstein, described in his famous equation $E = mc^2$, and an appreciation of the strong forces that bind nuclei together.

Einstein's equation

In Einstein's equation (known as the mass–energy equivalence relationship), E represents energy (in J), m represents mass (in kg) and c is the speed of light in a vacuum.

What the equation shows is that energy and mass are interchangeable quantities. During a chemical reaction, it is assumed that energy is conserved and that mass is conserved separately. However, during nuclear processes, we need only assume that the total quantity of mass and energy are conserved.

The numerical value of c is very high (approximately $3.00 \times 10^8\,\text{m s}^{-1}$) so a small mass, if converted to energy, releases enormous amounts of energy.

This is the basis of the enormous energy density of nuclear fuels. During fission and fusion processes, the masses of the nuclei involved are *not quite* conserved. Small amounts of mass (fractions of an atomic mass unit) are converted to energy during the processes.

Nuclear binding energy and mass defect

Section 24.3 includes a qualitative discussion of the energy changes during fission or fusion processes. To briefly recap, a nuclear process will occur if the binding energy of the nuclei of the products is greater than the binding energy of the reactant nuclei.

The binding energies of nuclei depend on a balance between the strong nuclear force (which dominates for small nuclei) and the electrostatic repulsion between the protons (which becomes more important in large nuclei, with many protons).

- *Binding energy* (ΔE): the energy required to separate a nucleus into protons and neutrons. It is expressed in kilojoules per mole of nuclei or megaelectronvolts (MeV).

  If the masses of the protons and neutrons in a particular nucleus are added up it is found that the total is slightly less than the actual mass of that nucleus. This arises because the binding energy of a nucleus has a small amount of mass associated with it (from $E = mc^2$) so the actual nuclear mass is slightly higher than its substituent protons and neutrons. This difference is called the mass defect (Δm).

- *Mass defect* (Δm): the difference between the mass of a nucleus and the total mass of its substituent nucleons.

Calculating the mass defect and binding energy of a nucleus

If we sum the masses of the nucleons in a given nucleus, and compare the total to the mass of the nucleus, we can use the mass defect to find the binding energy.

In the following examples, the atomic mass unit (amu) refers to a mass equal to one-twelfth that of a carbon-12 nucleus.

Worked example

Find the mass defect and binding energy of a helium-4 nucleus ($^{4}_{2}\text{He}$). Use the data in Table 24.15.

Actual mass of helium-4 nucleus	4.002602 amu
Mass of proton	1.007276 amu
Mass of neutron	1.008665 amu
Mass of 1 amu in kg	1.660539×10^{-27} kg
Speed of light in a vacuum	$299\,792\,500\ \text{m s}^{-1}$

■ **Table 24.15** Data for helium-4

A helium-4 nucleus consists of two protons and two neutrons.

Total mass of helium nucleus = (no. of neutrons × mass of neutron) + (no. of protons × mass of proton)

$$\text{Mass} = (2 \times 1.008665) + (2 \times 1.007276) = 4.031882\ \text{amu}$$

$$\text{Mass defect} = \text{mass of constituent particles} - \text{mass of nucleus}$$

$$= 4.031882\ \text{amu} - 4.002602\ \text{amu} = 0.029280\ \text{amu}$$

Hence the mass of the actual nucleus is smaller than the mass of its substituents. The 'missing mass' represents the energy released when the nucleus is formed.

To find the binding energy:

First, convert the mass defect into kilograms:

$$\text{Mass defect} = 0.029280 \times 1.660539 \times 10^{-27} = 4.862058 \times 10^{-29}\ \text{kg}$$

Apply Einstein's equation to convert this into energy (J):

$$\text{Energy} = \text{mass defect} \times (\text{speed of light})^2$$

$$E = 4.862058 \times 10^{-29} \times (299\,792\,500)^2 = 4.368927 \times 10^{-12}\ \text{J per nucleus}$$

To convert to energy change in kilojoules per mole (kJ mol^{-1}), multiply by the Avogadro constant to obtain the joules per mole, then divide by 1000:

$$4.368927 \times 10^{-12}\ \text{J} \times 6.022141 \times 10^{23}\ \text{mol}^{-1} = 2.631029 \times 10^{12}\ \text{J mol}^{-1}$$

$$= 2.631029 \times 10^{9}\ \text{kJ mol}^{-1}$$

Megaelectronvolts as a unit of energy:

The binding energy graph shown in Section 24.3 (see Figure 24.17 on p.27 or Section 36 of the IB *Chemistry data booklet)* uses the unit MeV, that is, megaelectronvolts.

The electronvolt (eV) is defined as the energy required to move one electron across a potential difference of one volt.

$$1\ \text{eV} = 1.6022 \times 10^{-19}\ \text{J}$$

In the example above, the binding energy of a helium nucleus is calculated as 4.368927×10^{-12} J. To convert into electron volts:

$$\frac{4.368927 \times 10^{-12}\ \text{J}}{1.6022 \times 10^{-19}\ \text{J eV}^{-1}} = 27\,268\,000\ \text{eV} = 27.3\ \text{MeV}$$

How much energy is produced in a fusion reaction?

The mass difference between the products and reactants can be used to calculate the energy released during a fusion process.

Application of the Einstein mass–energy equivalence relationship to determine the energy produced in a fusion reaction

Consider this fusion step in the nucleosynthesis of $^{4}_{2}\mathrm{He}$, which takes place in the Sun:

$$^{3}_{2}\mathrm{He} + ^{3}_{2}\mathrm{He} \rightarrow ^{4}_{2}\mathrm{He} + ^{1}_{1}\mathrm{H} + ^{1}_{1}\mathrm{H}$$

The masses of the species concerned are provided in Table 24.16.

Table 24.16 Mass data for helium and hydrogen isotopes

Particle	$^{3}_{2}\mathrm{He}$	$^{4}_{2}\mathrm{He}$	$^{1}_{1}\mathrm{H}$
Mass (amu)	3.016029	4.002602	1.007940

Total mass of reactants: $2 \times 3.016029 = 6.032058\,\mathrm{amu}$

Total mass of products: $4.002602 + (2 \times 1.007940) = 6.018482\,\mathrm{amu}$

$$\text{Mass difference: mass of reactants} - \text{mass of products} = 6.032058\,\mathrm{amu} - 6.018482\,\mathrm{amu}$$
$$= 0.013576\,\mathrm{amu}$$

$$\text{Mass difference in kilograms: } 0.013576\ \mathrm{amu} \times 1.660539 \times 10^{-27}\,\mathrm{kg\,amu^{-1}}$$
$$= 2.254348 \times 10^{-29}\,\mathrm{kg}$$

Apply Einstein's equation to convert this mass difference into energy (J):

$$\text{Energy} = \text{mass difference} \times (\text{speed of light})^{2}$$

$$E = 2.254348 \times 10^{-29} \times (299\,792\,500)^{2} = 2.026107 \times 10^{-12}\,\mathrm{J}\ \text{per nucleus}$$

Expressed in electronvolts this becomes:

$$\frac{2.026107 \times 10^{-12}\,\mathrm{J}}{1.6022 \times 10^{-19}\,\mathrm{J\,eV^{-1}}} = 12\,646\,000\,\mathrm{eV} = 12.6\,\mathrm{MeV}$$

To convert to kilojoules per mole ($\mathrm{kJ\,mol^{-1}}$), multiply by the Avogadro constant to obtain the answer in joules per mole, then divide by 1000:

$$2.026107 \times 10^{-12}\,\mathrm{J} \times 6.022141 \times 10^{23}\,\mathrm{mol^{-1}} = 1.22015 \times 10^{12}\ \mathrm{J\,mol^{-1}}$$
$$= 1.22015 \times 10^{9}\,\mathrm{kJ\,mol^{-1}}$$

How much energy is produced in a fission process?

Similarly, the mass difference between the products and reactants can be used to calculate the energy released during a fission process.

Application of the Einstein mass–energy equivalence relationship to determine the energy produced in a fission reaction

Consider the following fission reaction in which a neutron causes fission of a uranium-235 nucleus, leading to the formation of krypton-92 and barium-141, with three neutrons being released. Necessary data is provided in Table 24.17.

$$^{1}_{0}\mathrm{n} + ^{235}_{92}\mathrm{U} \rightarrow ^{92}_{36}\mathrm{Kr} + ^{141}_{56}\mathrm{Ba} + 3\,^{1}_{0}\mathrm{n}$$

Table 24.17 Mass data for uranium-235 fission

Particle	$^{1}_{0}\mathrm{n}$	$^{235}_{92}\mathrm{U}$	$^{92}_{36}\mathrm{Kr}$	$^{141}_{56}\mathrm{Ba}$
Mass (amu)	1.008665	235.043930	91.926156	140.914411

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Total mass of reactants: $1.008665 + 235.043930 = 236.052595\,\text{amu}$

Total mass of products: $91.926156 + 140.914411 + (3 \times 1.008665) = 235.866562\,\text{amu}$

$$\begin{aligned}\text{Mass difference: mass of reactants} - \text{mass of products} &= 236.052595\,\text{amu} - 235.866562\,\text{amu}\\ &= 0.186033\,\text{amu}\end{aligned}$$

Mass difference in kilograms: $0.186033\,\text{amu} \times 1.660539 \times 10^{-27}\,\text{kg}\,\text{amu}^{-1} = 3.089151 \times 10^{-28}\,\text{kg}$

Apply Einstein's equation to convert this mass difference into energy (J):

Energy = mass difference × (speed of light)^2

$$E = 3.089151 \times 10^{-28} \times (299\,792\,500)^2 = 2.776391 \times 10^{-11}\,\text{J per nucleus}$$

Expressed in electronvolts this becomes:

$$\frac{2.776391 \times 10^{-11}\,\text{J}}{1.6022 \times 10^{-19}\,\text{J}\,\text{eV}^{-1}} = 173\,290\,000\,\text{eV} = 173\,\text{MeV}$$

To convert to kilojoules per mole ($\text{kJ}\,\text{mol}^{-1}$), multiply by the Avogadro constant to obtain the energy change in joules per mole, then divide by 1000:

$$\begin{aligned}2.776391 \times 10^{-11}\,\text{J} \times 6.022141 \times 10^{23}\,\text{mol}^{-1} &= 1.671981 \times 10^{13}\,\text{J}\,\text{mol}^{-1}\\ &= 1.671981 \times 10^{10}\,\text{kJ}\,\text{mol}^{-1}\end{aligned}$$

One can compare this with the enthalpy of combustion of octane, which is $-5470\,\text{kJ}\,\text{mol}^{-1}$, smaller by a factor of a million.

13 Calculate the mass defect in kg and the binding energy in MeV of this fusion reaction which is part of the nucleosynthesis of nitrogen: ${}^{12}_{6}\text{C} + {}^{1}_{1}\text{H} \rightarrow {}^{13}_{7}\text{N}$. Necessary data is provided in Table 24.18.

Particle	${}^{1}_{1}\text{H}$	${}^{12}_{6}\text{C}$	${}^{13}_{7}\text{N}$
Mass (amu)	1.00794	12.00000	13.00574

Table 24.18 Mass data for nucleosynthesis of nitrogen

Producing nuclear fuel

In Section 24.3 it was noted that nuclear fission weapons contain a relatively small quantity of uranium-235 of high purity. Since U-235 is fissionable, a 'critical mass' of this substance can lead to a chain reaction, with the instantaneous release of enormous amounts of energy. However, nuclear power stations instead rely on the slow release of energy from the fission reaction. A runaway chain reaction leads to reactor meltdown. So in a power station, uranium containing a much smaller proportion of fissionable U-235 is used, with the remainder being mostly uranium-238.

In both situations however, the proportion of U-235 is greater than that which occurs naturally (see Table 24.19). It is therefore necessary to **enrich** natural uranium by a process of isotope separation, in order that the proportion of U-235 is sufficient for the stated purpose.

Table 24.19 Different enrichment grades of uranium

	Proportion of U-235
Natural uranium	0.7%
Low-enriched uranium (for reactors)	3–4%
High-enriched uranium (for weapons)	>90%

First stages of uranium production

Uranium is mined as U_3O_8, a yellow solid ore commonly known as yellowcake. This solid undergoes a series of reactions, via uranium dioxide (UO_2), ending with oxidation with fluorine gas, to form uranium hexafluoride (UF_6; uranium(VI) fluoride; commonly known as *hex*). Uranium hexafluoride is a solid at room temperature, but it sublimes at only 56.5 °C at 1 atmosphere pressure (Figure 24.60). The isotope separation of uranium uses UF_6 in the gas phase.

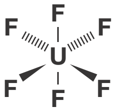


Figure 24.60 Uranium hexafluoride

UF_6 is a non-polar covalent molecular substance. In the solid phase, the molecules are held together in a lattice by dispersion forces. These require relatively little thermal energy to overcome them, leading to a low sublimation temperature.

Like other metallic halides with large degrees of covalency in their bonding, such as aluminium chloride, UF_6 hydrolyses when added to water, forming uranyl fluoride UO_2F_2 and hydrogen fluoride, according to the following equation:

$$UF_6(g) + 2H_2O(l) \rightarrow UO_2F_2(aq) + 4HF(g)$$

The different properties of UO_2 and UF_6 in terms of bonding and structure

Uranium dioxide is an ionic compound, containing uranium(IV) ions (U^{4+}) and oxide (O^{2-}) ions, arranged in a similar manner to the ions in calcium fluoride, CaF_2. As an ionic lattice comprised of highly charged ions (uranium(IV), 4+ and oxide, 2−) the melting point is very high, at 3140 K.

Uranium hexafluoride has a very high molar mass (349 $g\,mol^{-1}$) but is a gas at temperatures only slightly above room temperature. This might seem unusual but can be explained by considering the bonding within the substance. Fluorine forms short strong bonds with the central uranium atom, and the resulting molecule is a symmetrical octahedral molecule with no permanent dipole. The bonding within the UF_6 molecules is strong but the intermolecular forces binding it to its neighbours are weak dispersion forces.

Isotope separation

The different masses of the uranium atoms within uranium hexafluoride means that they can be separated:

If U-235 is present, the mass of a UF_6 molecule is 349 amu.

If U-238 is present, the mass is 352 amu.

This represents about a 0.8 per cent difference in mass between these two molecules. Although small, this mass difference affects the physical properties of UF_6 sufficiently that the molecules can be separated by physical means.

Separation by effusion

Effusion is a method by which gaseous substances can be separated according to their molecular masses. British scientists devised this method in 1940. When the USA entered World War II, the British atomic weapons effort was absorbed into the US Manhattan Project. The uranium used in the 'Little Boy' weapon dropped on Hiroshima was enriched by effusion.

The relationship between Graham's law of effusion and the kinetic theory

Effusion is defined as the process in which gas molecules pass through a small hole in their containment vessel. The rate at which the molecules pass through the hole is related to their mass. Heavier molecules pass through the hole at a lower rate. If a mixture of two gases is placed in the vessel, the gas with lighter molecules will escape through the hole at a higher rate, so the gas inside the vessel becomes richer in the heavier component.

This is explained by recalling that the kinetic energy is given by the expression $\frac{1}{2}mv^2$, where m is the mass and v is the average velocity of the gas molecules.

In a mixture of gases of different masses, at the same temperature, the average kinetic energy of the different gases must be the same. Since the lighter gas has a lower value of m, it must therefore have a higher value of v, so that $\frac{1}{2}mv^2$ reaches the same value. In short, the lighter gas has a higher average velocity of its molecules, so more of them will travel through the hole in the container wall, in a given time.

The relationship between mass of gas molecules and effusion rate is given by **Graham's law**:

$$\frac{\text{rate}_1}{\text{rate}_2} = \sqrt{\frac{\text{mass}_2}{\text{mass}_1}} = \sqrt{\frac{\text{density}_2}{\text{density}_1}}$$

In this equation rate_1 and rate_2 refer to the rates of effusion of two gases (measured in moles per unit time), and mass_1 and mass_2 are their formula masses. The equation can also be expressed in terms of the densities of the gases, density_1 and density_2.

Figure 24.61 shows how an effusion vessel operates. UF_6 vapour containing a mixture of the two uranium isotopes enters the vessel. The vessel is divided in two by a porous membrane. UF_6 containing uranium-235 effuses through the membrane more rapidly than that containing uranium-238 so the two isotopes are gradually separated.

Problems on the relative rate of effusion using Graham's law

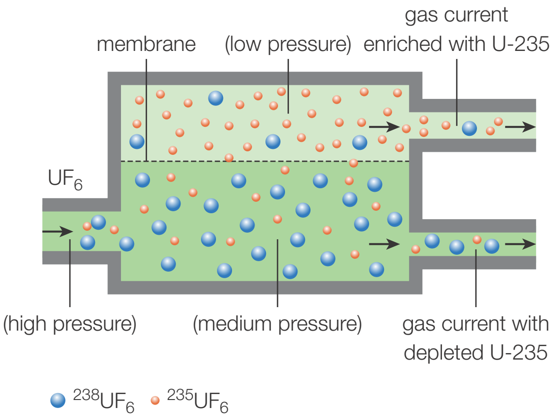
The masses of UF_6 molecules are slightly different, so the effusion rate will be slightly different also. The difference in effusion rate can be calculated using the molar masses cited above:

$$\frac{\text{rate}_{235UF6}}{\text{rate}_{238UF6}} = \sqrt{\frac{\text{mass}_{238UF6}}{\text{mass}_{235UF6}}} = \sqrt{\frac{352}{349}} = 1.004$$

Hence the rate of effusion of $^{235}UF_6$ is 1.004 times the rate of effusion of $^{238}UF_6$ (or 0.4 per cent faster). If a mixture of $^{235}UF_6$ and $^{238}UF_6$ is allowed to effuse through a hole in a vessel, the mixture of gases passing through the hole will be slightly richer in $^{235}UF_6$.

Figure 24.61 shows how an effusion vessel operates. UF_6 vapour containing a mixture of the two uranium isotopes enters the vessel. The vessel is divided in two by a porous membrane. UF_6 containing uranium-235 effuses through the membrane more rapidly than that containing uranium-238 so the two isotopes are gradually separated.

Figure 24.61 Separation of uranium isotopes by effusion



In practice, uranium hexafluoride is passed through a series of membranes, with the mixture becoming slightly richer in U-235 at each stage.

Isotope separation requires enormous amounts of energy and is incredibly expensive. Although this method dominated during the first decades of the Cold War, when both the USA and the USSR were determined to build up their atomic arsenals at all costs, it is now rarely used, having been mostly supplanted by centrifugation methods.

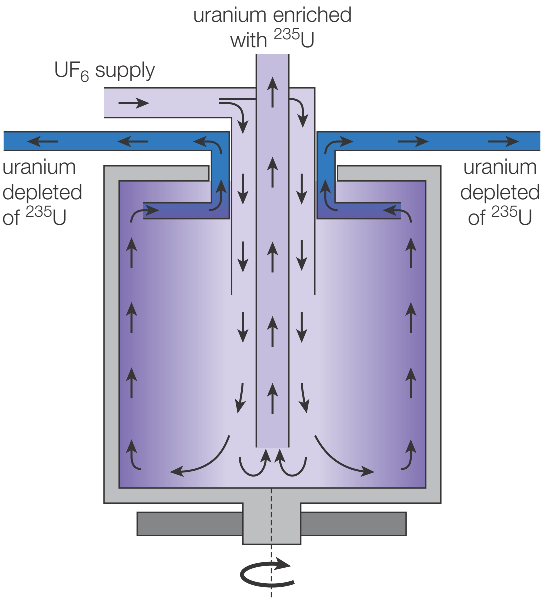


Figure 24.62 Gas centrifuge used for isotopic separation of uranium

Centrifugation methods

A **centrifuge** is often used in science laboratories to separate mixtures. Biology laboratories use them to separate blood cells from plasma for example.

A centrifuge consists of a rotating cylinder into which a mixture is placed. When the cylinder is spun at high speed, more dense components of the mixture are forced outwards, away from the centre of rotation, while less dense components remain nearer the centre.

A gas centrifuge can therefore be used to separate a sample of uranium hexafluoride into its isotopic components. Heavier $^{238}UF_6$ molecules are forced away from the centre of rotation with more force than lighter $^{235}UF_6$.

Figure 24.62 illustrates the process. UF_6 richer in uranium-235 is extracted from the vessel close to the axis of rotation (i.e. the centre of the diagram), and UF_6 richer in uranium-238 is extracted further from the axis of rotation (i.e. the edges of the diagram).

Gas centrifugation requires much less energy than the effusion-based method outlined above – only about one-fiftieth as much. It also requires fewer stages, as the separation ratio at each stage is about 1.3 rather than 1.004.

Uranium enrichment

At present, only a small number of countries have nuclear weapons, but many others claim to want to pursue peaceful nuclear energy. A country wishing to develop nuclear power will need to either buy enriched uranium from other countries, or develop their own centrifuges and process their own. The problem here is that the basic principle is the same whether you wish to enrich uranium to 4 per cent for a reactor or to 90 per cent for a nuclear bomb.

In 2010 it was discovered that a computer worm, called 'Stuxnet', had been introduced into the control systems of the Iranian uranium enrichment facilities. This worm, which is harmless to most other computer systems, appeared to have been specifically developed to damage the Iranian enrichment effort. The difficulty of getting this advanced piece of malware into Iran and into the software systems involved led many to believe that governments were involved, specifically those of Israel and the USA. These countries are highly suspicious of Iran's peaceful nuclear ambitions, citing the aggressive statements made by Iran towards Israel in the past.

Do countries in possession of nuclear technology have the right to deny it to other countries? International agencies exist to deter nuclear proliferation, but the 'nuclear club' is one that many nations still aspire to join. Should countries be sharing nuclear technology with one another in order to reduce reliance on fossil fuels around the world?

The dangers of nuclear energy

In Section 24.3 we outlined the three types of ionizing radiation and their potential for harm to humans. How does ionizing radiation actually damage human tissues? Why does radiation lead not only to tissue damage but also cancers later on?

Alpha, beta and gamma radiation are *ionizing*; that is, they have sufficient energy to promote electrons to higher energy levels and, ultimately, out of an atom altogether, forming an ion.

Direct effects of radiation

If the atom being ionized is part of a DNA molecule, then the ionization of the atom can affect the bonding within the DNA molecule. This may affect the DNA's ability to encode proteins and to replicate itself. This will then lead to the failure of cell processes and ultimately the death of the cell.

Indirect effects of radiation

The chances of a gamma ray photon or a beta particle, for example, interacting with a DNA molecule are actually quite small, because only a very small part of each cell, and therefore the larger organism, is actually composed of DNA. However, an enormous proportion of the tissues of the organism is composed of water.

Ionizing radiation, upon collision with a water molecule, can generate hydroxyl radicals:

$$H_2O \rightarrow HO^{\bullet} + H^{\bullet}$$

Hydroxyl radicals, $HO^{\bullet}$, having an unpaired electron, are highly reactive species, and their presence in a cell in elevated concentrations is highly dangerous. They can collide and react with DNA molecules, causing damage that leads to an inability to replicate the DNA, or to mutations in the DNA that might result in tumours later on.

Another highly dangerous radical is superoxide, $O_2^{-\bullet}$ (Figure 24.63).

This species is actually employed by the body itself as part of the immune response – it is generated by phagocytes (white blood cells) when attacking invading pathogens.

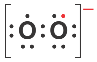


Figure 24.63 Lewis structure of a superoxide ion

Acute radiation syndrome (radiation sickness)

People exposed to large doses of radiation in a short time, such as victims of the atomic bombs in Japan or workers involved with nuclear accidents such as Chernobyl (1986) or Fukushima (2011), experience a range of symptoms.

The most sensitive system to the effects of ionizing radiation is the blood system. A large dose of radiation can cause rapid damage to bone marrow, meaning that victims experience symptoms related to their blood. A lack of platelets means that the blood cannot clot, leading to internal and external hemorrhaging. A lack of red blood cells leads to anemia, and a lack of white blood cells means that victims are highly susceptible to infections.

Figure 24.64 Nuclear testing at Maralinga, Australia

Longer-term effects of radiation

The damage to DNA and enzymes caused by ionizing radiation can have long-term health effects.

Cancer is the uncontrolled growth of cells. Normally, control processes ensure that cell repair and replacement occur at an appropriate rate to keep the body healthy. Radiation damage can interfere with these control processes, meaning that cells become 'immortal' and undergo uncontrolled cell division, leading to tumours. A tumour is a body of cells growing uncontrollably. These cells have their own blood supply and draw resources from the body. Cancer cells can then spread around the body leading to further tumours elsewhere. British, US and Australian servicemen and local islanders exposed to weapons tests in the Pacific in the 1950s experienced higher rates of cancers in later life (Figure 24.64).

In addition, ionizing radiation can cause a mutation in the DNA, meaning that the genetic sequence is changed. When the cells divide, they are no longer perfect healthy copies of the original. Sometimes, these mutations can lead to visible effects in the organism. In the aftermath of the atomic bombs on Japan, there was an increase in the number of fetal abnormalities, caused by the mothers' exposure to radiation.

Measuring radioactive doses

Doses of ionizing radiation are measured in sieverts (Sv). One sievert represents the effect on the body of one joule of energy from radiation on one kilogram of tissue. In SI unit terms, $1\,\text{Sv} = 1\,\text{J}\,\text{kg}^{-1}$.

The sievert can be used to estimate the increased risk of disease as radiation dose increases. For example, with each additional sievert of radiation exposure, the risk of cancer is estimated to increase by 5.5 per cent.

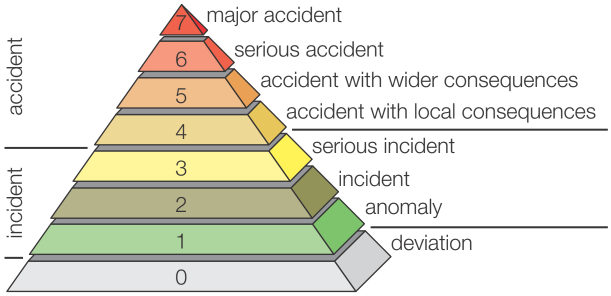
A typical radiation dose per year is 1 mSv (1 millisievert). Some activities increase the dose but are unlikely to lead to dangerous exposure. For example, aircrew receive more radiation due to time spent at high altitude, but this still only leads to about 1.5 mSv per year. A mammogram (X-ray) adds about 0.5 mSv.

Victims of the Hiroshima attack received doses ranging from 1 Sv to 10 Sv. Those receiving the higher doses all died quickly. Those receiving doses around 1 Sv experienced higher rates of cancers in subsequent years.

In 1946, Louis Slotin, a nuclear scientist, slipped while assembling the core of an experimental nuclear weapon and allowed the components to touch. For a fraction of a second, the mass went critical, and Slotin received an estimated dose of 21 Sv. He died 9 days later. Slotin gave permission for his illness to be filmed and used to educate others about the dangers of working with radioactive materials.

Nuclear accidents – cross-border disasters?

Despite strict safeguards, nuclear accidents do occur. They have the potential to be disastrous because radioactive material might leave the reactor and enter the oceans or the atmosphere, meaning that dangerous levels of radiation could be spread over a wide area, with no respect for international borders.



■ **Figure 24.65** The International Nuclear and Radiological Event Scale (INES)

In order that the severity of nuclear accidents can be rapidly communicated, in 1990 the International Atomic Energy Agency (IAEA) introduced the International Nuclear and Radiological Event Scale (INES; Figure 24.65). The INES is a logarithmic scale, so a category 7 event is ten times worse than a category 6 event.

In 1979 the Three Mile Island nuclear plant in Pennsylvania, USA, underwent a partial meltdown owing to a coolant leak. Radioactive gases were released into the atmosphere. INES did not exist at the time, but this event is now considered to be a level 5 event – an accident with wider consequences. Although there was no serious contamination on a national or international scale, some radioactive material was released into the atmosphere, and its spread was unpredictable.

The Chernobyl disaster of 1986 (Ukraine) was much more serious and is now categorized as a level 7 event. An explosion and fire at the plant led to enormous amounts of radioactive material entering the environment. The nearby cities of Chernobyl and Pripyat were completely abandoned. A 30 km exclusion zone was set up around the site, which still exists today, and elevated levels of radioactivity in air and soil were detected throughout Europe.

In 2011 a tsunami caused major damage to the reactor complex at Fukushima, Japan. Leaks of radioactive material into the sea and the atmosphere led to the establishment of a 20 km exclusion zone. The combined impact of damage to the six reactors in the complex warranted a level 7 event rating.

Kinetics of radioactive decay processes

In Section 24.3 we discussed that the time taken for the radioactivity of a sample to be halved is called the **half-life**. Radioactive decay processes are first-order processes – the half-life remains constant, but the number of radioactive atoms remaining in the sample decays exponentially.

Unlike chemical processes, radioactive decay rates are not affected by conditions such as temperature or pressure.

In first-order reactions, the half-life, $t_{\frac{1}{2}}$ is related to the decay constant λ by the following equation:

$$t_{\frac{1}{2}} = \frac{\ln 2}{\lambda} \text{ (where } \ln 2 = 0.693)$$

Hence the decay constant can be determined if the half-life is known:

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

The equation $N = N_0e^{-\lambda t}$ is given in Table 1 of the *IB Chemistry data booklet* and can be used to determine the amount of radioactivity in a sample (N) given the decay constant (λ), the time elapsed (t), and the original amount of radioactivity. Rearranging gives

$$\frac{N}{N_0} = e^{-\lambda t} \text{ where } \frac{N}{N_0} \text{ is the fraction of the orginal radioactivity present.}$$

In Section 24.3 the decay equation was also demonstrated to rearrange to:

$$t_{\frac{1}{2}} = t\frac{\ln 2}{\ln\left(\frac{N_0}{N}\right)}$$

Worked examples

Calculate the decay constant λ for the beta decay of iodine-131 (^{131}I), which has a half-life of 8.02 days. Find the fraction of the original radioactivity remaining after 30 days.

8.02 days = 8.02 × 24 × 60 × 60 seconds = 692 928 seconds

$$\lambda = \frac{0.693}{692928\text{ s}} = 1.00 \times 10^{-6}\text{ s}^{-1}$$

Time elapsed = 30 days = 30 × 24 × 60 × 60 = 2 592 000 seconds

$$\frac{N}{N_0} = e^{-\lambda t} = e^{-1.00 \times 10^{-6} \times 2592000} = 0.0749$$

So the fraction of the original radioactivity present is 0.0749 or 7.49 per cent.

Strontium-90 is a radioisotope found in fallout from nuclear weapon tests. It is particularly dangerous because its chemistry is similar to that of calcium, meaning that it is readily absorbed by the body and incorporated into tissues such as bone. It has a half-life of 28.8 years. If 50 g of Sr-90 was produced in a weapon test in 1954, how many grams will remain in 2014?

$$\lambda = \frac{0.693}{28.8\text{ y}} = 0.0241\text{ y}^{-1}$$

$$N = N_0e^{-t}$$

Where $N_0 = 50$ g and $t = 60$ years:

$$N = 50e^{-0.0241 \times 60} = 11.8\text{ g}$$

ToK Link

Predictions

'There is no likelihood that humans will ever tap the power of the atom.'

(Robert Millikan, Nobel Laureate Physics 1923, quoted in 1928)

'It's hard to make predictions, especially about the future.'

(attributed to various people, but often Niels Bohr, Nobel Laureate Physics 1922, quoted in 1918)

With hindsight, Millikan's quote seems ridiculous, as the scientific progress that led first to atomic weapons and then nuclear power seems inevitable. However, Millikan was a Nobel Prize-winning physicist – an expert in his field. His best judgement from the facts available was that harnessing atomic energy would be impossible. When Millikan was quoted in 1928, Leó Szilárd had yet to make his theoretical breakthrough conceiving the neutron-driven nuclear chain reaction in 1933.

The above story illustrates the difficulties faced by scientists in making predictions. Although scientists make and test predictions about the outcomes of their carefully designed scientific experiments all the time, predicting the impact that a new discovery will have is incredibly difficult, as there are so many variables at work. Refer back to the Nature of Science section on pages 77–8 although Leó Szilárd conceived that a nuclear chain reaction was theoretically possible, it took hundreds of scientists and millions of dollars to actually achieve a chain reaction.

The use of quotes such as Millikan's (and there are many others) to criticize the wisdom of experts is fun but it ignores a consideration of historical context. In the study of history, the injection of modern perspectives into a historical analysis is called presentism (meaning 'based in the present'). When applied to the history of science, this leads to a fallacious way of thinking in which those who promoted new ideas and instigated 'paradigm shifts' are seen as the 'heroes', and those who offered criticism and were reluctant to accept the new paradigm are the 'villains'. This view profoundly underserves many very important scientific figures in history, who in applying the scientific method were quite right to demand strong and clear evidence before rejecting an existing scientific theory.

ToK Link

Science and moral responsibility

'The only reaction I had…was a very considerable elation and excitement, and going to parties…It would make a tremendously interesting contrast between what was going on in [America] at the same time as what was going on in Hiroshima.'

(Manhattan Project physicist Richard Feynman on his reaction after the successful detonation of an atomic bomb over Hiroshima in 1945, quoted in 1981).

In the interview, originally broadcast by the BBC, Feynman goes on to express regret for not having considered the wider implications of his work on the bomb. He explains that when he started work, it was felt that the USA was in a race with the Nazi regime in Germany to develop the weapon. He felt there was a moral imperative to develop the bomb first to deter the Nazis. Feynman's regret was that when it became clear that the Germans were not going to reach their goal, he was so caught up in the research that he did not then stop to reconsider why he was doing his research and how the weapon might be used.

Does Feynman bear a moral responsibility for the deaths in Hiroshima? Some would say no – the decision to use the weapon lay with the US president, Harry S Truman. Others suggest that the scientists knew they were developing a weapon of mass destruction (they were more knowledgeable than anyone about the potential power of the bomb) and they should have protested.

Fritz Haber, the German scientist who pioneered poison gas research in World War I (see Chapter 7), claimed to believe that his new weapon was so horrible and indiscriminate that it would lessen people's willingness to wage war, leading to fewer deaths. Alfred Nobel, inventor of dynamite, thought the same.

Weapons research is an extreme case – it is hard for the scientists concerned to deny the ultimate purpose of their work (although in the case of the Manhattan Project, the US was at war at the time, which might influence your moral view).

What about examples in which the scientists intend to do good? The development of genetically–modified crops could prove invaluable in feeding the growing global population, but it could lead to unforeseen consequences in nature. The use of geo-engineering to cool down the planet (see in Section 24.5) could mitigate global warming, or it could lead to a worse climate disaster. Ostensibly the scientists here are working towards something they believe to be beneficial, but which nonetheless might present a risk.

Is the scale of the possible consequence a factor in the moral calculus? In the 19th century a factory machine or a steam engine could kill a small number of people. In the 21st century a nuclear war using hydrogen bombs could annihilate mankind. A climate disaster could displace millions and lead to flooding and famine. A genetically engineered virus escaping from a research facility could lead to a global pandemic.

The Precautionary Principle (see also Section 24.5) might be applied in these cases. This states that if an action has a risk of causing harm to the public or to the environment, the burden of proof that it is not harmful falls on those taking the action.

This means that in the absence of a scientific consensus that geo-engineering is safe, for example, it is up to the geo-engineers to prove that it is. It is their responsibility to examine the consequences before taking action, and in the event of a disaster they must accept the moral responsibility.

So are there any areas of research which can never be morally justified? This is a difficult question. It might depend upon the ethical framework that is applied. Animal experimentation is regarded as abhorrent by many, but can be justified on utilitarian grounds (saving the lives of humans is more important than harming animals). Could utilitarian arguments be used to justify experimenting on humans, such as convicted criminals? This idea would induce revulsion in most people, suggesting that there are elements of moral principle (a view of one's duty towards others, aside from the utilitarian calculation) at work as well. In 1796 Edward Jenner deliberately exposed an 8-year-old boy to smallpox to test his hypothesis that cowpox inoculation offered protection against the disease. Would this be acceptable today?

24.8 Photovoltaic and dye-sensitized solar cells

– when solar energy is converted to electrical energy the light must be absorbed and charges must be separated. In a photovoltaic cell both of these processes occur in the silicon semiconductor, whereas these processes occur in separate locations in a dye-sensitized solar cell (DSSC)

Solar cells are designed to capture sunlight and convert it into electricity. Although they were invented in the late 19th century, solar cells became very important in the 1950s, when it was realized that a solar cell would reduce the reliance of early satellites on on-board batteries.

Solar cells now find a range of applications, from large rooftop solar panels to small cells designed for powering calculators and phones.

Alternative energy advocates like to point out that there is an enormous amount of sunlight energy incident on the Earth. If the US state of West Virginia was covered in solar cells, and these captured 10 per cent of the Sun's energy, this would be enough to meet all our energy needs. However, the high cost of solar cells, combined with the logistical difficulties of capturing sunlight on such a scale and then distributing the electricity, mean that solar energy is likely to form only a small part of the energy mix for some time yet.

How do solar cells work?

There are several types of solar cells. Two important types are the silicon photovoltaic cell and the dye-sensitized solar cell (DSSC).

Silicon photovoltaic cells

Silicon is a non-metal in group 14 of the periodic table (Figure 24.66). It has a giant covalent structure closely related to that of diamond. Each silicon atom (electron arrangement 2,8,4) forms four single covalent bonds to four other silicon atoms (Figure 24.67a). These bonds are in a tetrahedral arrangement leading to a very rigid three-dimensional network (Figure 24.67b).

Silicon is near the boundary between the metals and non-metals in the periodic table (Chapter 3). Silicon is therefore a metalloid and has some properties intermediate between metals and non-metals. In particular, the allotrope of silicon used to make solar cells is a semiconductor – this is a class of substances that have electrical resistivity properties between those of electrical conductors and insulators. Their conductivity rises with temperature because their resistance falls with an increase in temperature.

Figure 24.66 A sample of the element silicon

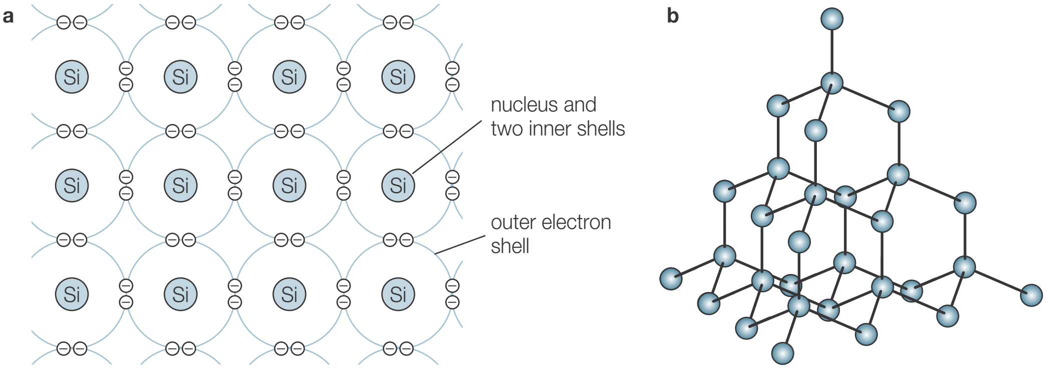


Figure 24.67 Representation of **a** the two-dimensional structure; **b** the three-dimensional structure of silicon

Semiconductors

Semiconductors that are composed of pure elements or compounds are described as intrinsic semiconductors. Silicon is the most important intrinsic semiconductor and is used for the production of a wide range of semiconductor devices. These include the transistor, many kinds of diodes, the silicon-controlled rectifier and integrated circuits. Solar photovoltaic panels are large semiconductor devices that convert light energy directly into electrical energy. However, the conductivity of pure silicon can be greatly increased by adding small amounts of other substances in a process known as 'doping'. Doping is normally done by exposing silicon, in a furnace, to the vapour of the substance to be added. The substance is added in tiny carefully controlled amounts. This ensures that the atoms of the dopant will be well spaced out in the silicon lattice so that its structure is not weakened. There are two types of extrinsic semiconductor: n-type and p-type.

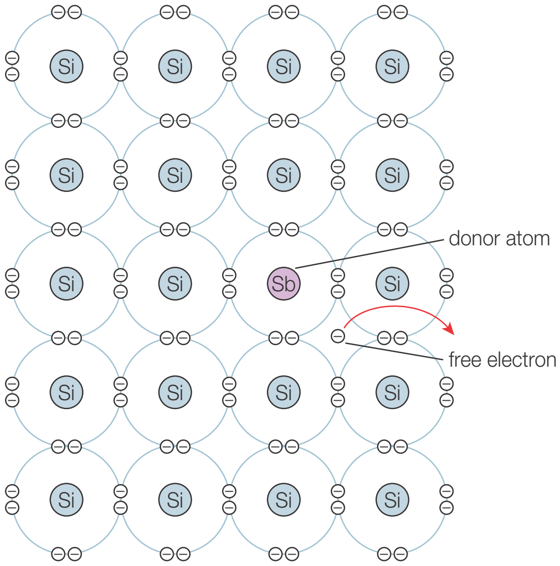


Figure 24.68 A representation of an n-type semiconductor

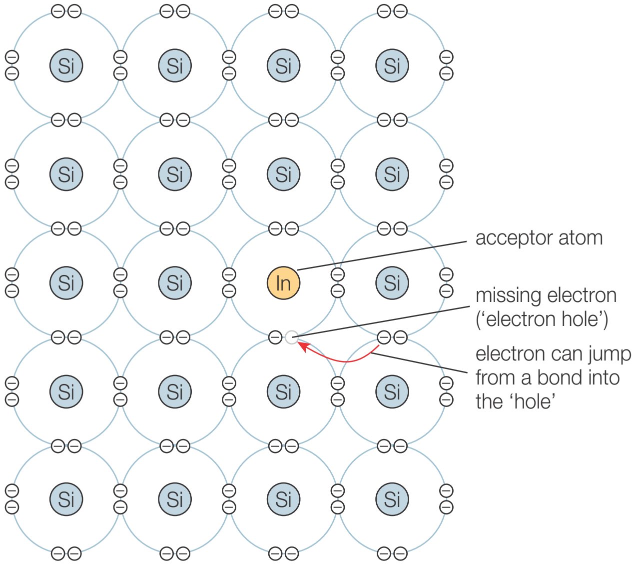


Figure 24.69 A representation of a p-type semiconductor

n-Type semiconductors

In an n-type semiconductor (Figure 24.68) the dopants are group 15 elements – such as phosphorus and antimony – which have five valence electrons. When a dopant atom replaces an atom of silicon in the lattice, it uses four of the five valence electrons to form single covalent bonds with silicon atoms. The fifth valence electron is delocalized into the lattice creating a mobile negative charge. Group 15 elements are called 'donor atoms' because they donate electrons to the silicon atoms. The presence of a small number of delocalized electrons makes the extrinsic semiconductor a significantly better electrical conductor than pure silicon (the parent intrinsic semiconductor). Note that the crystal of the extrinsic semiconductor is uncharged because the additional electrons are associated with a positive charge on the donor nucleus.

p-Type semiconductors

In a p-type semiconductor (Figure 24.69) the dopants are group 13 atoms – such as boron, indium and aluminium – which have three valence electrons. When a group 13 dopant atom replaces a silicon atom, it forms three single covalent bonds with three silicon atoms, but the fourth bond is incomplete – the adjoining silicon atom contributes an electron to the bond, but the group 13 atom does not. The resulting bond consists of only one shared electron. The vacancy is termed an 'electron hole'. The added group 13 atoms are termed 'acceptor atoms' because they can accept electrons to fill the holes in the bonds. Electrons can jump from nearby bonds into the holes. This leads to the hole reappearing somewhere else – in the location the electron came from. As electrons move to fill the hole, the hole effectively 'moves' through the conductor, like a bubble moving through a liquid. This moving hole is said to be positive.

The n in n-type semiconductor stands for negative – the dopants add electrons, which of course are negatively charged. The p in p-type semiconductor stands for positive – the dopants create positive holes. However, as noted, these semiconductors do not actually carry excess negative or positive charge.

Metal conductivity compared to semiconductors

Within any given period, the metals (on the left side of the periodic table) have the largest atomic radii. As the period is traversed left to right, the atomic radii decrease. The ionization energies of the atoms get larger, as the valence electrons are closer to the nucleus, and the nucleus contains more protons.

Metals have relatively low ionization energies compared to other elements, so are more able to give up their electrons into the delocalized 'sea of electrons', making them good conductors.

Non-metals hold on tightly to their electrons, making conduction very difficult. Semiconductors are somewhere in between – under certain conditions the electrons can be made to move to higher energy levels and then on to other atoms.

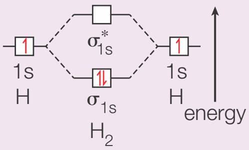
For more detail on how semiconductors conduct, see Band theory below.

Additional Perspective

Band theory

Band theory uses the idea of energy 'bands' to explain the conduction of electricity by semi-conductors.

For individual atoms, electrons occupy energy levels. These are the levels at which it is possible for the electrons to exist. The quantum model of the atom states that electrons can occupy these discrete energy level and nowhere else – they cannot exist in levels 'between' the energy levels or shells.



■ **Figure 24.70** Molecular orbital diagram for the H_2 molecule

The molecular orbital theory of bonding (Chapter 14) tells us that when two atoms bond with each other, their atomic orbitals combine to form two new 'molecular' orbitals (MOs) with different energy levels. In the case of a simple sigma (σ) bond between two atoms, two MOs are formed – one at an energy lower than the original atomic orbitals (this is called σ), and another at a higher energy (this is called σ* ; see Figure 24.70).

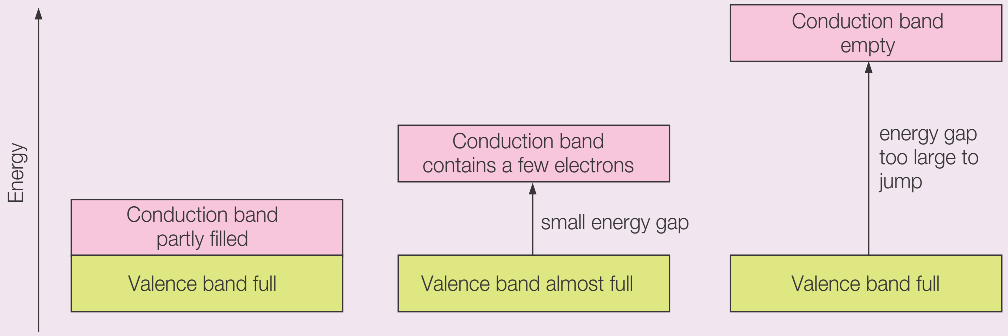
The larger the overlap, and the energy difference, between the atomic orbitals, the greater the energy separation between σ and σ*.

As more and more atoms are added (for example, to a giant molecular structure), each new atom's orbital overlaps with the others and new molecular orbitals are formed. In general *n* atomic orbitals will form *n* molecular orbitals. If *n* is large, as it is in a giant lattice-type structure, the *n* molecular orbitals are so close together that they create a continuous 'band' of energies, rather than a series of discrete levels. (If *n* is small, as in the molecular orbital diagram shown, there are few energy levels, with a clear separation between them.)

Depending on the degree of overlap between orbitals of atoms within the structure, there may be 'gaps' where no energy levels exist (Figure 24.71). These are called 'band gaps'.

In metals, there is no band gap. The atomic orbitals in the relatively large atoms in metals overlap with each other more than the smaller atoms within non-metals. This means that the energy levels 'spread out' more when the molecular orbitals are formed. The energy levels are so spread out that they overlap with each other and there are no 'gaps' in energy. In smaller non-metal atoms, the atomic orbitals overlap less. The bands are narrower and there are clear gaps in energy between higher and lower energy bands.

■ **Figure 24.71** Band theory



Metals
There is no energy gap between valence and conduction bands

Semi-conductors
At a sufficiently high temperature, some electrons can jump the gap

Insulators
The energy gap is too big to allow electrons to move between bands

In metals, electrons in the valence band can move to an unfilled energy level in a band of higher potential energy – this band is called the conduction band. Electrons in the conduction band are delocalized – they are not associated with any atom and move through the lattice when a potential difference (voltage) is applied across it.

In metals, there is no energy gap between the valence band and the conduction band. In insulators the energy gap is too big to allow electrons to move between the bands. In semiconductors the energy gap is smaller, and the probability of electrons jumping the gap increases as the temperature rises, or if light of suitable energy is absorbed.

This illustrates a key difference in the behaviour of metals and semiconductors. When the temperature of a metal increases, there is an increase in resistance, owing to the vibration of the atoms impeding the flow of electrons. However, in semiconductors, a temperature increase increases the likelihood that electrons can jump the energy gap between the valence and conduction bands, meaning that semiconductors are better conductors at high temperatures.

Photovoltaic cells

The band gap in pure silicon is 1.11 electronvolts (see Section 24.3) or 1.78×10^{-19} joules. This corresponds to a maximum absorption wavelength of 1100 nm which is in the infrared region. However, doping the silicon with other elements broadens the range of the absorbed frequencies so that many wavelengths are absorbed throughout the visible down to the infrared. When light is absorbed, valence electrons from the silicon atoms become temporarily delocalized. However, they eventually become valence electrons again – unless some process prevents them from doing this.

Photoconduction

According to band theory, when photons with sufficient energy are absorbed, valence electrons can move into the conduction band, leaving vacancies in the lower valence band (Figure 24.72). The electrons move around in the conduction band, but will eventually re-enter the valence band and occupy a vacant site – releasing energy in the process.

The operation of the photovoltaic solar cell

A photovoltaic cell consists of a pn-junction. When photons hit the n-type layer, electrons move across the junction from the n-type material into the p-type material (Figure 24.73). This creates a separation of charge on each side of the junction – a potential difference – which prevents any further movement of electrons.

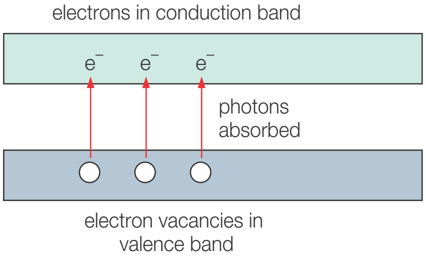
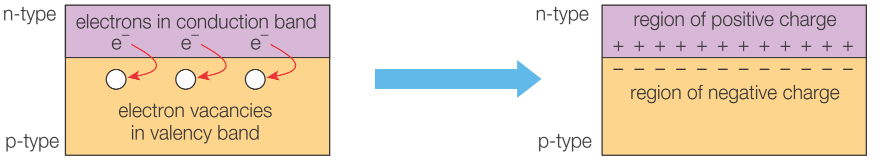


Figure 24.72 Photoconduction in a semiconductor



Movement of electrons across pn-junction…

… creates an electric field across the junction

Figure 24.73 Formation of an electric field at a pn-junction

If sunlight falls on the n-type material, electrons are excited to the conduction band. They are repelled away from the junction by the electric field and move towards the upper surface of the silicon wafer (Figure 24.74).

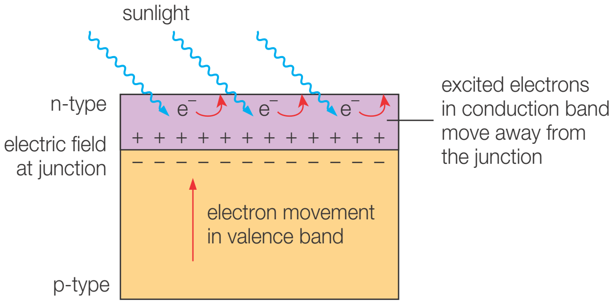


Figure 24.74 The effect of light on a photovoltaic cell

This leaves vacancies in the valence band in the n-type material, and electrons move across the junction from the valence band of the p-type material. If the upper and lower surfaces of the silicon wafer are connected through an electric circuit as shown in Figure 24.75, then electrons will flow from the top surface to the bottom surface to restore the balance of charge. The light energy of sunlight has been converted directly into electricity.

A typical photovoltaic cell is shown in cross section in Figure 24.76. The cell has an anti-reflectant coating over the upper n-type surface to increase the efficiency of light absorption. When the sunlight shines on the photovoltaic cell, the cell produces a small voltage and a current flows. The electric current is collected by strips of metal on the upper surface of the cell and channelled into an external circuit, which is connected to a metallic layer on the base of the cell. Cells are mounted in series and incorporated into a solar module.

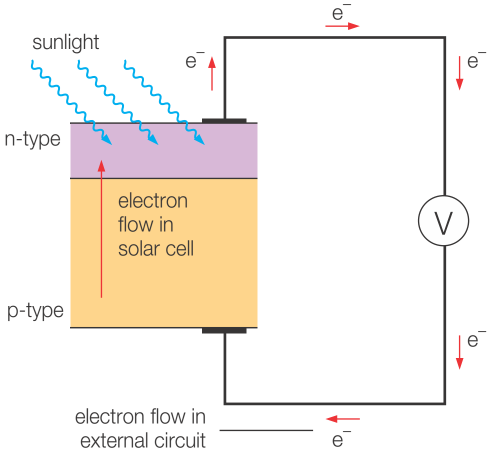


Figure 24.75 A silicon-based photovoltaic cell producing electric current in an external circuit

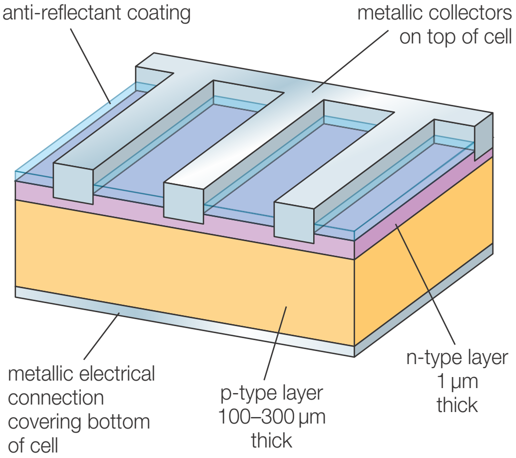


Figure 24.76 Cross section of part of a photovoltaic cell

Dye-sensitized solar cells

The dye-sensitized solar cell (DSSC) is an attempt to mimic the photochemical processes of photosynthesis in a solar cell (see Section 24.4). An organo-metallic dye captures photons, whose energy is used to drive electrons through an external circuit.

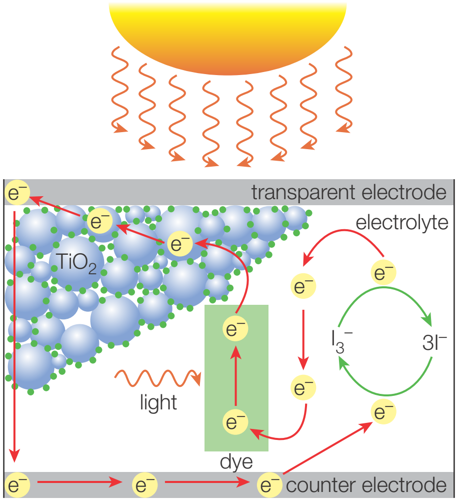
In a silicon photovoltaic cell, the silicon pn-junction converts the sunlight directly into electrical energy. Electrons leave the cell from the n-type silicon and return via the p-type silicon.

In a DSSC, there are two major components needed to allow the cell to operate. Firstly, a dye is used to absorb light and use the energy to drive electrons through the external circuit. Secondly, a chemical electrolyte is needed to provide an electron to reduce the dye molecule back to its original state.

Construction of the DSSC

The Grätzel DSSC is named for Michael Grätzel (Figure 24.77), who along with Brian O'Regan developed a cheap and easily constructed cell (Figure 24.78). It consists of a transparent electrode to which a highly porous layer of titanium dioxide (TiO_2) nanoparticles coated in the organic dye is attached. This assembly has a very large surface area, which makes it much more efficient at capturing photons.

■ **Figure 24.77** Michael Grätzel pictured with his record-breaking 15% efficient DSSC in 2013



■ **Figure 24.78** Schematic of a Grätzel DSSC

The dye absorbs photons which excite electrons. When the electron reaches a sufficient level of excitation, it enters the conduction band of the titanium dioxide semiconductor and then an external circuit. The electrons are re-introduced to the cell via a platinum electrode on the other side and electrons are returned to the dye via an electrolyte. The electrochemistry of the cell is complex, involving several pathways. One possible reaction scheme involves a mixture of iodide (I^-) and triiodide (I_3^-) ions in organic solvent. The iodide–triiodide mixture transfers electrons according to this half-equation:

$$I_3^- + 2e^- \rightarrow 3I^-$$

In the reaction scheme below, this equation is divided by 2, as the scheme follows the progress of a single electron through the electron transfer chain.

The operation of the DSSC

In the following reaction scheme, S represents the dye molecule and $h\nu$ represents a photon from the sunlight.

First, the dye molecule, S, absorbs a photon and an electron becomes excited (raised to a higher energy level, indicated by the asterisk *):

$$S \text{ (on } TiO_2) + h\nu \rightarrow S^* \text{ (on } TiO_2)$$

Next, the excited dye molecule gives up an electron to the TiO_2 network:

$$S^* \text{ (on } TiO_2) \rightarrow S^+ \text{ (on } TiO_2) + e^-$$

This electron flows through the TiO_2 and into the external circuit where it can drive a load such as a motor or a lamp. An electron re-enters the cell via the platinum counter electrode.

The iodide–triiodide electrolyte gains an electron from the counter electrode:

$$\frac{1}{2}\mathrm{I_3^-} + \mathrm{e^-} \rightarrow \frac{3}{2}\mathrm{I^-}$$

The iodide ion reduces the oxidized form of the dye, S^+, back to S:

$$\frac{3}{2}\mathrm{I^-} + S^+(\text{on TiO}_2) \rightarrow \frac{1}{2}\mathrm{I_3^-} + S\,(\text{on TiO}_2)$$

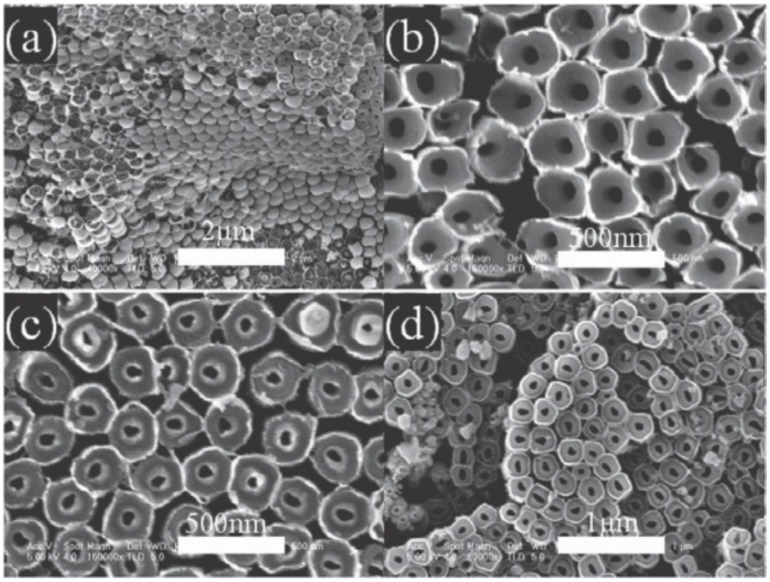
This cycle of reactions thus uses sunlight to drive a flow of electrons through an external circuit. The dye, S, is first oxidized to S^+, but is then reduced back to S, meaning that it is not consumed by the reaction.

How nanoparticles increase the efficiency of DSSCs

Inside the DSSC, the three components (dye, TiO_2 particles and electrolyte) are in close contact. The TiO_2 nanoparticles are tiny transparent spheres that pack together, touching each other. (Imagine a box full of polystyrene spheres.) The touching spheres therefore offer a continuous pathway for electrons to flow through the cell. The spheres are coated in dye everywhere they are not touching. However, spheres do not pack perfectly. The spaces between them are full of electrolyte solution.

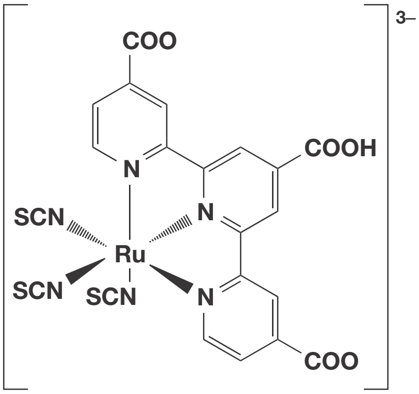
The DSSC therefore consists of a continuous network of touching TiO_2 particles (so electrons have a pathway from one side of the cell to the other), coated in dye. This network has a huge surface area covered in dye (owing to the tiny size of the TiO_2 particles), which in turn is in contact with a large area of electrolyte.

If the nanoparticles are too large, the area of dye (and hence absorption of light) decreases, and the area of contact with the electron-transferring electrolyte is also lower. If the nanoparticles are too small, the cell has a larger internal resistance, as it is more difficult for the electrons to find a pathway through the network. Nanoparticles for DSSCs fall in the range of 20–100 nm in diameter.



■ **Figure 24.79** Researchers at Shanghai Jiao Tong University in China have devised a material made of TiO_2 nanotubes that they hope will offer a good compromise between conductivity and surface area for use in DSSCs

The size of the nanoparticles is optimized to allow the right compromise between the area of light-absorbing dye in contact with the electrolyte, and the ability of the electrons to find a direct path through the network. Figure 24.79 shows a network of TiO_2 nanotubes which could have application in DSSCs.



■ **Figure 24.80** The Black Dye is a ruthenium-based complex ion dye with a π-conjugated system of pyridine rings. It absorbs across a wide range of visible light wavelengths, hence its name

The structure of the dye in a Grätzel DSSC

In Section 24.4, we discussed the importance of a conjugated system of double bonds to the absorption of visible light photons.

A conjugated system consists of a series of overlapping p-orbitals, often including alternating double and single bonds, or benzene rings. The wavelength of maximum absorption, λ_{max}, is greater when there is more conjugation. In the DSSC the choice of metal and structure of the dye is crucial in determining the range of frequencies at which the cell absorbs radiation.

An example of a dye used in a Grätzel DSSC is shown in Figure 24.80. It can be seen that it has a series of delocalized rings, similar to benzene, but with a nitrogen atom substituted for a carbon atom. These are called pyridine rings. The ring system is complexed with a central ruthenium atom, a transition metal. Conjugation is possible across the entire molecule. This dye is able to absorb photons over a wide range of frequencies in the visible region, all the way down the red end of the spectrum.

The advantages and disadvantages of photovoltaic cells and dye-sensitized solar cells

DSSCs have been under development for over 20 years and the technology is now rather mature. They are highly promising owing to their relative ease of manufacture and the high efficiencies already achieved. Silicon photovoltaic cells are an even more established technology which still receives a lot of attention and investment.

The advantages and disadvantages of each type of cell are summarized in Table 24.20.

Table 24.20 Comparison of silicon photovoltaics and DSSCs

	Advantages	Disadvantages
Silicon photovoltaic cell	Well-established technology is manufactured widely Efficiency of silicon photovoltaics is usually still higher – typically around 23%; so-called tandem cells, using several layers and multiple pn-junctions, have achieved 48%	Although economies of scale apply as they are widely made, they are still relatively expensive owing to the cost of processing silicon If they get hot (as they might on a sunny day), the silicon cells' efficiency decreases. For this reason they are often protected by a glass cover, which adds cost and weight
Dye-sensitized solar cell	The early stage of development means that significant advances are still being made to address the disadvantages of these cells. For example, gel or solid electrolytes are under development, which will remove the problem of the electrolyte solution DSSCs do not require any complicated manufacturing steps, and the dyes, although quite advanced, are cheap to make The dyes are more effective at capturing sunlight even at low light levels, whereas silicon cells need a minimum light intensity to work effectively	The electrolyte contains potentially harmful volatile organic compounds, which cannot be allowed to leak The electrolyte solution in iodide–triiodide cells makes the cell less resistant to temperature changes. At low temperatures it can freeze, which shuts the cell down. At high temperatures it can expand, causing sealing problems. However, more modern cells use solid-state or organic electrolytes which removes this problem DSSCs are typically less efficient than silicon-based cells, at around 11%, although 15% efficiency has been achieved in the laboratory. They are more useful for low-density applications such as rooftop solar panels, where physical size can be slightly larger with no real disadvantage. However, at present the cost of installation actually exceeds the cost of production, and this must be considered when calculating the payback time for the solar cell

Experimental work

A Grätzel DSSC can be constructed in a school laboratory using relatively simple equipment (Figure 24.81).

1. Grind titanium dioxide powder to a fine paste with dilute ethanoic acid. Apply this paste in a thin layer to the conducting side of a conducting glass slide and allow to dry.
2. Add a few drops of a brightly coloured dye to the TiO_2 paste on the slide. Fruit juices such as raspberry or blackberry are suitable.
3. Place a second conducting slide on top of the first, conducting side down. The conductivity of the cell can be improved by adding a thin layer of pencil graphite to the conducting side of the glass plate.
4. Prepare a solution of I_3^- and I^- by dissolving iodine in potassium iodide solution. I_3^- is formed by combination of $I_2 + I^-$.
5. Use binder clips to hold the cell together, and add the solution of I_3^- and I^- to the edge of the cell using a pipette. It will creep between the two layers by capillary action.
6. The cell is now ready. Use a multimeter to measure the voltage generated by the cell in bright sunlight.

The DSSC constructed in this way is much less efficient than commercial DSSCs but it illustrates the concept and the construction is similar.

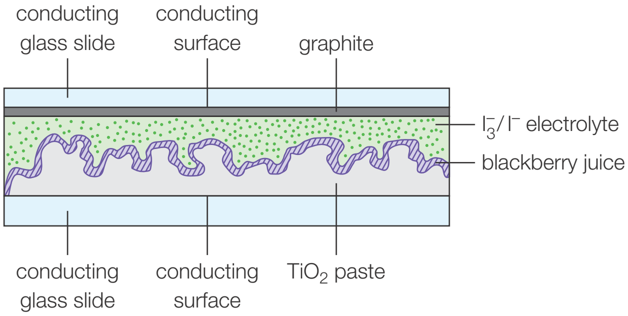


Figure 24.81 Schematic diagram of Grätzel DSSC using simple materials

Solar energy and worldwide energy needs

In his book *Sustainable Energy – Without the Hot Air* (Cambridge, 2009) David Mackay examines the feasibility of paving the Sahara desert with solar panels and using this to address the energy needs of European countries.

Mackay estimates that approximately 15 watts of electrical power can be generated from a square metre of land. This involves using a solar concentrator – a series of mirrors or lenses that concentrates sunlight into a photovoltaic collector. Given that world power consumption today is 15 000 gigawatts (1.5×10^{13} watts) then a land area of 1 million square kilometres (a 1000 km by 1000 km square) would be necessary. To supply just Europe and North Africa would require a 600 km by 600 km square, or an area the size of Germany. However, this would lead to a significant drop in the quantity of carbon added to the atmosphere from combustion of fossil fuels.

Assuming the logistical difficulties of actually constructing a solar power facility on this scale could be overcome, questions remain about the geopolitical implications of such a scheme:

Who would own the energy? Although the sunlight is incident on the countries concerned (possibly Algeria, Tunisia and Libya), it is likely that other countries or multinational energy corporations would develop the infrastructure. The African countries would have to be compensated for the energy, just as oil-rich countries are currently. What about the land itself? What is its value? Being optimistic, such projects could change the economic fortunes of hot, sunny countries around the world, with potential to raise living standards and lift many people out of poverty. However, good governance is required to ensure that the newfound income is used wisely to improve the countries' long-term economic prospects.

Mackay's book is highly theoretical and intended to illustrate the sheer scale of solar infrastructure needed to match the energy provided by fossil fuels. Realistically, the geopolitical situation does not allow for such projects. However, in 2006, Nathan Lewis and Daniel Nocera attempted a realistic analysis of the potential for solar energy to provide a useful proportion of worldwide energy needs.

Their main conclusions were that biologically derived solar cells, rather than those requiring silicon, are more likely to come down in cost sufficiently that they can offer large energy contributions. In addition, if solar energy is to be useful at higher latitudes, effective energy storage is needed, because solar energy on demand cannot be relied upon. An organic solar cell, which generates 'solar fuel' (perhaps by splitting hydrogen and oxygen from water) for use in a fuel cell, might offer a potential route to lowering our reliance on fossil fuels. Such cells would be less location-dependent, as even countries receiving much less sunlight than Saharan Africa would be able to make and store solar fuel during daylight hours.

Nature of Science

Transdisciplinary research

In Section 24.5 the transdisciplinary nature of climate science was discussed. The development of dye-sensitized solar cells also illustrates the overlap of different scientific fields.

The mechanism of action of the DSSC attempts to mimic the processes occurring during photosynthesis, so work done by biologists is incorporated. The use of TiO_2 nanoparticles requires the input of chemists with understanding of the kinetics of processes at the nanoscale. Chemists have also developed the dyes used, which aim to capture a wide range of solar radiation frequencies with a high efficiency.

Nature of Science

Funding

Scientific work has to be paid for. Sources of funding might include governments, charitable foundations or private companies. Private companies will naturally wish to see a return on their investment, and this will impact on the kinds of work done – it is likely to be focused on practical applications. Charitable foundations or governments might allocate some funding to purely theoretical research without any immediately obvious application – so-called 'blue skies research'. Government-funded research is susceptible to political concerns – for example, some political parties oppose stem cell research on moral grounds.

Sometimes research funding is justified in terms of one application, and then other potential applications are proposed. For example, much of the early work into fuel cells was carried out as part of the NASA Gemini programme in the 1960s and was funded as part of the enormous budget allocated to space flight at that time. The possibility of using fuel cells on Earth arose much later as part of a move away from fossil fuels.

ToK Link

Metaphors in science

The conjugated system in the dye molecules used in the dye-sensitized solar cell has some similarities with a violin string. The longer the conjugated system, the lower its natural frequency, meaning it absorbs radiation of longer wavelength. A violin string also has a natural frequency at which it vibrates, and this frequency is lower the longer the string. The behaviour of the violin string is a useful metaphor or memory aid at least, for the behaviour of the conjugated system.

However, is this metaphor really helpful in understanding why the conjugated system behaves as it does? Perhaps not. After all, the electrons in the conjugated system absorb light of specific wavelengths, but are they physically vibrating in the same way as the violin string? Some models propose the electron as a 'standing wave' vibrating at a specific frequency. Does the violin metaphor therefore oversimplify the complicated behaviour of the conjugated system, or overstate the similarity?

What are the purposes of metaphor in the acquisition of scientific knowledge? They are twofold: firstly, to help us get a 'sense' of the meaning of a scientific concept. As our understanding of science has increased, we have encountered many enormously complex phenomena that are not easily understood in terms of our everyday experience. Some phenomena such as quantum mechanics or the relativistic theory of gravitation can only be accurately described by mathematics. However, metaphors can be helpful in conveying the basics of an idea. The metaphor helps us to 'bridge the gap' between our own experience and the reality which might be impossible to conceive. For example, if the distortion of space–time by massive objects is likened to bowling balls resting on a rubber sheet, causing it to bend, this gives us an impression of how space–time might behave in the presence of larger or smaller objects.

This leads to metaphor's second purpose, which is to aid us in communicating our scientific knowledge. Your chemistry teacher may, at different times, have compared an electron to a particle, wave or a 'cloud' of charge. The electron is not exactly any of these things, but these metaphors can help us to make predictions about chemical behaviour, for example the formulae of compounds, their shapes or their properties.

You might argue that chemical understanding acquired on the basis of inaccurate metaphors is false understanding, and the knowledge gained is not actually knowledge at all, as it does not reflect reality. In practical terms, however, simplified ideas do have their uses. It is not necessary to use quantum mechanics to predict the formula of sodium chloride or to decide whether a metal or a non-metal will be a better conductor of electricity. In just the same way as simpler ideas have been augmented and sometimes replaced by more complex ideas in the history of science, you will learn new theories in chemistry which will augment and sometimes contradict the simpler ones you learnt in your pre-Diploma course.

Examination questions – a selection

Q1 Coal can be used to generate heat in our homes. Alternatively, it could be used in a power station to generate electricity, which can then be used for heating. Which approach is preferred? Outline some advantages and disadvantages of each option. [3]

Q2 Kerosene is used as fuel for jet aircraft. It is composed of hydrocarbons ranging from 6 to 16 carbon atoms.

a Assume kerosene is composed mainly of decane, $C_{10}H_{22}$. What is the specific energy of kerosene? Necessary data: ΔH_c: 6779 kJ mol^{-1}; M_r: 142.28 g mol^{-1}. [2]

b A Boeing 747 carries approximately 100 tonnes of fuel. How much energy is available in this mass of decane? [2]

Q3 Deduce equations for the production of decane $C_{10}H_{22}$ by:

a Direct hydrogenation of coal. [2]

b Liquefaction of coal gas, carbon monoxide, CO (g). [3]

Q4 A possible fission product of uranium-235 is xenon-137. This then undergoes beta decay forming caesium-137, releasing a gamma photon also. Caesium-137 also undergoes beta decay, and can be used as a beta radiation source to treat tumours. It has a half-life of 30 years. Caesium-137, although useful, is a hazardous isotope as it forms highly soluble salts which can enter the environment.

a Write an equation for the fission of uranium-235 to xenon-137, and identify the other element formed. [2]

b Write equations for the beta decay of xenon-137 and the subsequent beta decay of caesium-137. [2]

c Calculate the percentage of the original radioactivity left in a sample of caesium-137 after 180 years. [2]

d Why does the high solubility of caesium-137 salts make it a particularly dangerous radioisotope? [2]

Q5 Naturally occurring uranium-238 undergoes a series of radioactive decay processes terminating in lead-206. The first part of the decay chain takes uranium-235 to radium-226 in a series of steps.

a In the equation below, identify the type of radioactive particle (alpha, beta or neutron) emitted by the nucleus at each step:

$${}^{238}_{92}U \rightarrow {}^{234}_{90}Th \rightarrow {}^{234}_{91}Pa \rightarrow {}^{234}_{92}U \rightarrow {}^{230}_{90}Th \rightarrow {}^{226}_{88}Ra$$ [5]

Radium-226 is an alpha-emitting gas with a half-life of 1600 years.

b Calculate the time taken for the radioactivity of a sample of radium-226 to decay to 20 per cent of its original value. [2]

c Why does the fact that radium is an alpha-emitting gas make it particularly dangerous? [2]

Q6 Ethanol and biodiesel are examples of biofuels.

a Outline the advantages and disadvantages of biofuels in general. [4]

b Discuss the advantages and disadvantages of ethanol versus biodiesel made from palm oil. [3]

c Explain why vegetable oils are not usually suitable for use as fuels for cars. [2]

d Outline the process of transesterification and explain why the resultant mixture is more suitable as a fuel for motor vehicles. [2]

e One of the components of palm oil is a triglyceride of oleic acid, $(C_{17}H_{33}COO)_3CH(CH_2)_2$. Write a balanced equation for the transesterification of this triglyceride with methanol. [2]

Q7 Outline the possible environmental effects on the oceans of increasing atmospheric CO_2 levels. Include equations in your discussion. [5]

Q8 This question is about the greenhouse effect and global warming. Atmospheric warming arises because the amount of radiation incident on the Earth from the Sun is no longer matched by the amount of radiation leaving the Earth into space.

a What types of electromagnetic radiation are most prevalent in sunlight? [3]

b How does this radiation result in warming of the atmosphere? [2]

c Explain how a greenhouse gas such as carbon dioxide results in increased atmospheric warming. [3]

d What do you understand by the term 'global warming potential' (GWP)? [4]

e Explain how methane, a much less abundant atmospheric pollutant than carbon dioxide, is thought to make a significant contribution to anthropogenic global warming. [2]

f Describe the likely effects of anthropogenic global warming. [4]

Q9 This question is about the hydrogen fuel cell.

a Outline the function of each component in the hydrogen fuel cell:

i Platinum catalyst

ii Aqueous sodium hydroxide electrolyte. [4]

b The proton exchange membrane fuel cell replaces the sodium hydroxide with a polymer membrane. Suggest an advantage of using the membrane instead of the aqueous solution. [1]

c Write the half-cell equations for the reactions occurring at each electrode in an alkaline cell. State which is the negative and which the positive terminal of the cell. [4]

d State one disadvantage of using hydrogen as a fuel for fuel cells. [1]

Q10 Lithium-ion batteries and nickel–cadmium batteries are both examples of secondary cells.

a Define the term 'secondary cell'. [1]

b For each cell type, describe the electrolyte and identify the charge carrying species in the electrolyte during discharge. [4]

c Write the half-equations for the anode and cathode of each cell type. [8]

d Suggest two advantages of each cell type. [4]

Q11 Methanol fuel cells offer some advantages over hydrogen fuel cells.

a Suggest two advantages of a methanol fuel cell over a hydrogen fuel cell.

b i Deduce the oxidation state of carbon in methanol, CH_3OH. [1]

ii Deduce the oxidation state of carbon in carbon dioxide. [1]

iii Hence write the half-equation for the oxidation of methanol at the anode of the fuel cell. [2]

iv Write the half-equation for the reduction of oxygen gas at the cathode. [2]

c Some fuel cells run on ethanol as an alternative to methanol. Calculate the oxidation number of carbon in ethanol and hence write the anode half-equation for an ethanol fuel cell. [3]

Q12 The overall equation for the microbial fuel cell (MFC) can be expressed as:

$$CH_3COOH(aq) + \frac{3}{2}O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$$

a Calculate the thermodynamic efficiency of this cell, using the following data: [2]

Substance	Enthalpy of formation/ΔH_f kJ mol^{-1}	Gibbs free energy of formation/ΔG_f, kJ mol^{-1}
CH_3COOH (aq)	–486	–390
O_2(g)	0	0
CO_2(g)	–394	–394
H_2O(l)	–286	–237

b Give two advantages of the MFC. [2]

Q13 a For each of the following nuclear reactions, classify them as fusion or fission processes, and calculate the mass defect (in atomic mass units) and the energy released (in MeV). [12]

i ${}^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{144}_{56}\text{Ba} + {}^{89}_{36}\text{Kr} + 3{}^{1}_{0}\text{n}$

ii ${}^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \rightarrow {}^{4}_{2}\text{He} + {}^{1}_{0}\text{n}$

iii ${}^{6}_{3}\text{Li} + {}^{1}_{0}\text{n} \rightarrow {}^{4}_{2}\text{He} + {}^{3}_{1}\text{H}$

iv ${}^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{95}_{42}\text{Mo} + {}^{139}_{57}\text{La} + 2{}^{1}_{0}\text{n} + 7{}^{0}_{-1}\text{e}$

b For reaction (i) above, convert the energy value obtained to a value in kJ mol^{-1} of uranium-235. Comment on the value obtained. Necessary data:

Species	Mass (amu)
${}^{0}_{-1}\text{e}$	5.48580×10^{-4}
${}^{1}_{0}\text{n}$	1.00866
${}^{2}_{1}\text{H}$	2.01410
${}^{3}_{1}\text{H}$	3.01604
${}^{4}_{2}\text{He}$	4.00260
${}^{6}_{3}\text{Li}$	6.01512
${}^{89}_{36}\text{Kr}$	88.91764
${}^{95}_{42}\text{Mo}$	94.90584
${}^{139}_{57}\text{La}$	138.90635
${}^{144}_{56}\text{Ba}$	143.92295
${}^{235}_{92}\text{U}$	235.04393

[3]

Q14 This question is about the energy produced during nuclear reactions.

a Sketch a graph with nucleon number on the *x*-axis and energy on the *y*-axis. On these axes draw a curve showing the relationship between binding energy and nucleon number. [3]

b Explain why the graph in (a) has this shape, with reference to the electrostatic force and the strong nuclear force. [3]

c With reference to the fusion reactions of hydrogen forming helium, explain why the fusing of these nuclei leads to a release of energy. *(You need not calculate specific values in your answer.)* [2]

d With reference to the fission reaction of uranium-235 forming barium-139 and krypton-89, explain why the fission of uranium releases energy. *(You need not calculate specific values in your answer.)* [2]

Q15 Naturally occurring uranium consists mainly of uranium-238, with only 0.7 per cent uranium-235. It is necessary to increase the proportion of uranium-235, a process called enrichment.

a Why is it necessary to enrich uranium? [1]

b Uranium occurs naturally in an oxide ore called yellowcake, U_3O_8, which is converted to uranium dioxide, UO_2, and then to UF_6 in a two-step process.

i Write a balanced equation for the reaction of uranium dioxide with hydrogen fluoride, forming UF_4. State the type of reaction taking place here. [3]

ii Write a balanced equation for the conversion of UF_4 to UF_6 with fluorine gas. State the type of reaction taking place here. [3]

iii Explain why it is necessary to convert UO_2 to UF_6 for enrichment of uranium. [2]

c The uranium for the first atomic weapons was enriched by effusion of UF_6 containing each of the two isotopes of uranium in their natural abundances.

  i Use Graham's law to calculate the relative rate of effusion of the two forms of UF_6. [2]

  ii Given an original abundance of 0.7 per cent uranium-235, how many stages of effusion are necessary to reach an abundance of 90 per cent, which is viable for a weapon? [2]

  iii Gas centrifugation methods achieve a 1.3 separation ratio. How many stages of this process are required to reach 90 per cent abundance? [1]

Q16 This question is about the dangers of ionizing radiation. A water molecule in a cell can be split into two radicals by a high energy gamma ray photon:

$H_2O \rightarrow HO^\bullet + H^\bullet$

a Write an equation for the reaction of a hydroxyl radical, $HO^\bullet$, with a water molecule, H_2O. [1]

b A hydrogen radical, $H^\bullet$, can combine with an oxygen molecule O_2, forming a hydroperoxy (or hydroperoxyl) radical, which is dangerous as it has a longer lifetime than a $H^\bullet$ radical.

  i Write an equation for this reaction. [2]

  ii Draw the Lewis structure of the hydroperoxy radical. [1]

c Deprotonation of the hydroperoxy radical leads to formation of a superoxide radical, O_2^-. Draw the Lewis structure of the superoxide radical. [1]

d Explain why the presence of radicals in the body might lead to formation of tumours. [2]

Q17 This question is about radioactive decay and half-lives.

a Americium-241 emits alpha particles and gamma rays. It is used in smoke detectors and has a half-life of 432 years. A typical smoke detector contains 0.29 micrograms of Americium-241.

  i Americium-241 decays by alpha emission. What does it decay into? [1]

  ii A 20-year-old smoke detector is found in a landfill. How many grams of americium would you expect it to contain? [3]

b Spent nuclear fuel typically contains about 0.8 per cent plutonium-239. Plutonium-239 is an extremely hazardous substance. It is thought that 1 milligram of plutonium-239 is sufficient to kill a person. Its half-life is 23400 years.

  i Calculate the decay constant for the decay of plutonium-239. [2]

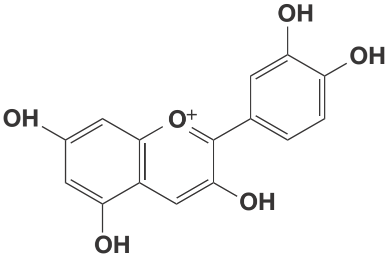
  ii How long would it take for a sample of 1 g of spent nuclear fuel to decay to such a level that it was below that necessary to kill a person (i.e. less than 1 milligram of plutonium-239 present)? [2]

c Cerium-144 exists in small amounts in fallout from atomic weapons and radioactive waste from power plants. Its half-life is 285 days. It decays by beta emission.

  i What product is formed from the beta emission of cerium-144? [1]

  ii A sample of radioactive waste is stored in a cooling pond for 12 weeks before being transferred to long-term storage. What proportion of the cerium has transmuted into the new element proposed in c(i)? [2]

Q18 A simple home-made dye-sensitized solar cell (DSSC) can be made using dyes obtained from natural sources such as fruits or flowers. The dye pictured is called cyanidin and is obtained from the red flowers of *Anthurium*.



a What structural feature of cyanidin makes it suitable for making a DSSC? [1]

b Cyanidin is placed on to a glass slide coated in a thin layer of finely divided titanium dioxide powder.

  i What is the purpose of the titanium dioxide powder? [1]

  ii Why is the titanium dioxide finely divided? [2]

c An electrolyte is also required, which is usually a mixture of iodide and triiodide ions in equilibrium. Give equations showing how the iodide–triiodide system enables:

  i Electrons to be transferred from the cell to the external circuit, by oxidizing the dye. [2]

  ii The reduction of the dye in the cell as electrons re-enter the cell. [2]

d A homemade DSSC such as this might reach an efficiency of 0.7 per cent. The best DSSCs in the laboratory have reached 15 per cent efficiency. Suggest ways in which the best DSSCs might differ from those you could construct from simple materials. [3]

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